Processing KODAK Motion Picture Films, Module 3

Analytical Procedures

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3 Analytical Procedures for Chemical Control

INTRODUCTION

Analysis of the critical chemicals in photographic processing solutions may be used as a basis for discarding a solution or for adjusting the composition of a solution for further use. Examples of the routine use of analysis include certification of replenisher solutions, start-up and daily tank analyses, and the measurement of silver in fixers. Chemical analyses are also used for determining proper replenisher formulas with their corresponding replenishment rates. The cost of the chemical analyses may be small when compared to the cost of using a substandard processing solution or the cost of process downtime.

The analytical procedures in this module are for analysis of chemicals in the solutions of KODAK Motion Picture Processes: ECN-2, ECP-2D, VNF-1 and RVNP. The numbers in the first column of the Table of Contents, identify the appropriate process for the procedure. A number with no letter prefix or the ULM- prefix, can be used with all Kodak film or paper processes. The ECN- prefix indicates the procedure is only for Process ECN-2 solutions, whereas ECP- procedures can be used for Process ECP-2D solutions. ECR- indicates use only with reversal Process VNF-1. The numbers are also assigned a suffix letter A, B, C, etc, indicating that the procedure is a revision of an earlier procedure or is based on an earlier procedure. The numbers found under the title of each procedure correspond to a Kodak internal system identifying the appropriate process.

The procedures are as short and simple as possible, commensurate with the accuracy and precision that is required for adequate chemical control of the process. We recommend the laboratory and personnel be supervised by a chemist. The analyses may be carried out by a trained technician. Essential equipment includes an analytical balance, a pH meter (with suitable electrodes, buffers and filling solutions), thermometers, hydometers, magnetic stirrers, a constant-temperature water bath, and a spectrophotometer.

A spectrophotometer equipped for making measurements in the ultraviolet and visible regions of the spectrum, provides a rapid means for making certain chemical analyses. Some models can also be used to check filters for sensitometers, densitometers and printers.

This module also includes some procedures for noncritical chemicals, and a collection of standard analytical practices which are not usually required for routine control. These may be used as a basis for diagnosing processing troubles as they arise. These practices are generally used by the supervisors and technicians in charge of the maintenance of analytical equipment.

Instructions for the preparation of the required reagents are given in Module 4, *Reagent Preparation Procedures.*

Note: The information presented herein is accurate and reliable to the best of our knowledge and belief, but is furnished without warranty of any kind. Customers must make their own determination of the suitability of completeness of any product, material, and/or procedure for a specific purpose and adopt such safety precautions as may be necessary.

Spectrophotometric Determination of EASTMAN Anti-fog No. 9 In Developer

ECN-2-1570C

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SD-49	—	—	—

INTRODUCTION

Ethyl acetate is used to extract the developing agent and other interfering constituents from the sample at mix pH. Carbon dioxide is evolved when acetic acid is added to lower the pH and must be completely removed before the extraction of EASTMAN Anti-fog No. 9 (AF No. 9). AF No. 9 is then extracted from the aqueous mixture with a measured amount of 4methyl-2-pentanone. The 4-methyl2-pentanone solution is dried over sodium sulfate. Sodium methoxide solution is pipetted into a volumetric flask, which is then filled to volume with the 4-methyl-2pentanone solution. In the presence of sodium methoxide, AF No. 9 and 4-methyl-2-pentanone react slowly to form an unstable dye. The absorbance at 550 nm is read after the optimum reaction time of 8 minutes. A glass-stoppered silica cell is used to prevent evaporation.

Note: Water destroys the dye. The volumetric flask must be dry.

It is necessary to ensure the complete removal of carbon dioxide evolved when acetic acid is added. Any remaining carbon dioxide will be extracted by the 4-methyl-2-pentanone and will react with the sodium methoxide to give a precipitate. A small precipitate, which dissolves with mixing, will not affect the analysis, but any permanent precipitate will give excessively high answers.

The reaction is sensitive to temperature. If the laboratory temperature is below 21°C or above 27°C, it is advisable to place the volumetric flask of dye in a 27°C constant-temperature bath for most of the 8-minute reaction time.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

Four developer mixes containing 0.10, 0.15, 0.20 and 0.25 g/L AF No. 9, respectively were analyzed by four analysts. Based on 26 data points, the 95percent confidence limits for an individual determination are ± 0.02 g/L AF No. 9. Recalibrate this method if AF No. 9 concentrations exceed 0.25 g/L.

SPECIAL APPARATUS

- Constant-temperature bath (optional)
- Spectrophotometer with a tungsten lamp
- 1-cm Silica Cell (glass-stoppered)

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use reagents that are ACS Reagent Grade unless specified otherwise.

- 10 g/L Cetyltrimethylammonium Bromide (CTAB)
- Ethyl Acetate, water-saturated
- 2 N Acetic Acid, CH_3COOH
- 4-Methyl-2-pentanone
- Sodium Sulfate, Na_2SO_4
- Sodium Methoxide in Methanol, 6 percent Solution or 59 g/L
- Methanol, Spectro-Reagent Grade

PROCEDURE

Extraction of Interferences

1. Pipet (wipe the pipet before leveling) 50.0 mL of sample into a 250-mL separatory funnel No. 1.
2. Add, from a tip-up pipet, 1 mL of 10 g/L CTAB.
3. Add, from a tip-up pipet, 50 mL of ethyl acetate, water-saturated.
4. Stopper and shake the funnel for a few seconds, then vent through the stopper. Continue to shake vigorously for 30 seconds, venting occasionally.
5. Allow the layers to separate; swirl the funnel and drain the lower (aqueous) layer into a 250-mL separatory funnel No. 2.

   Note: The ethyl acetate layer remaining in separatory funnel No. 1 may now be discarded. Use locally acceptable practices for disposal of waste ethyl acetate.
6. Using separatory funnel No. 2, repeat steps 3 and 4.
7. Allow the layers to separate, swirl the funnel, and drain the lower (aqueous) layer into a clean 250-mL separatory funnel No. 3.

Extraction of AF No. 9

1. Add, from a tip-up pipet, 20 mL of 2 N acetic acid to separatory funnel No. 3.
2. Stopper the funnel and begin mixing gently; vent through the stopper, very frequently until gas evolution ceases.
3. When gas evolution stops, remove the stopper and flush the remaining carbon dioxide out of the separatory funnel with a gentle stream of air or nitrogen. (Do not bubble through the solution in the separatory funnel.)
4. Pipet (wipe) 40.0 mL of 4-methyl-2-pentanone into the separatory funnel.
5. Stopper and shake the funnel for 30 seconds.
6. Allow the layers to separate; swirl the funnel, then discard the lower (aqueous) layer.

Drying the 4-methyl-2-pentanone

1. Weigh 25 grams of anhydrous sodium sulfate to the nearest gram.
2. Drain and discard about 1 mL of the 4-methyl-2pentanone to flush the water out of the stem of the separatory funnel No. 3.
3. Drain the 4-methyl-2-pentanone into a 150-mL beaker containing a magnetic stir bar.
4. Place the beaker on a magnetic mixer and begin stirring without splashing.
5. Add, while stirring, the 25 grams of sodium sulfate; continue stirring for 1 minute.

Dye Formation

Note: Water destroys the dye. The volumetric flask must be dry.

1. Pipet (wipe) 25.0 mL of sodium methoxide in methanol reagent into a clean dry 50-mL volumetric flask.
2. Fill the flask to volume with the 4-methyl-2-pentanone containing AF No. 9.

   Note: If necessary stir the sodium sulfate with a glass stirring rod to free more of the 4-methyl2-pentanone.
3. Immediately start a timer for 8 minutes; stopper and invert the flask to mix.
   a. If the solution is even slightly turbid after mixing, the results will be high. See Introduction.
   b. If the laboratory temperature is below 21°C, place the volumetric flask in a 27°C constant-temperature bath for most of the 8-minute reaction time. For more information, see the *INTRODUCTION*.

Absorbance Measurement

1. Rinse, at least twice, a clean glass-stoppered 1-cm silica cell with methanol.
2. With the contents of the volumetric flask, rinse twice. then fill the cell; stopper the cell.
3. When the alarm sounds, measure the absorbance at 550 nm against air on a spectrophotometer (A_{550}).

   Note:
   a. During the 8-minute wait, the sample should not be warmed (or chilled) by unnecessary handling or by storing in a warm (or cold) place.
   b. The cell should not be placed in the spectrophotometer for more than a minute before reading.

Calculation:

EASTMAN Anti-Fog No. 9, g/L = $0.547(A_{550}) + 0.06$

Potentiometric Determination of Bromide in Developer

ECN-926C
ECP-926C

Process	ECN-2	ECP-2B	VNF-1/LC	RVNP
Formulas	SD-49	SD-50/51	—	—

INTRODUCTION

This method contains two separate procedures for analysis of bromide. Procedure A is used for the analysis of fresh tank and fresh replenisher solutions. Procedure B is used for the analysis of seasoned tank and reconstituted replenisher solutions. Analysis of seasoned tank and reconstituted replenisher solutions using Procedure A will result in erroneously high results-as much as 0.3 g/L. This effect is dependent upon seasoning; aging is not a factor.

Procedure A—The sample is acidified and then titrated potentiometrically with silver nitrate.

Procedure B—Bromide enrichment by selective precipitation is utilized. All of the bromide is precipitated as silver bromide along with minor amounts of other silver salts, by the addition of a small excess of silver to an acidified sample of seasoned developer. The silver salts are filtered and developed by a silver halide developer, releasing soluble bromide. The sample is filtered again, the filtrate is acidified,

As an aid in selecting the proper inflection point and detecting instrument trouble or analytical errors, a set of standard titration curves of all developers should be kept on file. Such curves can be compared with the general shape and relative position of any routine titration curve. Typical titration curves are shown in Figures 1 and 2 as an aid in determining the increment size to use in the region of the end point and the expected potential change in millivolts.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

Figure 1 Typical Bromide Titration Curve in PROCESS ECN-2 Developer

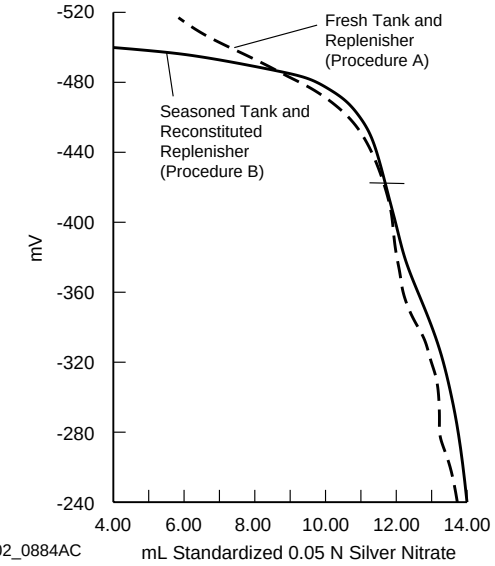
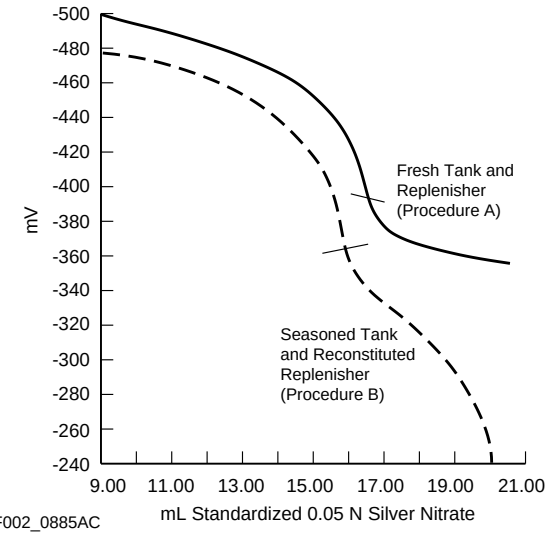


Figure 2 Typical Bromide Titration Curve in PROCESS ECP-2B Developer



RELIABILITY

Procedure A—The 95 percent confidence limits for an individual analysis of a fresh tank or replenisher sample are estimated to be slightly less than ± 0.05 g/L NaBr.

Procedure B—This procedure was specifically designed for current mix formulations and variance due to seasoning. Any change in mix formulation, especially in bromide concentration, may necessitate recalibration. This procedure will accurately analyze bromide in seasoned tank and reconstituted replenisher solutions containing as much as 1.5 g/L sodium bromide in SD-49 developer and 2.10 g/L sodium bromide in SD-50 or SD-51 developer. Analytical results will be low on solutions exceeding these concentrations of sodium bromide. Eight seasoned samples in the appropriate bromide concentration range were analyzed by three analysts. Based on 24 data points obtained, the 95 percent confidence limits for an individual determination are ± 0.05 g/L sodium bromide.

SPECIAL APPARATUS

- pH Meter
- Reference Electrode, Double Junction, Orion No.900200 or equivalent
- Indicator Electrode, Silver Billet, Beckman No. 39261 or equivalent
- Millipore Filter apparatus
- Millipore Filter membrane (0.45 micron porosity 47 mm)
- Exhaust Hood

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 1.0 M Ammonium Nitrate, NH_4NO_3
- Celite
- Silver Halide Developer
- 0.05 N Silver Nitrate, $AgNO_3$ (standardized to 4 decimal places)
- 18 N Sulfuric Acid, H_2SO_4

PROCEDURE A

For Fresh Tank and Replenisher

Note: Prepare the double junction/silver billet electrode pair and calibrate the electrode-instrument system according to the instructions given in Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revision.

Sample Treatment

(Perform in an Exhaust Hood)

1. Pipet, wipe the pipes before leveling, 50.0 mL of sample into a 250-mL beaker.

Warning

ACID. Avoid contact with skin and eyes. In case of contact, flush with water.

2. Stir the sample moderately on a magnetic stirrer and add very slowly from a tip-up pipes, the indicated volume of 18 N sulfuric acid.

Process	Formula	Acid
ECN-2	SD-49/49R	25 mL
ECP-2B	SD-50/50R SD-51/51R	50 mL 50 mL

Titration

1. Using a 25-mL buret, titrate the sample potentiometrically, according to Method ULM-0003-01, with standardized 0.05 N silver nitrate.

   Note: The titration may be performed most rapidly in the beginning where the potential change is the smallest. Refer to Figures 1 and 2 to determine the increment size to use in the region of the end point and the expected potential change in millivolts.

2. Determine the end point using concentric arcs from Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*.

Calculations

$$\text{NaBr, g/L} = \frac{(\text{N } AgNO_3)(\text{mL } AgNO_3) \times (\text{eq. wt. NaBr}) \times (1000)}{(\text{mL sample}) \times (1000)} =$$

$$\frac{(\text{N } AgNO_3)(\text{mL } AgNO_3) \times (102.91) \times (1000)}{(50) \times (1000)} =$$

$$2.058(\text{mL } AgNO_3)(\text{N } AgNO_3)$$

PROCEDURE B

For Seasoned Tank and Reconstituted Replenishers

Note: Prepare the double junction/silver billet electrode pair and calibrate the electrode-instrument system according to the instructions given in Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revision.

Sample Treatment

(Bromide Enrichment)

1. Pipet, wipe the pipes before leveling, 50.0 mL of sample into a 250-mL Phillips beaker. Stir moderately on a magnetic stirrer in an exhaust hood.

Warning

ACID. Avoid contact with skin and eyes. In case of contact, flush with water.

2. While stirring add very slowly, from a tip-up pipes, 50 mL of 18 N sulfuric acid to the Phillips beaker.
3. Add approximately 0.2 grams of Celite to the Phillips beaker. (One level scoop from a Coors No. 04 porcelain spatula is approximately 0.2 grams.)
4. Add, from a graduated cylinder, the indicated amount of standardized 0.05 N silver nitrate to the solution as it stirs. Immediately set a timer for 5 minutes and continue to stir during that period.

Process	Formula	Acid
ECN-2	SD-49/49R	15 mL
ECP-2B	SD-50/50R SD-51/51R	20 mL 20 mL

5. As the solution stirs, assemble a Millipore filter holder and filter membrane (type HAWP—0.45 micron porosity, 47 mm) on a 250-mL filter flask.
6. At the end of the five-minute stirring period, connect the aspirator hose and filter the solution through the Millipore apparatus, retaining the stirring bar in the Phillips beaker by means of another may-bar outside the beaker. When filtering is completed, disconnect the aspirator hose.
7. Rinse the sides of the Phillips beaker with 25 mL of 1.0 M ammonium nitrate from a tip-up pipet. Retaining the stirring bar in the Phillips beaker, rinse the sides of the Millipore funnel by pouring the solution through a long, thin-stemmed glass funnel. Reconnect the aspirator hose and filter the solution into the 250-mL filter flask. Disconnect the aspirator hose when the filtering is completed. Save both the long-stemmed funnel and the Phillips beaker.
8. Remove the 250-mL filter flask from the Millipore filter apparatus and discard the filtrate. Do not disassemble the Millipore filter apparatus.
9. Rinse the inside and outside of the stem only of the Millipore funnel with distilled water from a wash bottle, and place the filter apparatus on a clean 250-mL filter flask.

Silver Development

1. Add, from a graduated cylinder, 25 mL of silver halide developer to the 250-mL Phillips beaker.

   Note: Do not expose the silver halide developer to air any longer than necessary When not in use, store the silver-halide developer in a cool, dark place. A developer that has turned brown should not be used. The developer is still usable if it has a light tan color.

2. Swirl the Phillips beaker and immediately rinse the sides of the Millipore funnel (with no applied suction) by pouring the developer through the long-stemmed funnel. Set a timer for five minutes and allow the developer to remain in the Millipore funnel for that period. At one-minute intervals, swirl the Millipore funnel for several seconds.
3. During the five-minute period, add from a tip-up pipet, 25 mL of distilled water to the 250-mL Phillips beaker.
4. At the end of the five-minute period, connect the aspirator hose and filter the solution into the clean 250-mL filter flask. (Care must be taken to prevent loss of the filtrate through the aspirator hose.) With the aspirator hose still connected, rinse the sides of the Millipore funnel with the solution in the Phillips beaker by pouring the solution through the long-stemmed funnel. Disconnect the aspirator hose when the filtration is completed.
5. Quantitatively transfer the solution in the 250-mL filter flask into a 400-mL beaker using a maximum of 100 mL of distilled water.
6. Stir the solution moderately on a magnetic stirrer in an exhaust hood.

Warning

ACID. Avoid contact with skin and eyes. In case of contact, flush with water.

7. Add carefully from a tip-up pipet, 50 mL of 18 N sulfuric acid to the beaker.

Titration

1. Titrate the sample potentiometrically according to Method ULM-0003-01, with standardized 0.05 N silver nitrate using a 25-mL buret.

   Note: The titration may be performed most rapidly in the beginning where the potential change is the smallest. Refer to Figures 1 and 2, to determine the increment size to use in the region of the end point and the expected potential change in millivolts.

2. Determine the end point using the concentric arcs from Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*.

Calculations

$$\text{NaBr, g/L} = \frac{(\text{N } AgNO_3)(\text{mL } AgNO_3) \times (\text{eq. wt. NaBr}) \times (1000)}{(\text{mL sample}) \times (1000)} =$$

$$\frac{(\text{N } AgNO_3)(\text{mL } AgNO_3) \times (102.91) \times (1000)}{(50) \times (1000)} =$$

$$2.058(\text{mL } AgNO_3)(\text{N } AgNO_3)$$

Potentiometric Determination of Bromide in Ferricyanide Bleach

ECN-0004/1
ECP-0004/1
ECR-0004/1

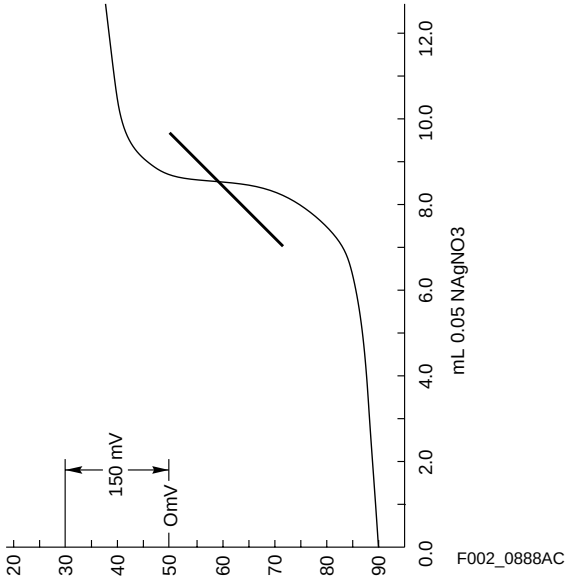
Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SR-29	SR-27	SR-40	—

INTRODUCTION

The ferricyanide and ferrocyanide ions in the bleach sample are precipitated using zinc sulfate and removed by centrifugation or filtration. A portion of the resulting solution is then titrated potentiometrically with silver nitrate solution.

The bleach has no chloride in its formula. However, chloride ions may be present in the water, or as an impurity in other chemicals. Because there is usually only a small amount of chloride present, the individual chloride and bromide "S" shaped curves ("breaks") tend to merge (see Figure 1). To separate them satisfactorily, more chloride is added prior to titration. In the resulting titration record, the first "break" is due to the bromide while the second (if the titration is allowed to continue) is due to the chloride.

Figure 1 S-shaped Curves



This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, the analyst who developed this method performed five (5) replicates on each of the following solutions:

a. A fresh ferricyanide bleach prepared with all components at their respective aim working tank concentrations.

b. A seasoned ferricyanide bleach analyzed, as received, at 17.805 g/L NaBr.

c. The same seasoned solution as in number b, above, analyzed after making an analytically weighed, standard addition of 9.248 g/L NaBr.

Sample	Mean Level (g/L NaBr)	(N)	Repeatability Standard Deviation, $1s_r$ (g/L NaBr)	95 Percent Confidence Estimate
"Fresh" at "Aim" (17.029 g/L NaBr)	16.606	5	0.20	± 0.55
"Seasoned", As Received	17.805	5	0.33	± 0.92
"Seasoned" with Standard Addition	26.725	5	0.56	± 0.36

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independently of the test method.

A statistically significant negative bias for NaBr of (± 2.5%) was found for a fresh tank ferricyanide bleach sample. However, this bias was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery is statistically significant from 100 percent. This was judged not to be practically significant.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The Reproducibility or customer standard deviation (1sc) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Three ferricyanide bleach samples were analyzed by four analysts, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

a. A fresh tank solution prepared at 17.029 g/L NaBr

b. A seasoned ferricyanide bleach sample analyzed, as received, at 30.546 g/L NaBr.

c. The same seasoned solution, as in number b, above, analyzed in the same manner, after making a standard addition of 10.687 g/L NaBr.

Sample	Mean Level (g/L NaBr)	(N)	Reproducibility Standard Deviation, $1S_c$ (g/L NaBr)	95 Percent Confidence Estimate
"Fresh" at "Aim" (17.029 g/L NaBr)	16.881	16	0.087	± 0.18
"Seasoned", as received	30.546	16	0.12	± 0.26
"Seasoned" with standard addition	40.573	16	0.32	± 0.67

APPARATUS

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E288, and E969, unless otherwise stated.

- Centrifuge, with rotor to accommodate 50-mL centrifuge tubes, capable of 1000 rpm.
- 50-mL centrifuge tubes (polypropylene)
- 10-mL pipette
- Volumetric flask, 100-mL
- Beakers, 150- and 250-mL
- ORION double-junction reference electrode 900200 or equivalent with (10% KNO3 outer filling solution)
- Silver billet indicator electrode BECKMAN Model 39261 or equivalent
- Automatic titrator with stirrer, METROHM E536 with an E665 Dosimat (20-mL burette) or equivalent.
- Whatman fluted filter paper - 32 cm (if needed)

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 190 g/L Zinc Sulfate, $ZnSO_4$
- 0.10 N Sodium Chloride, NaCl
- 0.05 N Silver Nitrate, $AgNO_3$, standardized to four significant figures
- Celite filter aid
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Sample Treatment

1. Pipette 5.0 mL of bleach into a 100-mL volumetric flask.
2. Add 25 mL of zinc sulfate. Dilute to volume with reagent water. Stopper and invert the flask 6 to 10 times to mix.

   Note: If unable to centrifuge, delete steps 3-5 and filter the treated sample through a 32-cm WHATMAN 2V fluted filter paper containing 2 g of Celite.
3. Pour nearly equal amounts of the mixture into two 50-mL centrifuge tubes. Do not fill the tubes to more than one inch from the top.
4. Place the tubes in opposite positions and centrifuge at maximum speed for at least two minutes. (Observe the safety precautions for the use of the centrifuge.)
5. Carefully decant the liquid phase from both centrifuge tubes into a 150-mL beaker.
6. Pipette 50.0-mL of the liquid phase or filtrate into a 250-mL beaker containing approximately 100-mL of reagent water.
7. Add 1 mL of 0.10 N sodium chloride to the beaker.

Titration

1. Titrate the sample, through the first break, on an automatic titrator with standardized 0.05 N silver nitrate. Use a silver billet as the indicator electrode and a double junction reference electrode

   Use the following settings for a METROHM titration system:

Horizontal chart span	= 500 mV
Maximum titration speed (min/100% volume)	= 15
Stop (%U)	= OFF
Vertical chart span (mm/100% volume)	= 400
Auto control	= OFF
Titration mode	= mV/pH
Titration “breaks” from	= right to left

2. Determine the end point using the concentric arcs method. (Refer to Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revisions.)

CALCULATIONS

$$\text{NaBr, g/L} = \frac{(\text{mL } AgNO_3)\ (\text{N } AgNO_3)\ (\text{eq. wt. NaBr})\ (1000)}{(\text{mL sample})\ (\text{fraction of treated sample})\ (1000)}$$

where:

mL $AgNO_3$	=	mL $AgNO_3$ consumed
N $AgNO_3$	=	Normality of $AgNO_3$ in meq./mL
eq. wt.	=	102.91 mg/meq NaBr
mL sample	=	mL sample pipetted into the 100-mL volumetric
fraction of treated sample	=	mL of filtrate used / total volume of solution
1000	=	factor to convert meq to eq in the numerator and mL to L in the denominator

Example:

$$\text{NaBr, g/L} = \frac{(8.24 \text{ mL } AgNO_3)\ (0.0494 \text{ N } AgNO_3)\ (102.91)\ (1000)}{(5.0)\ (50/100)\ (1000)}$$

$$= 16.6 \text{ g/L}$$

Potentiometric Determination of Bromide in KUL Bleach

ECN-0005/1
ECP-0005/1

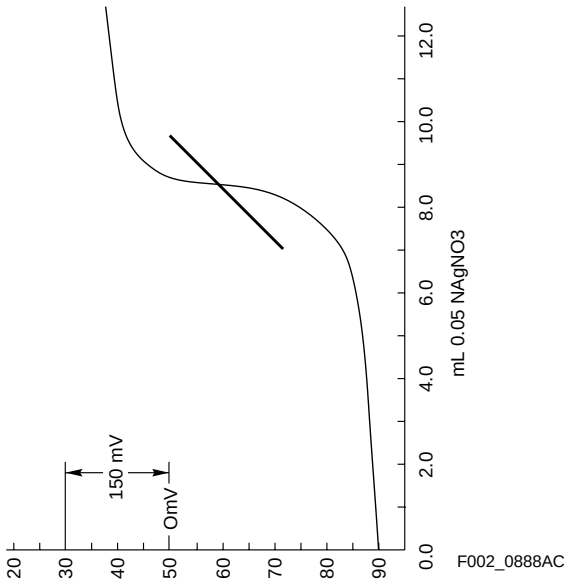
Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SB-34 SB-34R	SB-34 SB-34R	—	—

INTRODUCTION

The bromide ion level in an EASTMAN Color Films, Process ECN-2 or Process ECP-2D, KUL Bleach is determined potentiometrically by a silver nitrate titration. An aliquot of bleach is diluted with reagent water, combined with sulfuric acid, and titrated on an automatic titrator with standardized silver nitrate. A silver sulfide ion-specific electrode (ISE) (indicator) and a double-junction reference electrode are used to detect the end point. It was found that when using a silver bar indicator electrode, a conditioning layer had to be deposited on the electrode surface or a double break was seen. Using the silver sulfide ion-selective electrode eliminated this problem. All calibration data were generated using a silver sulfide ion-selective electrode. See Figure 1 for a representative titration curve.

Use of this method requires handling of potentially hazardous chemicals. Material Safety Data Sheets should be consulted for each chemical before use. These can be obtained from each chemical supplier.

Figure 1 Typical Bromide Titration Curve



PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate

Repeatability Standard Deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent Confidence Estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development:

a. A fresh EASTMAN Color Films, Process ECN-2 or Process ECP-2D, KUL Bleach prepared with all components at their respective working tank "aim" concentrations.

b. A seasoned EASTMAN Color Films, KUL Bleach analyzed as received at:
   - 52.448 g/L NaBr for Process ECN-2
   - 71.734 g/L NaBr for Process ECP-2D

c. The same seasoned solution as in number b, above, analyzed after making an analytically weighed, standard addition of:
   - 15.877 g/L NaBr for Process ECN-2
   - 21.792 g/L NaBr for Process ECP-2D

Samples (Process ECN-2 KUL Bleach)	Mean Level (g/L NaBr)	(N)	Repeatability Standard Deviation, $1S_r$ (g/L NaBr)	95 Percent Confidence Estimate
"Fresh" at "Aim" (44.066 g/L NaBr)	44.553	5	0.16	± 0.44
"Seasoned", As Received	52.448	5	0.12	± 0.33
"Seasoned" with Standard Addition	68.087	5	0.24	± 0.67

Samples (Process ECP-2D KUL Bleach)	Mean Level (g/L NaBr)	(N)	Repeatability Standard Deviation, $1S_r$ (g/L NaBr)	95 Percent Confidence Estimate
"Fresh" at "Aim" (77.764 g/L NaBr)	78.589	5	0.77	± 2.1
"Seasoned", As Received	71.734	5	0.43	± 1.2
"Seasoned" with Standard Addition	92.895	5	0.56	± 1.6

Bias

Bias is a statistically significant deviation from the known level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A statistically significant high bias of 1.2 percent for NaBr was found for a Process ECN-2 fresh tank sample, and 1.1 percent for a Process ECP-2D fresh tank sample. However, the bias was not practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery was not statistically different from 100 percent. Recovery was 98.5 percent for Process ECN-2 and 97.1 percent for Process ECP-2D.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Three EASTMAN Color Films, Process ECN-2 or Process ECP-2D, KUL bleach samples were analyzed by four trained analysts, each using different titration stations, on two different days. Duplicate analyses were performed on each sample, on each of two days. These samples were:

a. A “fresh” tank solution prepared at:
   - 44.096 g/L NaBr for Process ECN-2
   - 77.817 g/L NaBr for Process ECP-2D

b. An EASTMAN Color Films, “seasoned” tank KUL Bleach sample analyzed, in the same manner as the “fresh” sample, as received at:
   - 52.686 g/L NaBr for Process ECN-2
   - 72.226 g/L NaBr for Process ECP-2D

c. The same “seasoned” tank KUL Bleach sample as in number b, above, analyzed after making an analytically weighed, standard addition of:
   - 15.015 g/L of NaBr for Process ECN-2
   - 22.223 g/L of NaBr for Process ECP-2D

Samples (Process ECN-2 KUL Bleach)	Mean Level (g/L NaBr)	(N)	Reproducibility Standard Deviation, $1s_c$ (g/L NaBr)	95 Percent Confidence Estimate
“Fresh” at “Aim” (44.096 g/L NaBr)	44.133	16	0.34	± 0.72
“Seasoned”, as received	52.686	16	0.19	± 0.41
“Seasoned” with standard addition	67.357	16	0.29	± 0.62

Samples (Process ECP-2D KUL Bleach)	Mean Level (g/L NaBr)	(N)	Reproducibility Standard Deviation, $1s_c$ (g/L NaBr)	95 Percent Confidence Estimate
“Fresh” at “Aim” (44.096 g/L NaBr)	77.217	16	0.43	± 0.91
“Seasoned”, as received	78.226	16	0.24	± 0.51
“Seasoned” with standard addition	99.810	16	0.41	± 0.88

APPARATUS

All pipettes and volumetric glassware should be "Class A" as defined by the National Institute of Standards and Technology (NIST).

- 10.0-mL pipette
- 100-mL volumetric flask
- 250-mL beaker
- ORION double-junction reference electrode 900200 or equivalent:
- Filling Solutions:
  - ORION No. 900002 (inner chamber)
  - ORION No. 900003 (outer chamber)
- Silver Sulfide ion-selective electrode, ORION Model 941600 or equivalent
- METROHM Potentiograph, Model E536 automatic titrator with stirrer and 20-mL burette or equivalent

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise stated.

- Sulfuric acid, (7N) H_2SO_4
- Silver nitrate, (0.05 N) $AgNO_3$, standardized to four places past the decimal point.
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Sample Treatment

1. Pipette 10.0 mL of bleach sample into a 100-mL volumetric flask containing approximately 50 mL reagent water.
2. Bring to volume with reagent water and invert the flask 6 to 10 times to mix.
3. Pipette 10.0 mL from the 100-mL volumetric flask into a 250-mL beaker containing 100 mL of reagent water and a magnetic stir bar.
4. Add 10 mL of 7N sulfuric acid. Place the beaker on a magnetic stirrer. Turn on the stirrer.

Titration

1. Titrate the sample on an automatic titrator with standardized 0.05 N silver nitrate using a silver sulfide ion-selective electrode as the indicator and a double-junction reference electrode.

   Note: Place the titrant delivery tip so the titrant flows past the reference electrode before the silver sulfide ion-selective electrode.

2. Use the following settings for a METROHM E536 Potentiograph titration system:

Horizontal chart span	750 mV
Maximum titration speed	15 min/100% volume
Automatic titration stop (%U)	OFF
Vertical chart span	400 mm/100% volume
Automatic titration speed	OFF
Titration mode	mV/pH

3. Determine the end point using the concentric arcs method. (Refer to Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revisions.)

CALCULATIONS

$$\text{NaBr, g/L} = \frac{(\text{mL } AgNO_3) \times (\text{N } AgNO_3) \times (\text{eq. wt. NaBr}) \times (1000)}{(\text{mL sample}) \times (1000)}$$

where:

mL $AgNO_3$ = mL $AgNO_3$ consumed

N $AgNO_3$ = Normality of $AgNO_3$ in meq./mL used for titration

eq. wt. NaBr = 102.91 mg/meq

mL sample = 1.0 mL (effective sample size)

1000 = factor to convert meq to eq in the numerator and mL to L in the denominator

$$\text{NaBr, g/L} = \frac{(\text{mL } AgNO_3) \times (\text{N } AgNO_3) \times (102.91) \times (1000)}{(1.0) \times (1000)}$$

Example:

$$\text{NaBr, g/L} = \frac{(15.32 \text{ mL } AgNO_3)\ (0.0495 \text{ N } AgNO_3)\ (102.91)\ (1000)}{(1.0 \text{ mL}) \times (1000)}$$

NaBr, g/L = 78.7 g/L

Potentiometric Determination of Ammonium Bromide in UL Bleach

ECN-0022/1

INTRODUCTION

The ammonium bromide (NH_4Br) level in Process ECN-2 "UL" Bleach is determined potentiometrically by a silver nitrate titration. An aliquot of bleach sample is diluted with reagent water. An aliquot of the diluted sample is then combined with sulfuric acid and reagent water and it is then titrated on an automatic titrator with standardized silver nitrate. A silver sulfide ion-selective indicator electrode (ISE) and a double-junction reference electrode are used to determine the end point. It was found that when using a silver bar indicator electrode, a conditioning layer had to be deposited on the electrode surface or a double inflection was seen. Using the silver sulfide ion-selective electrode eliminated this problem. All precision and bias data were generated using a silver sulfide ion-selective electrode.

Use of this method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed three (3) replicates on each of the following solutions during methods development.

1. A fresh "UL" bleach was prepared with all components at their respective "working tank" aim concentrations (25.4255 g/L NH_4Br).
2. A seasoned "UL" bleach analyzed potentiometrically as received, at 40.171 g/L NH_4Br).

NH_4Br				
Sample	**Mean (g/L NH_4Br)**	**N**	**Repeatability Standard Deviation, $1s_r$ (g/L NH_4Br)**	**95 Percent Confidence Estimate (g/L NH_4Br)**
Fresh	25.393	3	0.042	± 0.181
Seasoned as received	40.171	3	0.083	± 0.357

Bias

Bias is a statistically significant deviation of the mean from the known ammonium bromide level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method.

A bias of –0.0325 g/L NH_4Br was found not to be statistically significant fir the Process ECN-2 "fresh" tank bleach sample.

REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ and 95 Percent Confidence Estimate

Reproducibility, or customer standard deviation, ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Three Process ECN-2 "UL" bleach samples were analyzed by four analysts, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. Three fresh "UL" bleach samples were prepared with all components at their respective working tank aim concentrations.
2. A seasoned "UL" bleach sample was analyzed potentiometrically, as received, at 39.9 g/L NH_4Br.
3. The same seasoned solution, as in number 2, above, was reanalyzed after, after making a standard addition of 8.0 g/L NH_4Br.

NH_4Br				
Sample	**N**	**Mean**	**Reproducibility Standard Deviation, $1s_c$ (g/L NH_4Br)**	**95 Percent Confidence Estimate (g/L NH_4Br)**
"Fresh" at 25 g/L NH_4Br	16	—	0.20	± 0.43
"Fresh" at 50 g/L NH_4Br	16	—	0.30	± 0.63
"Fresh" at 75 g/L NH_4Br	16	—	0.46	± 0.98
"Seasoned" As Received	16	39.9 g/L	0.32	± 0.69
"Seasoned" with Standard Addition	16	47.8 g/L	0.50	± 1.07

Bias

Bias is a statistically significant deviation of the mean from the known ammonium bromide level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample since the component concentration level was not determined independently of the test method.

A statistically significant bias was found at all levels for the Process ECN-2 "fresh" tank bleach samples (–0.184 g/L for the 25 g/L sample, –0.326 g/L for the 50 g/L sample, and –0.415 g/L for the 75 g/L sample. However, the bias was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

The recovery of the standard addition sample was 98.8 percent and found to not be statistically different from 100 percent at the 95 percent confidence level.

APPARATUS

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- METROHM 536 Titrator or equivalent with a DOSIMAT and a 20-mL burette
- Indicator electrode, Silver/Sulfide Ion Selective, Orion No. 941600 or equivalent
- Double junction reference electrode, ORION Model 900200 or equivalent
- Filling solutions:
  - ORION No. 900002 (inner chamber)
  - ORION No. 900003 (outer chamber)
- 2 Pipettes, (10.0-mL)
- Tip-up pipette, (10-mL)
- Volumetric flask, (100-mL)
- Beaker, (250-mL)

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 7 N Sulfuric Acid, H_2SO_4
- 0.05 N Silver Nitrate, $AgNO_3$ (standardized to 4 decimal places)
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

A. Sample Treatment

1. Pipet 10.0 mL of sample into a l00-mL volumetric flask containing approximately 50 mL of reagent water.
2. Bring to volume with reagent water and invert the flask 6 to 9 times to mix.
3. Pipet 10.0 mL from the l00-mL volumetric flask into a 250-mL beaker containing 100 mL of reagent water and a magnetic stir bar.
4. Add 10 mL of 7.0 N sulfuric acid from a tip-up pipet. Place the beaker on a magnetic stirrer. Turn on the stirrer.

B. Titration

1. Set the following parameters on the METROHM Titrator:

Titration mode	mV/pH
Horizontal chart span	750 mV
Autocontrol	OFF
Maximum titration speed	15 min/100% volume
Vertical chart span	400 mm/100% volume
Automatic titration stop (U%)	OFF
Indicator electrode	Silver/Sulfide Ion Selective, Orion Model 941600 or equivalent
Reference electrode	Double-Junction, Orion Model 900200 or equivalent

2. Place the 250-mL beaker on the METROHM titrator stand and add a magnetic stir bar. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the silver/silver electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex. Titrate the solution with standardized 0.05 N silver nitrate through the inflection.
3. Determine the end point using concentric arcs. Refer to Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revisions. If a microprocessor-controlled titrator is used, the endpoint will be picked automatically.

CALCULATIONS

For NH_4Br;

$$g/L\ NH_4Br = \frac{(mL\ AgNO_3)\ (N\ AgNO_3)\ (eq\ wt\ NH_4Br)\ (10)\ (1000)}{(mL\ sample)(1000)}$$

Where

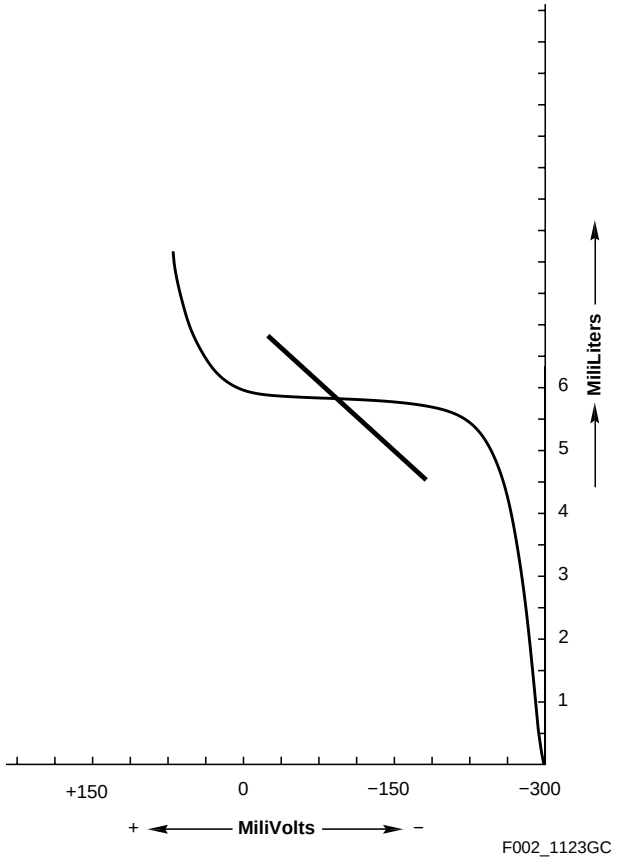
- $mL\ AgNO_3$ = volume of $AgNO_3$ in millilitres required to reach the equivalence point
- N = normality of the $AgNO_3$ in milliequivalents per millilitre (meq/mL)
- eq wt = equivalent weight of ammonium bromide in milligrams per milliequivalent (97.9 mg/meq)
- 10 = dilution factor for sample
- mL sample = millilitres of sample pipetted in step 1 of part A of procedure
- 1000 = factor to convert meq to eq in the numerator and mL to L in the denominator

If mL 0.0492 N $AgNO_3$ = 10.34 mLs:

$$g/L\ NH_4Br = \frac{(10.34)\ (0.0492)\ (97.9)\ (10)\ (1000)}{(10.00)\ (1000)}$$

$$= 49.8\ g/L\ NH_4Br$$

Figure 2 S-shaped Curves



Titrimetric Determination of Buffer Capacity of Accelerator Solution

ECN-2-755
ECR-755A

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SR-31	—	AB-3	AB-3

INTRODUCTION

Each process accelerator solution is buffered to a different pH. Buffer curves indicate that the optimum pH range for measuring buffering capacity is between pH 3.50 and pH 6.00. The buffer capacity is measured in terms of the volume of base required to change the pH from 3.5 to 6.0, and is expressed in terms of glacial acetic acid, mL/L, or sodium acetate, g/L.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

Process ECN-2—Four standard mixes were prepared containing 0.0, 10.0, 20.0, and 30.0 mL/L glacial acetic acid. They were analyzed in duplicate by three analysts in one laboratory The 95 percent confidence limits for a single determination are ± 0.20 mL/L glacial acetic acid.

Process VNF-1/RVNP—Four standard mixes were prepared containing 0.0, 6.89, 10.34, and 13.79 mL/L glacial acetic acid. They were analyzed in duplicate by three analysts in two laboratories. The 95 percent confidence limits for a single determination are ± 0.07 mL/L glacial acetic acid.

SPECIAL APPARATUS

- pH Meter
- Reference Electrode, Ceramic Junction, Calomel, Corning No. 476002, Beckman No. 38423 or equivalent (Filled with 3.5 M potassium chloride solution)
- Indicator Electrode, glass (pH), Rugged Bulb, Corning No. 476024 or equivalent
- 25 and 50-mL Burets

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 1 N Sodium Hydroxide, NaOH (standardized to 4 decimal places)
- 1.0 N Sulfuric Acid, H_2SO_4

PROCEDURE

Meter Preparation

1. Follow Method ULM-191-2, *pH Measurement of Photographic Processing Solutions*, to prepare the pH meter for making measurements below pH 9.

Titration

1. Pipet (wipe the pipet before leveling) the sample size below into a beaker containing a magnetic stirrer.

Process	Beaker Size	Sample Size
ECN-2, AB-2	200 mL	50.0 mL
VNF-1/RVNP, AB-3	400 mL	100.0 mL

2. Immerse the electrode assembly in the sample solution and start stirring.
3. Using 1.0 N sulfuric acid, adjust the pH of the sample to pH 3.5 (this volume does not have to be measured).
4. Using the buret size indicated below, titrate the sample to pH 6.00 with standardized 1 N sodium hydroxide. Record the volume of titrant used.

Process	Buret
ECN-2, AB-2	50 mL
VNF-1/RVNP, AB-3	25 mL

5. Remove the sample and rinse the electrode assembly with distilled water. If rinsing does not completely remove sample deposits, wipe the assembly with a cleansing tissue and rerinse. Place the electrode assembly in pH 4.01 potassium acid phthalate buffer for storage.

Calculations

ECN-2, AB-2

Buffer Capacity, mL/L =

1.22(N NaOH)(mL NaOH) – 0.52

VNF-1/RVNP, AB-3

Buffer Capacity, mL/L =

0.65(N NaOH)(mL NaOH) – 1.79

Buffer Capacity, g/L* =

0.94(N NaOH)(mL NaOH) – 2.6

* As sodium acetate.

Note: One gram of sodium acetate is equivalent to 0.689 mL of glacial acetic acid.

Buffering Capacity Determination of EASTMAN Color Films, Process ECN-2 Persulfate Bleach

ECN-0019-01

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SR-31 SR-31R	—	—	—

INTRODUCTION

The buffering capacity of an Eastman Color Films, Process ECN-2 persulfate bleach is determined by adjusting a 100 mL aliquot of sample to pH 1.600 (± 0.005) using 3N hydrochloric acid and then manually titrating to pH 2.800 (± 0.005) using standardized 1.0N sodium hydroxide solution. The volume of sodium hydroxide used is correlated to the amount of 85 percent phosphoric acid in the sample (buffering capacity) by a linear regression equation.

Repeatability and reproducibility studies were performed for both "fresh and "seasoned" solutions. The linear regression equations generated from individual "seasoned" solutions were different from each other and significantly different from those generated from "fresh" solutions, due to the differing amounts of seasoning products contributing to the buffering capacity. For this reason and since it is most representative of data generated by multiple analysts, the linear regression equation generated from the reproducibility study of a "fresh" persulfate bleach solution was chosen for inclusion in this method.

Use of this method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation ($1s_r$) & 95 Percent Confidence Estimate (not including bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions:

1. A "fresh" persulfate bleach prepared with components at their respective aim "working tank" concentrations, minus the phosphoric acid (85 percent H_3PO_4) component.
2. The same "fresh" solution as in number 1, above, reanalyzed after making standard additions of 2.0 mL/L, 3.0 mL/L and 5.0 mL/L 85 percent H_3PO_4.
3. A "seasoned" persulfate bleach analyzed, as received.
4. The same "seasoned" solution as in number 3, above, reanalyzed after making standard additions of 2.0 mL/L, 3.0 mL/L and 5.0 mL/L 85 percent H_3PO_4.

"Fresh" tank solutions

Based on 20 determinations by a single analyst, the Standard Error Estimate (Sy.x) for an individual determination of a "fresh" ECN-2 persulfate bleach is 0.11 mL/L 85 percent phosphoric acid (H_3PO_4), and the 95 percent confidence estimate at the midpoint of the line is ± 0.23 mL/L 85 percent phosphoric acid (H_3PO_4).

"Seasoned" tank solutions

Based on 20 determinations by a single analyst, the Standard Error Estimate (Sy.x) for an individual determination of a "seasoned" ECN-2 persulfate bleach is 0.18 mL/L 85 percent phosphoric acid (H_3PO_4), and the 95 percent confidence estimate at the midpoint of the line is ± 0.37 mL/L 85 percent phosphoric acid (H_3PO_4).

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed eight persulfate bleach samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were prepared identically to the solutions described in the repeatability section.

"Fresh" tank solutions

Based on 62 determinations by four analysts, the Standard Error Estimate (Sy.x) for an individual determination of a "fresh" ECN-2 persulfate bleach is 0.15 mL/L 85 percent phosphoric acid (H_3PO_4), and the 95 percent confidence estimate at the midpoint of the line is ± 0.29 mL/L 85 percent phosphoric acid (H_3PO_4).

Based on chemical theory and measurement of a "fresh" tank solution prepared at aim concentrations, this method is believed to provide an accurate measure of the buffering capacity of an ECN-2 persulfate bleach.

"Seasoned" tank solutions

Based on 63 determinations by four analysts, the Standard Error Estimate (Sy.x) for an individual determination of a "seasoned" ECN-2 persulfate bleach is 0.25 mL/L 85 percent phosphoric acid (H_3PO_4), and the 95 percent confidence estimate at the midpoint of the line is ± 0.49 mL/L 85 percent phosphoric acid (H_3PO_4).

Based on chemical theory and measurement of a "seasoned" tank solution, this method is believed to provide an accurate measure of the buffering capacity of ECN-2 persulfate bleach.

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- 100-mL pipette
- Beakers, 250-mL
- Dual channel pH meter, e.g. ORION EA 940 or equivalent.
- pH electrode, e.g. Corning Rugged Bulb pH electrode 476024 or equivalent
- Reference electrode, e.g. Corning 476002, reference, ceramic junction, calomel or equivalent

REAGENTS

Use ACS Reagent Grade reagents unless otherwise specified.

- pH 4 phthalate calibrating buffer (prepare from reagent grade chemicals, or purchase from vendor)
- pH 7 equimolar phosphate calibrating buffer (prepare from reagent grade chemicals, or purchase from vendor)
- pH 3.63 tartrate low pH control buffer (prepare from reagent grade chemicals, or purchase from vendor)
- 3.0 N Hydrochloric Acid (HCl)
- 1.00 N (± 0.02 N) Sodium Hydroxide (NaOH), standardized to 4 decimal places
- Water, Type I Reagent – This method was developed, and the resulting statistical data were obtained using reagent water equivalent to purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Preparation of the meter

1. Follow method *ULM-191-2* (or any subsequent pH method) for making pH measurements below pH 7.
   a. Adjust the temperature of the buffers.
   b. Calibrate the meter with the pH 7 and pH 4 buffers.
   c. Check the electrode calibration with pH 3.63 tartrate low control buffer.

Titration of Sample

1. Pipette (wipe the pipette before leveling) 100.0 mL of sample into a 250 mL beaker containing a magnetic stirrer.
2. Immerse the electrode assembly in the sample solution and stir without splashing.
3. Adjust the pH of the sample to approximately pH 1.5, using 3.0 N hydrochloric acid.
4. Add, from a pipette or burette, 1.000 N sodium hydroxide to attain a pH of 1.60 (1.595-1.605). This volume does not have to be measured.

Caution

Stir the solution rapidly without splashing. Do not rinse the sides of the beaker with reagent water because dilution will affect the results.

5. Using a 25-mL burette, titrate the sample to pH 2.80 (2.795-2.805) with 1.000 N sodium hydroxide. Record the volume of titrant used.

   Note: If the titration exceeds pH 2.8, discard the sample and repeat the analysis.

6. Remove the sample and rinse the electrode assembly with reagent water. If rinsing does not completely remove sample deposits, wipe the assembly with a cleansing tissue and rerinse. Replace the assembly in pH 7 buffer for storage.

Calculations

Buffering Capacity (mL/L 85% H_3PO_4) = m(x) + b

Where:

m = Slope of the regression line [(mL/L 85% H_3PO_4) / mL 1.00 N NaOH]

x = Volume of titrant consumed (mL 1.00 N NaOH)

b = Intercept of regression line (mL/L 85% H_3PO_4)

Example

Buffering Capacity = 1.491 (7.47) – 8.55

= 2.59 mL/L 85% H_3PO_4

Titrimetric Determination of EASTMAN Color Developing Agent, CD-3, in Process ECN-2 Developer with Sulfato Cerate

ECN-0003/1

Process	ECN-2	ECP-2B	VNF-1/LC	RVNP
Formulas	SD-49	—	—	—

INTRODUCTION

This method describes an analytical procedure for measuring EASTMAN Color Developing Agent, CD-3, in Process ECN-2 Developer. CD-3 in the aqueous developer sample is extracted with an organic solvent (butyl acetate). An inorganic salt (NaCI) and a surfactant (polystyrene sulfonate) are added to minimize the formation of emulsion layers during the extraction of CD-3. In seasoned samples, an emulsion layer is usually present. If the layer does not transfer to the sulfuric acid, no significant error is introduced. The CD-3 in the solvent layer is then back-extracted with sulfuric acid. This acid layer can then be titrated with sulfato cerate, using either an automatic titrator to record a potentiometric end point or manually titrated using ferroin indicator, to detect the end point visually.

The potentiometric titration is recommended over the visual end point titration. However, for those unable to use instrumentation, the manual titrimetric technique, using the visual ferroin indicator, is included. Judging end points with a visual color change, especially if the samples are highly seasoned and highly colored, can differ from person to person. The potentiometric method overcomes this problem because the end point is detected potentiometrically and displayed graphically by the titrator.

For the potentiometric measurement, a METROHM Potentiograph, Model E536 or equivalent should be used. The potentiometric titration requires a platinum indicator electrode and a double-junction reference electrode.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development (this procedure was performed by both potentiometric and visual end point detection):

a. A “fresh” EASTMAN Color Films, Process ECN-2 developer prepared with all components at their respective working tank aim concentrations (4.0023 g/L CD-3).

b. A “seasoned” EASTMAN Color Films, Process ECN-2 developer analyzed as received at 2.755 g/L CD-3 (potentiometrically) and 2.250 g/L CD-3 (visually).

c. The same “seasoned” solution as in number b, above, reanalyzed after making an analytically weighed, standard addition of 1.354 g/L CD-3 for the potentiometric study and 1.117 g/L CD-3 for the visual study.

Reproducibility (Customer Standard Deviation, $1s_c$)

Three EASTMAN Color Films, Process ECN-2 developer samples were analyzed by four trained analysts, each using different titration stations, on two different days. Each analyst analyzed each sample by both the potentiometric and the visual end point technique. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

a. A “fresh” tank solution prepared at 4.008 g/L CD-3.

b. An EASTMAN Color Films, Process ECN-2 “seasoned” tank developer sample analyzed, as received, in the same manner as the “fresh” developer.

c. The same (as in #b, above) EASTMAN Color Films, Process ECN-2 “seasoned” tank developer sample reanalyzed in the same manner as the “fresh” developer, after a standard addition of CD-3 was made. The “seasoned” sample of EASTMAN Color Films, Process ECN-2 developer, analyzed to be 3.7067 g/L CD-3 (potentiometrically) and 3.7270 g/L CD-3 (visually). A standard addition of 1.130 g/L CD-3 was made to that “seasoned” sample for the potentiometric and visual calibration study.

POTENTIOMETRIC TITRATION STATISTICS

Repeatability Standard Deviation, $1s_r$

Repeatability Standard Deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

CD-3 (Potentiometrically)				
Samples (Process ECN-2 Dev)	**Mean Level (g/L CD-3)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (g/L CD-3)**	**95 Percent Confidence Estimate (g/L CD-3)**
"Fresh" at "Aim" (4.0023 g/L CD-3)	3.866	5	0.028	± 0.078
"Seasoned", As Received	2.755	5	0.029	± 0.080
"Seasoned" with Standard Addition	4.041	4	0.016	± 0.051

Bias

Bias is a statistically significant deviation from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A statistically significant low bias (of –3.4 percent) for CD-2 was found for a Process ECN-2 "fresh" tank developer sample. However, the bias for was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 94.9 percent is statistically different from 100 percent. However, this was judged not to be practically significant.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

CD-3 (Potentiometrically)				
Samples (Process ECN-2 Dev)	**Mean Level (g/L CD-3)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (g/L CD-3)**	**95 Percent Confidence Estimate (g/L CD-3)**
"Fresh" at "Aim" (4.008 g/L CD-3)	3.8133	16	0.040	± 0.086
"Seasoned", As Received	3.707	16	0.033	± 0.069
"Seasoned" with Standard Addition	4.769	16	0.036	± 0.076

Bias

Bias is a statistically significant deviation from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A statistically significant low bias (of –4.9 percent) for CD-2 was found for a Process ECN-2 "fresh" tank developer sample. However, the bias for was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 94.1 percent is statistically different from 100 percent. However, this was judged not to be practically significant.

VISUAL TITRATION STATISTICS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate

Repeatability Standard Deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent Confidence Estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

CD-3 (Visually)				
Samples (Process ECN-2 Dev)	**Mean Level (g/L CD-3)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (g/L CD-3)**	**95 Percent Confidence Estimate (g/L CD-3)**
"Fresh" at "Aim" (4.008 g/L CD-3)	3.879	5	0.045	± 0.012
"Seasoned", As Received	2.250	5	0.020	± 0.056
"Seasoned" with Standard Addition	3.206	5	0.021	± 0.058

Bias

Bias is a statistically significant deviation from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A statistically significant low bias for CD-2 (of –3.1 percent) was found for a fresh tank Process ECN-2 developer sample. However, the bias for was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 85.6 percent is statistically different from 100 percent. However, this was judged not to be practically significant.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

CD-3 (Visually)				
Samples (Process ECN-2 Dev)	**Mean Level (g/L CD-3)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (g/L CD-3)**	**95 Percent Confidence Estimate (g/L CD-3)**
"Fresh" at "Aim" (4.008 g/L CD-3)	3.833	16	0.031	± 0.066
"Seasoned", As Received	3.727	16	0.039	± 0.084
"Seasoned" with Standard Addition	4.787	16	0.032	± 0.067

Bias

Bias is a statistically significant deviation from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A statistically significant low bias for CD-2 (of –4.4 percent) was found for a fresh tank Process ECN-2 developer sample. However, the bias for was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 93.8 percent is statistically different from 100 percent. However, this was judged not to be practically significant.

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- Pipette, (50-mL)
- Separatory funnels, (250-mL)
- Beakers, (250-mL)
- Exhaust hood
- METROHM 536 Titrator or equivalent with a DOSIMAT and a 20-mL burette
- Platinum indicator electrode, BECKMAN, Model 39273 or equivalent
- Double junction reference electrode, ORION Model 900200 or equivalent
  Filling solutions:
  - ORION No. 900002 (inner chamber)
  - ORION No. 900003 (outer chamber)
- Burette, (25-mL) / (visual method only)
- Magnetic stirrer / (visual method only)

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- Polystyrene Sulfonate, (0.1%)
- Butyl Acetate
- Ferroin Indicator
- Sulfuric Acid, H_2SO_4, (1.0 N)
- Sulfato Cerate, $(NH_4)_2Ce(NO_3)_6$, (0.05N) standardized to 4 places past the decimal point
- Sodium Chloride, NaCl

PROCEDURE

Extraction of the Developing Agent, CD-3, with Butyl Acetate

1. Pipette 50.0 mL (potentiometric titration) or 50.0 mL (visual titration) of sample into a 250-mL separatory funnel (No. 1).
2. Add 5.0 g NaCl to the separatory funnel.
3. Add 2 mL of 0.1% polystyrene sulfonate solution. Stopper the funnel and mix, by gently swirling or shaking, until all the salt completely dissolves.
4. Add 50 mL of butyl acetate. Swirl the funnel for 30 seconds. Stopper the funnel, invert and vent through the stopcock. Shake separatory funnel No. 1, horizontally, for a few seconds; invert and vent the funnel through the stopcock. Continue to shake vigorously for 30 seconds. The funnel should be vented at least 2 times.
5. Allow the layers to separate. Gently swirling the funnel will aid breaking up any emulsion at the aqueous-nonaqueous interface.
6. After separation of the layers occurs, transfer the lower (aqueous) layer, as completely as possible, including any emulsion that fails to separate, into another 250-mL separatory funnel (No. 2).
7. Swirl separatory funnel No. 1. Drain any additional lower (aqueous) layer that separates into separatory funnel No. 2. Save the top (butyl acetate) layer in separatory funnel No. 1.
8. Add 50 mL of butyl acetate to separatory funnel No. 2. Swirl the funnel for 30 seconds. Stopper the funnel; invert and vent through the stopcock. Shake the funnel horizontally for a few seconds; invert and vent through the stopcock. Continue to shake the funnel vigorously for 30 seconds, venting at least 2 times.
9. After the layers separate, discard the lower (aqueous) layer as completely as possible. Swirl the funnel and discard any additional aqueous layer that separates, taking care not to lose any of the butyl acetate layer. Discard any emulsion layer that fails to separate.

   Note: Additional separation time may be needed for highly seasoned samples.
10. Transfer the contents of separatory funnel No. 2 (butyl acetate layer) into funnel No. 1 (which contains the first butyl acetate layer).

Back-Extraction of the Developing Agent

1. Add 100 mL of 1.0 N sulfuric acid to separatory funnel No. 2 and swirl, rinsing the inside walls of the funnel. Save the funnel contents for step 3.
2. Gently swirl separatory funnel No. 1 and discard, as completely as possible, any lower (aqueous) layer that separates, taking care not to lose any of the butyl acetate layer.
3. Transfer the contents of separatory funnel No. 2 into funnel No. 1.
4. Swirl the funnel for 30 seconds. Stopper the funnel; invert and vent through the stopcock. Shake the separatory funnel horizontally for a few seconds; invert and vent through the stopcock. Continue to shake vigorously for 30 seconds, venting 2 times.
5. Allow enough time for complete separation of the phases.

   Note: It may take longer for complete separation of the phases in highly seasoned samples.
6. Transfer the lower (acid) layer from separatory funnel No. 1 to a 250-mL beaker without losing any of the top layer.
7. Swirl separatory funnel No. 1 and transfer any additional lower (acid) layer that separates, as completely as possible, into the beaker.

Titration of the Developing Agent with Sulfato Cerate

Note: The end-point of the titration step can be determined either potentiometrically (Step 1 below) or visually (Step 2 below).

1. Potentiometric Titration
   a. Add 5 drops of ferroin indicator and a magnetic stir bar to the 250-mL beaker (from steps 6 & 7 of the *Back-Extraction of the Developing Agent* procedure).

   Note: Do not omit the ferroin, it aids the definition of the end point.

   b. Set the following parameters, if using a METROHM 536 titrator:

Titration mode	mV/pH
Horizontal chart span	750 mV
Autocontrol	OFF
Maximum titration speed	15 min/100% volume
Vertical chart span	400 mm/100% volume
Automatic titration stop (U%)	OFF
Indicator electrode	Platinum, BECKMAN, Model 39373 or equivalent
Reference electrode	Double-junction ORION, Model 900200 or equivalent

   c. Place the 250-mL beaker on the METROHM titrator stand and add a magnetic stir bar. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex. Titrate the solution with standardized 0.05 N sulfato cerate through the inflection.

   d. Determine the end point using concentric arcs. (Refer to Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revisions.) Record the end point as **mL A**.

   e. Add 100 mL of 1.0 N sulfuric acid to a second 250-mL beaker containing a magnetic stir bar. Add 5 drops of ferroin indicator.

   f. Place the second beaker on the METROHM titrator stand and titrate through the inflection point with standardized 0.05 N sulfate cerate. Record any measurable end point as **mL B**. (This is the blank. This determination needs to be performed only once, if a series of analyses will be performed.)

2. Visual Titration:
   a. Place the 250-mL beaker (from steps 6 & 7 of the *Back-Extraction of the Developing Agent* procedure) on a magnetic stirrer after adding a magnetic stir bar. Add 5 drops of ferroin indicator. Turn the magnetic stirrer on and adjust the setting so that the solution stirs vigorously but without creating a vortex or splashing.
   b. Using a 25-mL burette, titrate the solution with standardized 0.05 N sulfato cerate to the first green color that persists for 15 seconds. Record the end point as **mL A**.
   c. Add 100 mL of 1.0 N sulfuric acid to a second 250-mL beaker containing a magnetic stir bar. Add 5 drops of ferroin indicator and place the beaker on a magnetic stirrer. Turn the magnetic stirrer on and adjust the setting so that the solution stirs vigorously without creating a vortex or splashing.
   d. Titrate the solution to the first light blue color that persists for 30 seconds. Record the end point as **mL B**. (This is the blank. This determination needs to be determined only once, if a series of analyses will be performed.)

Calculations

$$\text{mL A - mL B} = \text{mL 0.05 N sulfato cerate, consumed by the sample}$$

$$\text{g/L CD-3} = \frac{\text{(mL sulfate cerate)(N sulfate cerate)(eq. wt. CD-3)(1000)}}{\text{(mL sample)(1000)}}$$

$$\text{g/L CD-3} = \frac{\text{(mL sulfato cerate)(N sulfato cerate)(218.26)(1000)}}{\text{(50 mL)(1000)}}$$

Where:

eq. wt. CD-3 (218.26) = equivalent weight of CD-3 sesquisulfate monohydrate

Potentiometric Determination of Ferricyanide in Process ECN-2 Ferricyanide Bleach
ECN-00021/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SR-29 SR-29R	—	—	—

INTRODUCTION

Excess iodide ions and a zinc reagent are added to the bleach sample. The ferricyanide reacts with the iodide to produce an equivalent amount of iodine. The iodine is titrated with standard sodium thiosulfate, using either an automatic titrator to record a potentiometric end point, or it is titrated manually using starch indicator to detect the end point visually. The potentiometric titration is recommended over the visual end point titration. However, for those unable to use an automatic titrator, the visual titrimetric technique is included. Judging end points with a visual color change can differ from person to person. The potentiometric method overcomes this problem because the end point is detected potentiometrically and displayed graphically by the titrator.

For the potentiometric measurement, a Metrohm Potentiograph, Model E536 or equivalent should be used. The potentiometric titration requires a platinum indicator electrode and a double-junction reference electrode.

The reaction of ferricyanide and iodide is quantitative as long as zinc ions are present in excess. Any ferrocyanide present in the bleach, as well as the ferrocyanide produced by the reduction of ferricyanide, is precipitated as zinc ferrocyanide. See reactions 1-3, below.

Persulfate ions and some other oxidizing agents will also oxidize iodide. Thus, if present, they will be measured as ferricyanide by this method.

$$2[Fe(CN)_6]^{3-} + 2I^- \rightarrow 2[Fe(CN)_6]^{4-} + I_2 \qquad \text{(reaction 1)}$$

$$2[Fe(CN)_6]^{4-} + 2K^+ + 3Zn^{2+} \rightarrow K_2Zn_3[Fe(CN)_6]_2 \qquad \text{(reaction 2)}$$

$$2\ S_2O_3^{2-} + I_2 \rightarrow (S_4O_6)^{2-} + 2I^- \qquad \text{(reaction 3)}$$

Use of this method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Note: Separate statistics presented for potentiometric and visual titration methods.

Potentiometric Titrations

Repeatability Standard Deviation ($1s_r$) & 95 Percent Confidence Estimate (not including bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development (this procedure was performed by both potentiometric and visual end point detection):

1. A "fresh" ferricyanide bleach prepared with all components at their respective "working tank" aim concentrations.
2. A "seasoned" ferricyanide bleach analyzed potentiometrically as received at 46.202 g/L.
3. The same "seasoned" solution as in number 2, above, reanalyzed after making an analytically weighed, standard addition of 13.901 g/L $K_3Fe(CN)_6$.

$K_3Fe(CN)_6$ (Potentiometrically)				
Sample	**Mean (g/L $K_3Fe(CN)_6$)**	**N**	**Repeatability Standard Deviation, $1S_r$ (g/L $K_3Fe(CN)_6$)**	**95 Percent Confidence Estimate (g/L $K_3Fe(CN)_6$)**
"Fresh" at "Aim" (40.002 g/L $K_3Fe(CN)_6$)	39.878	6	0.032	± 0.08
"Seasoned", As Received	46.202	5	0.059	± 0.16
"Seasoned" with Standard Addition	59.820	5	0.057	± 0.16

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independently of the test method.

A statistically significant low bias of (-0.124 g/L) for $K_3Fe(CN)_6$ was found for a Process ECN-2 "fresh" tank developer sample. However, the bias was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 98.0 percent for Process ECN-2 was not statistically different from 100 percent.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Three ferricyanide bleach samples were analyzed by four analysts, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A "fresh" tank solution prepared at 40.000 g/L $K_3Fe(CN)_6$.
2. A "seasoned" ferricyanide bleach sample analyzed at 46.185 g/L $K_3Fe(CN)_6$.
3. The same "seasoned" solution, as in number 2, above, analyzed in the same manner, after making a standard addition of 13.901 g/L $K_3Fe(CN)_6$.

$K_3Fe(CN)_6$ (Potentiometrically)				
Sample	**Mean (g/L $K_3Fe(CN)_6$)**	**N**	**Reproducibility Standard Deviation, $1S_c$ (g/L $K_3Fe(CN)_6$)**	**95 Percent Confidence Estimate (g/L $K_3Fe(CN)_6$)**
"Fresh" at "Aim" (40.000 g/L $K_3Fe(CN)_6$)	40.400	16	0.090	± 0.19
"Seasoned", As Received	46.185	16	0.131	± 0.28
"Seasoned" with Standard Addition	59.795	16	0.188	± 0.40

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independently of the test method.

A statistically significant high bias of (+0.400 g/L) for $K_3Fe(CN)_6$ was found for a Process ECN-2 "fresh" tank developer sample. However, the bias was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. Statistically, the recovery of 97.9 percent for Process ECN-2 was significantly different from 100 percent, but was judged not to be practically significant.

Visual Titration

Repeatability Standard Deviation ($1s_r$) & 95 Percent Confidence Estimate (not including bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development (this procedure was performed by both potentiometric and visual end point detection):

1. A "fresh" ferricyanide bleach prepared with all components at their respective "working tank" aim concentrations.
2. A "seasoned" ferricyanide bleach analyzed as received at 46.350 g/L.
3. The same "seasoned" solution as in number 2, above, reanalyzed after making an analytically weighed, standard addition of 13.901 g/L $K_3Fe(CN)_6$.

$K_3Fe(CN)_6$ (Visually)				
Sample (ECN-2)	**Mean (g/L $K_3Fe(CN)_6$)**	**N**	**Repeatability Standard Deviation, $1S_r$ (g/L $K_3Fe(CN)_6$)**	**95 Percent Confidence Estimate (g/L $K_3Fe(CN)_6$)**
"Fresh" at "Aim" (40.002 g/L $K_3Fe(CN)_6$)	39.935	6	0.034	± 0.09
"Seasoned", As Received	46.350	5	0.069	± 0.19
"Seasoned" with Standard Addition	59.778	5	0.046	± 0.13

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independently of the test method.

A statistically significant low bias of (-0.067 g/L) for $K_3Fe(CN)_6$ was found for a Process ECN-2 "fresh" tank developer sample. However, the bias was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. Statistically, the recovery of 96.6 percent for Process ECN-2 was significantly different from 100 percent, but was judged not to be practically significant.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Three ferricyanide bleach samples were analyzed by four analysts, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A “fresh” ferricyanide bleach prepared with all components at their respective “working tank” aim concentrations.
2. A “seasoned” ferricyanide bleach sample analyzed at 46.041 g/L $K_3Fe(CN)_6$.
3. The same “seasoned” solution, as in number 2, above, analyzed in the same manner, after making a standard addition of 13.901 g/L $K_3Fe(CN)_6$.

$K_3Fe(CN)_6$ (Visually)				
Sample	**Mean (g/L $K_3Fe(CN)_6$)**	**N**	**Reproducibility Standard Deviation, $1S_c$ (g/L $K_3Fe(CN)_6$)**	**95 Percent Confidence Estimate (g/L $K_3Fe(CN)_6$)**
“Fresh” at “Aim” (40.000 g/L $K_3Fe(CN)_6$)	40.282	16	0.122	± 0.26
“Seasoned”, As Received	46.041	16	0.072	± 0.15
“Seasoned” with Standard Addition	59.615	16	0.112	± 0.24

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for “fresh” samples only. Bias is not determined for “seasoned” samples, since the component concentration level was not determined independently of the test method.

A statistically significant high bias of (+0.282 g/L) for $K_3Fe(CN)_6$ was found for a Process ECN-2 “fresh” tank developer sample. However, the bias was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. Statistically, the recovery of 97.7 percent for Process ECN-2 was significantly different from 100 percent, but was judged not to be practically significant.

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- Pipette, (25.0-mL)
- Tip-up pipettes, (20-mL and 25-mL)
- Beakers, (250-mL)
- METROHM 536 Titrator or equivalent with a DOSIMAT and a 20-mL burette
- Platinum indicator electrode, BECKMAN, Model 39273 or equivalent
- Double junction reference electrode, ORION Model 900200 or equivalent
  Filling solutions:
  ORION No. 900002 (inner chamber)
  ORION No. 900003 (outer chamber)
- Burette, (50-mL) / (visual method only)
- Magnetic stirrer / (visual method only)
- Magnetic stir bar / (visual method only)

REAGENTS

Use ACS Reagent Grade reagents unless otherwise specified.

- 0.6 N potassium iodide
- Zinc sulfate - 7.0 N sulfuric acid reagent
- Starch indicator
- Sodium thiosulfate, ($Na_2S_2O_3$), (0.1 N) standardized to 4 places past the decimal point
- Water, Type I Reagent – This method was developed, and the resulting statistical data were obtained using reagent water equivalent to purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Removal of the Interfering Constituents

1. Pipette 25.0 mL of sample into a 250-mL beaker.
2. Add 25 mL of 0.6 potassium iodide from a tip-up pipet.
3. Add 20 mL of zinc sulfate - 7.0 N sulfuric acid reagent from a tip-up pipet; mix thoroughly.

Titration with Sodium Thiosulfate

Note: The end-point of the titration step can be determined either potentiometrically (Step 1) or visually (Step 2)

1. *Potentiometric Titration*:
   a. Set the following parameters on the METROHM Titrator:

Titration mode	mV/pH
Horizontal chart span	250 mV
Autocontrol	OFF
Maximum titration speed	15 min/100% volume
Vertical chart span	400 mm/100% volume
Automatic titration stop (U%)	OFF
Indicator electrode	Platinum, BECKMAN, Model 39273 or equivalent
Reference electrode	Double-junction ORION, Model 900200 or equivalent

   b. Place the 250-mL beaker on the METROHM titrator stand and add a magnetic stir bar. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex. Titrate the solution with standardized 0.1 N sodium thiosulfate through the inflection.
   c. Determine the end point using concentric arcs (Refer to method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revisions.) If a microprocessor controlled titrator is used, the endpoint will be picked automatically.
2. *Visual Titration*:
   a. Place the 250-mL beaker (from the *Removal of the Interfering Constituents* procedure) on a magnetic stirrer after adding a magnetic stir bar. Turn the magnetic stirrer on and adjust the setting so that the solution stirs vigorously but without creating a vortex or splashing.
   b. Using a 50-mL burette, titrate the solution with standardized 0.1 N sodium thiosulfate to a light yellow color.
   c. Add 5 mL of starch indicator from a tip-up pipet, and continue the titration until the blue color just disappears.

CALCULATIONS

For $Na_3Fe(CN)_6$

$$g/L\ Na_3Fe(CN)_6 = \frac{(mL\ Na_2S_2O_3)\ (N\ Na_2S_2O_3)\ (eq\ wt\ Na_3Fe(CN)_6)\ (1000)}{(mL\ sample)\ (1000)}$$

For $K_3Fe(CN)_6$

$$g/L\ K_3Fe(CN)_6 = \frac{(mL\ Na_2S_2O_3)\ (N\ Na_2S_2O_3)\ (eq\ wt\ K_3Fe(CN)_6)\ (1000)}{(mL\ sample)\ (1000)}$$

Where:

mL $Na_2S_2O_3$	=	volume of $Na_2S_2O_3$ in milliliters required to reach the equivalence point
N	=	normality of the $Na_2S_2O_3$ in milliequivalents per milliliter (meq/mL)
eq. wt	=	equivalent weight of ferricyanide in milligrams per milliequivalents [280.92 for $Na_3Fe(CN)_6$, 329.25 for $K_3Fe(CN)_6$]
1000	=	factor to convert milligrams to grams of ferricyanide
mL sample	=	milliliters of sample pipetted in step 1 of *Removal of the Interfering Constituents*
1000	=	factor to convert mLs of sample to Litres

If mL 0.1000 N $Na_2S_2O_3$ = 34.77

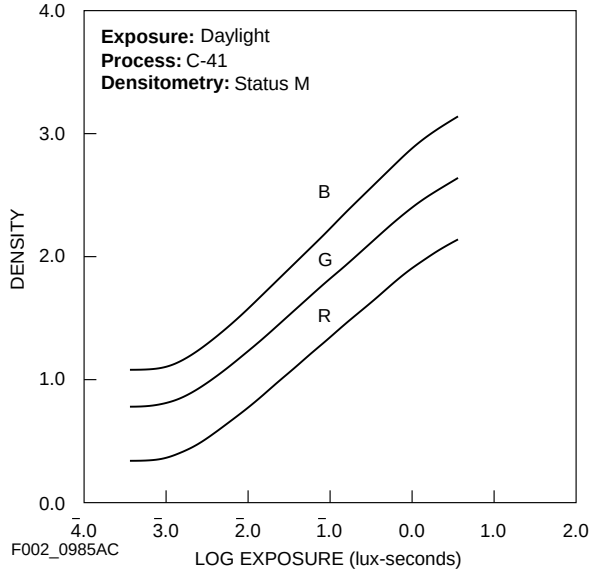
$$(g/L)\ Na_3Fe(CN)_6 = \frac{(34.77)\ (0.1000)\ (280.92)\ (1000)}{(25)\ (1000)}$$

$$(g/L)\ Na_3Fe(CN)_6 = 39.07$$

$$(g/L)\ K_3Fe(CN)_6 = \frac{(34.77)\ (0.1000)\ (329.25)\ (1000)}{(25)\ (1000)}$$

$$(g/L)\ K_3Fe(CN)_6 = 45.79$$

Figure 1 Typical Titration Curve, Ferricyanide in ECN-2 Ferricyanide Bleach



Cerimetric Determination of Sodium Ferrocyanide in Ferricyanide Bleach

ECN-2-1101
ECP-2D-1101
ECR-1101E

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SR-29	SR-27	SR-40	—

PRINCIPLE

Ferrocyanide is oxidized in an acid solution by sulfato cerate. This reaction is:

$$Ce^{+4} + Fe(CN)_6^{-4} \rightarrow Ce^{+3} + Fe(CN)_6^{-3}$$

Sodium diphenylamine sulfonate indicator is used. The indicator has a blank of 0.1 mL sulfato cerate. This value is used in the calculations.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

RELIABILITY

It is difficult to see the color change of the indicator in dark-colored seasoned samples. Thus, the resulting analyses may vary by approximately ± 3 g/L ferrocyanide. If greater precision is needed, refer to Method 1102, *Potentiometric Determination of Ferrocyanide in Ferricyanide Bleach and Ferrocyanide Stock Solutions*, (or the most recent revision).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 7.0 N Sulfuric Acid, H_2SO_4
- 0.01 M Sodium Diphenylamine Sulfonate Indicator
- 0.05 N Sulfato Cerate (standardized to 4 decimal places)

PROCEDURE

Sample Treatment

1. Add approximately 500 mL of distilled water to a 1000-mL conical flask.
2. Pipet (wipe the pipet before leveling) the sample into the flask according to the table below.

Solution	Sample Size
Fresh or regenerated Bleach	10.0 mL
Seasoned Bleach	5.0 mL

3. Add 10 mL of 7.0 N sulfuric acid from a tip-up pipet.

Titration

1. Add, with swirling, 20 drops (approximately 1 mL) of 0.01 M sodium diphenylamine sulfonate indicator.
2. Titrate immediately with standardized 0.05 N sulfato cerate to the *first scarlet color that persists for 1 minute*.

Calculations

$$\Delta mL\ cerate = mL\ cerate - blank = mL\ cerate - 0.1$$

$Na_4Fe(CN)_6 \cdot 10H_2O$, g/L =

$$\frac{(N\ cerate)(\Delta cerate)(eq\ wt\ Na_4Fe(CN)_6 \cdot 10H_2O)(1000)}{(mL\ sample)(1000)} =$$

10-mL sample

$$\frac{(N\ cerate)(\Delta mL\ cerate)(484.1)(1000)}{(10)(1000)} =$$

$$48.41(N\ cerate)(\Delta mL\ cerate)$$

5-mL sample

$$\frac{(N\ cerate)(\Delta mL\ cerate)(484.1)(1000)}{(5)(1000)} =$$

$$96.82(N\ cerate)(\Delta mL\ cerate)$$

Potentiometric Determination of Ferrocyanide in Process ECN Ferricyanide Bleach and Ferrocyanide Stock Solutions

ECN-0020-01

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SR-29	—	—	—

INTRODUCTION

Ferrocyanide is determined by an oxidation titration with standardized sulfato cerate in an acid solution. The reaction is:

$$Ce^{+4} + Fe(CN)_6^{4-} \rightarrow Ce^{+3} + Fe(CN)_6^{3-}$$

The endpoint of the titration is detected potentiometrically. The electrodes used for the titration are a platinum indicator electrode and a double junction reference electrode. Results are reported in terms of potassium ferrocyanide trihydrate, $K_4Fe(CN)_6 \cdot 3H_2O$.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed three (3) replicates on each of the following solutions during methods development.

1. A “fresh” ferricyanide bleach prepared with all components at their respective “working tank” aim concentrations.
2. The same “fresh” solution as in number 1, above, reanalyzed after making an analytically weighed, standard addition of 4.9452 g/L $K_4Fe(CN)_6 \cdot 3H_2O$.
3. A “seasoned” ferricyanide bleach analyzed potentiometrically as received, at 3.5057 g/L $K_4Fe(CN)_6 \cdot 3H_2O$.
4. The same “seasoned” solution as in number 3, above, reanalyzed after making an analytically weighed, standard addition of 1.0280 g/L $K_4Fe(CN)_6 \cdot 3H_2O$.

$K_4Fe(CN)_6 \cdot 3H_2O$				
Sample	**Mean (g/L $K_4Fe(CN)_6 \cdot 3H_2O$)**	**N**	**Repeatability Standard Deviation, $1s_r$ (g/L $K_4Fe(CN)_6 \cdot 3H_2O$)**	**95 Percent Confidence Estimate g/L $K_4Fe(CN)_6 \cdot 3H_2O$)**
“Fresh”	0.073	3	0.0037	± 0.016
“Fresh” plus Standard Addition	5.000	3	0.0024	± 0.010
“Seasoned”, As Received	3.506	3	0.0002	± 0.001
“Seasoned” plus Standard Addition	4.526	3	0.0023	± 0.010

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. Instead, a recovery was calculated for the component in a fresh sample.

Statistically the recovery of 99.27 percent was significantly different from 100 percent, but was judged not to be practically significant.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically the recovery of 99.27 percent was significantly different from 100 percent, but was judged not to be practically significant.

REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed four ferricyanide bleach samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A fresh tank solution prepared at 40.000 g/L $K_3Fe(CN)_6$
2. The same "fresh" ferricyanide bleach sample as in number 1, above, analyzed in the same manner, after making a standard addition of 3.5540 g/L $K_4Fe(CN)_6 \cdot 3H_2O$.
3. A seasoned ferricyanide bleach sample analyzed, as received, at 3.5540 g/L $K_4Fe(CN)_6 \cdot 3H_2O$.
4. The same seasoned solution, as in number 3, above, analyzed in the same manner, after making a standard addition of 1.0917 g/L $K_4Fe(CN)_6 \cdot 3H_2O$.

$K_4Fe(CN)_6 \cdot 3H_2O$				
Sample	**Mean (g/L $K_4Fe(CN)_6 \cdot 3H_2O$)**	**N**	**Reproducibility Standard Deviation, $1s_c$ (g/L $K_4Fe(CN)_6 \cdot 3H_2O$)**	**95 Percent Confidence Estimate g/L $K_4Fe(CN)_6 \cdot 3H_2O$)**
"Fresh"	0.096	15	0.0065	± 0.014
"Fresh" plus Standard Addition	3.627	16	0.0210	± 0.045
"Seasoned", As Received	3.506	16	0.0063	± 0.013
"Seasoned" plus Standard Addition	4.598	16	0.0146	± 0.031

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. Instead, a recovery was calculated for the component in a fresh sample. Statistically, the recovery of 99.33 percent was significantly different from 100 percent, but was judged not to be practically different

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 100.01 percent was not statistically significantly different from 100 percent.

APPARATUS

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E288, and E969, unless otherwise stated.

- Pipette, (50.0-mL)
- Tip-up pipette, (50-mL)
- Beaker, (600-mL, 400-mL)
- METROHM 536 Titrator or equivalent with a DOSIMAT and a 20-mL burette
- Platinum indicator electrode, BECKMAN, Model 39273 or equivalent
- Double junction reference electrode, ORION Model 900200 or equivalent
- Filling solutions:
  - ORION No. 900002 (inner chamber)
  - ORION No. 900003 (outer chamber)

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 0.0500 N Sulfato Cerate
  (standardized to 4 decimal places)
- 7.0 N Sulfuric Acid
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Treatment of Sample

1. Pipet (wipe the pipet before leveling) the sample of ferricyanide bleach into a beaker according to the following table:

Expected Concentration of $K_4Fe(CN)_6 \cdot 3H_2O$ (g/L)	Beaker Size (mLs)	Sample (mLs)	Reagent Water (mLs)	7.oN H_2SO_4
Below 5	600	200.00	100	50
Between 5 and 10	600	100.00	200	50
Between 10 and 20	400	50.00	200	50
Between 20 and 40	400	25.00	200	50
Between 40 and 80	400	10.00	200	50
Between 80 and 200	400	5.00	200	50
Over 200	400	2.00	200	50

2. Add reagent water from a graduated cylinder according to the table in step 1.
3. Add 7.0 N sulfuric acid from a tip-up pipet according to the table in step 1. Mix thoroughly.

Potentiometric Titration of Sample

1. Titrate the solution with 0.0500 N sulfato cerate, using a METROHM Titrator or equivalent.
   a. Set the following parameters on the METROHM Titrator:

Titration mode	mV/pH
Horizontal chart span	500 mV
Autocontrol	OFF
Maximum titration speed	15 min/100% volume
Vertical chart span	400 mm/100% volume
Automatic titration stop (U%)	OFF
Indicator electrode	Platinum, BECKMAN, Model 39273 or equivalent
Reference electrode	Double-junction ORION, Model 900200 or equivalent

   b. Place the beaker on the METROHM titrator stand and add a magnetic stir bar. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex. Titrate the solution with standardized 0.0500 N sulfato cerate through the inflection.

   c. Determine the end point using concentric arcs (refer to Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revisions.) If a microprocessor controlled titrator is used, the endpoint will be picked automatically.

CALCULATIONS

For $K_4Fe(CN)_6$;

$$g/L\ K_4Fe(CN)_6 \cdot 3H_2O = \frac{(mL\ sulfato\ cerate)\ (N\ sulfato\ cerate)\ (eq.\ wt.\ K_4Fe(CN)_6 \cdot 3H_2O)\ (1000)}{(mL\ sample)\ (1000)}$$

where:

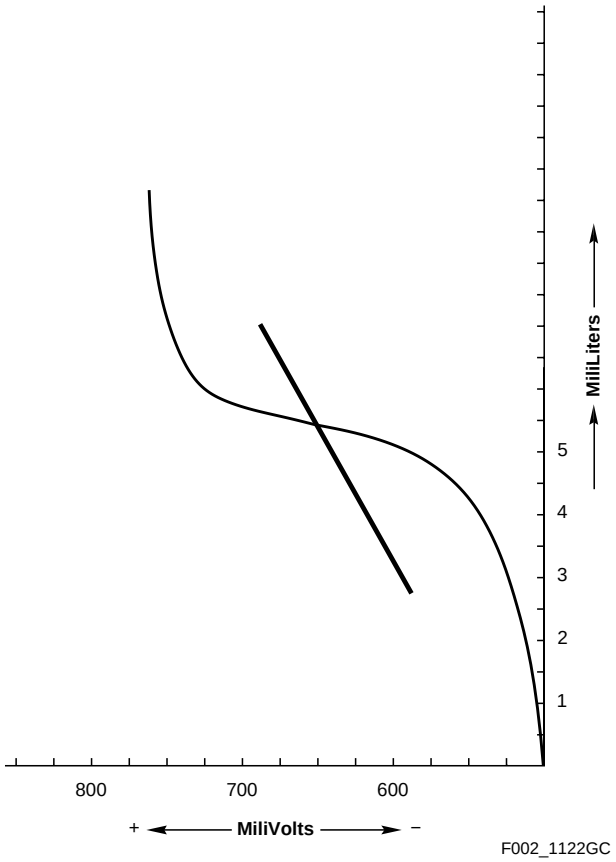
mL sulfato cerate	=	volume of sulfato cerate in milliliters required to reach the equivalence point
N	=	normality of sulfato cerate in milliequivalents per milliliter (meq/mL)
eq. wt.	=	equivalent weight of ferrocyanide in milligrams per milliequivalents [422.41 for $K_4Fe(CN)_6 \cdot 3H_2O$]
1000	=	factor to convert milligrams to grams of ferrocyanide
mL sample	=	milliliters of sample pipetted in step 1 of the *Treatment of Sample*
1000	=	factor to convert mLs of sample to liters

If mL 0.0500 N sulfato cerate = 16.41 mLs;

$$g/L\ K_4Fe(CN)_6 \cdot 3H_2O = \frac{(16.41\ (0.0500)\ (422.41)\ (1000)}{(50.0)\ (1000)}$$

$$g/L\ K_4Fe(CN)_6 \cdot 3H_2O = 6.93$$

Figure 1 S-shaped Curves



Spectrophotometric Determination of Ferrocyanide in Effluents

ECN-0025-1

INTRODUCTION

This method is used to determine the concentration of ferrocyanide ion in photoprocessing solution effluents. The ion concentration is determined spectrophotometrically. The sample is diluted, if necessary, such that the ferrocyanide ion [$Fe(CN)_6^{4-}$] concentration falls within a range of 0.5 to 5 mg/L. Results are reported as mg/L of potassium ferrocyanide trihydrate [$K_4Fe(CN)_6 \cdot 3H_2O$]. A dilution of 25 mL of effluent to 250 mL is sufficient for samples as high as 100 mg/L $K_4Fe(CN)_6 \cdot 3H_2O$ concentration. In most cases, this is adequate. However, this method can be used for samples of potassium ferrocyanide trihydrate concentrations as high as one g/L by making a second dilution of 25 mL to 250 mL.

After dilution, the sample is made alkaline to dissolve ferrocyanide. The sample is then filtered to remove any insolubles. The filtrate is acidified and ferrous/ferric reagent added. After 15 minutes, the intensity of the blue color produced is measured at 700 nm using a spectrophotometer equipped with a tungsten lamp.

Use of this method requires handling potentially hazardous chemicals. Material Safety Data Sheets (MSDS) should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

A. Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development.

1. An effluent sample analyzed as received, at 6.85 mg/L $K_4Fe(CN)_6 \cdot 3H_2O$.
2. The same effluent sample as in number 1, above, reanalyzed after making an analytically weighed, standard addition of 2.36 mg/L $K_4Fe(CN)_6 \cdot 3H_2O$.

Potassium Ferrocyanide, trihydrate				
Sample	**Mean mg/L $K_4Fe(CN)_6 \cdot 3H_2O$**	**N**	**Repeatability Standard Deviation, $1s_r$ mg/L $K_4Fe(CN)_6 \cdot 3H_2O$**	**95 Percent Confidence Estimate mg/L $K_4Fe(CN)_6 \cdot 3H_2O$**
Effluent	6.85	5	0.123	± 0.34
Effluent plus Standard Addition	9.40	5	0.105	± 0.29

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method.

Bias was not determined, since this is an effluent sample with an unknown level of potassium ferrocyanide trihydrate.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically the recovery of 108.05 percent was significantly different from 100 percent at the 95 percent confidence level, but was judged not to be practically significant.

B. REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed two effluent samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. An effluent sample was analyzed as received as 6.57 mg/L $K_4Fe(CN)_6 \cdot 3H_2O$.
2. The same effluent sample, as in number 1, above, analyzed in the same manner, after making a standard addition of 2.68 mg/L $K_4Fe(CN)_6 \cdot 3H_2O$.

Potassium Ferrocyanide, trihydrate				
Sample	**Mean mg/L $K_4Fe(CN)_6 \cdot 3H_2O$**	**N**	**Reproducibility Standard Deviation, $1s_r$ mg/L $K_4Fe(CN)_6 \cdot 3H_2O$**	**95 Percent Confidence Estimate mg/L $K_4Fe(CN)_6 \cdot 3H_2O$**
Effluent	6.57	16	0.207	± 0.44
Effluent plus Standard Addition	9.67	16	0.340	± 0.72

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method.

Bias was not determined, since this is an effluent sample with an unknown level of potassium ferrocyanide trihydrate.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically, the recovery of 115.67 percent was significantly different from 100 percent at the 95 percent confidence level, however it was judged not to be practically significant.

APPARATUS

- Pipet (40-mL)
- Graduated Cylinder (100 mL)
- (2) Beakers (150 mL)
- Conical Flask (250-mL)
- Filter apparatus

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E288, and E969, unless otherwise stated.

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 2.5 N Sodium hydroxide, NaOH
- Concentrated Hydrochloric acid, HCl
- Ferrous/Ferric Reagent
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

1. Pipet (wipe the pipet before leveling) 25.0 mL of effluent sample (Solution A) into a 250 mL volumetric flask. Dilute to volume with reagent water; stopper and invert the flask several times to mix (this is solution B).
2. Add, from a graduated cylinder, 100 mL of the diluted sample (Solution B) from step 1 to a 250 mL conical flask, and make it alkaline by adding 10 drops of 2.5 N sodium hydroxide.
3. Mix thoroughly and filter the solution through Whatman 2V filter paper.
4. Make the filtrate acid by the dropwise addition of concentrated hydrochloric acid. (Use 0-14 pH indicating paper as an indicator. The paper will turn red when solution is acidic.)
5. Pipet (wipe the pipet before leveling) 40.0 mL of the filtrate into each of two 150 mL beakers. (One will be the sample and the other will be the blank.)
6. Add 2 drops of ferrous/ferric reagent to the first beaker (sample); allow both beakers to stand for 15 minutes.
7. If a blue color is apparent, rinse and fill a 1-cm silica cell with solution from the first 150 mL beaker (step 6). Rinse the outer faces of the silica cell with reagent water and wipe dry with a clean tissue. Measure the absorbance of the sample vs. air at 700 nm on a spectrophotometer equipped with a tungsten lamp. Record this reading as A_{700} spl.

   Note: If no blue color is produced by Solution B in the first beaker in Step 6, repeat Steps 2 through 8 using the undiluted effluent sample (Solution A).
8. Rinse and fill the 1-cm silica cell from step 7 with the filtrate in the second 150 mL beaker from step 5. Measure the absorbance of this solution as in step 7. Record this reading as A_{700} blk.

CALCULATIONS

$y = mx + b$

Definition of the equation is found in the Regression section of Appendix A.

$$mg/L\ Fe(CN)_6^{4-} = m\ (A_{700}spl - A_{700}blk) + b$$

Where:

m = slope of the calibration line [(mg/L) mg/L $Fe(CN)_6^{4-}$ / $ABU_{@700}$]

$A_{700}spl - A_{700}blk$ = Absorbance of sample at 700 nm minus the absorbance of blank at 700 nm

b = the intercept of the calibration line with the y-axis (mg/L $Fe(CN)_6^{4-}$)

Each laboratory should establish its own regression equation based on a set of calibration standards. Appendix A explains this calibration procedure. The regression equation may be different for each spectrophotometer. A typical regression equation line for the effluent is described by the following equation:

$$mg/L\ Fe(CN)_6^{4-} = 28.942\ (A_{700}spl - A_{700}blk) - 0.2072$$

$$mg/L\ K_4Fe(CN)_6 \cdot 3H_2O = mg/L\ Fe(CN)_6^{4-} \times 1.99$$

$$mg/L\ Na_4Fe(CN)_6 \cdot 10H_2O = mg/L\ Fe(CN)_6^{4-} \times 2.28$$

Example of calculations:

Spectrophotometric readings: $A_{spl} = 0.146$ $A_{blk} = 0.020$

$$mg/L\ Fe(CN)_6^{4-} = 28.942\ (0.146 - 0.020) - 0.2072$$
$$= 28.942\ (0.126) - 0.2072$$
$$= 3.44$$

$$mg/L\ K_4Fe(CN)_6 \cdot 3H_2O = 3.44\ (1.99)$$
$$= 6.85$$

$$mg/L\ KNa_4Fe(CN)_6 \cdot 10H_2O = 2.44(2.28)$$
$$= 7.84$$

APPENDIX A

Calibration of Spectrophotometer for Ferrocyanide in Effluents

This Appendix should be used to establish the initial calibration equation, whenever the instrument has been adjusted, or to recheck the calibration (at least every six months)

A. Preparation of Standards

A 4.0 g/L $Fe(CN)_6^{4-}$ stock standard solution is prepared by dissolving 8.0 grams of potassium ferrocyanide trihydrate ($K_4Fe(CN)_6 \cdot 3\ H_2O$) in a 1 liter volumetric flask and diluting to the mark with reagent water.

1. Pipet 10.0 mL of this stock standard solution to a second 1 liter volumetric flask and dilute to volume with reagent water. This solution contains 0.040 g/L of $Fe(CN)_6^{4-}$.
2. Label five 100 mL volumetric flasks as follows: 0.0 mg/L; 1.0 mg/L; 2.5 mg/L; 5.0 mg/L; and 10.0 mg/L.
3. Using a 25 mL buret, add the following amounts of 0.040 g/L ferrocyanide standard solution to the flasks as indicated:

Volumetric Flask Identification	Volume of Standard Solution, mL
0.0 mg/L	0.0
1.0 mg/L	2.5
2.5 mg/L	6.3
5.0 mg/L	12.5
10.0 mg/L	25.0

4. Dilute to volume with reagent water.

B. Analysis of Standards

1. Run each sample by the method described in the preceding Procedure.
2. Table of Data gathered from Analysis of Standards

Standard (g/L $Fe(CN)_6^{4-}$	ABS_{spl}	ABS_{blk}	Net ABS@700 nm
0.0	0.038	0.038	0.000
1.0	0.078	0.038	0.040
2.5	0.133	0.038	0.095
5.0	0.236	0.038	0.198
10.0	0.380	0.038	0.342

C. Regression

1. This data was processed by a least squares linear regression to develop the line represented by equation, $y = mx + b$:

Where:

$y =$ mg/L $Fe(CN)_6^{4-}$

$m =$ slope of the line or the relation between absorbance and concentration determined during calibration [(mg/L)/absorbance]

$x =$ net absorbance of the sample at 700 nm (ABS_{spl} - ABS_{blk})

$b =$ the intercept of the calibration line with the y-axis (in mg/L Ferrocyanide)

2. The equation generated using the above data was:

$$Fe(CN)_6^{4-}, \text{ mg/L} = 28.942 \text{ (Net } ABS_{@700\ nm}) - 0.2072$$

3. The calibration equation was done in the following manner on a (SHIMADZU Model UV 160 U) spectrophotometer. Five fresh solutions were prepared (see Step #1 of Preparation of Standards). Each solution was analyzed to create a linear regression, based on 5 data points, for each spectrophotometer being used. Each laboratory should calibrate their spectrophotometer, otherwise an unknown bias may exist.

Determination of Ferrous Iron in EASTMAN Color Films, "KUL" Bleach

ECN-0007/1
ECP-0007/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SB-34/34R	SB-34/34R	—	—

INTRODUCTION

The determination of iron(II) in EASTMAN Color Films, Process ECN-2 or Process ECP-2D, KUL Bleach is accomplished by a spectrophotometric technique. The iron(II) concentration is determined by adding a sample to deaerated 1,10-phenanthroline/sodium acetate to form a colored complex. The absorbance of this complex is then measured at 510 nm on a spectrophotometer. Bleach samples should be run as quickly as possible, because the iron(II) content of closed samples increases gradually upon standing. The 1,10-phenanthroline/sodium acetate is deaerated with nitrogen to minimize oxidation of the iron(II) in the sample as the colored complex is formed. This method is calibrated between 0.25 and 3.0 g/L iron(II).

Use of this method requires handling of potentially hazardous chemicals. Material Safety Data Sheets should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including bias)

Repeatability Standard Deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed three (3) replicates on a "fresh" EASTMAN Color Films, Process ECN-2 or Process ECP-2D, "KUL" bleach and five (5) replicates on each of a "seasoned" and a "seasoned" plus standard addition EASTMAN Color Films, Process ECN-2 or Process ECP-2D, "KUL" bleach solutions during methods development:

1. A fresh EASTMAN Color Films, Process ECN-2 or Process ECP-2D, KUL Bleach prepared with all components at their respective working tank "aim" concentrations:
   - 1.012 g/L total iron for Process ECN-2
   - 1.024 g/L total iron for Process ECP-2D
2. A seasoned EASTMAN Color Films, KUL Bleach analyzed as received at:
   - 0.367 g/L iron(II) for Process ECN-2
   - 0.504 g/L iron(II) for Process ECP-2D
3. The same seasoned solution as in number 2, above, analyzed after making an analytically weighed, standard addition of:
   - 0.115 g/L iron(II) for Process ECN-2
   - 0.157 g/L iron(II) for Process ECP-2D

Sample (Process ECN-2 KUL Bleach)	Mean (g/L Iron(II))	(N)	Repeatability Standard Deviation, $1S_r$ (g/L Iron(II))	95 Percent Confidence Estimate (g/L Iron(II))
"Fresh" at (1.012 g/L Iron(II))	1.011	3	0.003	± 0.013
"Seasoned", As Received	0.367	5	0.006	± 0.017
"Seasoned" with Standard Addition	0.462	5	0.008	± 0.022

Sample (Process ECP-2D KUL Bleach)	Mean (g/L Iron(II))	(N)	Repeatability Standard Deviation, $1S_r$ (g/L Iron(II))	95 Percent Confidence Estimate (g/L Iron(II))
"Fresh" at (1.024 g/L Iron(II))	1.017	3	0.007	± 0.030
"Seasoned", As Received	0.504	5	0.005	± 0.015
"Seasoned" with Standard Addition	0.656	5	0.003	± 0.009

Bias

Bias is a statistically significant deviation from the known level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independent of the test method.

No statistically significant bias was found for the Process ECN-2 or Process ECP-2D "fresh" tank samples.

Recovery

Recovery is used instead of bias for "seasoned" samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the "seasoned" sample with a standard addition of the component minus the mean for the "seasoned" sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery was not statistically different from 100 percent.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Three EASTMAN Color Films KUL bleach samples were analyzed by four trained analysts, each using different titration stations, on two different days. Duplicate analyses were performed on each sample, on each of two days. These samples were:

1. A "fresh" tank solution prepared at:
   - 0.509 g/L iron(II) for Process ECN-2
   - 0.516 g/L iron(II) for Process ECP-2D
2. An EASTMAN Color Films "seasoned" tank KUL Bleach sample analyzed, in the same manner as the "fresh" sample, as received at:
   - 0.449 g/L iron(II) for Process ECN-2
   - 0.486 g/L iron(II) for Process ECP-2D
3. The same (as in number 2, above) EASTMAN Color Films "seasoned" tank KUL Bleach sample, analyzed after making an analytically weighed, standard addition of:
   - 0.158 g/L iron(II) for Process ECN-2
   - 0.159 g/L iron(II) for Process ECP-2D

The Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Samples (Process ECN-2 KUL Bleach)	Mean (g/L Iron(II))	(N)	Reproducibility Standard Deviation, $1s_c$ (g/L Iron(II)	95 Percent Confidence Estimate (g/L Iron(II)
"Fresh" at (0.509 g/L iron(II))	0.514	16	0.014	± 0.030
"Seasoned", as received	0.449	16	0.029	± 0.062
"Seasoned" with standard addition	0.604	16	0.033	± 0.070

Samples (Process ECN-2D KUL Bleach)	Mean (g/L Iron(II))	(N)	Reproducibility Standard Deviation, $1s_c$ (g/L Iron(II)	95 Percent Confidence Estimate (g/L Iron(II)
"Fresh" at (0.516 g/L iron(II))	0.503	16	0.031	± 0.066
"Seasoned", as received	0.486	16	0.025	± 0.053
"Seasoned" with standard addition	0.639	16	0.036	± 0.077

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- Double Beam Spectrophotometer equipped with a tungsten lamp (i.e., PERKIN-ELMER Lambda 4 series)
- Two, 1-cm silica cells
- 200-µL EPPENDORF micropipet or equivalent micropipet

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 1,10-Phenanthroline/Sodium Acetate reagent
- Ferrous Ammonium Sulfate Hexahydrate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$
- Water, Type I Reagent - This method was developed, and the statistical data were obtained, using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Blank

1. Set a double-beam spectrophotometer to a wavelength of 510 nm.
2. Rinse two, clean 1.0-cm cells with reagent water, at least three times. Fill the cells with reagent water and dry the outside surfaces with a tissue.
3. Place both cells into the double-beam spectrophotometer and zero the instrument.
4. Leave the reference cell in the instrument and remove the sample cell.

Sample Preparation

1. Bubble nitrogen through the 1,10-phenanthroline/ sodium acetate reagent, contained in a conical flask, for 15 minutes. Only de-gas 5 mL of reagent per sample plus 30 mL excess.
2. Using a serological pipet, add 5 mL of the deaerated 1,10-phenanthroline/sodium acetate reagent to a 100-mL volumetric flask.
3. Pipet 200-µL of sample into the flask with a micropipet (EPPENDORF or equivalent) containing the 1,10-phenanthroline/sodium acetate. Swirl the flask to mix.
4. Dilute to volume with reagent water. Invert the flask, 6-10 times, to thoroughly mix the solution.
5. Within 20 seconds, rinse the 1.0-cm cell from the spectrophotometer sample compartment, at least three times, with the above solution, and fill the cell. Rinse the outer surfaces of the cell with reagent water and dry with a tissue.
6. Place the cell into the sample compartment of the spectrophotometer. Measure and record the absorbance at 510 nm vs. reagent water.

Calculations

$$\text{Iron(II), g/L} = m\,(A_{510}) + b$$

where:

m = slope of the calibration line (in g/L/Abs. units)

A_{510} = absorbance (ABU) of sample at 510 nm

b = the calibration intercept of the line with the y-axis (g/L, Fe(II))

Each laboratory should establish its own calculation based on a linear regression of a set of calibration standards. *APPENDIX A* explains this calibration procedure. The regression line may be different for each spectrophotometer. A, typical calibration line is described by the following equation:

$$\text{iron(II), g/L} = 2.49\,(A_{510}) - 0.068$$

APPENDIX A

Calibration of Spectrophotometer For Iron(II)

Use this Appendix to recheck the spectrophotometer linear calibration for iron(II) on a regular basis of at least every 6 months. Also, use it the first time this method is performed and whenever the spectrophotometer has been repaired.

Preparation of Standards

A litre of "fresh" Process ECN-2 or Process ECP-2D, "KUL" Bleach solution should be prepared that contains all the constituents of the mix at the aim tank concentrations.

1. For the iron(II) standards in Process ECN-2 or Process ECP-2D, "KUL" Bleach, weigh out 0.088, 0.410, 0.740, and 1.065 g portions of assayed ferrous ammonium sulfate, hexahydrate (see *APPENDIX B* for assay procedure) to the nearest 0.0001 g.
2. Quantitatively transfer each portion of ferrous ammonium sulfate to 50-mL volumetric flasks, respectively labeled with the corresponding weights, with the "fresh" Process ECN-2 or Process ECP-2D, "KUL" Bleach mix. Swirl the flasks to dissolve the ferrous ammonium sulfate. (NOTE: the iron(II) material takes some time to dissolve.)
3. When the ferrous ammonium sulfate has dissolved, fill each volumetric to the mark with the "fresh" Process ECN-2 or Process ECP-2D, "KUL" Bleach mix. Invert each flask, 6-10 times, to thoroughly mix the solutions.
4. Run each sample in (at least) duplicate by the method described in the preceding *PROCEDURE*.

Determination of Iron(II)

The calculation to determine the amount of iron(II) in the standards from the weighed amount of ferrous ammonium sulfate is as follows:

$$\underset{\text{iron(II)}}{\text{g/L}} = \frac{\text{g wt of } Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O}{50\text{ mL}} \times \frac{55.85}{391.85} \times \frac{1000\text{ mL}}{1\text{L}}$$

where:

g wt of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ = weight recorded in step 1 of Preparation of Standards

55.85 = atomic weight of iron

391.85 = molecular weight of ferrous ammonium sulfate, 6-hydrate

1000 mL/1L = conversion factor from mL to L

If the assay from *APPENDIX B* is not 100 percent, the result of the above calculation must be multiplied by the wt/wt%, iron (II) assay value to obtain the correct value.

Regression

The data collected may be used to construct the regression equation for the calibration line.

The reliability of the calibration line generated was done in the following manner on a SHIMADZU Model UV16OU Spectrophotometer. Four "fresh" ECN-2 and ECP-2D, "KUL" bleach solutions were prepared containing 0.2515, 1.0235, 2.0296, and 3.0401 g/L iron(II). Each solution was analyzed in triplicate to create a linear regression (based on 12 data points). The average standard deviation (1s) for the linear regression was 0.007 g/L iron(II), corresponding to a 95 percent confidence estimate of ± 0.015 g/L. Each laboratory should calibrate its spectrophotometer; otherwise, an unknown bias may exist.

Process ECN-2

g wt of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	g/L Iron(II)	Absorbance at 510 nm
0.0887	0.2520	0.117
0.0887	0.2520	0.114
0.0887	0.2520	0.117
0.3562	1.0121	0.422
0.3562	1.0121	0.420
0.3562	1.0121	0.422
0.7101	2.0177	0.835
0.7101	2.0177	0.821
0.7101	2.0177	0.839
1.0658	3.0381	1.239
1.0658	3.0381	1.231
1.0658	3.0381	1.234

Process ECP-2D

g wt of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	g/L Iron(II)	Absorbance at 510 nm
0.0885	0.2515	0.132
0.0885	0.2515	0.129
0.0885	0.2515	0.132
0.3602	1.0235	0.435
0.3602	1.0235	0.435
0.3602	1.0235	0.435
0.7143	2.0296	0.844
0.7143	2.0296	0.842
0.7143	2.0296	0.840
1.0665	3.0401	1.250
1.0665	3.0401	1.245
1.0665	3.0401	1.255

Figure 1
Calibration of Iron(II) in ECN-2, "KUL" Bleach

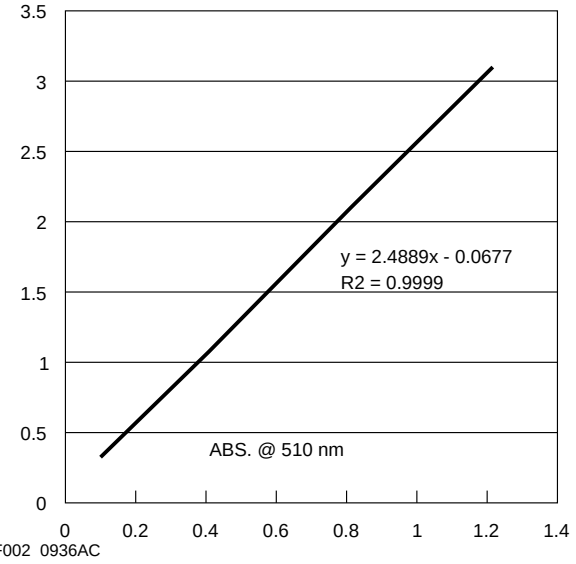
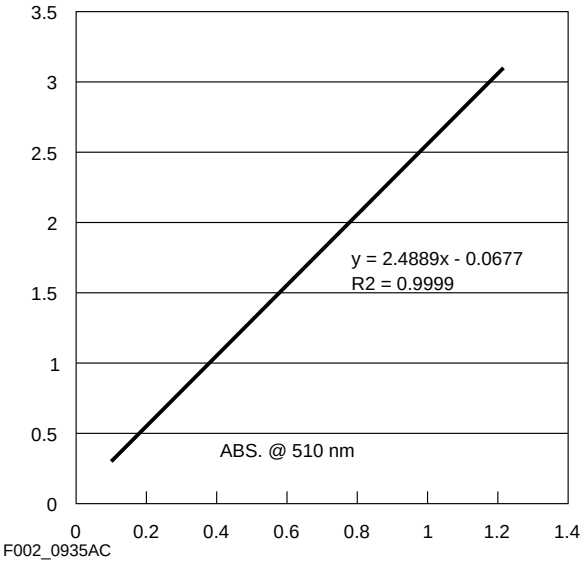


Figure 2
Calibration of Iron(II) in ECP-2D, "KUL" Bleach



This data was then processed by a least squares linear regression to develop the line, y = mx + b.
where:

- y = grams per litre of iron(II)
- m = Slope of the line or the relation between absorbance and iron(II) concentration determined during calibration [(g/L)/absorbance]
- x = absorbance of sample at 510 nm
- b = the calibration intercept of the line with the y-axis (g/L, Fe(II))

The equation generated using the above data was:

$$\text{iron(II), g/L} = 2.49\ (A_{510}) - 0.068$$

APPENDIX B

This appendix contains two assay procedures for Ferrous Ammonium Sulfate. The first procedure uses Potassium Dichromate; while the alternate procedure uses Potassium Permanganate titrant.

Assay Procedure for Ferrous Ammonium Sulfate, Hexahydrate

Reagents

All reagents are ACS Reagent Grade unless otherwise stated.

- Potassium Dichromate, $K_2Cr_2O_7$, NIST Primary Standard, 136e, dried for 2 hours at 110°C
- Ferroin Indicator, 1,10-Phenanthroline Iron(II) Sulfate solution (0.025 M) $[(C_{12}H_8N_2)_3FeSO_4]$
- Sulfuric Acid, concentrated, H_2SO_4
- Ferrous Ammonium Sulfate-6-Hydrate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$

Procedure

1. Weigh 14.0 g of ferrous ammonium sulfate, hexahydrate to the nearest 0.0001 g and record the weight.
2. Quantitatively transfer to a 200-mL volumetric flask and swirl the flask to dissolve the ferrous ammonium sulfate.
3. Dilute the solution to the mark with reagent water. Invert the flask, 6-10 times, to thoroughly mix.
4. Weigh 1.0 g of dried, potassium dichromate to the nearest 0.0001 g and record the weight.
5. Quantitatively transfer to a 100-mL volumetric flask containing 50 mL of reagent water. Swirl the flask to dissolve the potassium dichromate.
6. Dilute the solution to the mark with reagent water. Invert the flask, 6-10 times, to mix thoroughly.
7. Fill a 50-mL buret with the ferrous ammonium sulfate solution (step 3, above).
8. Add 20 mL concentrated sulfuric acid to a 150-mL beaker containing 25 mL of reagent water and a magnetic stirring bar.

Caution

Hot acid solution is formed.

9. Pipet 15.0 mL of the potassium dichromate solution into the beaker.
10. Add 2 drops of ferroin indicator to the beaker and place the beaker on a magnetic stirrer.
11. Slowly add the ferrous ammonium sulfate solution from the buret to the beaker. The solution will change colors as the titrant is added, going from a green-blue color to a reddish-brown color. The point that produced the first reddish-brown color change is the end point.
12. Record the volume of ferrous ammonium sulfate titrant consumed at the end point to the nearest 0.05 mL.
13. Repeat steps 7-12, two more times.

Calculations

N Potassium Dichromate

$$N\ K_2Cr_2O_7 = \frac{\text{g wt of } K_2Cr_2O_7}{100\ \text{mL}} \times \frac{1000}{294.2/6}$$

where:

294.2/6 = the eq. wt of $K_2Cr_2O_7$

g wt of $K_2Cr_2O_7$ = recorded wt from step 4

1000 = factor to convert equivalents to milliequivalents

N of Ferrous Ammonium Sulfate

$$N\ Fe(NH_4)_2(SO_4)_2 = \frac{(\text{mL } K_2Cr_2O_7)(N\ K_2Cr_2O_7)}{\text{mL } Fe(NH_4)_2(SO_4)_2}$$

where:

mL $Fe(NH_4)_2(SO_4)_2$ = average* volume of the three titrations required to reach the end point color change

mL $K_2Cr_2O_7$ = 15.0 mL

N $K_2Cr_2O_7$ = normality calculated in *N Potassium Dichromate*

* The average volume for the three titrations should not have a standard deviation (1s) greater than 0.50 mL.

g/L, Iron(II) in Ferrous Ammonium Sulfate

$$\text{g/L, Iron(II) (actual)} = N\ Fe(NH_4)_2(SO_4)_2 \times 55.85$$

where:

55.85 = gram-equivalent weight of Iron(II) in $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$

Theoretical wt of Ferrous in Solution

$$\text{g/L iron(II)} = \frac{\text{wt of } Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O}{200\ \text{mL}} \times \frac{55.85}{391.85} \times \frac{1000\ \text{mL}}{1\text{L}}$$

where:

391.85 = molecular weight of ferrous ammonium sulfate, 6-hydrate

55.85 = atomic weight of iron

wt of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ = weight recorded in step 1 of this procedure.

1000 mL = factor to convert mL to L

Assay Percentage

$$\%\text{Iron(II)} = \frac{\text{g/L Iron(II) (actual)}}{\text{g/L Iron(II) (theoretical)}} \times 100$$

Alternate Assay Procedure for Ferrous Ammonium Sulfate, Hexahydrate

Note: This procedure is based on the method in Reagent Chemicals, 8th Edition, Amercian Chemical Society, 1993.

Assay Procedure

Note: This procedure should be repeated in triplicate with the average of the three results used as the assay value.

1. Accurately weigh 1.6 grams of sample to the nearest milligram and dissolve in a mixture of 100 mL reagent water and 3 mL of concentrated sulfuric acid contained in a 250 mL Erlenmeyer flask.

Caution

Always add acid to water and not water to acid.

2. Titrate while stirring with standardized 0.1 N potassium permanganate ($KMnO_4$) from a 50 mL buret to a permanent faint pink endpoint that lasts for at least 15 seconds.
3. Repeat steps 1 and 2 without any sample. This is the blank.

Calculations

$$\%\ (wt./wt.)\ \text{ferrous ammonium sulfate, hexahydrate} = \frac{(mL\ KMnO_4\ sample - mL\ KMnO_4\ blank) \times N\ KMnO_4 \times 0.3921 \times 100}{\text{sample size in grams}}$$

Titrimetric Determination of Hypo Index, Thiosulfate, and Sulfite in EASTMAN Color Films, Process ECN-2 Fixer

ECN-0002/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	F-34a/F-34aR	—	—	—

INTRODUCTION

This method describes the titrimetric determination of hypo index (total reductants), thiosulfate, and sulfite in EASTMAN Color Films, Process ECN-2, fixers. It is recommended that these determinations be carried out by a potentiometric titrimetric approach, using an auto-titrator. However, for those unable to use instrumentation, the manual titrimetric technique, using the visual starch indicator, is included.

For the potentiometric measurement, a *Metrohm* Potentiograph, Model E536 or equivalent should be used. The potentiometric titration requires a platinum indicator electrode and a double-junction reference electrode.

The **Hypo Index** (HI) or total reductants of a fixer is defined as the millilitres of 0.1 N iodine consumed by the thiosulfate and sulfite combined (reaction 1 & 2), in a specified volume of fixer. The fixer is added to an excess of iodine (liberated from the reaction of potassium iodate and potassium iodide under acidic conditions - reaction 3). The unreacted iodine is titrated either potentiometrically or visually with standardized sodium thiosulfate from the appropriate capacity burette. The difference between the blank titration and the sample titration represents the milliequivalents of iodine consumed by the sample. Dividing the milliequivalents of iodine by 0.1 meq/mL yields the HI of the sample. Hypo index is reported in the terms of HI(1), mL which is the millilitres of 0.1000 N I_2 consumed by 1.0 mL of sample.

$$2\ S_2O_3^{=} + I_2 \rightarrow 2I^- + S_4O_6^{=} \quad \text{(reaction 1)}$$

$$HSO_3^{=} + I_2 + H2O \rightarrow SO_4^{=} + 2I^- + 3H^+ \quad \text{(reaction 2)}$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad \text{(reaction 3)}$$

$$Na_2SO_3 + HCHO + H2O \rightarrow CH_3(OH)\ SO_3Na + NaOH \quad \text{(reaction 4)}$$

The **thiosulfate** is determined potentiometrically by adding 6 percent formaldehyde to a second sample aliquot in reagent water. Under these conditions, the sulfite in the sample forms a formaldehyde bisulfite complex (reaction 4). This sample is then added to an excess of acidified iodine. The unreacted iodine is titrated either potentiometrically with standardized sodium thiosulfate from a 50-mL capacity burette. The difference between the blank titration and the sample titration represents the milliequivalents of iodine consumed by the thiosulfate in the sample. The thiosulfate is expressed as g/L thiosulfate ion ($S_2O_3^{=}$).

The **thiosulfate** is determined by the visual titration by adjusting the pH of a sample aliquot to 8.5. At this pH, the sulfite rapidly forms the stable sulfite - formaldehyde adduct. Upon acidification, which prevents the adduct from reacting with iodine, the thiosulfate from the sample is titrated with standardized iodine reagent to a starch end point.

The **sulfite** content is calculated by subtracting the milliequivalents of iodine consumed by the thiosulfate from the milliequivalents of iodine consumed by the thiosulfate and sulfite. The sulfite is reported as sodium sulfite.

Use of this method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions (this procedure was done by both potentiometric and visual end point detection):

a. A “fresh” EASTMAN Color Films, Process ECN-2, Fixer prepared with all components at their respective aim concentrations in a working tank.

b. A “seasoned” EASTMAN Color Films, Process ECN-2, Fixer analyzed as received at 125.67 g/L thiosulfate ion and 28.92 g/L sodium sulfite.

c. The same “seasoned” solution as in number b, above, reanalyzed after making standard additions of 37.850 g/L thiosulfate ion and 8.415 g/L sodium sulfite.

Reproducibility

Three EASTMAN Color Films, Process ECN-2, Fixer samples were analyzed by four analysts, each using different titration stations, on two different days. Each analyst analyzed each sample by both the potentiometric and the visual end point technique. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

a. a “fresh” tank solution prepared at 109.212 g/L thiosulfate ion and 21.335 g/L sodium sulfite.

b. an EASTMAN Color Films, Process ECN-2 “seasoned” tank fixer sample analyzed, as received, in the same manner as the “fresh” fixer.

c. the same (as in number b, above) EASTMAN Color Films, Process ECN-2 “seasoned” tank fixer sample reanalyzed in the same manner as the “fresh” fixer, after standard additions of thiosulfate and sulfite were made. The “seasoned” sample of EASTMAN Color Films, Process ECN-2 fixer, analyzed to be 115.17 g/L thiosulfate ion and 15.69 g/L sodium sulfite. Standard

additions of 34.57 g/L thiosulfate ion and 5.444 g/L sodium sulfite were made to that “seasoned” sample.

POTENTIOMETRIC TITRATION STATISTICS

Repeatability Standard Deviation, $1s_r$ & 95 Percent Confidence Estimate (not including bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

HYPO INDEX (1 mL)				
Samples (Process ECN-2 Fixer)	**Mean Level (mL 0.1 N I_2)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (mL 0.1 N I_2)**	**95 Percent Confidence Estimate (mL 0.1 N I_2)**
“Fresh” at “Aim”	10.02	5	0.086	± 0.24
“Seasoned”, As Received	15.80	5	0.073	± 0.20
“Seasoned” with Standard Addition	19.38	5	0.14	± 0.39

THIOSULFATE				
Samples (Process ECN-2 Fixer)	**Mean Level (g/L $S_2O_3^{=}$)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (g/L $S_2O_3^{=}$)**	**95 Percent Confidence Estimate (g/L $S_2O_3^{=}$)**
“Fresh” at “Aim”	81.18	5	0.67	± 1.9
“Seasoned”, As Received	125.67	5	0.47	± 1.3
“Seasoned” with Standard Addition	153.79	5	0.60	± 1.7

SULFITE				
Samples (Process ECN-2 Fixer)	**Mean Level (g/L Na_2SO_3)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (g/L Na_2SO_3)**	**95 Percent Confidence Estimate (g/L Na_2SO_3)**
“Fresh” at “Aim”	17.55	5	0.69	± 1.9
“Seasoned”, As Received	28.92	5	0.65	± 1.8
“Seasoned” with Standard Addition	35.69	5	1.18	± 3.3

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for “fresh” samples only. Bias is not determined for “seasoned” samples, since the component concentration level was not determined independently of the test method.

A statistically significant bias for thiosulfate of (-1.09 percent) was found for a “fresh” tank Process ECN-2 Fixer sample. The biases for Hypo Index and Sodium Sulfite were not statistically significant. However, the bias for thiosulfate was judged not to be practically significant.

Recovery

Recovery is used instead of bias for "seasoned" samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the "seasoned" sample with a standard addition of the component minus the mean for the "seasoned" sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The table below shows whether or not a recovery is statistically or practically different from 100 percent.

POTENTIOMETRIC RECOVERY, Process ECN-2			
Analyte	**Recovery Value**	**Statistically Significant**	**Practically Significant**
Hypo Index (1 mL)	76%	Yes	No
Thiosulfate ($S_2O_3^{=}$)	74%	Yes	No
Sodium Sulfite (Na_2SO_3)	80.4%	No	No

Reliability

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The customer standard deviation is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

HYPO INDEX				
Samples (Process ECN-2 Fixer)	**Mean Level (mL 0.1 N I_2)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (mL 0.1 N I_2)**	**95 Percent Confidence Estimate (mL 0.1 N I_2)**
"Fresh" at "Aim"	12.88	16	0.25	± 0.54
"Seasoned", As Received	12.73	16	0.13	± 0.27
"Seasoned" with Standard Addition	15.83	16	0.16	± 0.33

THIOSULFATE				
Samples (Process ECN-2 Fixer)	**Mean Level (g/L $S_2O_3^{=}$)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (g/L $S_2O_3^{=}$)**	**95 Percent Confidence Estimate (g/L $S_2O_3^{=}$)**
"Fresh" at "Aim"	108.14	16	0.94	± 2.00
"Seasoned", As Received	114.86	16	0.73	± 1.56
"Seasoned" with Standard Addition	142.23	16	0.78	± 1.67

SULFITE (Na_2SO_3)				
Samples (Process ECN-2 Fixer)	**Mean Level (g/L Na_2SO_3)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (g/L Na_2SO_3)**	**95 Percent Confidence Estimate (g/L Na_2SO_3)**
"Fresh" at "Aim"	20.79	15	0.59	± 1.26
"Seasoned", As Received	15.70	16	0.68	± 1.45
"Seasoned" with Standard Addition	19.85	16	0.76	± 1.63

VISUAL TITRATION STATISTICS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

HYPO INDEX (3.0 mL)				
Samples (Process ECN-2 Fixer)	**Mean Level (mL 0.1 N I_2)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (mL 0.1 N I_2)**	**95 Percent Confidence Estimate (mL 0.1 N I_2)**
"Fresh" at "Aim"	29.42	5	0.089	± 0.25
"Seasoned", As Received	47.29	5	0.060	± 0.17
"Seasoned" with Standard Addition	57.65	5	0.084	± 0.23

THIOSULFATE ($S_2O_3^{=}$)				
Samples (Process ECN-2 Fixer)	**Mean Level (g/L $S_2O_3^{=}$)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (g/L $S_2O_3^{=}$)**	**95 Percent Confidence Estimate (g/L $S_2O_3^{=}$)**
"Fresh" at "Aim"	81.37	5	0.10	± 0.28
"Seasoned", As Received	125.29	5	0.24	± 0.67
"Seasoned" with Standard Addition	155.73	5	0.19	± 0.53

SULFITE (Na_2SO_3)				
Samples (Process ECN-2 Fixer)	**Mean Level (g/L Na_2SO_3)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (g/L Na_2SO_3)**	**95 Percent Confidence Estimate (g/L Na_2SO_3)**
"Fresh" at "Aim"	16.08	5	0.18	± 0.50
"Seasoned", As Received	28.93	5	0.24	± 0.67
"Seasoned" with Standard Addition	33.43	5	0.31	± 0.86

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independently of the test method.

Statistically significant biases were found for hypo index, thiosulfate, and sodium sulfite (see the table below) for a "fresh" tank Process ECN-2 Fixer sample. However, the individual biases for hypo index, thiosulfate, or sodium sulfite were judged not to be practically significant.

Analyte	Bias (Measurement Unit of Analyte)	Bias (%)
Hypo Index (mL 0.1 N I_2)	– 0.82	– 2.71%
Thiosulfate (g/L $S_2O_3^{=}$)	– 0.696	– 0.85%
Sodium Sulfite (Na_2SO_3)	– 1.322	– 7.6%

Recovery

Recovery is used instead of bias for “seasoned” samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the “seasoned” sample with a standard addition of the component minus the mean for the “seasoned” sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The table below show whether or not a recovery is statistically or practically significant from 100 percent.

VISUAL RECOVERY, Process ECN-2			
Analyte	**Recovery Value**	**Statistically Significant**	**Practically Significant**
Hypo Index (1 mL)	73.3%	Yes	No
Thiosulfate ($S_2O_3^{=}$)	80.4%	Yes	No
Sodium Sulfite (Na_2SO_3)	53.4%	Yes	No

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

HYPO INDEX (1.0 mL)				
Samples (Process ECN-2 Fixer)	**Mean Level (mL 0.1 N I_2)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (mL 0.1 N I_2)**	**95 Percent Confidence Estimate (mL 0.1 N I_2)**
“Fresh” at “Aim”	12.97	16	0.18	± 0.39
“Seasoned”, As Received	12.70	16	0.15	± 0.31
“Seasoned” with Standard Addition	15.93	16	0.20	± 0.43

THIOSULFATE ($S_2O_3^{=}$)				
Samples (Process ECN-2 Fixer)	**Mean Level (g/L $S_2O_3^{=}$)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (g/L $S_2O_3^{=}$)**	**95 Percent Confidence Estimate (g/L $S_2O_3^{=}$)**
“Fresh” at “Aim”	107.95	16	0.93	± 1.99
“Seasoned”, As Received	114.95	16	0.97	± 2.06
“Seasoned” with Standard Addition	142.59	16	1.07	± 2.28

SULFITE (Na_2SO_3)				
Samples (Process ECN-2 Fixer)	**Mean Level (g/L Na_2SO_3)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (g/L Na_2SO_3)**	**95 Percent Confidence Estimate (g/L Na_2SO_3)**
“Fresh” at “Aim”	21.17	16	1.18	± 2.52
“Seasoned”, As Received	15.46	16	1.14	± 2.43
“Seasoned” with Standard Addition	20.23	16	1.58	± 3.38

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

For Potentiometric Titration:

- *Metrohm Potentiograph,* Model E536 or equivalent titrator
- *Metrohm* Model 665 *Dosimat* with a 50-mL burette size (no substitution)
- Electrodes:

Indicator electrode	=	Platinum inlay (i.e., *Beckman* Model 39273 or equivalent)
Reference electrode	=	Double-junction (i.e., *Orion* 900200 or equivalent) (10% KNO_3 outer filling solution)

For Visual Titration:

- Burette, Class A, 50 mL capacity, *Teflon stopcock*
- Magnetic Stirrer

REAGENTS

Use ACS Reagent Grade reagents unless otherwise specified.

- Potassium Iodate, KIO_3 (0.1 N), - standardized to four decimal places
- Acetic Acid, CH_3COOH (2.0 N)
- Potassium Iodide, KI (0.6 M)
- Sodium Thiosulfate, $Na_2S_2O_3$ (0.1 N) - standardized to four decimal places
- Formaldehyde (6%), pH 3.9
- Starch Indicator
- Phenolphthalein Indicator
- Sodium Hydroxide, NaOH (1.0 N)
- Sulfuric Acid, H_2SO_4 (1.0 N)
- Iodine, I_2 (0.1 N) - standardized to four decimal places
- Water, Type I Reagent – This method was developed, and the resulting statistical data were obtained using reagent water equivalent to or purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

For Potentiometric Titration

A. Hypo Index (HI) or Total Reductants

1. To a 400-mL beaker with a magnetic stir-bar, add 100 mL reagent water.
2. Pipette 40.0 mL (use a 20-mL pipette, twice) of standardized 0.1 N potassium iodate into the 400-mL beaker.
3. While stirring, add 10 mL of 2.0 N acetic acid and 25 mL of 0.6 M potassium iodide (KI) to the 400-mL beaker.
4. With continued stirring, immediately pipette 1.0 mL of sample *near the surface of the liquid*. Rinse the sides of the beaker with reagent water.
5. Titrate with standardized 0.1 N sodium thiosulfate on an E536 *Metrohm* Potentiograph or equivalent titrator. If using an E536, titrate the solution from step 4, using the following parameters:

Rate	=	10 min/100% vol
Auto Control	=	OFF
Mode	=	mV/pH
Range	=	500 mV
Burette Size	=	50 mL
Indicator Electrode	=	Platinum inlay or platinum wire (i.e., *Beckman* Model 39273)
Reference Electrode	=	Double-junction reference (i.e., *Orion* Model 90-02)

6. Determine the volume of 0.1 N sodium thiosulfate at the end point using concentric arcs (see Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or subsequent revision).
7. Run a blank (do steps 1–6, but omit the addition of the sample in step 4).

B. Thiosulfate Determination

1. Sample Pretreatment:
   a. To a 250-mL beaker with a magnetic stir-bar, add 75 mL of reagent water.
   b. Pipette 2.0 mL of sample into the 250-mL beaker.
   c. Add 5 mL of 6% formaldehyde (pH 3.9) to the beaker.
   d. Start stirring the contents of the 250-mL beaker, set and start a timer for 2 minutes of stirring.
2. Titration of Sample:
   a. Into a 400-mL beaker with a magnetic stir-bar, pipette 40.0 mL of standardized 0.1 N potassium iodate while the timer from step 1.d. is running.
   b. While stirring, add 10 mL of 2.0 N acetic acid to the 400-mL beaker (continue stirring through step 2e.).
   c. When the timer goes off, add 25 mL of 0.6 M KI to the 400-mL beaker.
   d. Immediately after the 0.6 M KI has been added, add the solution in the 250-mL beaker, from step 1, *Sample Pretreatment:*, to the 400-mL beaker.
   e. Rinse the 250-mL beaker three times with reagent water and add the rinses to the 400-mL beaker.
   f. Titrate the contents of the 400-mL beaker with standardized 0.1 N sodium thiosulfate on an E536 Metrohm Potentiograph or equivalent titrator. If using a Metrohm E536, titrate the solution from step 2e. using the parameters found in step 5 of the *Hypo Index (HI) or Total Reductants* procedure.
   g. Determine the volume of 0.1 N sodium thiosulfate at the end point using concentric arcs (see Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revision.
3. Run a blank, following all the steps in 1 and 2 above, except omit the addition of sample in step 1b.

C. Sulfite

1. Sulfite is a calculated value and requires no additional measurement.

For Visual Titration

A. Hypo Index (HI) or Total Reductants

Treatment and Titration of Sample:

1. Pipette (wipe before leveling) 40.0 mL of standardized 0.1 N potassium iodate solution into a 250-mL conical flask containing a magnetic stir bar.
2. Add 10 mL of 2.0 N acetic acid solution from a tip-up (or equivalent) pipette.
3. Stir the solution with a magnetic stirrer and add 25 mL of 0.6 M potassium iodide solution from a tip-up pipette.
4. Immediately pipette (wipe) 1.0 mL of the fixer sample into the 250-mL flask while the solution is stirring (hold the tip of the pipette against the wall of the flask and as close to the surface of the stirring solution as possible while the sample is draining but do not immerse the tip of the pipette in the stirring solution).
5. Titrate with standardized 0.1 N sodium thiosulfate solution to a light yellow color.
6. Add 5 mL of the starch indicator, from a tip-up pipette and continue the titration until the blue color just disappears for 15 seconds.
7. Run a blank (do steps 1–6, but omit the addition of the sample in step 4).

B. Thiosulfate (Hypo)

1. Treatment of the Sample:
   a. Pipette 2.0 mL of the fixer sample into a 250-mL conical flask containing a magnetic stir bar.
   b. Add 5 mL of formalin from a tip-up pipette.
   c. Add 3 or 4 drops of phenolphthalein indicator to the flask.
      - If the solution is pink, titrate with 1.0 N sulfuric acid to colorless.
      - If the solution is colorless, titrate with 1.0 N sodium hydroxide to the first light pink color.
   d. Let the solution stand for 2 minutes.
   e. Add 10 mL of 2.0 N acetic acid from a tip-up pipette.
2. Titration with Iodine:
   a. Add, from a tip-up pipette, 5 mL of the starch indicator to the conical flask.
   b. Titrate with standardized 0.1 N iodine solution to the first distinct blue color that persists for 15 seconds.

C. Sulfite

1. Sulfite is a calculated value and requires no additional measurement.

CALCULATIONS

For Potentiometric Titration

A. Hypo Index (HI) or Total Reductants:

$$\text{HI (1), mL} = \frac{(\text{mL Blank A} - \text{mL Sample A})\ (\text{N } Na_2S_2O_3)}{0.1000\ \text{N } Na_2S_2O_3}$$

Where:

HI (1), mL = mL of 0.1000 N I_2 consumed by 1.0 mL sample

mL Blank A = millilitres of titrant at the end point of the blank titration of potentiometric Procedure A.

mL Sample A = millilitres of titrant at the end point of the sample titration of potentiometric Procedure A.

N $Na_2S_2O_3$ = normality of the titrant (meq/mL)

0.1000 = nominal value for the normality of the titrant, in meq/mL

B. Thiosulfate ($S_2O_3^{=}$):

$$\text{g/L } S_2O_3^{=} = \frac{(\text{mL Blank B} - \text{mL Sample B})(\text{N } Na_2S_2O_3)(112.13)(1000)}{\text{sample size } (1000)}$$

Where:

mL Blank B = millilitres of titrant at the end point of the blank titration of potentiometric Procedure B

mL Sample B = millilitres of titrant at the end point of the sample titration of potentiometric Procedure B.

N $Na_2S_2O_3$ = normality of the titrant (meq/mL)

112.13 = equivalent weight of thiosulfate expressed in mg/meq

1000 = conversion factor of milligrams to grams

1000 = conversion factor of millilitres to litres

sample size = sample size used in potentiometric Procedure B (2.0 mL)

C. Sodium Sulfite (Na_2SO_3):

mL Blank A – mL Sample A = D mL A

mL Blank B – mL Sample B = D mL B

$$\text{g/L } Na_2SO_3 = \frac{[(\text{D mL A})(2.0) - (\text{D mL B})](\text{N } Na_2S_2O_3)(63.02)(1000)}{\text{sample size } (1000)}$$

Where:

N $Na_2S_2O_3$ = normality of the titrant

2.0 = conversion of hypo index to 2.0 mL sample size

63.02 = equivalent weight of sodium sulfite in mg/meq

1000 = conversion factor of milligrams to grams

sample size = sample size used in potentiometric Procedure B (2.0 mL)

1000 = conversion factor of millilitres to litres

Example Potentiometric Calculations:

Titration		mL 0.1 N $Na_2S_2O_3$ Titrant
Blank A	=	40.50
Sample A	=	21.85
Blank B	=	40.55
Sample B	=	19.80

Hypo Index (HI) or Total Reductants:

$$\text{HI (1), mL} = \frac{(40.50 - 21.85)(0.0989)}{0.1000}$$

$$= 18.4 \text{ mL } 0.1000 \text{ N } I_2$$

Thiosulfate ($S_2O_3^{=}$):

$$\text{g/L } S_2O_3^{=} = \frac{(40.55 - 19.80)(0.0989)(112.13)(1000)}{(2.0)(1000)}$$

$$= 57.5 \text{ g/L}$$

Sodium Sulfite (Na_2SO_3):

$$\text{g/L } Na_2SO_3 = \frac{[(40.50 - 21.85)(2.0) - (40.55 - 19.80)](0.0989)(63.02)(1000)}{(2.0)(1000)}$$

$$= 51.4 \text{ g/L}$$

For Visual Titration

A. Hypo Index (HI) or Total Reductants:

$$\text{HI (1), mL} = \frac{(\text{mL Blank A} - \text{mL Sample A})\ (\text{N } Na_2S_2O_3)}{0.1000\ \text{N } Na_2S_2O_3}$$

Where:

HI (1), mL = mL of 0.1000 N I_2 consumed by 1.0 mL sample

mL Blank A = millilitres of titrant at the end point of the blank visual titration, Procedure A.

mL Sample A = millilitres of titrant at the end point of the sample visual titration, Procedure A.

N $Na_2S_2O_3$ = normality of the titrant (meq/mL)

0.1000 = nominal value for the normality of the titrant, in meq/mL

B. Thiosulfate ($S_2O_3^{=}$):

$$\text{g/L } S_2O_3^{=} = \frac{(\text{mL } I_2)(\text{N } I_2)[\text{eq. wt. } S_2O_3^{=}](1000)}{(\text{mL Sample size})(1000)}$$

Where:

mL I_2 = millilitres of iodine titrant measured at the visual end point

N I_2 = normality of the titrant (meq/mL)

[eq. wt. $S_2O_3^{=}$] = equivalent weight of thiosulfate expressed in mg/meq (112.13)

1000 = factors to convert mg/mL to g/L

C. Sodium Sulfite (Na_2SO_3):

$$\text{g/L } Na_2SO_3 = \frac{[(\text{HI})(\text{N* } I_2)(3)] - [(\text{mL } I_2)(\text{N } I_2)](\text{eq. wt. } S_2O_3^{=})(1000)}{(\text{mL Sample size})(1000)}$$

Where:

HI = mL of 0.1000 N I2 consumed by 1.0 mL sample

N* I_2 = nominal 0.1000 normality of iodine used in the Hypo Index calculation (meq/mL)

3 = conversion of Hypo Index to a 3.0 mL sample size

mL I_2 = millilitres of iodine titrant measured at the visual end point, Procedure B

N I_2 = normality of the iodine titrant (meq/mL) used in Procedure B, visual end point

eq. wt. $S_2O_3^{=}$ = equivalent weight of thiosulfate expressed in mg/meq (112.13)

mL Sample = sample size used in Procedure B, visual end point

1000 = conversion factors for milligrams to grams and milliliters to liters

Spectrophotometric Determination of Iron (II) in "UL" Bleach

ECN-2-3275-2

INTRODUCTION

The determination of iron (II) in Process ECN-2 "UL" bleach employs a spectrophotometric technique. The iron (II) concentration is determined by adding sample to deaerated 1,10-phenanthroline/sodium acetate to form a colored complex. The absorbance of the complex is measured at 510 nm on a spectrophotometer. Protect bleach samples from oxidation between sampling and analysis to avoid the accidental loss of iron (II). It is essential to complete the analysis within four hours of sampling because the ferric complex is thermally unstable and will yield iron (II) when sealed samples are kept for extended periods. The 1,10-phenanthroline/sodium acetate is deaerated with nitrogen to prevent oxidation of the iron (II) in the sample as the colored complex is formed.

Use of this method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed three (3) replicates on each of the following solutions during methods development.

1. A fresh "UL" bleach was prepared with all components at their respective "working tank" aim concentrations 0.492 g/L iron (II).
2. A seasoned "UL" bleach analyzed as received, at 0.270 g/L iron (II).
3. The same "seasoned" solution as in number 2, above, was reanalyzed after making an analytically weighed, standard addition of 0.483 g/L iron (II).

Iron II				
Sample	**Mean g/L Iron (II)**	**N**	**Repeatability Standard Deviation, $1s_r$ g/L Iron (II)**	**95 Percent Confidence Estimate g/L Iron (II)**
Fresh 0.492 g/L Iron (II)	0.498	4	0.002	± 0.006
Seasoned as Received	0.270	4	0.004	± 0.013
Seasoned plus Addition	0.748	4	0.016	± 0.051

Bias

Bias is a statistically significant deviation of the mean from the known iron (II) level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method.

A bias of 0.006 g/L iron (II) was found not to be statistically significant fir the Process ECN-2 "fresh" tank "UL" bleach sample. However, the difference at the 95 percent confidence level was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

The recovery of the standard addition sample was 98.96 percent and found to not be statistically different from 100 percent at the 95 percent confidence level. However, it was judged not to be practically different from 100 percent.

REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ and 95 Percent Confidence Estimate

Reproducibility, or customer standard deviation, ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Three Process ECN-2 "UL" bleach samples were analyzed by four analysts, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. Three fresh "UL" bleach samples were prepared with all components at their respective working tank aim concentrations.
2. A seasoned "UL" bleach sample was analyzed spectrophotometrically, as received, at 0.078 g/L iron (II).
3. The same "seasoned" solution, as in number 2, above, was reanalyzed after, after making an analytically weighed, standard addition of 0.229 g/L iron (II).

Iron II				
Sample	**N**	**Mean**	**Reproducibility Standard Deviation, $1s_c$ g/L Iron (II)**	**95 Percent Confidence Estimate g/L Iron (II)**
"Fresh" at 0.247 g/L Iron (II)	16	0.246 g/L	0.005	± 0.010
"Fresh" at 0.492 g/L Iron (II)	16	0.493 g/L	0.007	± 0.015
"Fresh" at 1.001 g/L Iron (II)	16	1.010	0.014	± 0.029
"Seasoned" as Received	16	0.078 g/L	0.005	± 0.010
"Seasoned" with Standard Addition	16	0.271 g/L	0.005	± 0.011

Bias

Bias is a statistically significant deviation of the mean from the known iron (II) level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample since the component concentration level was not determined independently of the test method.

No statistically significant bias was found at all levels for the Process ECN-2 "fresh" tank "UL" bleach samples (–0.001 g/L for the 0.25 g/L sample, 0.001 g/L for the 0.492 g/L sample, and 0.009 g/L for the 1.001 g/L sample.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

The recovery of the standard addition sample was 84.28 percent and found to be statistically different from 100 percent at the 95 percent confidence level. However, it was not practically different from 100 percent because the seasoned solution result was below the calibration range of the method. When the seasoned sample is in the calibration range, the recovery of the standard addition is not statistically different from 100 percent.

APPARATUS

- Double Beam Spectrophotometer with a tungsten lamp (i.e., Perkin-Elmer Lambda 4 series)
- 1-cm Silica Cells (two)
- 200-µL Eppendorf micropipet or equivalent micropipet

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- Nitrogen Gas, N_2
- 1,10 Phenanthroline/Sodium Acetate Reagent
- Ferrous Ammonium Sulfate 6-hydrate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$
- Potassium Dichromate, $K_2Cr_2O_7$, NIST Oxidimetric Primary Standard SRM-136e (or subsequent lot of SRM-136)
- Ferroin Indicator
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

A. Blank Determination

1. Adjust the spectrophotometer wavelength to 510 nm.
2. Rinse two, clean 1-cm cells with reagent water, at least three times. Fill the cells with reagent water and dry the outside surfaces with a tissue.
3. Place both cells into the spectrophotometer and zero the instrument.
4. Leave a cell in the reference path of the instrument and remove the sample cell.

Sample Treatment

1. Bubble nitrogen through the 1,10-phenanthroline/ sodium acetate reagent, contained in a conical flask, for 15 minutes.

   Note: Only degas 5 mL of reagent per sample plus 30 mL extra.
2. After degassing the 1,10-phenanthroline/sodium acetate reagent for 15 minutes, use a serological pipet to add 5.00 mL to a l00-mL volumetric flask.
3. With a micropipet (Eppendorf or equivalent), pipet 200.0 µL of sample into the flask that contains the 5 mL of 1,10-phenanthroline/sodium acetate reagent. Swirl the flask to mix.
4. Dilute to volume with distilled water. Invert the flask 6 to 10 times to thoroughly mix the solution.
5. Immediately (within 20 sec) rinse the 1-cm cell from the spectrophotometer sample compartment, at least three times, with the above solution, and fill the cell. Rinse the outer surfaces of the cell with reagent water and dry with a tissue.
6. Place the cell into the sample compartment of the spectrophotometer. Measure and record the absorbance at 510 nm vs reagent water.

Calculations

$y = mx + b$

Where:

- y = concentration of iron(II) in g/L
- m = slope of the line

  Note: Slope is the relation between absorbance and iron (II) concentration determined during calibration [in g/L /abs].
- x = absorbance of sample at 510 nm
- b = the intercept of the calibration line with the y-axis [in g/L, iron (II)]

$\text{Iron (II), g/L} = m(A_{510}) + b0.046$

Each laboratory should establish its own calculation based on a linear regression of a set of calibration standards. *APPENDIX I* explains this calibration procedure. The calibration line may be different for each spectrophotometer. The following is a typical calibration line:

$\text{Iron (II), g/L} = 2.57(A_{510}) + 0.046$

APPENDIX I

Spectrophotometer Calibration for Iron (II) Determination

Note: Use this appendix to recheck the spectrophotometer linear calibration for iron (II) at least every 6 months. Also use it the first time this method is performed, and whenever the spectrophotometer has been adjusted or repaired.

Preparation of Standard

Prepare a litre of fresh Process ECN-2 "UL" bleach solution containing all the constituents of the mix at the aim tank concentrations.

1. For the four iron (II) standards in "UL" bleach, weigh out 0.088, 0.176, 0.355, and 0.710 g portions of assayed ferrous ammonium sulfate, 6-hydrate, record to the nearest 0.1 mg. See Module 4, *Reagent Preparation Procedures*, for the assay procedure for ferrous ammonium sulfate, 6-hydrate.
2. Quantitatively transfer each of the four weighings of ferrous ammonium sulfate to four 50-mL volumetric flasks, labeled with the corresponding weights. Rinse each weighing boat into the corresponding flask with the fresh "UL" bleach mix. Swirl each flask to dissolve the ferrous ammonium sulfate.

   Note: The iron (II) material (ferrous ammonium sulfate) takes some time to dissolve.
3. When the ferrous ammonium sulfate has dissolved, fill each volumetric flask to the mark with the fresh "UL" bleach mix. Invert each flask 6-10 times to thoroughly mix the solutions.
4. Run each sample in (at least) duplicate by the method described in the preceding *PROCEDURE*, p. -3.

Determination of Iron (II)

The calculation to determine the amount of iron (II) in the standards from the weighed amount of ferrous ammonium sulfate is as follows:

g/L iron (II) =

$$\text{g/L iron (II)} = \frac{\text{g of } Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O}{(50\text{ mL})} \times \frac{55.85}{391.85} \times \frac{1000\text{ mL}}{1\text{ L}} \times \frac{\text{wt/wt assay}}{100}$$

Where:

g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	=	weight recorded in Step 1
55.85	=	atomic weight of Iron
1000 mL	=	factor to convert mL to L
50 mL	=	volume of the ferrous ammonium sulfate standard
392.13	=	molecular weight of ferrous ammonium sulfate, 6-hydrate
100	=	correction for wt/wt% to wt/wt
wt/wt assay	=	assay of $Fe(NH_4)_2(SO_4)_2$ based on determination in Appendix II

Regression

The data collected from above was used to construct the regression equation for the calibration line.

The reliability of the resulting calibration line was determined in the following manner on a spectrophotometer in a Kodak laboratory. Four fresh "UL" bleach solutions were prepared containing 0.2503, 0.4995, 1.006, and 2.013 g/L iron (II). Each solution was analyzed in duplicate to create a linear regression (based on 12 data points) for each spectrophotometer being used. The average standard deviation (1s) for the linear regression was 0.011 g/L iron (II), corresponding to a 95 percent confidence estimate of ± 0.02 g/L. Each laboratory should calibrate their spectrophotometer; otherwise, an unknown bias may exist.

Ferrous Ammonium Sulfate, g/L	g/L Iron (II)	Absorbance of Sample
0.0882	0.2503	0.081
0.0882	0.2503	0.081
0.0882	0.2503	0.083
0.1760	0.4995	0.174
0.1760	0.4995	0.174
0.1760	0.4995	0.175
0.3545	1.0062	0.376
0.3545	1.0062	0.374
0.3545	1.0062	0.372
0.7091	2.0126	0.766
0.7091	2.0126	0.763
0.7091	2.0126	0.769

The data was then processed by a least squares linear regression to develop the line, y = mx + b. Definition of the equation is found in the *Calculations* section (page -3).

The equation generated using the above data was:

$$\text{Iron (II), g/L} = 2.57(A_{spl}) + 0.046$$

APPENDIX II

This appendix contains two assay procedures for Ferrous Ammonium Sulfate. The first procedure uses Potassium Dichromate; while the alternate procedure uses Potassium Permanganate titrant.

Assay Procedure for Ferrous Ammonium Sulfate, Hexahydrate

Reagents

All reagents are ACS Reagent Grade unless otherwise stated.

- Potassium Dichromate, $K_2Cr_2O_7$, NIST Primary Standard, 136e, dried for 2 hours at 110°C
- Ferroin Indicator, 1,10 Phenanthroline ferrous sulfate (0.025 M)
- Sulfuric Acid, concentrated, H_2SO_4
- Ferrous Ammonium Sulfate 6-Hydrate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$

Procedure

1. Weigh 14.0 g of ferrous ammonium sulfate to the nearest 0.0001 g and record the weight.
2. Quantitatively transfer to a 200-mL volumetric flask with reagent water and swirl the flask to dissolve the ferrous ammonium sulfate.
3. Dilute the solution to the mark with reagent water. Invert the flask, 6-10 times, to thoroughly mix.
4. Weigh 1.0 g of dried, potassium dichromate to the nearest 0.0001 g and record the weight.
5. Quantitatively transfer to a 100-mL volumetric flask containing 50 mL of reagent water. Swirl the flask to dissolve the potassium dichromate.
6. Dilute the solution to the mark with reagent water. Invert the flask 6-10 times, to mix thoroughly.
7. Fill a 50-mL buret with the ferrous ammonium sulfate solution (step 3, above).
8. Add 20 mL concentrated sulfuric acid to a 150-mL beaker containing 25 mL of distilled water and a magnetic stirring bar.

Caution

Hot acid solution is formed. Always add acid to water and not the converse

9. Pipet 15.0 mL of the potassium dichromate solution into the beaker.
10. Add 2 drops of ferroin indicator to the beaker and place the beaker on a magnetic stirrer.
11. Slowly add the ferrous ammonium sulfate solution from the buret to the beaker. The solution will change colors as the titrant is added, going from a green-blue color to a reddish-brown color. The point the produces the first *reddish-brown* color change is the end point.
12. Record the volume of the ferrous ammonium sulfate titrant consumed to the nearest 0.05 mL at the end point.
13. Repeat steps 7–12, two more times.

Calculations

To calculate the Assay Percentage, four preliminary calculations must first be performed. first, the normality of the potassium dichromate must be determined.

1) N Potassium Dichromate

$$N\ K_2Cr_2O_7 = \frac{\text{g wt of N } K_2Cr_2O_7 \times 1000}{100 \times 49.03}$$

Where:

g wt of $K_2Cr_2O_7$	=	recorded weight from step 4
1000	=	factor to convert equivalent wt. to milliequivalent wt.
100	=	volume of $K_2Cr_2O_7$ solution in mL
49.03	=	g/equivalent wt. of $K_2Cr_2O_7$

Once the normality of the potassium dichromate is known, the value is used in the second calculation to determine the normality of the ferrous ammonium sulfate.

2) N of Ferrous Ammonium Sulfate

$$N\ Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O = \frac{(mL\ K_2Cr_2O_7)(N\ K_2Cr_2O_7)}{mL\ Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$$

Where:

mL $K_2Cr_2O_7$	=	15.0 mL volume of $K_2Cr_2O_7$ solution taken
N $K_2Cr_2O_7$	=	Normality (meq./mL) calculated, above
mL $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	=	average volume* of the three titrations required to reach the end point color change.

* The average volume for the three titrations should not have a standard deviation (1_s) greater than 0.50 mL

Once the normality of the ferrous ammonium sulfate has been calculated, it is used to determine the actual iron (II) concentration in g/L in the third calculation.

3) g/L, Iron (II) in Ferrous Ammonium Sulfate

$$g/L,\ Iron\ (II)\ (actual) = N\ Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O \times 55.85$$

Where:

55.85	=	equivalent weight (g/equivalent) of Iron (II) in $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$

The theoretical concentration of iron (II) is calculated in the fourth step.

4) Theoretical wt of Iron (II) in Solution

$$\text{g/L iron (II)} = \frac{\text{wt of } Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O}{200 \text{ mL}} \times \frac{55.85}{392.13} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

Where:

wt of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	=	weight (g) recorded in Step 1
55.85	=	atomic weight of iron (g/mole)
1000 mL	=	factor to convert mL to Litre
200 mL	=	preparation volume for $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$
392.13	=	molecular weight (g/mole) of ferrous ammonium sulfate, 6-hydrate

Finally, the assay percentage of the ferrous ammonium sulfate hexahydrate is determined using the actual iron concentration (determined in step 3) and the theoretical iron concentration (determined in step 4) as follows:

5) Assay Percentage

$$\text{\% iron (II)} = \frac{\text{g/L iron (II) (actual)}}{\text{g/L iron (II) (Theo.)}} \times 100$$

Alternate Assay Procedure for Ferrous Ammonium Sulfate, Hexahydrate

Note: This procedure is based on the method in Reagent Chemicals, 8th Edition, Amercian Chemical Society, 1993.

Assay Procedure

Note: This procedure should be repeated in triplicate with the average of the three results used as the assay value.

1. Accurately weigh 1.6 grams of sample to the nearest milligram and dissolve in a mixture of 100 mL reagent water and 3 mL of concentrated sulfuric acid contained in a 250 mL Erlenmeyer flask.

Caution

Always add acid to water and not water to acid.

2. Titrate while stirring with standardized 0.1 N potassium permanganate ($KMnO_4$) from a 50 mL buret to a permanent faint pink endpoint that lasts for at least 15 seconds.
3. Repeat steps 1 and 2 without any sample. This is the blank.

Calculations

$$\text{\% (wt./wt.) ferrous ammonium sulfate, hexahydrate} = \frac{(\text{mL } KMnO_4 \text{ sample} - \text{mL } KMnO_4 \text{ blank}) \times \text{N } KMnO_4 \times 0.3921 \times 100}{\text{sample size in grams}}$$

Spectrophotometric Determination of Iron (Total) and Iron (II) in "ML" Bleach

ECN-2-ML-3260

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SR-32/SR-32R	—	—	—

INTRODUCTION

This method contains analytical procedures for measuring Iron(II) and total Iron in KODAK Process ECN-2, Type ML Bleach. Calculations, derived from the analytical data, are included for determining Iron(III).

Total Iron is determined by oxidizing any Iron(II) Iron(III) with Persulfate. A Thiocyanate complex of the Iron(III) is formed in a dilute acid solution. A direct measurement of the Iron-Thiocyanate is made using a calibrated spectrophotometer at 474 nm. Each spectrophotometer is calibrated for the Iron-Thiocyanate complex using standard samples. The standard samples are prepared and analyzed using this procedure. An average absorptivity measurement is calculated from the standard data. This average absorptivity is used to calculate a sample concentration.

The Iron(II) is determined by adding a sample to deaerated 1,10-Phenanthroline/Sodium Acetate reagent. Any Iron(II) present in the sample will form a colored complex with the reagent that can be measured on a spectrophotometer at 510 nm. Bleach samples should be protected from aeration between the time of sampling and analysis. The Iron(II) content of the bleach increases gradually upon standing. Bleach solutions should be analyzed for Iron(II) within 4 hours of sampling. The 1,10-Phenanthroline/Sodium Acetate reagent is deaerated with Nitrogen prior to use to prevent any additional oxidation.

Iron(III) is Calculated by subtracting the g/L Iron(II) from the g/L total Iron.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

Total Iron

Three fresh samples of concentration 6.0, 14.0 and 20.0 g/L total Iron were prepared in KODAK Process ECN-2-ML bleach solution. Each solution was run in duplicate by four analysts on one day. Based on this data (n = 24), the 95 percent confidence estimate is ± 0.4 g/L total Iron (1s± = ± 0.2 g/L) for fresh solutions.

A seasoned KODAK Process ECN-2-ML bleach and that sample containing a 2 g/L total Iron standard addition were analyzed in duplicate by four analysts. Based on this data (n = 16), the 95 percent confidence estimate is ± 0.4 g/L total Iron (is ± 0.2 g/L) for seasoned samples. The recovery of the 2 g/L total Iron addition indicated no bias due to the analytical technique.

Iron(II)

Ten mixes of aqueous solutions of Ferrous Ammonium Sulfate were analyzed by three analysts in two laboratories and over two ranges.

Range 1: 0.5-2.5 g/L of Ferrous Iron

The 95 percent confidence estimate for a single determination based on a 2-variable linear regression of 13 data points is ± 0.1 g/L Ferrous Iron.

Range 2: 2.5-12.5 g/L Ferrous Iron

The 95 percent confidence estimate for a single determination based on 2-variable linear regression of 13 data points is ± 0.45 g/L Ferrous Iron.

SPECIAL APPARATUS

- 50-µL Eppendorf micropipet or equivalent micropipet
- 100-µL Eppendorf micropipet or equivalent micropipet
- Rapid-delivery glass transfer pipes or automatic pipet
- Spectrophotometer equipped with a tungsten lamp

Note: Follow the manufacturer's instructions for care and use of micropipets.

Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

- 2.5 N Sulfuric Acid, H_2SO_4
- 40 g/L Potassium Persulfate, $K_2S_2O_8$
- 200 g/L Ammonium Thiocyanate, NH_4SCN
- 1,10-Phenanthroline/Sodium Acetate reagent
- Ferric Nitrate, $Fe(NO_3)_3 \cdot 9H_2O$ ACS reagent grade
- 0.1 N Sodium Thiosulfate, standardized $Na_2S_2O_3$
- Potassium Iodide, KI ACS reagent grade
- Starch indicator
- 0.1 N Nitric Acid, HNO_3
- Hydrochloric Acid, HCl concentrated

PROCEDURE

Determination of Absorptivity

See *APPENDIX 1, Determination of the Absorptivity of the Iron-Thiocyanate Complex*.

Total Iron

Sample Procedure

1. Prepare a blank solution by adding 25 mL 2.5 N Sulfuric Acid, 10 mL of 40 g/L Potassium Persulfate and 25 mL 200 g/L Ammonium Thiocyanate to a 100-mL volumetric flask. *Swirl to mix* and dilute to volume with distilled water.
2. Adjust the wavelength on the spectrophotometer to 474 nm. Zero the spectrophotometer vs air.
3. Rinse a clean 1-cm silica cell several times with the blank solution prepared in #1. Rinse the outer faces of the cell with water and dry with a tissue. Place in the sample-cell compartment of the spectrophotometer. Record the absorbance at 474 nm. This is A_{blk}.
4. Pipet 2.0 mL of a bleach sample into a 250-mL volumetric flask. Dilute to volume with distilled water. *Invert several times to mix*.
5. To a second 100-mL volumetric flask, add 25 mL of 2.5 N Sulfuric Acid and 10 mL of 40 g/L Potassium Persulfate. *Swirl to mix*.
6. Pipet 3.0 mL of the diluted bleach sample from step 4 into the 100-mL volumetric flask. *Swirl to mix*.
7. Add 25 mL of 200 g/L Ammonium Thiocyanate to the 100-mL volumetric flask. *Swirl to mix*. Dilute to volume with distilled water. *Invert several times to mix*.
8. Remove the 1-cm silica cell, containing the blank, from the cell compartment of the spectrophotometer and rinse with distilled water several times.
9. Rinse the cleaned silica cell several times with the sample prepared in step 7, and fill with the sample solution.
10. Rinse the outer faces of the cell with distilled water, wipe, and dry with a tissue.
11. Place the cell with the sample solution into the sample-cell compartment of the spectrophotometer and determine the absorbance of the sample at 474 nm vs air. This is A_{Spl}.

Calculation

$$A_{474} = A_{spl} - A_{blk}$$

$$\text{g/L Fe} = \frac{A_{474} \times 4166.7}{\text{Absorptivity}}$$

Where:

Absorptivity is the absorptivity of the Iron/ Thiocyanate complex (see *APPENDIX 1*)

4166.7 is the dilution factor

$$\left(\frac{250\ \text{mL}}{2\ \text{mL}} \times \frac{100\ \text{mL}}{3\ \text{mL}} \right)$$

Ferrous Iron, Fe (II)

1. Bubble Nitrogen through an appropriate volume of 1,10-Phenanthroline/Sodium Acetate reagent in a conical flask for 15 min. Allow 5 mL of reagent for each sample and an extra 25-30 mL for ease in bubbling.
2. After 15 min. pipes 5 mL of the deaerated 1,10-Phenanthroline/Sodium Acetate reagent, using a fast-delivery glass transfer pipes or equivalent automatic device, into the indicated volumetric flask (see Note 1).

g/L Iron(II)		Volumetric Flask
a.	0.5-2.5 g/L (see Note 2)	100-mL
b.	2.5-12.5 g/L	250-mL

Note: 1: Because of the large excess of reagent used, absolute accuracy in pipetting is not essential. The transfer should be rapid to prevent excessive aeration of the reagent. Continue bubbling the 1,10-Phenanthroline/Sodium Acetate reagent remaining in the conical flask for use on subsequent samples.

Note: 2: Initially use a 100-mL volumetric flask (Step 2a). If the absorbance obtained in Step 5 is greater than 0.550, discard the results and follow the procedure using a 250-mL volumetric flask (Step 2b).

3. Using an EPPENDORF (or equivalent) micropipet, pipes the indicated volume of sample into the volumetric flask containing the 1,10-Phenanthroline/ Sodium Acetate reagent and swirl to mix:

a.	100-mL volumetric flask	use 100 µL
b.	250-mL volumetric flask	use 50 µL

4. Dilute to volume with distilled water; invert several times to mix.
5. *Immediately* measure the absorbance of the solution on a spectrophotometer at 510 nm using a 1-cm silica cell vs air (zeroed @ 510 nm, air vs air) (see Step 2, Note 2).

Calculations

a. Range: 0.5–2.5 g/L Iron (II) (100 µL)

Calculation:

$$\text{Iron (II), g/L} = 5.40\ (A_{510}) - 0.27$$

b. Range: 2.5–12.5 g/L Iron (II) (50 µL)

Calculation:

$$\text{Iron (II), g/L} = 25.66\ (A_{510}) - 0.69$$

Iron (III)

Iron(III), g/L - Total Iron, g/L - Iron(II), g/L

APPENDIX 1

Determination of the Absorptivity of the Iron-Thiocyanate Complex

Reagents

- Distilled water
- Ammonium Thiocyanate, 200 g/L
- Potassium Persulfate, 40 g/L
- Ferric Nitrate, 9-hydrate, ACS reagent grade
- Potassium Iodide
- Hydrochloric Acid, concentrate
- Starch indicator
- Sodium Thiosulfate, 0.1 N standardized to 4 decimal places
- Nitric Acid, 0.1 N

Procedure

1. Weigh 9.0 g of Ferric Nitrate, 9-hydrate, ± 0.001 g, and transfer to a 250-mL volumetric flask. Dissolve and dilute to volume with distilled water. *Invert several times to mix*. This solution is labeled as 5 g/L Fe.
2. Prepare a blank by adding 25 mL 2.5 N Sulfuric Acid, 10 mL 40 g/L Potassium Persulfate, and 25 mL 200 g/L Ammonium Thiocyanate to a 100-mL volumetric flask. *Swirl to mix*. Dilute to volume with distilled water. *Invert several times to mix*.
3. Rinse a clean 1-cm silica cell several times with the blank solution and then fill the cell with the blank solution. Clean (with distilled water) and dry (with a tissue) the outer faces of the cell.
4. Zero the spectrophotometer at 474 nm vs air.
5. Place the cell containing the blank in the sample cell compartment. Read the absorbance at 474 nm. This is A_{blk}.
6. Pipet 5.0 mL of the 5 g/L Fe solution prepared in step 1 into a 500-mL volumetric flask. Dilute to volume with 0.1 N Nitric Acid. *Invert several times to mix*.
7. To a 100-mL volumetric flask, add 25 mL 2.5 N Sulfuric Acid and 10 mL of 40 g/L Potassium Persulfate. *Swirl to mix*.
8. Pipet 3.0 mL of the solution from step 6 into the volumetric flask from step 7. *Swirl to mix.*
9. Add 25 mL of 200 g/L Ammonium Thiocyanate to the 100-mL volumetric flask. Swirl to mix. Dilute to volume with distilled water. *Invert several times to mix*.
10. Remove the sample cell containing the blank from the spectrophotometer. Rinse the cell several times and fill with the solution from step 9. Clean the outer faces of the cell with distilled water and dry with a tissue.
11. Determine the absorbance of the solution in step 10 at 474 nm vs air. This is $A_{Std\ \#1}$.

12. Substitute the following sample sizes in Step 8.

Sample size	A_{std}
4 mL	$A_{std\ \#2}$
5 mL	$A_{std\ \#3}$
10 mL	$A_{std\ \#4}$

13. Each of the standards needs to be analyzed at least three times.

Calculation of the Absorptivity

$$\text{Absorptivity, L/(g-cm)} = \frac{A \times DF}{Assay}$$

Where:

A = absorbance measured at 474 rnm

Assay = the value determined below

DF = the dilution factor,

$$\left(\frac{500}{5} \times \frac{100}{\text{sample size}}\right)$$

3333 for std. #1

2500 for std. #2

2000 for std. #3

1000 for std. #4

$$\text{Absorptivity for std. \#1} = \frac{3333 \times A_{std\ \#1}}{Assay}$$

$$\text{Absorptivity for std. \#2} = \frac{2500 \times A_{std\ \#2}}{Assay}$$

$$\text{Absorptivity for std. \#3} = \frac{2000 \times A_{std\ \#3}}{Assay}$$

$$\text{Absorptivity for std. \#4} = \frac{1000 \times A_{std\ \#4}}{Assay}$$

A typical absorptivity is 190.0 L/(g-cm) (see *APPENDIX 2, Typical Absorptivity*). Calculate a mean absorptivity using the data from the triplicate analysis of the standards. The mean value should have a RSD < 1.0%.

$$\text{Mean} = \bar{A} = \frac{\Sigma A}{n} \quad ; \quad \text{Standard Deviation(s)} = \sqrt{\frac{\Sigma(A - \bar{A})^2}{n-1}}$$

where: A = individual absorbance measurements
n = 12

$$RSD = \frac{s}{\bar{A}} \times 100\%$$

See *APPENDIX 2, Typical Absorptivity* for an example of sample data.

Assay of 5 g/L Iron Solution

1. This assay procedure should be performed in triplicate.
2. Pipet 25.0 mL of the stock solution of 5 g/L Fe into a 500-mL glass stoppered ERLEMMEYER flask containing 100 mL of distilled water.
3. Add 5 mL of concentrated Hydrochloric Acid and 3 ± 0.1 g of Potassium Iodide.
4. Stopper and swirl the flask to dissolve the Potassium Iodide. Store in a dark place for 30 minutes.
5. After the 30 minutes, remove the flask from the dark and titrate with standardized 0.1 N Sodium Thiosulfate (50-mL buret) from a red color to a yellow-red color change.
6. Add 3 mL Starch indicator solution and continue titrating until the blue to colorless endpoint persists for 15 seconds. This is mL_{spl}.
7. Into another 500-mL ERLENMEYER flask, add 100 mL distilled water, 5 mL concentrated Hydrochloric Acid and 3 g Potassium Iodide.
8. Stopper the flask and swirl as in Step 4. Store in the dark for 30 minutes.
9. After 30 minutes, add 3 mL Starch indicator solution.
10. Swirl and titrate with standardized 0.1 N Sodium Thiosulfate (50-mL beret). Titrate to the same persistent color observed in step 6, above. This is mL_{blk}.
11. Each of the standards needs to be analyzed at least three times.

Calculation of the Absorptivity

$$\text{g/L Fe)} = \frac{mL \times E_w \times N}{25.0}$$

Where:

E_w = Equivalent weight of Iron, 55.85

25.0 = Sample size in mL

N = Normality of the Sodium Thiosulfate

mL = $mL_{Spl} - mL_{blk}$

Calculate the mean, standard deviation and RSD of the assay. The RSD should be < 0.5%.

$$\text{Mean} = \bar{X} = \frac{\Sigma X}{n}$$

$$\text{Standard Deviation(s)} = \sqrt{\frac{\Sigma(X - \bar{X})^2}{n-1}}$$

$$RSD = \frac{s}{\bar{X}} \times 100\%$$

F010_0088

Where:

E_w = the individual result

n = the number of replicates (3)

APPENDIX 2
Typical Absorptivity

mL Diluted Stock	Absorbance	Absorptivity
3	0.279	189.48
3	0.279	189.48
3	0.286	192.19
4	0.381	192.04
4	0.374	188.50
4	0.381	192.04
5	0.467	188.31
5	0. 475	191.53
5	0.475	191.53
10	0.935	188.51
10	0.939	189.31
10	0.939	189.31
		$\overline{X}$ = 190.2
		S = ± 1.5
		RSD = ± 0.8%

Spectrophotometric Determination of Total Iron in EASTMAN Color Films, "KUL" Bleach

ECN-0006/1
ECP-0006/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SB-34/ SR-34R	SB-34/ SR-34R	—	—

INTRODUCTION

The determination of total iron in Eastman Color Films, Process ECN-2 or Process ECP-2D, "KUL" Bleach utilizes a spectrophotometric procedure. Total Iron is determined by oxidizing any iron (II) present to iron (III) with persulfate. A thiocyanate complex of the iron (III) is formed in a dilute acid solution. A direct measurement of the iron-thiocyanate complex is made using a calibrated spectrophotometer with wavelength set at 477 nm. The calibration of the spectrophotometer is described in Appendix A.

Use of this method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development:

a. A "fresh" EASTMAN Color Films, Process ECN-2 or Process ECP-2D, "KUL" bleach prepared with all components at their respective working tank aim concentrations:
   - 4.946 g/L total iron for Process ECN-2
   - 8.728 g/L total iron for Process ECP-2D

b. A "seasoned" EASTMAN Color Films, Process ECP-2, "KUL" bleach analyzed as received at:
   - 5.285 g/L total iron for Process ECN-2
   - 9.219 g/L total iron for Process ECP-2D

c. The same "seasoned" solution as in letter b, above, analyzed after making an analytically weighed, standard addition of:
   - 0.529 g/L total iron for Process ECN-2
   - 1.386 g/L total iron for Process ECP-2D

Repeatability Standard Deviation, $1s_r$ & 95 Percent Confidence Estimate (not including bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

Samples (Process ECN-2, "KUL" Bleach)	Mean Level (g/L Total Iron)	(N)	Repeatability Standard Deviation, $1S_r$ (g/L Total Iron)	95 Percent Confidence Estimate (g/L Total Iron)
"Fresh" at "Aim" (4.946 g/L Total Iron)	4.943	5	0.055	± 0.15
"Seasoned", As Received	5.285	5	0.12	± 0.32
"Seasoned" with Standard Addition	5.797	5	0.039	± 0.11

Samples (Process ECP-2, "KUL" Bleach)	Mean Level (g/L Total Iron)	(N)	Repeatability Standard Deviation, $1S_r$ (g/L Total Iron)	95 Percent Confidence Estimate (g/L Total Iron)
"Fresh" at "Aim" (8.728 g/L Total Iron)	8.598	5	0.046	± 0.13
"Seasoned", As Received	9.219	5	0.13	± 0.36
"Seasoned" with Standard Addition	10.610	5	0.075	± 0.21

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independently of the test method.

No statistically significant bias was found for a Process ECN-2, "KUL" "fresh" tank bleach sample.

A statistically significant low bias (–1.5 percent) was found for a Process ECP-2, KUL "fresh" tank bleach sample. This was judged not to be practically significant.

Recovery

Recovery is used instead of bias for "seasoned" samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample, which contains the standard addition minus the mean of the "seasoned" sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

For the Process ECN-2, KUL "fresh" tank bleach sample, the recovery (96.8 percent) was not statistically different from 100 percent.

For the Process ECP-2, KUL "fresh" tank bleach sample, the recovery (100.3 percent) was not statistically different from 100 percent.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The customer standard deviation ($1s_c$)is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Two EASTMAN Color Films, Process ECN-2, "KUL" bleach samples were analyzed by four trained analysts, using multiple calibrated spectrophotometers, on two different days. Duplicate analyses were performed on each sample, on each of two days. These samples were:

a. A "fresh" tank solution prepared at 4.937 g/L total iron.

b. An EASTMAN Color Films, Process ECN-2, "KUL" "seasoned" bleach tank sample analyzed, as received, in the same manner as the "fresh" bleach.

Samples (Process ECN-2, "KUL" Bleach)	Mean Level (g/L Total Iron)	(N)	Reproducibility Standard Deviation, $1S_c$ (g/L Total Iron)	95 Percent Confidence Estimate (g/L Total Iron)
"Fresh" at "Aim" (4.937 g/L Total Iron)	4.992	16	0.11	± 0.23
"Seasoned", As Received	3.634	16	0.072	± 0.15

Three EASTMAN Color Films, Process ECP-2, "KUL" bleach samples were analyzed by four trained analysts, using multiple calibrated spectrophotometers, on two different days. Duplicate analyses were performed on each sample, on each of two days. These samples were:

a. A "fresh" bleach tank solution prepared at 8.712 g/L total iron with all components at their respective working tank "aim" concentrations.

b. An EASTMAN Color Films, Process ECP-2, "KUL" "seasoned" bleach tank sample analyzed, as received at 10.442 g/L total iron, in the same manner as the "fresh" bleach.

c. The same "seasoned" solution, as in number b above, analyzed after making an analytically weighed, standard addition of 2.0032 g/L Total Iron.

Samples (Process ECP-2, "KUL" Bleach)	Mean Level (g/L Total Iron)	(N)	Reproducibility Standard Deviation, $1S_c$ (g/L Total Iron)	95 Percent Confidence Estimate (g/L Total Iron)
"Fresh" at "Aim" (8.712 g/L Total Iron)	8.716	16	0.11	± 0.23
"Seasoned", As Received	10.441	16	0.013	± 0.28
"Seasoned" with Standard Addition	12.349	16	0.15	± 0.32

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- 1.0-cm silica cell
- 2.0- and 3.0-mL pipettes
- 100- and 250-mL volumetric flasks
- Double-beam spectrophotometer, equipped with a tungsten light source (i.e., Shimadzu Model UV160U)

REAGENTS

Use ACS Reagent Grade reagents unless otherwise specified.

- Nitric Acid, HNO_3 (5.0 N)
- Potassium Persulfate, $K_2S_2O_8$ (40 g/L)
- Ammonium Thiocyanate, NH_4SCN (200 g/L)
- Water, Type I Reagent-This method was developed, and the resulting statistical data were obtained using reagent water equivalent to or purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

1. Zero the Spectrophotometer
   a. Adjust the wavelength on the spectrophotometer to 477 nm.
   b. Zero the spectrophotometer vs air.
2. Blank
   a. Prepare a blank solution by adding 10 mL of 5 N nitric acid, 1 mL of 40 g/L potassium persulfate, and 25 mL of 200 g/L ammonium thiocyanate to a 100-mL volumetric flask.
   b. Swirl to mix reagents, dilute to the mark with reagent water & invert 6 to 10 times to mix.
   c. Rinse a clean, 1-cm silica cell 3-5 times with blank solution from step b and fill the silica cell with the blank. Rinse the outer surfaces of the cell with reagent water and wipe dry with a tissue. Place the cell into the sample beam cell holder of the spectrophotometer.
   d. Read the absorbance of the blank within 2 minutes at 477 nm vs. air as (ABS_{blk}).
   e. Remove the silica cell and rinse 3 to 5 times with reagent water.
3. Sample
   a. Add approximately 200 mL of reagent water to a 250-mL volumetric flask.
   b. Pipette 2.0 mL of the sample into the 250-mL flask. Fill to volume with reagent water. Invert the flask 6 to 10 times to mix.
   c. To a 100-mL volumetric flask, add 10 mL of 5 N nitric and 1 mL of 40 g/L potassium persulfate. Swirl to mix.
   d. Pipette 3.0 mL of the diluted sample from step 3b, into the 100-mL flask.
   e. Add 25 mL of 200 g/L ammonium thiocyanate solution to the 100-mL flask, while swirling the flask. Fill to volume with reagent water. Invert the flask 6 to 10 times to mix.
   f. Rinse the 1-cm silica cell 3-5 times with the sample from step 3e, and then fill the silica cell with the sample. Rinse the outer surfaces of the cell with reagent water and wipe dry with a tissue. Place the cell into the spectrophotometer's sample beam cell holder.
   g. Record the absorbance of sample at 477 nm vs. air as (ABS_{spl}). Absorbance should be recorded within 2 minutes of sample preparation.

Note: When using a single-beam spectrophotometer, as opposed to a double-beam spectrophotometer, the procedure is the same. However, a new blank should be prepared for each sample due to the instability of the blank.

CALCULATIONS

$$ABS_{477} = ABS_{spl} - ABS_{blk}$$

$$g/L\ Fe = \frac{ABS_{477} \times DF}{Absorptivity}$$

Where:

DF = dilution factor, e.g., = $\frac{(250\ mL)(100\ mL)}{(2.0\ mL)(3.0\ mL)}$ = 4166.7

250 mL = volume of first dilution

2.0 mL = volume of sample pipetted into first volumetric flask

100 mL = volume of second dilution

3.0 mL = volume pipetted from first dilution into second volumetric flask

Absorptivity = 205 ABU-L/g-cm*

* NOTE: Use the *APPENDIX* to determine absorptivity of the iron thiocyanate complex, since each spectrophotometer may yield a different absorptivity value.

If:

ABS_{spl} = 0.286

ABS_{blk} = 0.044

Then:

ABS_{477} = 0.242

$$g/L\ Iron = \frac{0.242 \times 4166.7}{205}$$

g/L Iron = 4.9

APPENDIX

Calibration of the Spectrophotometer for the Iron-Thiocyanate Complex

This appendix should be used to recheck the iron thiocyanate absorptivity **at least every 6 months**. Also, it is to be used the first time this method is performed and whenever the spectrophotometer has been adjusted or repaired.

Reagents

Use ACS Reagent Grade reagents unless otherwise specified.

- Water, Type I Reagent-This method was developed, and the resulting statistical data were obtained using reagent water equivalent to purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.
- Nitric Acid, HNO_3 (Concentrated)
- Nitric Acid, HNO_3 (5.0 N)
- Nitric Acid, HNO_3 (0.5 N)
- Potassium Persulfate, $K_2S_2O_8$ (40 g/L)
- Ammonium Thiocyanate, NH_4SCN (200 g/L)
- Iron, wire, 0.5 mm diameter, 99.99 percent pure available from:

  Aldrich Chemical Company, Inc.

  940 West Saint Paul Ave.

  Milwaukee, WI 53233

  CAT No. 26,624-8 in either 0.75 g or 7.5 g quantities

Procedure

Preparation of 10 g/L Iron Stock Solution.

1. Measure 200 mL of concentrated nitric acid into a 250-mL graduated cylinder. Slowly pour the acid into a 1-L beaker containing 300 mL of reagent water and a magnetic stir bar. Mix thoroughly.
2. Weigh 2.50 g of iron wire and record the weight to the nearest 0.1 mg. Wear white cotton gloves to keep finger oils and moisture from the wire. Use complete packs of wire to avoid contamination from wire cutting devices. Two or three of the 0.75-g packs will contain a weight close to the stated amount (each typically contains more than the nominal 0.75 g).
3. Place the iron wire into a 1-L beaker with a magnetic stirring bar. Place the beaker on a warm, hot-plate/ stirrer.
4. Slowly add about 125 mL of the diluted nitric acid (prepared in step 1) to the iron wire in the beaker. The iron wire will begin to dissolve and the acid will begin to boil.
5. Once the wire has totally dissolved, immediately allow the solution to cool to room temperature. Quantitatively transfer the cooled solution into a 250-mL volumetric flask.
6. Fill the volumetric flask to the mark with reagent water. Invert the flask 6–10 times to mix.

Note: This solution is stable for six months and should be stored in either plastic or colorless glass bottles (do not store in brown glass bottles as extraneous iron will be extracted from the glass).

Calculations

$$\text{Conc. of 10 g/L stock standard solution} = \frac{\text{weight from step 2} \times 0.9999 \times 4}{250 \times 4}$$

Where:

0.9999 = assay value of iron wire supplied by Aldrich

4 = factor to convert 250 mL to 1 L

250 = volume of stock solution (mL)

Absorptivity of Iron-Thiocyanate Complex

1. Zero the spectrophotometer as described in the *Zero the Spectrophotometer* Procedure of the above method. Prepare and record the absorbance of a reagent blank described in the *Blank* Procedure of the above method (ABS_{blk}).
2. Pipette 3.0 mL of the 10 g/L iron stock solution into a 1-L volumetric flask containing 500 mL of 0.5 N nitric acid. Dilute to volume with 0.5 N nitric acid, stopper, and invert several times (6-10) to mix. This is the absorptivity stock solution (approximately 30 mg/L Fe).
3. To a 100-mL volumetric flask, add 10 mL of 5 N nitric acid and 1 mL 40 g/L potassium persulfate. Swirl to mix.
4. Pipette 3.0 mL of the stock solution from step 2, into the flask in step 3, with swirling.
5. Add 25 mL of 200 g/L ammonium thiocyanate to the flask (step 4) with swirling. Dilute to volume with reagent water. Stopper and invert 6–10 times to mix. This is Std 1.
6. Rinse the 1-cm silica spectrophotometer cell several times with the sample. Fill the cell and rinse the outer surfaces with reagent water. Wipe dry with a soft tissue and place the cell into the sample beam cell holder of the spectrophotometer.
7. Record the absorbance of Std 1 at 477 nm as $ABS_{std\ 1}$. Absorbance should be recorded within 2 minutes of sample preparation.
8. Repeat steps 3 to 7, two more times.
9. Repeat steps 2 to 8, substituting the following pipette sizes into step 4 (see the following table). Record absorbances with the corresponding Std #.

Pipette Size (mL)	Std #
5.0	Std 2
10.0	Std 3
15.0	Std 4

10. The linear nature of the relationship between absorbance at 477 nm and iron concentration is shown in the *Typical Absorptivity* Table with the accompanying Figure, *Calibration of Total Iron in ECN-2 or ECP-2 "KUL" Bleach.*

Calculation of Absorptivity

$$\text{Absorptivity (ABU-L/g-cm)} = \frac{ABS_{std}\ \#\ \text{x df}}{\text{Iron Stock Conc.}}$$

Where:

ABS_{std} # = recorded absorbance for each standard measured at 477 nm

df = dilution factor for corresponding standard

$$\frac{1000\ \text{mL}}{3.0\ \text{mL}} \times \frac{100\ \text{mL}}{\text{pipet size}}$$

Iron Stock Conc. = calculated amount of iron in iron wire stock solution (refer to section on *Preparation of 10 g/L Iron Stock Solution.*)

Example

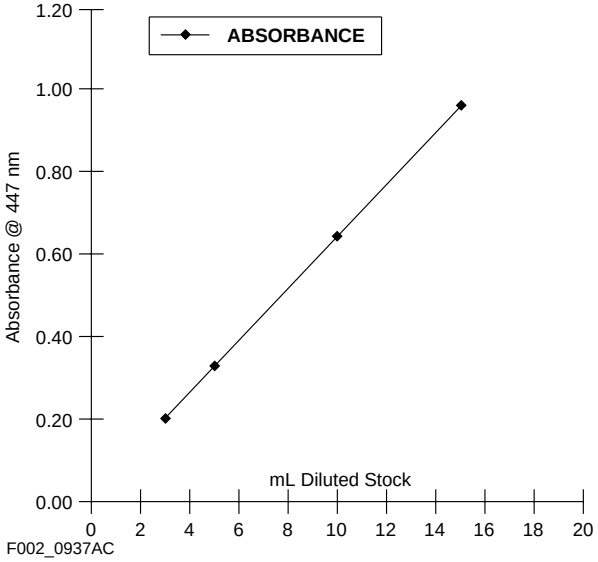
$$\text{Absorptivity (ABU-L/g-cm)} = \frac{0.330 \times 6666.7}{10.695}$$

$$= 205.7$$

Typical Absorptivity

mL Diluted Stock	Absorbance	Absorptivity
3.0	0.192	204.85
3.0	0.195	204.05
3.0	0.194	206.99
5.0	0.322	206.13
5.0	0.319	204.21
5.0	0.322	206.13
10.0	0.638	204.21
10.0	0.642	205.49
10.0	0.641	205.17
15.0	0.955	203.78
15.0	0.953	203.36
15.0	0.958	204.42
		$\bar{x}$ = 205.2
		s = 1.4

Figure 1 Calibration of Total Iron in ECN-2 or ECP-2 "KUL" Bleach



Determination of Total Iron in Eastman Color Films, Process ECN-2, “ML” Type Bleach Using HACH Calorimeter Test Kit

ECN-2-ML-3280

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SR-32/SR-32R	—	—	—

INTRODUCTION

This test kit (MACH catalog no. 41100-10) is used to determine total iron in Kodak Color Films, Process ECN-2, “ML” type bleach samples. The bleach samples are diluted and mixed with a FerroVer Iron Reagent Powder Pillow to create a colored solution. This colored solution is measured using the HACH DR 100 Colorimeter provided with the test kit. The absorbance is then used to calculate the amount of iron in the bleach.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

The reliability data given below applies only to ECN-2 “ML” Bleach. No calibration was performed using ECN-2 “UL” Bleach.

Three fresh mixes of Process ECN-2, “ML” Bleach (5.0, 10.0, 15.0 g/L total iron) were analyzed in duplicate on one day by three Kodak processing machine operators. A pooled standard deviation (1s) of 0.39 g/L (n = 16) was calculated. The 95 percent confidence estimate, based on the pooled standard deviation, was ± 1.00 g/L. A high bias of 12.5 percent, 9.0 percent and 7.6 percent were found at the low, aim and high levels, respectively.

A seasoned bleach sample analyzed to be 3.94 g/L total iron, and a standard addition to that sample of 2.09 g/L iron (added as solution 3422), were analyzed in the same manner as the fresh samples. For the seasoned samples, the standard deviation (1s) was 0.13 g/L (n = 5) and the 95 percent confidence estimate was ± 0.36 g/L. Recovery was 97 percent.

APPARATUS

Use pipets and volumetric glassware meeting the “Class A” definition by the National Institute of Standards and Technology (NIST).

- 500-mL volumetric flasks
- 5.0-mL pipets

The following are provided with the HACH test kit:

- 2.5-cm sample cells
- Clippers
- 1-cm cell holder
- HACH DR-100 Colorimeter

REAGENTS

All reagents are provided with the HACH test kit.

- FerroVer Iron Reagent Powder Pillow

PROCEDURE*

1. Pipet 5.0 mL of bleach sample into a 500-mL volumetric flask. Dilute to volume with distilled water. Invert six times to mix.
2. Pipet 5.0 mL of the solution contained in the 500-mL volumetric flask (prepared in step 1) into another 500-mL volumetric flask. Dilute to volume with distilled water. Invert six times to mix.
3. Rinse both of the 2.5-cm sample cells using the solution prepared in step 2.
4. Fill one of the sample cells to the 10-mL mark (white line) with the solution prepared in step 2.
5. Use the clippers to open one FerroVer Iron Reagent Powder Pillow and add its contents to the sample cell from step 4. Cap the cell and shake to mix. (An orange color will develop if iron is present.)

Note: After preparation of the sample in step 5, the remaining steps of this procedure must be performed within 30 minutes.

6. Open the Light Shield (black lid) of the DR 100 Colorimeter and turn the Right Set control knob fully clockwise.
7. Place the black plastic 1-cm Cell Holder into the Left Set position of the sample well by aligning the white line of the cell holder with the white line of the Left Set position.
8. Press down firmly to seat the Cell Holder into place. Close the Light Shield
9. While holding the On button down, adjust the Left Set control to align the meter needle with the arrow at the far left of tile scale arc.
10. Open the Light Shield and remove the Cell Holder.
11. Fill the other sample cell from step 3 to the 10-mL mark (white line) with the solution from step 2.
12. Cap the sample cell. Wipe the outside of the cell with a clean tissue.
13. Place the cell into the sample well and press down firmly to seat it into place.
14. Close the Light Shield. While holding the On button down, adjust the Right Set control for a reading of zero mg/L.
15. Open the Light Shield and remove the cell.
16. Wipe the outside of the sample cell prepared in step 5 with a clean tissue.
17. Place the sample cell into the sample well and press down firmly to seat it into place
18. Close the Light Shield. While holding the On button down, allow the meter reading to stabilize. Read and record the mg/L iron from the 0-2 mg/L scale (bottom scale).
19. Open the Light Shield and remove the sample cell
20. Multiply the mg/L iron (Fe) reading (obtained in step 18) by 10 to obtain the iron content of the sample in g/L:

$$\text{g/L iron} = (\text{reading in mg/L iron}) \frac{(10{,}000 \text{ fold dilution})}{1000 \text{ mg/g}}$$

Where:

g/L iron = (reading in mg/L iron) (10)

Example: g/L iron = (0.55)(10)

g/L iron = 5.5 g/L

* Test instructions are adapted from DR 100 Colorimeter Manual (1987) of HACH COMPANY, Loveland, Colorado with the exception of steps 1, 2, and 20.

Determination of Total Iron in Eastman Color Films, Process ECN-2, "UL" Type Bleach Using HACH Calorimeter Test Kit

ECN-2-UL-3280

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SR-33	—	—	—

INTRODUCTION

This test kit (MACH catalog no. 41100-10) is used to determine total iron in Eastman Color Films, Process ECN-2, "UL" type bleach samples. The bleach samples are diluted and mixed with a FerroVer® Iron Reagent Powder Pillow to create a colored solution. This colored solution is measured using the HACH DR 100 calorimeter provided with the test kit. The absorbance is then used to calculate the amount of iron in the bleach.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

Three fresh mixes of Process ECN-2, "UL" Bleach (5.0, 10.0, 15.0 g/L total iron) were analyzed in duplicate on one day by three Kodak processing machine operators. A pooled standard deviation (1s) of 0.70 g/L (n = 16) was calculated. The 95 percent confidence estimate, based on the pooled standard deviation, was ± 1.94 g/L. High biases of 18.8 percent, 9.4 percent and 9.6 percent were found at the low, aim, and high levels, respectively.

A seasoned bleach sample analyzed to be 5.00 g/L total iron, and a standard addition to that sample of 1.06 g/L iron were analyzed in the same manner as the fresh samples. For the seasoned samples, the standard deviation (1s) was 0.089 g/L (n = 6) and the 95 percent confidence estimate was ± 0.23 g/L. Recovery of the standard addition was 95 percent.

APPARATUS

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

- 100, 500-mL volumetric flasks
- 2.0, 5.0-mL pipets

The following are provided with the HACH test kit:

- 2.5-cm sample cells
- Clippers
- 1-cm cell holder
- HACH DR-100 Colorimeter

REAGENTS

All reagents are provided with the HACH test kit.

- FerroVer® Iron Reagent Powder Pillow

PROCEDURE

1. Pipet 5.0 mL of bleach sample into a 500-mL volumetric flask. Dilute to volume with distilled water. Invert six times to mix.
2. Pipet 2.0 mL of the solution contained in the 500-mL volumetric flask (prepared in step 1) into a 100-mL volumetric flask. Dilute to volume with distilled water. Invert six times to mix.
3. Rinse both of the 2.5 cm sample cells using the solution prepared in step 2.
4. Fill one of the sample cells to the 10-mL mark (white line) with the solution prepared in step 2.
5. Use the clippers to open one FerroVer® Iron Reagent Powder Pillow and add its contents to the sample cell from step 4. Cap the cell and shake to mix. (An orange color will develop if iron is present.)

   Note: After preparation of the sample in step 5, the remaining steps of this procedure must be performed within 30 minutes.
6. Open the Light Shield (black lid) of the DR 100 Colorimeter and turn the Right Set control knob fully clockwise.
7. Place the black plastic 1-cm cell holder into the Left Set position of the sample well by aligning the white line of the cell holder with the white line of the Left Set position.
8. Press down firmly to seat the Cell Holder into place. Close the Light Shield.
9. While holding the On button down, adjust the Left Set control to align the meter needle with the arrow at the far, left of the scale arc.
10. Open the Light Shield and remove the Cell Holder.
11. Fill the other sample cell from step 3 to the 10-mL mark (white line) with the solution from step 2.
12. Cap the sample cell. Wipe the outside of the cell with a clean tissue.
13. Place the cell into the sample well and press down firmly to seat it into place.
14. Close the Light Shield. While holding the On button down, adjust the Right Set control for a reading of zero mg/L.
15. Open the Light Shield and remove the cell.
16. Wipe the outside of the sample cell prepared in step 5 with a clean tissue.

17. Place the sample cell into the sample well and press down firmly to seat it into place.
18. Close the Light Shield. While holding the On button down, allow the meter reading to stabilize. Read and record the mg/L iron from the 0-2 mg/L scale (bottom scale).
19. Open the Light Shield and remove the sample cell.
20. Multiply the mg/L iron (Fe) reading (obtained in step 18) by 5 to obtain the iron content of the sample in g/L:

$$\text{g/L iron} = (\text{reading in mg/L iron}) \frac{\text{5000 fold dilution}}{\text{1000 mg/g}}$$

$$\text{g/L iron} = (\text{reading in mg/L iron})\ (5)$$

Example $\text{g/L iron} = (0.89\ \text{mg/L})\ (5)$

$\text{g/L iron} = 4.45\ \text{g/L}$

* Test instructions are adapted from DR 100 Colorimeter Manual (1987) of HACH COMPANY, Loveland, Colorado with the exception of steps 1, 2, and 20.

Determination of Total Iron in EASTMAN Color Films, Process ECN-2 "UL" Type Bleach Using a HACH Pocket Colorimeter Test Kit

ECN-0026-01

INTRODUCTION

This test kit (HACH catalog no. 46700-22) is used to determine total iron in Eastman Color Films, Process ECN-2, "UL" type bleach samples. The bleach samples are diluted and mixed with a FerroVer® Iron Reagent Powder Pillow to create a colored solution. This colored solution is measured using the HACH Pocket Colorimeter provided with the test kit. The absorbance is then used to calculate the amount of iron in the bleach.

"Determination of Total Iron in Eastman Color Films, Process ECN-2, UL Type Bleach Using HACH Colorimeter Test Kit" (*ECN-2-UL-3280*) is used with the previous analog colorimeter Model DR 100.

Use of this method requires handling of potentially hazardous chemicals. Material Safety Data Sheets (MSDS) should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation ($1s_r$) & 95 Percent Confidence Estimate (not including bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development.

1. A "fresh" UL type bleach tank prepared with all components at their respective "working tank" aim concentrations.
2. A "seasoned" UL type bleach tank analyzed colorimetrically as received, at 5.59 g/L iron.
3. The same "seasoned" solution as in number 2, above, reanalyzed after making an analytically weighed, standard addition of 1.68 g/L iron.

Iron				
Sample	**Mean (g/L Iron)**	**N**	**Repeatability Standard Deviation, $1S_r$ (g/L Iron)**	**95 Percent Confidence Estimate (g/L Iron)**
"Fresh" (Prepared at 4.94 g/L)	5.04	5	0.065	± 0.18
"Seasoned" As Received	5.59	5	0.022	± 0.06
"Seasoned" plus Standard Addition	7.06	5	0.065	± 0.18

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level is not determined independently of the test method.

A bias of 0.10 g/L iron was found to be statistically significant at the 95 percent confidence level, but was judged not to be practically significant.

Recovery

Recovery is used for seasoned samples, since the component concentration level is not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically, the recovery of 87.50 percent was statistically different from 100 percent at the 95 percent confidence level, but was judged not to be practically significant.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Because the results of the repeatability study show similar variability to the method *ECN-2-UL-3280* that used an analog model colorimeter, and the reagent chemistry is unchanged, it is expected that the newer instrument with digital readout will exhibit comparable or superior performance under reproducibility conditions. Therefore, a reproducibility study was not performed. The results of the previous method reliability are duplicated below as a reference.

Three fresh mixes of Process ECN-2, "UL" Bleach (5.0, 10.0, 15.0 g/L total iron) were analyzed in duplicate on one day by three skilled analysts. A pooled standard deviation (1s) of 0.70 g/L (n=16) was calculated. The 95 percent confidence estimate, based on the pooled standard deviation, was ± 1.94 g/L. High biases of 18.8 percent, 9.4 percent, and 9.6 percent were found at the low, aim, and high levels, respectively.

A seasoned bleach sample analyzed to be 5.00 g/L total iron, and a standard addition to that sample of 1.06 g/L iron were analyzed in the same manner as the fresh samples. For the seasoned samples, the standard deviation (1s) was 0.089 g/L (n=6) and the 95 percent confidence estimate was ± 0.23 g/L. Recovery of the standard addition was 95 percent.

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- 100, 500 mL volumetric flasks
- 2.0, 5.0 mL pipets
- Included in HACH test kit:
  - (2) 2.5 cm sample cell
  - HACH Pocket Colorimeter

REAGENTS

Use ACS Reagent Grade reagents unless otherwise specified.

- FerroVer® Iron Reagent Powder Pillow
- Water, Type I Reagent – This method was developed using reagent water equivalent to purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Refer to the POCKET COLORIMETER™ Analysis System Instruction Manual for additional information including safety precautions, a general description, and calibration routines for Hi and Lo range samples.

1. Pipet 5.0 mL of bleach sample into a 500 mL volumetric flask. Dilute to volume with reagent water. Invert six times to mix.
2. Pipet 2.0 mL of the solution contained in the 500 mL volumetric flask (prepared in step 1) into a 100 mL volumetric flask. Dilute to volume with reagent water. Invert six times to mix.
3. Rinse both the 2.5 cm sample cells using the solution prepared in step 2. One cell will be used for sample reagent and the other as a blank.
4. Fill one of the sample cells to the 10 mL mark (white line) with the solution prepared in step 2. This will be sample reagent one.
5. Tear open one of the FerroVer® Iron Reagent Powder Pillows and add its contents to the sample cell from step 4. Cap the cell and shake to mix. Wipe the outside of the cell with a clean tissue. (An orange color will develop if iron is present.)

   Note: After preparation of the sample in step 5, the remaining steps of this procedure must be performed within 30 minutes.

   Note: Accuracy is not effected by undissolved powder.
6. Set and start a timer for three minutes.
7. After three minutes have elapsed, fill the second 2.5 cm sample cell from step 3 to the 10 mL mark (white line) with the solution from step 2. This will be blank one.
8. Cap the blank sample cell. Wipe the outside of the cell with a clean tissue. This cell is used as a sample blank to zero the instrument. No FerroVer® reagent is added.
9. Remove the instrument cap from the Pocket Colorimeter.
10. Place the blank sample cell from step 8 into the cell holder with the diamond mark facing the keypad.
11. Tightly cover the blank sample cell with the instrument cap (flat side facing the back of the instrument).

12. Press ‘ZERO’. The instrument will display “---” followed by “0.00”.
13. Within 30 minutes after the 3 minute waiting period, place the reagent sample cell prepared in step 5 into the cell holder with the diamond mark facing the keypad.
14. Tightly cover the reagent sample cell with the instrument cap (flat side facing the back of the instrument).
15. Press ‘READ’. The instrument will display “---” followed by the results in mg/L iron.

CALCULATIONS

Multiply the mg/L iron reading (obtained in step 15, above) by 5 to obtain the iron content of the sample in g/L:

$$\text{g/L iron} = (\text{reading in mg/L iron from step 15}) \times \frac{\text{5000 fold dilution}}{\text{1000 mg/g}}$$

g/L iron = (reading in mg/L iron from step 15) (5)

Example:

g/L iron = (0.89 mg/L) (5)

g/L iron = 4.45 g/L

Spectrophotometric Determination of Total Iron in "UL" Bleach

ECN-2-3263-2

INTRODUCTION

The determination of total iron in Process ECN-2, "UL" bleach, utilizes a spectrophotometric technique. The total iron concentration is determined by oxidizing any iron (II) present to iron (III) with persulfate. A thiocyanate complex of the iron (III) is formed in a dilute acid solution. A direct measurement of the iron-thiocyanate complex is made using a calibrated spectrophotometer at 477 nm.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed two (2) replicates on each of the following solutions over two days during methods development.

1. A fresh "UL" bleach was prepared with all components at their respective "working tank" aim concentrations (3.87 g/L total iron).
2. A seasoned "UL" bleach analyzed as received, at 4.91 g/L total iron.
3. The same "seasoned" solution as in number 2, above, was reanalyzed after making an analytically weighed, standard addition of 0.99 g/L total iron.

Total Iron				
Sample	**Mean (g/L Total Iron**	**N**	**Repeatability Standard Deviation, $1s_r$ (g/L Total Iron**	**95 Percent Confidence Estimate (g/L Total Iron)**
Fresh	3.78	4	0.025	± 0.08
Seasoned as received	4.91	4	0.030	± 0.10
Seasoned plus Addition	5.76	4	0.033	± 0.11

Bias

Bias is a statistically significant deviation of the mean from the known ammonium total iron level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method.

A bias of –0.09 g/L total iron was found to be statistically significantly different for the Process ECN-2 "fresh" tank "UL" bleach sample. However, the difference was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

The recovery of the standard addition sample was 85.86 percent and found to be statistically different from 100 percent at the 95 percent confidence level. However, it was judged not to be practically different from 100 percent.

REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ and 95 Percent Confidence Estimate

Reproducibility, or customer standard deviation, ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Five Process ECN-2 "UL" bleach samples were analyzed by four analysts, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. Three "fresh" "UL" bleach samples were prepared with all components at their respective "working tank" aim concentrations.
2. A "seasoned" "UL" bleach sample was analyzed spectrophotometrically as received, at 4.91 g/L total iron.
3. The same "seasoned" solution as in number 2, above, was reanalyzed after making an analytically weighed, standard addition of 0.99 g/L iron.

Total Iron				
Sample	**N**	**Mean**	**Reproducibility Standard Deviation, $1s_c$ (g/L Total Iron)**	**95 Percent Confidence Estimate (g/L Total Iron)**
"Fresh" at 1.05 g/L Total iron	16	1.00 g/L	0.019	± 0.04
"Fresh" at 3.87 g/L Total iron	16	3.78 g/L	0.037	± 0.08
"Fresh" at 7.48 g/L Total iron	16	7.46 g/L	0.056	± 0.13
"Seasoned" As Received	16	4.91 g/L	0.032	± 0.07
"Seasoned" with Standard Addition	16	5.74 g/L	0.038	± 0.08

Bias

Bias is a statistically significant deviation of the mean from the known total iron level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample since the component concentration level was not determined independently of the test method.

A statistically significant low bias of -0.05 g/L and -0.09 total iron was found for the fresh "UL" bleach tank sample at the 1.05 g/L and 3.87 g/L iron level (aim), respectively. However, the bias was judged not to be practically significant. A bias of -0.02 g/L at the 7.48 g/L total iron was not statistically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independent of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

The recovery of the standard addition sample was 83.84 percent and found to be statistically different from 100 percent at the 95 percent confidence level. However, it was judged not to be practically different from 100 percent.

APPARATUS

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- Double Beam Spectrophotometer with a tungsten lamp (i.e., Perkin-Elmer Lambda 4 series)
- 1-cm Silica Cells

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 2.5 N Sulfuric Acid, H_2SO_4
- 40 g/L Potassium Persulfate, $K_2S_2O_8$
- 200 g/L Ammonium Thiocyanate, NH_4SCN
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

A. Spectrophotometer Zeroing

1. Adjust the spectrophotometer wavelength to 477 nm.
2. Zero the spectrophotometer versus air.

B. Blank Determination

1. Add 25 mL of 2.5 N sulfuric acid, 10 mL of 40 g/L potassium persulfate, and 25 mL of 200 g/L ammonium thiocyanate to a 100-mL volumetric flask.
2. Swirl to mix the reagents and dilute to the mark with reagent water. Invert the flask 6 to 10 times to mix.
3. Rinse a clean 1-cm silica cell 3 to 5 times with blank solution from Step 2 and fill the silica cell with the blank solution. Rinse the outer surfaces of the cell with reagent water and wipe dry with a tissue. Place the cell into the spectrophotometer sample cell holder.
4. Record absorbance of blank at 477 nm as A_{blk}.

C. Sample Treatment

1. Add approximately 200 mL of reagent water to a 250-mL volumetric flask.
2. Pipet 5.00 mL of the sample into the 250-mL flask. Fill to volume with reagent water. Invert flask 6 to 10 times to mix.
3. Add 25 mL of 2.5 N sulfuric acid and 10 mL of 40 g/L potassium persulfate to a 100 mL volumetric flask. Swirl to mix.
4. Pipet 3.00 mL of diluted sample from Step 2, into a l00-mL volumetric flask.
5. Add 25 mL of 200 g/L ammonium thiocyanate to the l00-mL volumetric flask while swirling the flask. Fill to volume with reagent water. Invert the flask 6 to 10 times to mix.
6. Rinse the 1-cm silica cell 3 to 5 times with sample from Step 5, and then fill the silica cell with the sample. Rinse the outer surfaces of the cell with reagent water and wipe dry with a tissue. Place the cell into the spectrophotometer sample cell holder.
7. Record absorbance of sample at 477 nm as A_{spl}.

Note: If using a single-beam spectrophotometer (as opposed to a double-beam spectrophotometer) the procedure is the same.

Calculations

$$\Delta A_{477} = A_{spl} - A_{blk}$$

$$\text{g/L Fe} = \frac{(\Delta A_{477})(DF)}{(\text{Absorptivity})} =$$

Where:

$$DF = \text{Dilution factor} = \frac{(250\text{ mL})(100\text{ mL})}{(5.00\text{ mL})(3.00\text{ mL})} = 1666$$

250 mL = volume of first dilution

5.00 mL = volume of sample pipeted into first volumetric flask

100 mL = volume of second dilution

3.00 mL = volume of first dilution pipeted into second volumetric flask

Absorptivity = 196 L/g-cm)

Note: Use *APPENDIX 1* to determine the absorptivity of the iron-thiocyanate complex. Each spectrophotometer may yield a different absorptivity value.

Example Calculation:

$$\Delta A_{477} = A_{spl} - A_{blk}$$

$$\Delta A_{477} = 0.479 - 0.043 = 0.436$$

$$\text{g/L Fe} = \frac{(\Delta A_{477})(DF)}{(\text{Absorptivity})} =$$

$$\frac{(0.436)(1666)}{(196)} = 3.7$$

APPENDIX 1

Determination of the Absorptivity of the Iron-Thiocyanate Complex

Note: Use this procedure to recheck the iron thiocyanate absorptivity at least every six months. Also use it the first time this method is performed and whenever the spectrophotometer has been adjusted or repaired.

Reagents

All reagents are ACS Reagent Grade unless otherwise stated.

- 2.5 N Sulfuric Acid, H_2SO_4
- 40 g/L Potassium Persulfate, $K_2S_2O_8$
- 200 g/L Ammonium Thiocyanate, NH_4SCN
- Ferric Nitrate, 9-hydrate, $Fe(NO_3)_3 \cdot 9H_2O$
- Potassium Iodide, KI
- Hydrochloric Acid, concentrated, HCl
- Starch Indicator
- 0.1 N Sodium Thiosulfate, $Na_2S_2O_3$ (standardized to 4 decimal places)
- 0.10 N Nitric Acid, HNO_3

Procedure

Standard Iron Solution Preparation

1. Weigh 9.0 ± 0.001 g ferric nitrate, 9-hydrate and transfer to a 250-mL volumetric flask.
2. Dissolve and dilute to volume with reagent water.
3. Stopper and invert the flask 6 to 10 times to mix. Label this flask 5 g/L Fe solution.

Solution Assay

1. Pipet 25.0 mL of 5 g/L Fe solution into a 500-mL glass-stoppered Erlenmeyer flask containing 100 mL of reagent water.
2. Add 5 mL of concentrated hydrochloric acid and 3 ± 0.1 g of potassium iodide.
3. Stopper and swirl the flask to dissolve the potassium iodide. Place in a dark area for 30 minutes.
4. After 30 minutes, remove the flask from the dark. Begin titrating with standardized 0.1 N sodium thiosulfate until the red color changes to a yellow-red color.
5. Add 3 mL starch indicator and continue titrating until the solution changes from blue to colorless and remains so for 15 seconds. Record the mL of 0.1 N sodium thiosulfate as mL_{spl}.
6. Repeat Steps 1 to 5 two more times. Record the mL of 0.1 N sodium thiosulfate as stated in Step 5.
7. Then repeat Steps 1 to 5 without the 5 g/L Fe solution and record the mL of 0.1 N sodium thiosulfate as mL_{blk}.

Calculation

Note: Calculate the assay result separately for each of the three sample titrations.

$$\text{g/L Fe} = \frac{(\Delta mL)(\text{eq wt Fe})(N\ Na_2S_2O_3)(1000)}{(\text{sample size})(1000)} =$$

$$\frac{(\Delta mL)(55.85)(N\ Na_2S_2O_3)(1000)}{(25.0)(1000)} =$$

$$2.23(\Delta mL)(N\ Na_2S_2O_3)$$

Where:

ΔmL = $mL_{spl} - mL_{blk}$

1000 = Conversion of millilitres to litres and milligrams to grams

Calculate the mean iron content (Xbar), standard deviation (s) and RSD of the assay using the data from the three analyses of the standards. The mean value should have an RSD < 0.10%.

$$\bar{X} = \frac{\Sigma X}{n}$$

$$s = \sqrt{\frac{\Sigma(X - \bar{X})^2}{n-1}}$$

$$RSD^* = \frac{s}{\bar{X}} \times 100\%$$

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Where:

X = individual g/L Fe assay results

n = the number of replicates (3)

Absorptivity of Iron-Thiocyanate Complex

1. Zero the spectrophotometer as described in *A. Spectrophotometer Zeroing*. Prepare and record the absorbance of a reagent blank as described in the *B. Blank Determination* procedure (A_{blk}).
2. Pipet 2.00 mL of the assayed 5 g/L Fe solution into a 500-mL volumetric flask containing 250 mL 0.1 N nitric acid.
3. Fill the flask to volume with 0.1 N nitric acid. Stopper and invert the flask 6 to 10 times to mix thoroughly.
4. Add 25 mL 2.5 N sulfuric acid and 10 mL of 40 g/L potassium persulfate to a 100-mL volumetric flask. Swirl to mix.
5. Pipet 2.00 mL of the solution (Step 3) into the flask (Step 4) while swirling.
6. Add 25 mL of 200 g/L ammonium thiocyanate to the flask while swirling. Dilute to volume with reagent water. Stopper and invert the flask 6 to 10 times to mix. Label the flask, STD 1.
7. Rinse the 1-cm silica cell 3 to 5 times with sample from Step 6, and fill the silica cell with the sample. Rinse the outer surfaces of the cell with reagent water and wipe dry with a tissue. Place the cell into the spectrophotometer sample cell holder.
8. Record absorbance of sample at 477 nm as A_{std} 1.

   Note: The absorbance should be recorded within 2 minutes of sample preparation.
9. Repeat Steps 4 to 8 and record absorbance of sample at 477 nm as A_{std} 2.
10. Repeat Steps 4 to 8, substituting the following sample sizes in Step 5 and record absorbance of results as A_{st2} 1, A_{st2} 2, A_{st3} 1, etc.

STD #	Sample Size
STD 2	5.0 mL
STD 3	10.0 mL
STD 4	15.0 mL

Calculation of Absorptivity

$$\text{Absorptivity, L/(g-cm)} = \frac{(\Delta A_{477})(DF)}{\text{Assay}}$$

Where:

ΔA_{477} = $(\Delta A_{std}\ \# - \Delta A_{blk})$

$\Delta A_{std}\ \#$ = absorbance for each STD measured at 477 nm

ΔA_{blk} = absorbance of the blank measured at 477 nm

DF = Dilution factor for each standard = $\frac{(500)(100)}{(2.00)}$

500 mL = volume of first dilution

2.00 mL = volume of sample pipeted into first volumetric flask

100 mL = volume of second dilution

STD sample size = volume of first dilution pipeted into second volumetric flask

Assay = assay value determined for the 5 g/L STD Fe solution

Typical Absorptivity		
Fe STD #	**ΔA**	**Absorptivity**
STD 1	0.081 0.081 0.081	198.0 198.0 198.0
STD 2	0.200 0.199 0.200	195.6 195.6 195.6
STD 3	0.403 0.395 0.397	197.0 193.1 194.1
STD 4	0.597 0.601	194.6 195.9

$\overline{X}$ = 195.9

1s = 1.71

RSD = 0.9%

RSD should be = <1.0%

Potentiometric Determination of Uncomplexed 1,3-PDTA In ECN-2-ML Bleach

ECN-2-ML-3255

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SR-32/SR-32R	—	—	—

INTRODUCTION

The sample is buffered at a pH of approximately 4.5. A small amount of Ferrous Ammonium Sulfate (0.001 N) is added. The sample is then titrated with standardized 0.1 N Ferric Ammonium Sulfate. The endpoint is determined potentiometrically using a Platinum indicator electrode and a double-junction reference electrode. At a pH of approximately 4.5, the uncomplexed 1,3-Propylene-diamine-N,N,N',N'-tetraacetic Acid (1,3-PDTA) in the sample forms a complex with the Fe(III) in the titrant, while the Fe(II) from the Ferrous Ammonium Sulfate (0.001 N.) remains weakly complexed. A large potential change occurs at the equivalence point due to an abrupt change in the relative concentrations of the Fe(II) and Fe(III) ions.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

Three fresh hand-weighed standards containing 2, 6, and 10 g/L 1,3-PDTA were obtained. Three analysts tested each solution in duplicate, on two separate days, resulting in 36 data points. Based on this data, the pooled standard deviation (1s) was 0.04 g/L 1,3-PDTA with a 95 percent confidence estimate (CE) for a single determination of ± 0.08 g/L 1,3-PDTA. A low bias was observed, but was insignificant compared to the product specifications.

One seasoned sample was also obtained. To this seasoned sample, a 1 g/L standard addition was made. Each of these samples was analyzed in duplicate by three analysts, on two separate days, for a total of 12 data points for each sample. The mean analysis for excess 1,3-PDTA in the seasoned sample was 4.79 g/L with a standard deviation (1s) and a 95 percent CE of 0.05 and ± 0.10 g/L, respectively. The average recovery of the 1 g/L standard addition was 101 percent.

SPECIAL APPARATUS

- pH Meter with glass electrode (CORNING #476024 or equivalent) and calomel reference electrode (CORNING #476002 or equivalent)
- METROHM Automatic Titrator (or equivalent), with a Platinum indicator electrode (BECKMAN #39273 or equivalent) and a double-junction reference electrode (ORION #90-02 or equivalent)

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

- Glacial Acetic Acid
- 0.001 N Ferrous Ammonium Sulfate•6Hydrate $[Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O]$
- 0.1 N Ferric Ammonium Sulfate•12Hydrate $[Fe(NH_4)(SO_4)_2 \cdot l2H_2O]$, standardized to 4 decimal places

PROCEDURE

Treatment of the Sample

1. Pipet 50 mL of sample into a 250-mL beaker containing 75 mL of distilled water and a Teflon stirring bar.
2. Immerse the pH electrodes into the solution and turn on the stirrer.
3. Adjust the pH of the solution to 4.5 ± 0.1, dropwise, with Glacial Acetic Acid.
4. Rinse the electrode assembly with distilled water. Collect all rinses in the beaker containing the sample.

Titration

1. Place the beaker containing the sample on a magnetic stirrer. Turn on the stirrer and immerse the Platinum indicator and double-junction reference electrodes into the solution.
2. Add 10 drops of 0.001 N Ferrous Ammonium Sulfate to the solution.
3. Wait 2 minutes for the electrodes to equilibrate.
4. If using a METROHM 536 titrator, adjust the parameters to the following settings:

Automatic Titration Stop (stop % U)	off
Vertical Chart Span (min/100% vol)	400
Automatic Titration Speed (auto control)	off
Maximum Titration Speed (min/100% vol)	15
Titration Mode	mV/pH
Horizontal Chart Span (mV)	250

5. Titrate the sample with standardized 0.1 N Ferric Ammonium Sulfate using a 20 mL buret.
6. Determine the equivalence point on the titration curve using a concentric arcs template. (Refer to Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or subsequent revisions.)

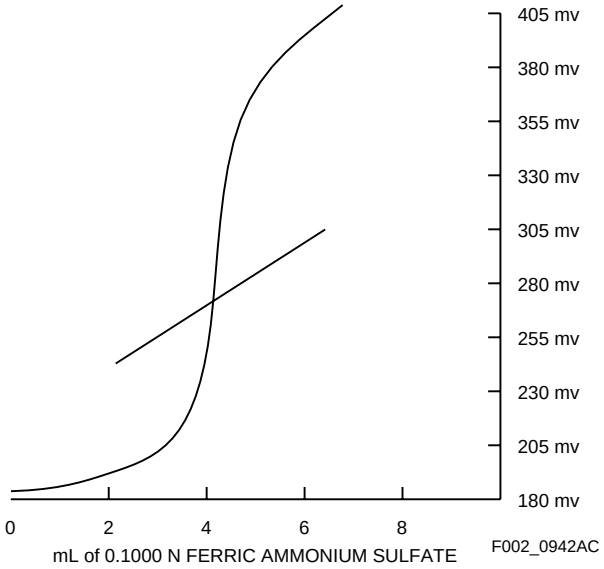
Calculations

$$\text{Uncomplexed 1,3-PDTA g/L} = \frac{\text{(mL titrant) (N titrant) (306)}}{\text{mL sample}}$$

where:

306 = equivalent weight of 1,3-PDTA

Figure 1 Typical Titration Curve of Free 1,3-PDTA in ECN-2 ML Bleach



Note: A seasoned solution may exhibit a slightly more shallow curve shape due to extraneous components.

Potentiometric Determination of Kodak Persulfate Bleach Accelerator PBA-1 in Accelerator Solution

ECN-2-2100B
ECR-2100B

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SR-31	—	SR-45	SR-45

INTRODUCTION

Strong base is added to the sample to hydrolyze the KODAK Persulfate bleach accelerator PBA-1 to a titratable mercaptan. The PBA-1 content is measured by means of a potentiometric titration with silver nitrate titrant using a silver/sulfide electrode as an indicator and a double junction electrode as a reference. This analysis is performed using an automatic titrator.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

Fresh Process ECN-2, ECP-2D and VNF-1/RVNP bleach accelerator samples were analyzed by three analysts in two laboratories. A linear regression of the data generated the standard deviation (s), and 95 percent confidence estimates (CE) given below. No bias from stoichiometry was found.

Process	ECN-2	ECP-2D	VNF/RVNP
Sample Range, g/L	2–8	1–8	1–7
Sample No.	3	4	4
Data pts.	18	24	24
(s), g/L	± 0.05	± 0.04	± 0.02
95% CE, g/L	± 0.10	± 0.10	± 0.10

A seasoned sample from processes ECN-2 and ECP-2D was analyzed five times by each of three analysts over two days. The 95 percent confidence estimate was ± 0.04 g/L PBA-1 (s = ± 0.02 g/L) for both Process ECN-2 and ECP-2D. No statistically significant day-to-day or analyst-to-analyst variability was found.

A standard addition of 0.5 g/L PBA-1 was made to two seasoned samples from processes ECN-2 and ECP-2D. Each sample was analyzed in duplicate by three analysts. Based on the 12 data points for each process, the method found 97 percent for ECN-2 and 100 percent for ECP-2D.

SPECIAL APPARATUS

- Automatic Titrator (with a 20-mL buret)
- Orion Double Junction Reference Electrode, Cat. No. 900200 or equivalent
- Orion Silver/Silver Sulfide Indicator Electrode, Cat. No. 941600 or equivalent

Note: Do not use a silver billet or bar electrode as prepared by the obsolete method 900 “Procedure For Electroplating A Silver-Silver Iodide Electrode.”

Note: Use pipets and volumetric glassware meeting the “Class A” definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use reagents that are ACS Reagent Grade unless specified otherwise.

- 10 N Sodium Hydroxide, NaOH
- 0.05 N Silver Nitrate, $AgNO_3$ (standardized to 4 decimal places)

PROCEDURE

Preparation of the Sample

1. Pipet 50.0 mL of sample into a 400-mL beaker equipped with a magnetic stirring bar.

Warning

Sodium hydroxide is caustic. Avoid contact with skin and eyes. In case of contact, flush with water.

2. Using a tip-up pipet, add 10 mL of 10 N sodium hydroxide to the beaker containing the sample.
3. Place the beaker on a magnetic stirrer and set a timer for 3 minutes.
4. After the solution has stirred for 3 minutes, add 250 mL of distilled water from a graduated cylinder.

Titration

1. Titrate potentiometrically (refer to Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*) with standardized 0.05 silver nitrate. Use a silver/silver sulfide (indicator) and a double junction (reference) as the electrode pair at a titration speed of 1 mL/min.

Warning

Silver nitrate is poisonous, causes burns, and stains skin. Avoid contact.

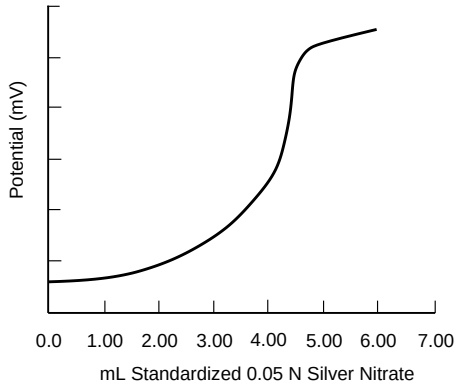
If a Metrohm Automatic Titrator is used, the following settings are recommended:

Potentiograph E536 Control	Setting
Stop %U	Off
mm/100% Volume	400
Auto Control	8
min/100% Volume	20
mV x 100	–1
mV - pH Switch (range)	750 mV
mV/pH	100%
°C	Auto

Dosimat 655 Control	Setting
Mode Switch	Mode 1

2. Determine the end point using the Concentric Arcs Technique (see Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or subsequent revision). Figure 1, *Typical PBA-1 Titration Curve* shows a typical titration curve.

Figure 1 Typical PBA-1 Titration Curve



F002_0899AC

Calculation

PBA-1, g/L =

$$\frac{(N\ AgNO_3)(mL\ AgNO_3)(eq\ wt\ PBA\text{-}1)(1000)}{(mL\ sample)(1000)} =$$

$$\frac{(N\ AgNO_3)(mL\ AgNO_3)(220.2)(1000)}{(50.0)(1000)} =$$

$$4.404(N\ AgNO_3)(mL\ AgNO_3)$$

Where:

eq wt PBA-1 = 220.2 g/equivalent

Titrimetric Determination of Persulfate in ECN-2 Persulfate Bleach

ECN-0024/1

INTRODUCTION

This method is based upon the oxidation of ferrous ion by persulfate in an acid solution at room temperature. A known excess of ferrous ion is added to the sample and the residual ferrous ion is titrated with standardized sulfato cerate. A blank determination should be run daily because ferrous solutions are slowly oxidized by air during use.

Use of this method requires handling potentially hazardous chemicals. Material Safety Data Sheets (MSDS) should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development.

1. A "fresh" Persulfate bleach tank solution prepared with all components at their respective "working tank" aim concentrations.
2. A "seasoned" Persulfate bleach tank solution analyzed as received, at 28.74 g/L $Na_2S_2O_8$.
3. The same "seasoned" solution as in number 2, above, reanalyzed after making an analytically weighed, standard addition of 8.5920 g/L $Na_2S_2O_8$.

$Na_2S_2O_8$				
Sample	**Mean g/L $Na_2S_2O_8$**	**N**	**Repeatability Standard Deviation, $1s_r$ g/L $Na_2S_2O_8$**	**95 Percent Confidence Estimate g/L $Na_2S_2O_8$**
"Fresh" (prepared at 33.27 g/L)	32.27	5	0.059	± 0.16
"Seasoned" as Received	28.74	5	0.065	± 0.18
"Seasoned" plus Standard Addition	37.20	5	0.065	± 0.18

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A bias of –1.00 g/L $Na_2S_2O_8$ was found to be statistically significant at the 95 percent confidence level, however it was judged not to be practically significant.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically the recovery of 98.46 percent was significantly different from 100 percent at the 95 percent confidence level, but it was judged not to be practically significant.

REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed four Persulfate bleach tank samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A "fresh" Persulfate bleach tank solution prepared with all components at their respective "working tank" aim concentrations.
2. A "seasoned" Persulfate bleach tank solution analyzed as received, at 27.19 g/L $Na_2S_2O_8$.
3. The same "seasoned" solution as in number 2, above, analyzed in the same manner, after making a standard addition of 8.5912 g/L $Na_2S_2O_8$.

Potassium Ferrocyanide, trihydrate				
Sample	**Mean g/L $Na_2S_2O_8$**	**N**	**Reproducibility Standard Deviation, $1s_c$ g/L $Na_2S_2O_8$**	**95 Percent Confidence Estimate g/L $Na_2S_2O_8$**
"Fresh" (prepared at 33.01 g/L)	32.57	16	0.216	± 0.46
"Seasoned" as Received	27.19	16	0.233	± 0.50
"Seasoned" plus Standard Addition	35.41	16	0.197	± 0.42

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A bias of – 0.44 g/L $Na_2S_2O_8$ was found to be statistically significant at the 95 percent confidence level, however it was judged not to be practically significant.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically, the recovery of 95.68 percent was significantly different from 100% at the 95 percent confidence level, however it was judged not to be practically significant.

APPARATUS

- Conical Flask with stopper (250-mL)
- 2 Tip-up pipettes (50-mL, 15-mL)
- Pipet (5-mL, 10-mL)

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 7.0 N sulfuric acid
- 0.25 N ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$
- 0.0500 N sulfato cerate (standardized to four decimal place
- Ferroin indicator solution
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Determination of Persulfate

1. Pipet (wipe the pipet before leveling) 5.00 mL of sample into a 250 mL conical flask containing a magnetic stir bar.
2. Add 50 mL of reagent water from a tip-up pipet.
3. Add 15 mL of 7.0 N sulfuric acid from a tip-up pipet.

Caution

Acid, avoid contact with skin and eyes. In case of contact, flush with water.

4. Pipet (wipe the pipet before leveling) 10.0 mL of 0.25 N ferrous ammonium sulfate into the flask. Using a squeeze bottle, wash down the sides of the flask with reagent water.
5. Swirl the solution to mix, stopper the flask and let it stand for 3 minutes.

   Note: Longer standing times do not adversely affect the titration providing the solution is protected from air.
6. Add 4 drops of ferroin indicator and titrate with 0.0500 N sulfato cerate to the first light cyan color.
7. Record the end point as mL A.

Determination of Reagent Blank

Note: A reagent blank should be run at least once per day because the 0.25 N ferrous ammonium sulfate will slowly change with usage.

1. Add 50 mL of reagent water, with a tip up pipet, to a 250 mL conical flask containing a magnetic stir bar.
2. Repeat steps 3 through 6 of Section A.
3. Record the end point as mL B.

CALCULATIONS

For Sodium Persulfate, g/L

$$\text{g/L } Na_2S_2O_8 = \frac{(\text{mLs B - mLs A})\ (\text{N cerate})\ (\text{eq wt } Na_2S_2O_8)}{\text{mL Sample}}$$

Where:

mLs B = volume of sulfato cerate in milliliters required to reach the equivalence point without the addition of sample (Blank)

mLs A = volume of sulfato cerate in milliliters required to reach the equivalence point with the addition of sample

N cerate = normality of the sulfato cerate in milliequivalents per milliliter (meq/mL)

eq wt $Na_2S_2O_8$ = equivalent weight of sodium persulfate in milligrams per milliequivalent (119.05 mg/meq)

mL Sample = volume of sample pipetted in step 1 of part A of procedure

If mL 0.0497 N sulfato cerate = 32.85 mLs

mLs Blank = 49.90 mLs

$$\text{g/L } Na_2S_2O_8 = \frac{(49.90 - 32.85)\ (0.0497)\ (119.05}{5.00}$$

g/L $Na_2S_2O_8$ = 20.18

Potentiometric Determination of Silver in Process ECN Fixing Baths

ECN-0023-01

INTRODUCTION

The sample containing silver is titrated potentiometrically with standardized sodium sulfide using a silver billet/double junction electrode pair. The sample is made alkaline to prevent the decomposition of sodium thiosulfate, which occurs in acid solutions. Ethylenedinitrilotetraacetic acid (EDTA) is added to minimize interference of other metal ions. The EDTA reagent does not prevent interference from zinc ions. Gelatin is added to prevent the coagulation of the silver sulfide that is formed. This prevents the coagulated silver sulfide from occluding the silver ions.

Changes in the volume of sample and of sodium hydroxide/EDTA reagent affect the silver results. If a small amount of sample is used, the sample volume must be adjusted to about 300 mL with 1.0 M sodium thiosulfate.

Use of this method requires handling potentially hazardous chemicals. Material Safety Data Sheets (MSDS) should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

A. Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed three (3) replicates on each of the following solutions during methods development.

1. A “fresh” fixing tank prepared with all components at their respective “working tank” aim concentrations.
2. The same “fresh” solution as in number 1, above, reanalyzed after making an analytically weighed, standard addition of 1.0745 g/L Ag.
3. A “seasoned” fixing tank analyzed potentiometrically as received, at 1.1488 g/L Ag.
4. The same “seasoned” solution as in number 3, above, reanalyzed after making an analytically weighed, standard addition of 0.2686 g/L Ag.

Ag				
Sample	**Mean (g/L Ag)**	**N**	**Repeatability Standard Deviation, $1s_r$ (g/L Ag)**	**95 Percent Confidence Estimate (g/L Ag)**
“Fresh”	0.0060	3	0.00000	± 0.0000
“Fresh” plus Standard Addition	1.0830	3	0.00251	± 0.0108
“Seasoned”, As Received	1.1488	3	0.00374	± 0.0161
“Seasoned” plus Standard Addition	1.3658	3	0.00492	± 0.0212

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. Instead, a recovery was calculated for the component in a fresh sample.

The recovery of 106.23 percent was not significantly different from 100 percent at the 95 percent confidence level.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

The recovery of 102.16 percent* was not statistically significantly different from 100 percent at the 95 percent confidence level.

* Note: Recovery was calculated by accounting for a 5 percent error from dilution of 1 liter of seasoned fixer by a 50.00 mL aliquot of silver nitrate.

$$\text{Example: } \frac{(1.3658) - (1.1488 \times 0.95)}{0.2686} \times 100 = 102.16\%$$

B. REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed four fixing bath samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A "fresh" fixing tank prepared with all components at their respective "working tank" aim concentrations.
2. The same "fresh" fixing tank sample as in 1 above, analyzed in the same manner, after making a standard addition of 1.0745 g/L Ag.
3. A "seasoned" tank solution analyzed as received as 1.0488 g/L Ag.
4. The same "seasoned" solution, as in number 3, above, analyzed in the same manner, after making a standard addition of 0.2686 g/L Ag.

Ag				
Sample	**Mean (g/L Ag)**	**N**	**Reproducibility Standard Deviation, $1s_c$ (g/L Ag**	**95 Percent Confidence Estimate (g/L Ag)**
"Fresh"	0.0397	16	0.01765	± 0.0376
"Fresh" plus Standard Addition	0.5745	16	0.00753	± 0.0160
"Seasoned", As Received	1.1236	16	0.01245	± 0.0265
"Seasoned" plus Standard Addition	1.3415	16	0.01895	± 0.0404

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. Instead, a recovery was calculated for the component in a fresh sample. Statistically, the recovery of 99.55 percent was not significantly different from 100 percent at the 95 percent confidence level.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 102.07 percent* was not statistically significantly different from 100 percent at the 95 percent confidence level.

* Note: Recovery was calculated by accounting for a 5 percent error from dilution of 2 liters of seasoned fixer by a 100.00 mL aliquot of silver nitrate.

$$\text{Example: } \frac{(1.3415) - (1.1236 \times 0.95)}{0.2686} \times 100 = 102.07\%$$

APPARATUS

- METROHM 536 Titrator or equivalent with a DOSIMAT and a 50-mL burette
- Beaker (600-mL)
- Tip-up pipette (50-mL, 10-mL)
- Graduated Cylinder (500-mL, 250-mL)
- Pipet (50-mL, 100-mL)
- Indicator electrode, Silver Billet, BECKMAN, Model 39261 or equivalent
- Double junction reference electrode, ORION Model 900200 or equivalent
- Filling solutions:
  - ORION No. 900002 (inner chamber filling solution)
  - ORION No. 900003 (outer chamber filling solution)

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E288, and E969, unless otherwise stated.

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 0.1 M Sodium Thiosulfate, $Na_2S_20_3$
- 70.1 N Sodium Hydroxide/Ethylenedinitrilotetraacetic Acid (EDTA) reagent, 1 N NaOH/EDTA
- 4 g/L Gelatin
- 0.06 N Sodium Sulfide, Na_2S (standardized to 4 decimal places)
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

A. Treatment of Sample

1. Pipet (wipe the pipet before leveling) the sample of fix solution into a 600 mL beaker according to the following table:

Note: Fresh solutions will have less than 1.0 g/L silver, for seasoned samples a 50 mL sample size may be used to determine approximate level of silver in sample.

Silver Concentration g/L	Sample, mL	1.0 M Sodium Thiosulfate, mL
Less than 1	300*	0
1 to 3	100.0	200
More than 3	50.0	250

* Use a graduated cylinder.

2. From a 250-mL graduated cylinder, add to the 600-mL beaker the amount of 1.0 M sodium thiosulfate indicated in the table.
3. Add 100 mL of 1 N NaOH/EDTA reagent from a 50-mL tip-up pipet.
4. Add 10 mL of 4 g/L gelatin from a tip-up pipet.

B. Potentiometric Titration of Sample

1. Titrate the solution with 0.0600 N sodium sulfide, using a METROHM E536 Titrator or equivalent.
   a. Set the following parameters on the METROHM E536 Titrator:

Titration mode	mV/pH
Horizontal chart span	750 mV
Autocontrol	OFF
Maximum titration speed	15 min/100% volume
Vertical chart span	400 mm/100% volume
Automatic titration stop (U%)	OFF
Indicator electrode	Silver Billet BECKMAN, Model 39261 or equivalent
Reference electrode	Double-junction ORION, Model 900200 or equivalent

   b. Place the beaker on the METROHM titrator stand and add a magnetic stir bar. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex. Titrate the solution with standardized 0.0600 N sodium sulfide through the inflection.

Note: Avoid unnecessary exposure of the standardized sodium sulfide to air. The reagent should be standardized each week. Discard all unused reagent remaining in any open bottles at the end of each day (60 mL reagent bottles are suggested for storage of 0.06 N sodium sulfide).

c. Determine the end point using concentric arcs (refer to Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revisions.) If a microprocessor controlled titrator is used, the endpoint will be picked automatically.

CALCULATIONS

For Silver, g/L;

$$\text{g/l Ag} = \frac{(\text{mL } Na_2S)\ (\text{N } Na_2S)\ (\text{eq wt Ag})\ (1000)}{(\text{mL sample})\ (1000)}$$

Where:		
mL Na_2S	=	volume of sodium sulfide in milliliters required to reach the equivalence point
N Na_2S	=	normality of the sodium sulfide in milliequivalents per milliliter (meq/mL)
eq. wt. Ag	=	equivalent weight of silver in milligrams per milliequivalents [107.88 for Ag]
1000	=	factor to convert milligrams to grams of Ag
mL sample	=	milliliters of sample pipetted in step 1 of part A of procedure
1000	=	factor to convert mLs of sample to Liters

For samples containing less than 1 g/L silver:

$$\text{g/l Ag} = \frac{(\text{mL } Na_2S)\ (\text{N } Na_2S)\ (107.88)\ (1000)}{(300)\ (1000)}$$

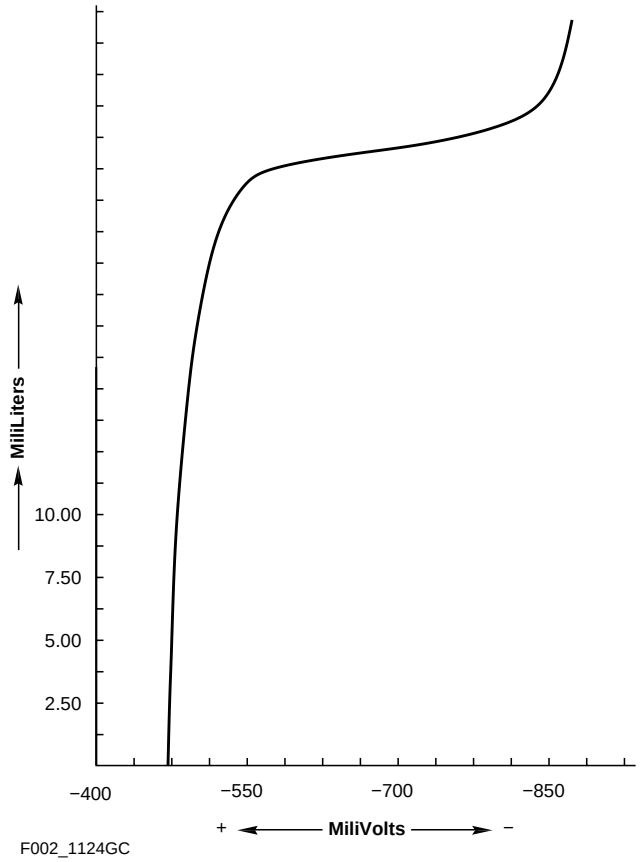
For samples containing 1 to 3 g/L silver:

$$\text{g/l Ag} = \frac{(\text{mL } Na_2S)\ (\text{N } Na_2S)\ (107.88)\ (1000)}{(100.00)\ (1000)}$$

For samples containing more than 3 g/L silver:

$$\text{g/l Ag} = \frac{(\text{mL } Na_2S)\ (\text{N } Na_2S)\ (107.88)\ (1000)}{(50.00)\ (1000)}$$

Figure 2 S-shaped Curve



Potentiometric Determination of Sodium Chloride in EASTMAN Color Films, Persulfate Bleach

ECN-0009/1
ECP-0009/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SR-31	SR-30	—	—

INTRODUCTION

The chloride concentration of an Eastman Color Films, Process ECN-2 or ECP-2D persulfate bleach sample is determined by potentiometric titration with silver nitrate solution after acidification with acetic acid. See Figure 1, *Chloride Titration Curve for ECN-2 Persulfate Bleach*, and Figure 2, *Chloride Titration Curve for ECP-2D Persulfate Bleach*, for typical titration curves.

This method was developed using a 50-mL burette. If a 20-mL burette is utilized, the burette will refill at 20 mL, depending on sample chloride concentration. No studies have been performed to determine the impact of this substitution.

Use of this method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$ & 95 Percent Confidence Estimate (not including bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

To obtain the repeatability data, the analyst who developed this method performed five (5) replicates on each of the following solutions:

1. A "fresh" persulfate bleach prepared with all components at their respective aim "working tank" concentrations:
   - 15.052 g/L NaCl for Process ECN-2
   - 15.016 g/L NaCl for Process ECP-2D
2. A "seasoned" persulfate bleach analyzed, as received at:
   - 17.547 g/L NaCl for Process ECN-2
   - 23.021 g/L NaCl for Process ECP-2D
3. The same "seasoned" solution as in number 2, above, reanalyzed after making a standard addition of:
   - 5.291 g/L NaCl for Process ECN-2
   - 6.943 g/L NaCl for Process ECP-2D

Samples (Process ECN-2)	Mean (g/L NaCl)	(N)	Repeatability Standard Deviation, $1S_r$ (g/L NaCl)	95 Percent Confidence Estimate (g/L NaCl)
"Fresh" at "Aim" (15.052 g/L NaCl)	15.076	5	0.018	± 0.05
"Seasoned", as received	17.547	5	0.050	± 0.14
"Seasoned" with Standard Addition	22.815	5	0.015	± 0.04

Samples (Process ECP-2D)	Mean (g/L NaCl)	(N)	Repeatability Standard Deviation, $1S_r$ (g/L NaCl)	95 Percent Confidence Estimate (g/L NaCl)
"Fresh" at "Aim" (15.016 g/L NaCl)	14.961	5	0.040	± 0.11
"Seasoned", as received	23.021	5	0.024	± 0.07
"Seasoned" with Standard Addition	29.855	5	0.022	± 0.06

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independently of the test method.

A statistically significant positive bias for NaCl of (0.16 percent) was found for a Process ECN-2 "fresh" persulfate bleach tank sample. However, this bias was judged not to be practically significant.

A statistically significant negative bias for NaCl of (-0.37 percent) was found for a Process ECP-2D "fresh" persulfate bleach tank sample. However, this was judged not to be practically significant.

Recovery

Recovery is used instead of bias for "seasoned" samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with the standard addition of the component minus the mean for the "seasoned" sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

For the Process ECN-2 sample, the recovery was not statistically different from 100 percent.

For the Process ECP-2D, KUL sample, the recovery of 98.4 percent is statistically different from 100 percent. This was judged not to be practically significant.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Three persulfate bleach samples were analyzed by four analysts, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A "fresh" tank solution prepared at:
    - 15.001 g/L NaCl for Process ECN-2
    - 15.014 g/L NaCl for Process ECP-2D
2. A seasoned persulfate bleach sample analyzed, "as received" at:
    - 17.608 g/L NaCl for Process ECN-2
    - 22.701 g/L NaCl for Process ECP-2D
3. The same "seasoned" solution, as in number 2, above, analyzed in the same manner, after making a standard addition of:
    - 5.269 g/L NaCl for Process ECN-2
    - 6.990 g/L NaCl for Process ECP-2D

Samples (Process ECN-2)	Mean (g/L NaCl)	(N)	Reproducibility Standard Deviation, $1S_c$ (g/L NaCl)	95 Percent Confidence Estimate (g/L NaCl)
"Fresh" at "Aim" (15.001 g/L NaCl)	14.949	16	0.052	± 0.11
"Seasoned" as received	17.608	16	0.155	± 0.33
"Seasoned" with Standard Addition	22.789	16	0.052	± 0.11

Samples (Process ECP-2D)	Mean (g/L NaCl)	(N)	Reproducibility Standard Deviation, $1S_c$ (g/L NaCl)	95 Percent Confidence Estimate (g/L NaCl)
"Fresh" at "Aim" (15.014 g/L NaCl)	14.946	16	0.050	± 0.11
"Seasoned" as received	22.701	16	0.093	± 0.20
"Seasoned" with Standard Addition	29.619	16	0.113	± 0.24

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- 5-mL pipette
- Beakers, 250-mL
- ORION double-junction reference electrode 900200 or equivalent with (10 percent KNO_3 outer filling solution)
- Silver billet indicator electrode BECKMAN Model 39261 or equivalent
- Automatic titrator with stirrer, METROHM E536 with an E665 Dosimat (50-mL burette) or equivalent.

REAGENTS

Use ACS Reagent Grade reagents unless otherwise specified.

- Glacial Acetic Acid
- Sodium Chloride, NaCl
- 0.05 N Silver Nitrate, $AgNO_3$, standardized to four decimal places
- Water, Type I Reagent—This method was developed using reagent water equivalent to purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Treatment of the Sample

1. Pipette 5.0 mL of the bleach into a 250-mL beaker containing approximately 100 mL of reagent water.
2. Add 10 mL of glacial acetic acid to the beaker.

Titration

1. Place the 250-mL beaker on the METROHM titrator stand and add a magnetic stir bar. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the silver electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex.
2. Titrate the sample, through the first break, on an automatic titrator with standardized 0.05 N silver nitrate. Use a silver billet as the indicator electrode and a double junction reference electrode. If using a METROHM titration system, the following settings should be used:

Horizontal chart span	=	500 mV
Maximum titration speed (min/100% volume)	=	15
Stop (%U)	=	OFF
Vertical chart span (mm/100% volume)	=	400
Auto control	=	OFF
Titration mode	=	mV/pH
Titration “breaks” from	=	right to left

3. Determine the end point using the concentric arcs method. (Refer to Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revisions.) See Figure 1, *Chloride Titration Curve for ECN-2 Persulfate Bleach*, and Figure 2, *Chloride Titration Curve for ECP-2D Persulfate Bleach*.

Figure 1 Chloride Titration Curve for ECN-2 Persulfate Bleach

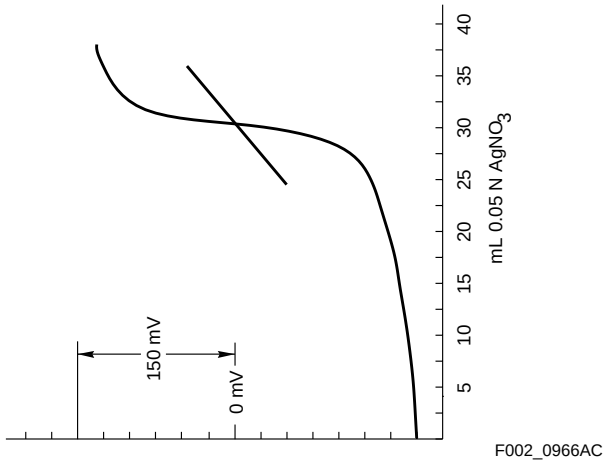
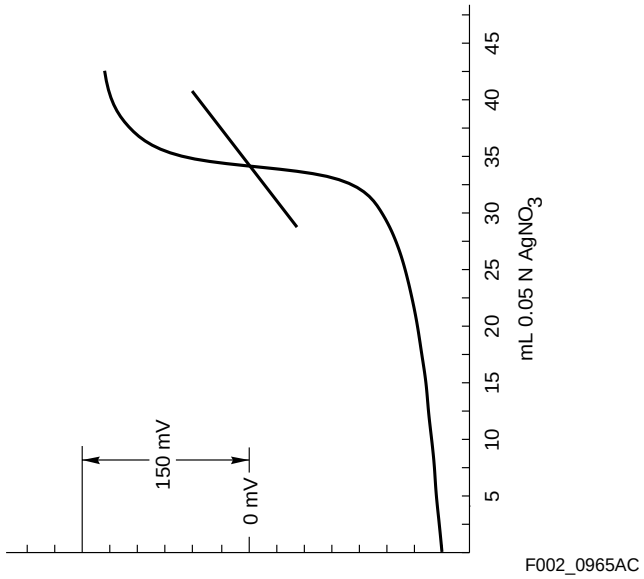


Figure 2 Chloride Titration Curve for ECP-2D Persulfate Bleach



CALCULATIONS

$$\text{NaCl, g/L} = \frac{(\text{mL } AgNO_3)\ (\text{N } AgNO_3)\ (\text{eq. wt. NaCl})\ (1000)}{(\text{mL sample})\ (1000)}$$

Where:

N $AgNO_3$	=	Normality of $AgNO_3$ in meq/mL
eq. wt.	=	58.44 mg/meq NaCl
mL sample	=	mL sample pipetted into the 250-mL beaker
1000	=	factor to convert mg to g in numerator and mL to L in denominator

Example:

$$\text{NaCl, g/L} = \frac{(25.77 \text{ mL } AgNO_3)\ (0.0499 \text{ } AgNO_3)\ (58.44)\ (1000)}{(5.00)\ (1000)}$$

$$= 15.0$$

Iodometric Determination of Sodium Metabisulfite in Accelerator Solution

ECN-2-1340
ECR-1340A

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	AB-2	—	AB-3	AB-3

PRINCIPLE

The sample is added to an excess of iodine, formed by acidifying standard potassium iodate solution and adding potassium iodide. Part of the iodine is reduced to iodide by the sodium metabisulfite ($Na_2S_2O_5$) and the KODAK Bleach Accelerator PBA-1, in the sample. The unreduced part is measured by titration against standard sodium thiosulfate with starch as the indicator. Since the quantity of sodium thiosulfate used in the titration is equivalent to the quantity of unreduced iodine, the concentration of sodium metabisulfite is calculated from the difference between the total iodine and the quantity of sodium thiosulfate used in the titration. A stoichiometric factor in the calculation corrects for the KODAK Persulfate Bleach Accelerator PBA-1, contribution in the titration. KODAK Persulfate Bleach Accelerator PBA-1 must be analyzed prior to the analysis of sodium metabisulfite (see Method 2100B, *Potentiometric Determination of Kodak Persulfate Bleach Accelerator PBA-1 in Accelerator Solution*).

The method is accurate in that it measures the amount of sodium metabisulfite existing in the mix. In some mixes containing a relatively small amount of sodium metabisulfite, an appreciable portion of the sodium metabisulfite is oxidized during mixing, producing results lower than mix level.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use reagents that are ACS Reagent Grade unless specified otherwise.

- 0.1 N Potassium Iodate, KIO_3 (standardized to 4 decimal places)
- 7.0 N Sulfuric Acid, H_2SO_4
- 0.60 M Potassium Iodide, KI
- 0.1 N Sodium Thiosulfate, $Na_2S_20_3$ (standardized to 4 decimal places)
- Starch Indicator

PROCEDURE

Sample Treatment

1. Pipet (wipe the Pipet before leveling) 50.0 mL of standardized 0.1 N potassium iodate into a 250-mL conical flask.
2. Add 25 mL of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 25 mL of 0.60 M potassium iodide from a tip-up pipet.
4. Pipet (wipe) 10.0 mL of sample into the flask.

Titration

1. Titrate with standardized 0.1 N sodium thiosulfate to a *yellow* color.
2. Add approximately 5 mL of starch indicator and continue the titration until the *blue* color disappears.

Calculation

$Na_2S_2O_5$, g/L =

$$\frac{[(N\ KIO_3)(mL\ KIO_3)-(N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)](eq\ wt\ Na_2S_2O_5)(1000)}{(mL\ sample)(1000)} - 0.216(g/L\ PBA\text{-}1) =$$

$$\frac{[(N\ KIO_3)(50)-(N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)](47.53)(1000)}{(10.00)(1000)} - 0.216(g/L\ PBA\text{-}1) =$$

$$\frac{47.53[(N\ KIO_3)(50.0)-(N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)] - 0.216(g/L\ PBA\text{-}1)}{}$$

Determination of Sodium Sulfite in KODAK Color Developer

ECN-2-1305B
ECP-2-1305C
ECR-1305L

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SD-49	SD-50/51	DR-100/101 DR-150/151	DR-105 DR-150

INTRODUCTION

This method is used to determine sodium sulfite in a Process ECN-2, ECP-2D, or VNF/RVNP Color Developer sample. The sulfite content is determined by reacting the sample with excess iodine (liberated from the reaction of potassium iodine under acidic conditions). The unreacted iodine is titrated with standard sodium thiosulfate either potentiometrically or to a visual starch end point. The sulfite content is equivalent to the reacted iodine, which is the difference between the total iodine formed and the unreacted iodine titrated.

The potentiometric titration is recommended over the visual end point titration. With the visual method, it is difficult to pick the end point in highly seasoned (colored) samples. Also, there is a tendency to over-titration, visually, which leads to low sulfite results. The potentiometric method overcomes both these problems because the end point is detected potentiometrically and displayed graphically by the titrator.

Use of this methods requires handling of potentially hazardous chemicals. Material Safety Data Sheets should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PROCEDURE A – POTENTOMETRIC TITRATION

Precision and Bias

Process ECN-2—Three fresh and two seasoned samples of Process ECN-2 Color Developer were analyzed by four analysts on two separate days using multiple titrators. The samples were run in duplicate on each day. The fresh samples were prepared at 1, 3, and 5 g/L Na_2SO_3. The seasoned sample consisted of Process ECN-2 Color Developer from a processor, analyzed as received (at 1.658 g/L Na_2SO_3) and with a standard addition of 0.35 g/L Na_2SO_3.

Process ECP-2D—Three fresh and two seasoned samples of Process ECP-2D Color Developer were analyzed by three analysts on two separate days using multiple titrators. The samples were run in duplicate on each day. The fresh samples were prepared at 1, 3, and 5 g/L Na_2SO_3. The seasoned sample consisted of Process ECP-2D Color Developer from a processor, analyzed as received (at 3.35 g/L Na_2SO_3) and with a standard addition of 0.65 g/L Na_2SO_3.

Process VNF/RVNP—No reliability information was generated for the reversal process VNF-1 and RVNP.

Customer Standard Deviation, s_c

Thew customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any analyst could test the sample using any instrument on any day.

ECN-2 Sample	N	Customer Standard Deviation, $1S_c$
Fresh 1 g/L Na_2SO_3	16	0.029 g/L
Fresh 3 g/L Na_2SO_3	16	0.042 g/L
Fresh 5 g/L Na_2SO_3	16	0.090 g/L
Seasoned Sample (mean = 1.66 g/L Na_2SO_3)	16	0.042 g/L
Seasoned Sample with Addition (mean = 1.99 g/L Na_2SO_3)	16	0.032 g/L

ECP-2D Sample	N	Customer Standard Deviation, $1S_c$
Fresh 1 g/L Na_2SO_3	12	0.045 g/L
Fresh 3 g/L Na_2SO_3	12	0.046 g/L
Fresh 5 g/L Na_2SO_3	12	0.055 g/L
Seasoned Sample (mean = 3.35 g/L Na_2SO_3)	12	0.122 g/L
Seasoned Sample with Addition (mean = 3.99 g/L Na_2SO_3)	12	0.130 g/L

95 Percent Confidence Estimate (not including bias)

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the sodium sulfite level 95 percent of the time.

ECN-2 Sample	95 Percent Confidence Estimate
Fresh 3 g/L Na_2SO_3	± 0.090 g/L
Seasoned Sample (mean = 1.66 g/L Na_2SO_3)	± 0.090 g/L

ECP-2D Sample	95 Percent Confidence Estimate
Fresh 3 g/L Na_2SO_3	± 0.098 g/L
Seasoned Sample (mean = 3.35 g/L Na_2SO_3)	± 0.260 g/L

Bias

Bias is a statistically significant deviation of the mean from the known sodium sulfite level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level cannot be determined independently of the test method.

A statistically significant bias was found at all levels for the Process ECN-2 samples. A low bias of 4.1 percent, 2.4 percent, and 2.9 percent was found at the 1 g/L, 3 g/L, and 5 g/L levels, respectively. These bias were judged not to be practically significant.

A low bias of 4.9 percent, 2.5 percent, and 3.6 percent was found at the 1 g/L, 3 g/L, and 5 g/L levels, respectively for the Process ECP-2D samples. These bias were judged not to be statistically or practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level cannot be determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component, divided by the calculated mean for the seasoned sample plus the actual amount of the standard addition. It is expressed as a percentage.

The recovery of the standard addition was not statistically different from 100 percent.

Apparatus

All volumetric glassware should meet all “Class A” specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, E 969, and E 1272 and all referenced documents.

- 10.0-, 15.0-, and 20.0-mL pipets
- 250-mL beakers
- Automatic titrator with stirrer, METROHM Potentiograph, Model E536 or equivalent
- ORION double-junction reference electrode 900200 or equivalent (10% KNO_3 outer filling solution)
- Platinum inlay electrode, BECKMAN #39373 or equivalent

Reagents

All chemicals are ACS Reagent Grade unless otherwise stated.

- 0.1 N Potassium Iodate, KIO_3 (standardized to 4 places)
- 0.6 M Potassium Iodide, KI
- 0.1 N Sodium Thiosulfate, $Na_2S_2O_3$ (standardized to 4 places)
- 7 N Sulfuric Acid, H_2SO_4
- Water, Type I Reagent – This method was developed, and the resulting statistical data were obtained using reagent water equivalent to purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

Procedure

Treatment and Titration of the Sample

1. Pipet 20.0 mL of standardized 0.1 N potassium iodate into a 250-mL beaker containing 75 mL reagent water and a TEFLON-coated stirring bar.
2. While stirring, add 25 mL of 7.0 N sulfuric acid and 25 mL of 0.6 M potassium iodide.
3. While stirring, immediately pipet the sample size indicated below into the flask *near the surface of the liquid*. Rinse the sides of the beaker with reagent water.

Process	Sample Size
ECN-2	20.0 mL
ECP-2D	10.0 mL
VNF-1/LC	2.00 mL
RVNP	2.00 mL

4. Place the electrodes in the beaker.

   Note: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.

   Titrate the solution potentiometrically with standardized 0.1 N sodium thiosulfate solution while stirring. Use the following parameters with a METROHM E536 Potentiograph:

Rate:	15 min/100% volume
Auto Control:	OFF
Mode:	mV/pH
Range:	500 mV
Buret size:	20 mL
Chart speed:	400 mm/100% volume

5. Determine the volume, in mL, of 0.1 N sodium thiosulfate added to reach the end point using concentric arcs (Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or subsequent revision). Record this as mL A
6. Repeat steps 1–5 pipetting 15.0 mL of standardized 0.1 N potassium iodate instead of 20.0 mL and substituting reagent water for the sample. This is the blank. Record this as mL B.

   Note: The blank only needs to be determined once when running a series of samples.

Calculations

$$Na_2SO_3,\ g/L = \frac{[(mL\ B \times 1.33) - mL\ A] \times (N\ Na_2S_2O_3) \times (eq.\ wt.) \times (1000)}{(ml\ sample) \times (1000)}$$

ECN-2

$$Na_2SO_3,\ g/L = \frac{[(mL\ B \times 1.33) - mL\ A] \times (N\ Na_2S_2O_3) \times (63.02) \times (1000)}{(20) \times (1000)}$$

ECP-2D

$$Na_2SO_3,\ g/L = \frac{[(mL\ B \times 1.33) - mL\ A] \times (N\ Na_2S_2O_3) \times (63.02) \times (1000)}{(10) \times (1000)}$$

VNF-1/RVNP

$$Na_2SO_3,\ g/L = \frac{[(mL\ B \times 1.33) - mL\ A] \times (N\ Na_2S_2O_3) \times (63.02) \times (1000)}{(2) \times (1000)}$$

Where:

mL A = mL of $Na_2S_2O_3$ consumed by sample

mL B = mL of $Na_2S_2O_3$ consumed by blank

$$1.33 = \frac{\text{mL of 0.1 N potassium iodate used for sample}}{\text{mL of 0.1 N potassium iodate used for blank}}$$

PROCEDURE B – VISUAL TITRATION

Reliability

No statistical calibration was performed on this method at the time it was written. Procedure B is reproduced here from previous Methods ECN-2-1305A, ECP-2-1305B, and ECR-1305L for those without access to the preferred auto-titration method.

Apparatus

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- 20.0-, 25.0-, and 50.0-mL pipets
- 250-mL conical flask
- 50.0-mL buret

Reagents

All chemicals are ACS Reagent Grade unless otherwise stated.

- 0.1 N Potassium Iodate, KIO_3
- 0.6 M Potassium Iodide, KI
- 0.1 N Sodium Thiosulfate, $Na_2S_2O_3$, standardized to 4 places
- 7 N Sulfuric Acid, H_2SO_4
- Starch Indicator

Procedure

Treatment and Titration of the Sample

1. Pipet 50.0 mL of 0.1 N potassium iodate into a 250-mL conical flask containing a TEFLON-coated stirring bar
2. While stirring, add 25 mL of 7.0 N sulfuric acid and 25 mL of 0.60 M potassium iodide
3. While stirring, immediately pipet the sample size indicated below into the flask *near the surface of the liquid*. Rinse the sides of the flask with reagent water.

Process	Sample Size
ECN-2	50.0 mL
ECP-2D	25.0 mL
VNF-1/LC	5.00 mL
RVNP	5.00 mL

4. While stirring, immediately titrate with standardized 0.1 N sodium thiosulfate solution (50-mL buret) to a *light yellow* color. Add 5 mL of starch indicator and titrate, drop by drop, until the disappearance of the *blue color* for at least 15 seconds. Record this volume as mL A.
5. Repeat Steps 1 through 4 using 40.0 mL (pipet two 20.0-mL portions) of standardized 0.1 N potassium iodate instead of 50.0 mL, and substituting distilled water for the sample. This is the blank. Record this volume as mL B.

Calculations

$$Na_2SO_3, g/L = \frac{[(mL\ B \times 1.25) - mL\ A] \times (N\ Na_2S_2O_3) \times (eq.\ wt.) \times (1000)}{(ml\ sample) \times (1000)}$$

ECN-2

$$Na_2SO_3, g/L = \frac{[(mL\ B \times 1.25) - mL\ A] \times (N\ Na_2S_2O_3) \times (63.02) \times (1000)}{(50) \times (1000)}$$

ECP-2D

$$Na_2SO_3, g/L = \frac{[(mL\ B \times 1.25) - mL\ A] \times (N\ Na_2S_2O_3) \times (63.02) \times (1000)}{(25) \times (1000)}$$

VNF-1/RVNP

$$Na_2SO_3, g/L = \frac{[(mL\ B \times 1.25) - mL\ A] \times (N\ Na_2S_2O_3) \times (63.02) \times (1000)}{(5) \times (1000)}$$

Where:

mL A = mL of $Na_2S_2O_3$ consumed by sample

mL B = mL of $Na_2S_2O_3$ consumed by blank

$$1.25 = \frac{mL\ of\ 0.1\ N\ potassium\ iodate\ used\ for\ sample}{mL\ of\ 0.1\ N\ potassium\ iodate\ used\ for\ blank}$$

Iodometric Determination of Sulfite in Prebath PB-6

ECN-1315
ECP-1315

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	PB-6	PB-6	—	—

INTRODUCTION

The sample is added to an excess of iodine, formed by acidifying standard potassium iodide. Part of the iodine is reduced to iodide by the sodium sulfite and sodium metabisulfite in the sample; the remaining iodine is measured by titrating it with standardized sodium thiosulfate using starch indicator. Since the quantity of sulfite is equivalent to the quantity of reduced iodine, and the quantity of sodium thiosulfate used in the titration is equivalent to the quantity of remaining iodine, the difference between the total iodine and the volume of sodium thiosulfate is a measure of the sodium sulfite and sodium metabisulfite total.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

RELIABILITY

The method is reliable in that it measures the true total amount of sulfite in the mix. In some mixes containing a relatively small amount of sulfite, an appreciable portion of the sulfite is oxidized during mixing, leading to low sulfite results.

Reagents

Use ACS Reagent Grade reagents unless otherwise specified.

- 0.1 N Potassium Iodate, KIO_3 (standardized to 4 decimal places)
- 7.0 N Sulfuric Acid, H_2SO_4
- 0.60 M Potassium Iodide, KI
- 0.1 N Sodium Thiosulfate, $Na_2S_20_3$ (standardized to 4 decimal places)
- Starch Indicator

PROCEDURE

Sample Treatment

1. Pipet, wipe the pipet before leveling, 50.0 mL of standardized 0.1 N potassium iodate into a 250-mL conical flask.
2. Add 25 mL of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 25 mL of 0.60 M potassium iodide from a tip-up pipet.
4. Pipet (wipe) 10.0 mL of sample into the flask.

Titration

1. Titrate with standardized 0.1 N sodium thiosulfate to a *light yellow color*.

   Note: Highly seasoned samples may not turn light yellow but an observable color change will take place.
2. Add, from a tip-up pipet, 5 mL of starch indicator and continue the titration until the iodine-starch (*dark blue or black*) color disappears.

   Note: The final color of the solution will be *clear or tinted* depending upon the degree of seasoning.

Calculations

Na_2SO_3, g/L =

$$\frac{[(N\ KIO_3)(mL\ KIO_3) - (N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)](eq\ wt\ Na_2SO_3)(1000)}{(mL\ sample)(1000)} =$$

$$\frac{[(N\ KIO_3)(50.0) - (N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)](63.03)(1000)}{(10.0)(1000)} =$$

$$6.303[(N\ KIO_3)(50.0) - (N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)]$$

Potentiometric Determination of Total Alkalinity of EASTMAN Color Films Developer

ECN-0001/1
ECP-0001/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	SD-49	SD-50 SD-51	TBD	TBD

INTRODUCTION

The total alkalinity of a photoprocessing solution is defined as the millilitres of 0.1000 N sulfuric acid required to adjust a specified volume of photoprocessing solution to a pH of 4.3. To determine total alkalinity, a pH meter with a pH indicator electrode and a calomel reference electrode is calibrated according to the procedure described in Method ULM-191-2, *pH Measurement of Photographic Processing Solutions*, or subsequent pH method. A specified volume of photoprocessing solution is titrated to a pH of 4.3 with 0.1000 N sulfuric acid. The volume of sample used in the titration must be reported along with the mL of 0.1000 N sulfuric acid required for the titration

A pH of 4.3 was chosen for the end point because, when titrated with acid, most buffering constituents in photoprocessing solutions show an inflection point near 4.3. The end point determination will be more precise when the pH of the solution is changing quickly (near an inflection point) than when the pH is changing very gradually.

Use of this methods requires handling of potentially hazardous chemicals. Material Safety Data Sheets should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

A fresh tank solution was analyzed four times on one day by both a manual and an automated titration. The manual titration was performed by an experienced analyst. The automated titration was supported by a robotic sample handling system.

A replenisher sample and a seasoned developer tank sample were obtained from a processor and were analyzed as received in the same manner as the fresh sample.

Repeatability Standard Deviation, $1s_r$

All values are expressed in units of mL of 0.1000 N sulfuric acid, and were determined using a sample size of 5.00 mL.

ECN-2 Developer	Manual Method, $1S_r$	Automated Method, $1S_r$
Fresh Tank	0.0	0.06
Seasoned Tank	0.0	0.81
Replenisher	0.082	1.92

ECP-2D Developer	Manual Method, $1S_r$	Automated Method, $1S_r$
Fresh Tank	0.05	0.05
Seasoned Tank	0.08	0.71
0.05	0.05	0.70

95 Percent Confidence Estimate (not including bias)

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean total alkalinity 95 percent of the time.

ECN-2 Developer Sample	95 Percent Confidence Estimate	
	Manual Method	Automated Method
Fresh Tank	± 0.0	± 0.18
Seasoned Tank	± 0.0	± 2.60
Replenisher	± 0.26	± 6.12

ECP-2D Developer Sample	95 Percent Confidence Estimate	
	Manual Method	Automated Method
Fresh Tank	± 0.16	± 0.16
Seasoned Tank	± 0.26	± 2.25
Replenisher	± 0.16	± 2.24

Comparison of Precision for Manual and Automated Procedures

The total alkalinity of forty-one photoprocessing solutions from fourteen different photoprocesses* were determined four times each by both the manual and automated procedures described here. The manual procedure was performed by an experienced analyst. The standard deviations resulting from the manual titrations were pooled, as were the standard deviations of the automated titration results. The pooled standard deviations (n=41) represent a good estimate of the variability for each procedure.

Procedure	Pooled Standard Deviation
Manual	0.13
Automated	0.41

Note: The precision study for the manual method was performed by a single, experienced analyst. If a multiple analyst study were performed, the pooled standard deviation would likely be greater than the pooled standard deviation of the automated method.

* PROSTAR, POLYMAX, RP X-OMAT, ULTRTEC, X-OMAT RA/30, C-41, E-6, ECN-2, ECP-2, EP-2, R-3, RA/RA4, RA 100, RA/RT

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by the American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969 unless otherwise stated.

Manual Titration

- pH Meter, ORION EA 940, or equivalent
- pH Indicator electrode, CORNING Model 476024, or equivalent
- Calomel reference electrode filled with 3.5 N KCl, CORNING Model 476002, or equivalent
- 50-mL Buret

Automatic Titration

- Titrator, METROHM 682, or equivalent
- pH Indicator electrode, CORNING Model 476024, or equivalent
- Calomel reference electrode filled with 3.5 N KCl, CORNING Model 476002, or equivalent

REAGENTS

All reagents used are ACS Reagent Grade unless otherwise stated.

- Water, Type I Reagent – This method was developed using reagent water equivalent to purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.
- 0.1 N Sulfuric Acid, standardized to four decimal places. If an autotitration system is being used, then the sulfuric acid should be standardized by using an automated system.

PROCEDURE

Manual Titration

Titration of the Sample

1. Using Method ULM-191-2, *pH Measurement of Photographic Processing Solutions* (or any subsequent pH method), calibrate the pH meter for making pH measurements below pH 7.
2. Pipet (wipe the pipet before leveling) 5.0 mL of sample into a 150-mL beaker containing 50 mL of reagent water and a Teflon-coated stir bar.
3. Rinse the electrodes with reagent water and blot the electrodes with a tissue.
4. Place the electrode assembly and the tip of the buret (if possible) into the solution. Turn on the stirrer.
5. Using a 50-mL buret, titrate the sample solution with 0.1000 N sulfuric acid to a pH of 4.3.
   a. Add 1 mL increments of sulfuric acid to the sample solution until the pH of the solution is 5.
   b. Add 0.1 mL of sulfuric acid to the sample solution. When the pH of the solution reaches 4.5, record the volume of acid corresponding to the pH value. Continue to titrate until the pH of solution is less than 4.3 and record the pH after each 0.1 mL addition.
   c. For the calculation of total alkalinity, use the volume of acid that resulted in the solution pH that was closest to 4.300. For example, if 29.9 mL of acid resulted in a pH of 4.309, and 30.0 mL of acid resulted in a pH of 4.297, use 30.0 mL of acid in the calculation.

Calculations

1. To calculate the total alkalinity (TA), use the following formula:

$$TA = (N_{acid})(mL_{acid})/0.1$$

Where:

N_{acid} = actual normality of sulfuric acid used

mL_{acid} = millilitres of sulfuric acid used

0.1 = corrects the actual normality of sulfuric acid to 0.1000 N sulfuric acid

2. The total alkalinity is reported to a tenth of a millilitre (0.1 mL).

   Note: The sample size used to determine the total alkalinity of a solution must be included when reporting results. For example, the total alkalinity of solution X is 24.5 mL for a 5.0 mL sample size.

Automated Titration

An example of a program listing for the determination of total alkalinity using a METROHM 682 titrator is shown in *APPENDIX 1*.

pH Calibration Procedure

1. Fill a beaker half-full with pH 7 calibrating buffer and a second beaker half-full with pH 4 calibrating buffer.
2. Place the electrodes into a constantly stirred pH 7 calibrating buffer.
3. Press the "MEAS" key on the titrator panel. The display will read, "MEAS pH***."
4. Press the "PREP STEP" key until the display reads "EL CAL 0/1."
5. Enter "1" and press the "ENTER" key until the display reads "pH(s)1 7.00."
6. Allow the electrodes to equilibrate for 2 minutes, then enter the assigned value of the pH 7 calibrating buffer and press the "ENTER" key.
7. Remove the electrodes from the cup, rinse the electrodes with reagent water, blot with a tissue, and place the electrodes into the pH 4 calibrating buffer.
8. Type in 4.00.
9. Press the "ENTER" key until the display reads "pH(s)2 4.00."
10. Allow the electrodes to equilibrate. The slope will be printed out. The slope should be between 98 and 102 percent. If not, repeat steps 2 through 10.
11. Press the "QUIT" key to continue with the procedure.

Titration of the Sample

1. Pipet (wipe the pipet before leveling) 5.0 mL of sample into a 150-mL beaker containing 50 mL of reagent water and a Teflon-coated stir bar.
2. Rinse the electrodes with reagent water and blot the electrodes with a tissue.
3. Place the electrode assembly and the tip of the buret (if possible) into the solution. turn on the stirrer.
4. Press "GO."

Calculations

1. The total alkalinity results are printed on the titrator's printer.
2. The total alkalinity is reported to a tenth of a millilitre (0.1 mL).

   Note: The sample size used to determine the total alkalinity of a solution must be included when reporting results. For example, the total alkalinity of solution X is 24.5 mL for a 5.0 mL sample size.

APPENDIX 1

METROHM 682 Titrator Example Programs Total Alkalinity Determination

Set pH 4.3

Prep. Steps

Pause 10 s

Titr.dosimat 1

Electr. input 1

Parameters:

EP1 pH 4.30

Dyn.pH 1 3.0

Drift1 10.0 mV/s

T(delay) 1 s

Temp. 25°C

Stop V 99.99 mL

Formula: F1 = (F1 = (EP1*C01)

Formula Constant:

C01 = correction factor for the normality of the sulfuric acid. C01 can be calculated as follows:

$$\frac{\text{Actual normality of sulfuric acid}}{0.1000}$$

Buffering Capacity Determination of EASTMAN Color Films, Process ECP-2 Accelerator Bath

ECP-0020-01

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	AB-1b AB-1bR	—	—

INTRODUCTION

The buffering capacity of an Eastman Color Films, Process ECP-2 accelerator bath is determined by adjusting a 100.0 mL aliquot of sample to pH 3.500 (± 0.005) using 1.0N sulfuric acid and then manually titrating to pH 6.000 (± 0.005) using standardized 1.00N sodium hydroxide solution. The volume of sodium hydroxide used is related to the amount of glacial acetic acid in the sample (buffering capacity) by a linear regression equation.

Repeatability and reproducibility studies were performed for both "fresh" and "seasoned" solutions. The linear regression equations generated from individual "seasoned" solutions were different from each other and significantly different from those generated from "fresh" solutions, due to the differing amounts of seasoning products contributing to the buffering capacity. For this reason, and since it is most representative of data generated by multiple analysts, the linear regression equation generated from the reproducibility study of a "fresh" accelerator bath solution was chosen for inclusion in this method.

Use of this method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation ($1s_r$) & 95 Percent Confidence Estimate (not including bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

To obtain the repeatability data, the analyst who developed this method performed five (5) replicates on each of the following solutions:

1. A "fresh" accelerator bath prepared with components at their respective aim "working tank" concentrations, minus the glacial acetic acid component.
2. The same "fresh" solution as in number 1, above, reanalyzed after making standard additions of 3.0 mL/L, 7.0 mL/L and 10.0 mL/L glacial acetic acid.
3. A "seasoned" accelerator bath analyzed, as received.
4. The same "seasoned" solution as in number 3, above, reanalyzed after making standard additions of 3.0 mL/L, 7.0 mL/L and 10.0 mL/L glacial acetic acid.

"Fresh" tank solutions

Based on 20 determinations by a single analyst, the Standard Error Estimate (Sy.x) for an individual determination of a "fresh" ECP-2 accelerator bath is 0.08 mL/L glacial acetic acid, and the 95 percent confidence at the midpoint of the line is ± 0.18 mL/L glacial acetic acid.

"Seasoned" tank solutions

Based on 20 determinations by a single analyst, the Standard Error Estimate (Sy.x) for an individual determination of a "seasoned" ECP-2 accelerator bath is 0.03 mL/L glacial acetic acid, and the 95 percent confidence at the midpoint of the line is ± 0.07 mL/L glacial acetic acid.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed eight "fresh" accelerator bath samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were prepared identically to the "fresh" solutions described in the repeatability section above.

Two analysts analyzed eight "seasoned" accelerator bath samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were prepared identically to the "seasoned" solutions described in the repeatability section.

"Fresh" tank solutions

Based on 64 determinations by four analysts, the Standard Error Estimate (Sy.x) for an individual determination of a "fresh" ECP-2 accelerator bath is 0.06 mL/L glacial acetic acid, and the 95 percent confidence at the midpoint of the line is ± 0.13 mL/L glacial acetic acid.

Based on chemical theory and measurement of a "fresh" tank solution prepared at aim concentrations, this method is believed to provide an accurate measure of the buffering capacity of an ECP-2 accelerator bath.

"Seasoned" tank solutions

Based on 31 determinations by two analysts, the Standard Error Estimate (Sy.x) for an individual determination of a "seasoned" ECP-2 accelerator bath is 0.04 mL/L glacial acetic acid, and the 95 percent confidence at the midpoint of the line is ± 0.09 mL/L glacial acetic acid.

Based on chemical theory and measurement of a "seasoned" tank solution, this method is believed to provide an accurate measure of the buffering capacity of ECP-2 accelerator bath.

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- 100-mL pipette
- 25-mL burette
- Beakers, 250-mL
- Dual channel pH meter, e.g. ORION EA 940 or equivalent.
- pH electrode, e.g. Corning Rugged Bulb pH electrode 476024 or equivalent
- Reference electrode, e.g. Corning 476002, reference, ceramic junction, calomel or equivalent
- Magnetic stirrer and magnetic stir bar

REAGENTS

Use ACS Reagent Grade reagents unless otherwise specified.

- pH 4 phthalate calibrating buffer (prepare from reagent grade chemicals, or purchase from vendor)
- pH 7 equimolar phosphate calibrating buffer (prepare from reagent grade chemicals, or purchase from vendor)
- pH 3.63 tartrate low pH control buffer (prepare from reagent grade chemicals, or purchase from vendor)
- 1.0 N Sulfuric Acid (H_2SO_4)
- 1.00 N (± 0.02 N) Sodium Hydroxide (NaOH), standardized to 4 decimal places
- Water, Type I Reagent – This method was developed, and the resulting statistical data were obtained using reagent water equivalent to purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Preparation of the meter

1. Follow method *ULM-191-2* (or any subsequent pH method) for making pH measurements below pH 7.
   a. Adjust the temperature of the buffers.
   b. Calibrate the meter with the pH 4 and pH 7 buffers.
   c. Check the electrode calibration with pH 3.63 tartrate low control buffer.

Titration of Sample

1. Pipette (wipe the pipette before leveling) 100.0 mL of sample into a 250 mL beaker containing a magnetic stirr bar.
2. Place beaker on magnetic stirrer
3. Immerse the electrode assembly in the sample solution and stir without splashing.
4. Adjust the pH of the sample to approximately pH 3.5, using 1.0 N sulfuric acid.
5. Add, from a pipette or burette, 1.00 N sodium hydroxide to attain a pH 3.500 (3.495 - 3.505). This volume does not have to be measured.

Caution

Stir the solution rapidly without splashing. Do not rinse the sides of the beaker with reagent water because dilution will affect the results.

6. Using a 25-mL burette, titrate the sample to pH 6.000 (5.995 - 6.005) with 1.00 N sodium hydroxide. Record the volume of titrant used.

   Note: If the titration exceeds pH 6.000, discard the sample and repeat the analysis.

7. Remove the sample and rinse the electrode assembly with reagent water. If rinsing does not completely remove sample deposits, wipe the assembly with a cleansing tissue and re-rinse. Replace the assembly in pH 7 buffer for storage.

Calculation

Buffering Capacity (mL/L glacial acetic acid) = m(x) + b

Where:

m = Slope of the regression line
[(mL/L glacial acetic acid) / mL 1.00 N NaOH]

x = Volume of titrant consumed (mL 1.00 N NaOH)

b = Intercept of regression line (mL/L glacial acetic acid)

Example

Buffering Capacity = 0.648 (7.47) – 0.311

= 4.53 mL/L glacial acetic acid

Buffering Capacity Determination of EASTMAN Color Films, Process ECP-2 Persulfate Bleach

ECP-0019-01

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	SR-30 SR-30R	—	—

INTRODUCTION

The buffering capacity of an Eastman Color Films, Process ECP-2 persulfate bleach is determined by adjusting a 100 mL aliquot of sample to pH 1.600 (± 0.005) using 3N hydrochloric acid and then manually titrating to pH 2.800 (± 0.005) using standardized 1.0N sodium hydroxide solution. The volume of sodium hydroxide used is correlated to the amount of 85 percent phosphoric acid in the sample (buffering capacity) by a linear regression equation.

Repeatability and reproducibility studies were performed for both "fresh and "seasoned" solutions. The linear regression equations generated from individual "seasoned" solutions were different from each other and significantly different from those generated from "fresh" solutions, due to the differing amounts of seasoning products contributing to the buffering capacity. For this reason and since it is most representative of data generated by multiple analysts, the linear regression equation generated from the reproducibility study of a "fresh" persulfate bleach solution was chosen for inclusion in this method.

Use of this method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation ($1s_r$) & 95 Percent Confidence Estimate (not including bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions:

1. A "fresh" persulfate bleach prepared with components at their respective aim "working tank" concentrations, minus the phosphoric acid (85 percent H_3PO_4) component.
2. The same "fresh" solution as in number 1, above, reanalyzed after making standard additions of 2.0 mL/L, 3.0 mL/L and 5.0 mL/L 85 percent H_3PO_4.
3. A "seasoned" persulfate bleach analyzed, as received.
4. The same "seasoned" solution as in number 3, above, reanalyzed after making standard additions of 2.0 mL/L, 3.0 mL/L and 5.0 mL/L 85 percent H_3PO_4.

"Fresh" tank solutions

Based on 20 determinations by a single analyst, the Standard Error Estimate (Sy.x) for an individual determination of a "fresh" ECP-2 persulfate bleach is 0.08 mL/L 85 percent phosphoric acid (H_3PO_4), and the 95 percent confidence estimate at the midpoint of the line is ± 0.17 mL/L 85 percent phosphoric acid (H_3PO_4).

"Seasoned" tank solutions

Based on 20 determinations by a single analyst, the Standard Error Estimate (Sy.x) for an individual determination of a "seasoned" ECP-2 persulfate bleach is 0.13 mL/L 85 percent phosphoric acid (H_3PO_4), and the 95 percent confidence estimate at the midpoint of the line is ± 0.27 mL/L 85 percent phosphoric acid (H_3PO_4).

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed eight persulfate bleach samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were prepared identically to the solutions described in the repeatability section.

"Fresh" tank solutions

Based on 55 determinations by four analysts, the Standard Error Estimate (Sy.x) for an individual determination of a "fresh" ECP-2 persulfate bleach is 0.16 mL/L 85 percent phosphoric acid (H_3PO_4), and the 95 percent confidence estimate at the midpoint of the line is ± 0.31 mL/L 85 percent phosphoric acid (H_3PO_4).

Based on chemical theory and measurement of a "fresh" tank solution prepared at aim concentrations, this method is believed to provide an accurate measure of the buffering capacity of an ECP-2 persulfate bleach.

"Seasoned" tank solutions

Based on 62 determinations by four analysts, the Standard Error Estimate (Sy.x) for an individual determination of a "seasoned" ECP-2 persulfate bleach is 0.29 mL/L 85 percent phosphoric acid (H_3PO_4), and the 95 percent confidence estimate at the midpoint of the line is ± 0.57 mL/L 85 percent phosphoric acid (H_3PO_4).

Based on chemical theory and measurement of a "seasoned" tank solution, this method is believed to provide an accurate measure of the buffering capacity of ECP-2 persulfate bleach.

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- 100-mL pipette
- Beakers, 250-mL
- Dual channel pH meter, e.g. ORION EA 940 or equivalent.
- pH electrode, e.g. Corning Rugged Bulb pH electrode 476024 or equivalent
- Reference electrode, e.g. Corning 476002, reference, ceramic junction, calomel or equivalent

REAGENTS

Use ACS Reagent Grade reagents unless otherwise specified.

- pH 4 phthalate calibrating buffer (prepare from reagent grade chemicals, or purchase from vendor)
- pH 7 equimolar phosphate calibrating buffer (prepare from reagent grade chemicals, or purchase from vendor)
- pH 3.63 tartrate low pH control buffer (prepare from reagent grade chemicals, or purchase from vendor)
- 3.0 N Hydrochloric Acid (HCl)
- 1.00 N (± 0.02 N) Sodium Hydroxide (NaOH), standardized to 4 decimal places
- Water, Type I Reagent – This method was developed, and the resulting statistical data were obtained using reagent water equivalent to purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Preparation of the meter

1. Follow method *ULM-191-2* (or any subsequent pH method) for making pH measurements below pH 7.
   a. Adjust the temperature of the buffers.
   b. Calibrate the meter with the pH 7 and pH 4 buffers.
   c. Check the electrode calibration with pH 3.63 tartrate low control buffer.

Titration of Sample

1. Pipette (wipe the pipette before leveling) 100.0 mL of sample into a 250 mL beaker containing a magnetic stirrer.
2. Immerse the electrode assembly in the sample solution and stir without splashing.
3. Adjust the pH of the sample to approximately pH 1.5, using 3.0 N hydrochloric acid.
4. Add, from a pipette or burette, 1.000 N sodium hydroxide to attain a pH of 1.60 (1.595-1.605). This volume does not have to be measured.

Caution

Stir the solution rapidly without splashing. Do not rinse the sides of the beaker with reagent water because dilution will affect the results.

5. Using a 25-mL burette, titrate the sample to pH 2.80 (2.795-2.805) with 1.000 N sodium hydroxide. Record the volume of titrant used.

   Note: If the titration exceeds pH 2.8, discard the sample and repeat the analysis.

6. Remove the sample and rinse the electrode assembly with reagent water. If rinsing does not completely remove sample deposits, wipe the assembly with a cleansing tissue and rerinse. Replace the assembly in pH 7 buffer for storage.

Calculations

$$\text{Buffering Capacity (mL/L 85\% } H_3PO_4) = m(x) + b$$

Where:

m = Slope of the regression line [(mL/L 85% H_3PO_4) / mL 1.00 N NaOH]

x = Volume of titrant consumed (mL 1.00 N NaOH)

b = Intercept of regression line (mL/L 85% H_3PO_4)

Example

Buffering Capacity = 1.479 (7.47) – 7.49

= 3.56 mL/L 85% H_3PO_4

Titrimetric Determination of EASTMAN Color Developing Agent, CD-2, in Process ECP-2 Developer with Sulfato Cerate

ECP-0003/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	SD-50/51	—	—

INTRODUCTION

This method describes an analytical procedure for measuring EASTMAN Color Developing Agent, CD-2, in Process ECP-2 Developer. CD-2 in the aqueous developer sample is extracted with an organic solvent (butyl acetate). An inorganic salt (NaCI) and a surfactant (polystyrene sulfonate) are added to minimize the formation of emulsion layers during the extraction of CD-2. In seasoned samples, an emulsion layer is usually present. If the layer does not transfer to the sulfuric acid, no significant error is introduced. The CD-2 in the solvent layer is then back-extracted with sulfuric acid. This acid layer can then be titrated with sulfato cerate, using either an automatic titrator to record a potentiometric end point or manually titrated using ferroin indicator, to detect the end point visually.

The potentiometric titration is recommended over the visual end point titration. However, for those unable to use instrumentation, the manual titrimetric technique, using the visual ferroin indicator, is included. Judging end points with a visual color change, especially if the samples are highly seasoned and highly colored, can differ from person to person. The potentiometric method overcomes this problem because the end point is detected potentiometrically and displayed graphically by the titrator.

For the potentiometric measurement, a METROHM Potentiograph, Model E536 or equivalent should be used. The potentiometric titration requires a platinum indicator electrode and a double-junction reference electrode.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development (this procedure was performed by both potentiometric and visual end point detection):

a. A “fresh” EASTMAN Color Films, Process ECP-2 developer prepared with all components at their respective working tank aim concentrations (2.9590 g/L CD-2).

b. A “seasoned” EASTMAN Color Films, Process ECP-2 developer analyzed as received at 1.0537 g/L CD-2 (potentiometrically) and 1.1041 g/L CD-2 (visually).

c. The same “seasoned” solution as in number b, above, reanalyzed after making an analytically weighed, standard addition of 1.0216 g/L CD-2 for the potentiometric study and 1.0108 g/L CD-2 for the visual study.

Reproducibility

Three EASTMAN Color Films, Process ECP-2 developer samples were analyzed by four analysts, each using different titration stations, on two different days. Each analyst analyzed each sample by both the potentiometric and the visual end point technique. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

a. A “fresh” tank solution prepared at 2.9620 g/L CD-2.

b. An EASTMAN Color Films, Process ECP-2 “seasoned” tank developer sample analyzed, as received, in the same manner as the “fresh” developer. The “seasoned” sample of EASTMAN Color Films, Process ECP-2 developer, analyzed to be 2.5321 g/L CD-2 potentiometrically and 2.568 g/L CD-2 visually.

c. The same (as in #2, above) EASTMAN Color Films, Process ECP-2 “seasoned” tank developer sample reanalyzed in the same manner as the “fresh” developer, after a standard addition of CD-2 was made. A standard addition of 0.8406 g/L CD-2 was made to that “seasoned” sample for the potentiometric and visual calibration study.

POTENTIOMETRIC TITRATION STATISTICS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate

Repeatability Standard Deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent Confidence Estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

CD-2 (Potentiometrically)				
Samples (Process ECP-2 Dev)	**Mean Level (g/L CD-2)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (g/L CD-2)**	**95 Percent Confidence Estimate (g/L CD-2)**
"Fresh" at "Aim" (2.959 g/L CD-2)	2.8802	5	0.020	± 0.056
"Seasoned", As Received	1.0537	5	0.026	± 0.072
"Seasoned" with Standard Addition	2.0451	5	0.004	± 0.011

Bias

Bias is a statistically significant deviation from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independent of the test method.

A statistically significant low bias (of 2.6 percent) for CD-2 was found for a "fresh" tank Process ECP-2 developer sample. However, the bias for was judged not to be practically significant.

Recovery

Recovery is used instead of bias for "seasoned" samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the "seasoned" sample with a standard addition of the component minus the mean for the "seasoned" sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 97 percent is statistically different from 100 percent. However, this was judged not to be practically significant.

Reproducibility (Customer) Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

CD-2 (Potentiometrically)				
Samples (Process ECP-2 Dev)	**Mean Level (g/L CD-2)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (g/L CD-2)**	**95 Percent Confidence Estimate (g/L CD-2)**
"Fresh" at "Aim" (2.9620 g/L CD-2)	2.8299	16	0.040	± 0.086
"Seasoned", As Received	2.5321	16	0.033	± 0.071
"Seasoned" with Standard Addition	3.3449	16	0.036	± 0.077

VISUAL TITRATION STATISTICS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate

Repeatability Standard Deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent Confidence Estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

CD-2 (Visually)				
Samples (Process ECP-2 Dev)	**Mean Level (g/L CD-2)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (g/L CD-2)**	**95 Percent Confidence Estimate (g/L CD-2)**
"Fresh" at "Aim" (2.9590 g/L CD-2)	2.8755	5	0.006	± 0.016
"Seasoned", As Received	1.1041	5	0.010	± 0.029
"Seasoned" with Standard Addition	2.0985	5	0.002	± 0.006

Bias

Bias is a statistically significant deviation from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independent of the test method.

A statistically significant low bias (of 2.8 percent) for CD-2 was found for a "fresh" tank Process ECP-2 developer sample. However, the bias for was judged not to be practically significant.

Recovery

Recovery is used instead of bias for "seasoned" samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the "seasoned" sample with a standard addition of the component minus the mean for the "seasoned" sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 98.4 percent is statistically different from 100 percent. However, this was judged not to be practically significant.

Reproducibility (Customer) Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

CD-2 (Visually)				
Samples (Process ECP-2 Dev)	**Mean Level (g/L CD-2)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (g/L CD-2)**	**95 Percent Confidence Estimate (g/L CD-2)**
"Fresh" at "Aim" (2.962 g/L CD-2)	2.8652	16	0.006	± 0.013
"Seasoned", As Received	2.5678	16	0.014	± 0.030
"Seasoned" with Standard Addition	3.3712	16	0.020	± 0.043

SPECIAL APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- Pipette, (25 & 50-mL)
- Separatory funnels, (250-mL)
- Beakers, (250-mL)
- Exhaust hood
- METROHM 536 Titrator or equivalent with a DOSIMAT and a 20-mL burette
- Platinum indicator electrode, BECKMAN, Model 39273 or equivalent
- Double junction reference electrode, ORION Model 900200 or equivalent
  Filling solutions:
  - ORION No. 900002 (inner chamber)
  - ORION No. 900003 (outer chamber)
- Burette, (25-mL) / (visual method only)
- Magnetic stirrer / (visual method only)

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- Polystyrene Sulfonate, (0.1%)
- Butyl Acetate
- Ferroin Indicator
- Sulfuric Acid, H_2SO_4, (1.0 N)
- Sulfato Cerate, $(NH_4)_2Ce(NO_3)_6$, (0.05N) standardized to 4 places past the decimal point
- Sodium Chloride, NaCl

PROCEDURE

Extraction of the Developing Agent, CD-2, with Butyl Acetate

1. Pipette 25.0 mL (potentiometric titration) or 50.0 mL (visual titration) of sample into a 250-mL separatory funnel (No. 1).
2. Add 5.0 g NaCl to the separatory funnel.
3. Add 2 mL of 0.1% polystyrene sulfonate solution. Stopper the funnel and mix, by gently swirling or shaking, until all the salt completely dissolves.
4. Add 50 mL of butyl acetate. Swirl the funnel for 30 seconds. Stopper the funnel, invert and vent through the stopcock. Shake separatory funnel No. 1, horizontally, for a few seconds; invert and vent the funnel through the stopcock. Continue to shake vigorously for 30 seconds. The funnel should be vented at least 2 times.
5. Allow the layers to separate. Gently swirling the funnel will aid breaking up any emulsion at the aqueous-nonaqueous interface.
6. After separation of the layers occurs, transfer the lower (aqueous) layer, as completely as possible, including any emulsion that fails to separate, into another 250-mL separatory funnel (No. 2).
7. Swirl separatory funnel No. 1 and drain any additional lower (aqueous) layer that separates into separatory funnel No. 2. Save the top (butyl acetate) layer in separatory funnel No. 1.
8. Add 50 mL of butyl acetate to separatory funnel No. 2. Swirl the funnel for 30 seconds. Stopper the funnel; invert and vent through the stopcock. Shake the funnel horizontally for a few seconds; invert and vent through the stopcock. Continue to shake the funnel vigorously for 30 seconds, venting at least 2 times.
9. After the layers separate, discard the lower (aqueous) layer as completely as possible. Swirl the funnel and discard any additional aqueous layer that separates, taking care not to lose any of the butyl acetate layer. Discard any emulsion layer that fails to separate.

   Note: Additional separation time may be needed for highly seasoned samples.
10. Transfer the contents of separatory funnel No. 2 (butyl acetate layer) into funnel No. 1 (which contains the first butyl acetate layer).

Back-Extraction of the Developing Agent

1. Add 100 mL of 1.0 N sulfuric acid to separatory funnel No. 2 and swirl, rinsing the inside walls of the funnel. Save the funnel contents for step 3.
2. Gently swirl separatory funnel No. 1 and discard, as completely as possible, any lower (aqueous) layer that separates, taking care not to lose any of the butyl acetate layer.
3. Transfer the contents of separatory funnel No. 2 into funnel No. 1.
4. Swirl the funnel for 30 seconds. Stopper the funnel; invert and vent through the stopcock. Shake the separatory funnel horizontally for a few seconds; invert and vent through the stopcock. Continue to shake vigorously for 30 seconds, venting 2 times.
5. Allow enough time for complete separation of the phases.

   Note: It may take longer for complete separation of the phases in highly seasoned samples.
6. Transfer the lower (acid) layer from separatory funnel No. 1 to a 250-mL beaker without losing any of the top layer.
7. Swirl separatory funnel No. 1 and transfer any additional lower (acid) layer that separates, as completely as possible, into the beaker.

Titration of the Developing Agent with Sulfato Cerate

Note: The end-point of the titration step can be determined either potentiometrically (Step 1 below) or visually (Step 2 below).

1. Potentiometric Titration
   a. Add 5 drops of ferroin indicator and a magnetic stir bar to the 250-mL beaker (from steps 6 & 7 of the *Back-Extraction of the Developing Agent* procedure).

      Note: Do not omit the ferroin, it aids the definition of the end point.

   b. Set the following parameters, if using a METROHM 536 titrator:

Titration mode	mV/pH
Horizontal chart span	750 mV
Autocontrol	OFF
Maximum titration speed	15 min/100% volume
Vertical chart span	400 mm/100% volume
Automatic titration stop (U%)	OFF
Indicator electrode	Platinum, BECKMAN, Model 39373 or equivalent
Reference electrode	Double-junction ORION, Model 900200 or equivalent

   c. Place the 250-mL beaker on the METROHM titrator stand. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex. Titrate the solution with standardized 0.05 N sulfato cerate through the inflection.

   d. Determine the end point using concentric arcs. (Refer to Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revisions.) Record the end point as **mL A**.

   e. Add 100 mL of 1.0 N sulfuric acid to a second 250-mL beaker containing a magnetic stir bar. Add 5 drops of ferroin indicator.

   f. Place the second beaker on the METROHM titrator stand and titrate through the inflection point with standardized 0.05 N sulfate cerate. Record any measurable end point as **mL B**. (This is the blank. This determination needs to be performed only once, if a series of analyses will be performed.)

2. Visual Titration:
   a. Place the 250-mL beaker (from steps 6 & 7 of the *Back-Extraction of the Developing Agent* procedure) on a magnetic stirrer. Add 5 drops of ferroin indicator. Turn the magnetic stirrer on and adjust the setting so that the solution stirs vigorously but without creating a vortex or splashing.

   b. Using a 25-mL burette, titrate the solution with standardized 0.05 N sulfato cerate to the first green color that persists for 15 seconds. Add the titrant dropwise when within an estimated 2 mL of the end point, allowing sufficient time for mixing before making another addition. Record the end point as **mL A**.

   c. Add 100 mL of 1.0 N sulfuric acid to a second 250-mL beaker containing a magnetic stir bar. Add 5 drops of ferroin indicator and place the beaker on a magnetic stirrer. Turn the magnetic stirrer on and adjust the setting so that the solution stirs vigorously without creating a vortex or splashing.

   d. Titrate the solution to the first light blue color that persists for 30 seconds. Record the end point as **mL B**. (This is the blank. This determination needs to be determined only once, if a series of analyses will be performed.)

Calculations

mL A - mL B = mL 0.05 N sulfato cerate, consumed by the sample

$$\text{g/L CD-2} = \frac{(\text{mL sulfate cerate})(\text{N sulfate cerate})(\text{eq. wt. CD-2})(1000)}{(\text{mL sample})(1000)}$$

$$\text{g/L CD-2} = \frac{(\text{mL sulfato cerate})(\text{N sulfato cerate})(107.37)(1000)}{(50\ \text{mL})(1000)}$$

Where:

eq. wt. CD-2 (107.37) = equivalent weight of CD-2 monohydrochloride

Cerimetric Determination of CD-2 Contamination in Eastman Color Print-2 First Fixer
ECP-2-2020

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	F35B, 35D	—	—

PRINCIPLE
A sample of fix is made alkaline (over pH 9.0) and the CD-2 is extracted with chloroform. The CD-2 in the chloroform is then extracted into dilute acid and titrated with sulfato cerate using ferroin as an indicator.

RELIABILITY
CD-2 additions were made to a sample of seasoned fix. Four samples were each run by two analysts. Using the stoichiometric equation:

0.0107 (mL of cerate) – .001 = g/L CD-2

The results were:

CD-2 Added g/L	CD-2 Found g/L
0	0.03 , 0.03
0.10	0.12, 0.12
0.20	0.22, 0.22
0.40	0.41, 0.41

REAGENTS
- 10 N Sodium Hydroxide, NaOH
- pH 11.1 Sodium Carbonate Buffer, Na_2CO_3
- 1.0 N Sulfuric Acid, H_2SO_4
- 0.0500 N Sulfato Cerate, $(NH_4)_2Ce(NO_3)_6$
- Ferroin Indicator

PROCEDURE
Extraction of CD-2 into Chloroform
1. Add from graduated cylinder 500 mL of sample to a one-litre separatory funnel.
2. Add 25 mL of 10 N sodium hydroxide from a tip-up pipet to the funnel.
3. Add 100 mL of pH 11.1 sodium carbonate buffer with a 50-mL tip-up pipet to the funnel.
4. Add 100 mL of chloroform with a tip-up pipet to the funnel stopper and shake 30 seconds, venting occasionally.

Extraction of CD-2
1. Add 50 mL of 1.0 N sulfuric acid to a 250-mL separatory funnel.
2. Drain the chloroform layer from the one-litre separatory funnel into the 250-mL funnel. Shake for 30 seconds.
3. Allow the layers to separate and discard the lower chloroform layer.
4. Drain the acid layer into a 150-mL beaker equipped with a magnetic stirring bar. Rinse the 250-mL funnel with distilled water, adding the rinse to the beaker.
5. Ad 4 drops of ferroin indicator to the beaker and titrate with 0.0500 N sulfato cerate to a green end point.

Calculations
0.0107 (mL cerate) – .001 = CD-2, g/L

Cerimetric Determination of KODAK Color Developing Agent, CD-2, in Stop Bath

ECP-2-2010A

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	SB-14	—	—

INTRODUCTION

Using this analytical procedure you can measure the amount of KODAK Color Developing Agent, CD-2, carried into a Process ECP-2D Stop Bath. The pH of the stop bath sample is adjusted to the approximate pH of an ECP-2D developer, using 6 N sodium hydroxide. The CD-2 is then extracted with water-saturated ethyl acetate. The CD-2 in the solvent layer is then extracted with sulfuric acid and titrated with sulfato cerate, using an automatic titrator.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Three fresh and two seasoned samples of Process ECP-2 Stop Bath were analyzed by four analysts on two separate days using multiple titrators. The samples were run in duplicate on each day. The fresh samples were prepared at 1, 3, and 5 g/L CD-2.

The seasoned samples consisted of Process ECP-2 Stop Bath from a processor, analyzed as received (at 2.22 g/L CD-2) and with a standard addition of 0.428 g/L CD-2.

Customer Standard Deviation, $1s_c$

The customer standard deviation ($1s_c$) is an estimate of the variability* a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

Samples	(N)	Customer Standard Deviation, $1S_c$
Fresh 1 g/L CD-2	16	0.052 g/L
Fresh 3 g/L CD-2	14	0.040 g/L
Fresh 5 g/L CD-2	15	0.091 g/L
Seasoned (mean = 2.22 g/L CD-2)	16	0.073 g/L
Seasoned (mean = 2.60 g/L CD-2)	16	0.048 g/L

95 Percent Confidence Estimate (not including bias)

The 95 percent Confidence Estimate (calculated using the repeatability standard deviation) around a single test will include the mean CD level 95 percent of the time.

Samples	95 Percent Confidence Estimate
Fresh 3 g/L CD-2	± 0.086 g/L
Seasoned	± 0.156 g/L

Bias

Bias is a statistically significant deviation of the mean from the known CD-2 level at the 95 percent confidence level. It is determined for fresh samples only Bias is not determined for seasoned samples, since the component concentration level cannot be determined independently of the test method.

A statistically significant bias was found at all levels. A low bias of 19 percent was found at the 1 g/L level. A low 10 percent bias was also found at both the 3 and 5 g/L level. These biases are felt to be caused by air oxidation during pH adjustment and less than complete extraction of the samples.

Recovery

Recovery is used instead of bias for seasoned samples, since the component level cannot be determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component, divided by the calculated mean for the seasoned sample plus the actual amount of the standard addition. It is expressed as a percentage.

The recovery of the standard addition sample was statistically different from 100 percent, but was not practically significant.

* This assumes the customer laboratory meets the same certification requirements as the Kodak laboratory that developed this method.

SPECIAL APPARATUS

- Exhaust Hood
- Metrohm Potentiograph E536 Titrator or equivalent with Dosimat with a 20-mL buret
- Reference Electrode, Double Junction, Orion No. 900200 or equivalent [Filling solutions: Sat. Silver Chloride solution, or Orion No. 900002 (inner chamber) and 10 percent potassium nitrate, or Orion No. 900003 (outer chamber)]
- Indicator Electrode, Platinum Inlay/Disc, Beckman No. 39273 or equivalent
- pH meter capable of two-point calibration
- Reference Electrode, Ceramic Junction, Calomel, Corning No. 476002, Beckman No. 38423 or equivalent (Filled with 3.5 M potassium chloride bridge solution in outer chamber)
- Indicator Electrode, Glass Rugged Bulb, Corning No. 476024 or equivalent

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 6 N Sodium Hydroxide, NaOH
- 0.1% Polystyrene Sulfonate
- Ethyl Acetate, water-saturated
- Ferroin Indicator
- 1.0 N Sulfuric Acid, H_2SO_4
- 0.05 N Sulfato Cerate, $(NH_4)_2Ce(NO_3)_6$, (standardized to 4 decimal places)

PROCEDURE

Sample Treatment

1. Pour approximately 100 to 120 mL of sample into a 250-mL beaker containing a Teflon-coated stirring bar.
2. Follow Method ULM-191-2, *pH Measurement of Photographic Processing Solutions*, (or any subsequent pH method) for making high-range pH measurements.
3. Immerse the electrode assembly in the sample and start the magnetic stirrer.
4. Adjust the pH of the sample to pH 10.30 ~ 0.03 using 6 N sodium hydroxide. This volume does not have to be measured.
5. Once the pH has been adjusted, pipes 25.0 mL of the sample into a 250-mL separatory funnel (No. 1).
6. Add 2 mL of 0.1% polystyrene sulfonate solution and mix by gently swirling for 10 seconds.
7. Add 25 mL of water-saturated ethyl acetate. Swirl the funnel for 30 seconds. Stopper the funnel; invert and vent through the stopcock. Shake separatory funnel No. 1 horizontally for a few seconds; invert and vent the funnel through the stopcock. Continue to shake vigorously for 30 seconds. The funnel should be vented at least 2 times.
8. Allow the layers to separate. Gently swirling the funnel will aid breaking up any emulsion at the aqueous/nonaqueous interface.
9. After separation of the layers occurs, transfer as completely as possible the lower (aqueous) layer into another 250-mL separatory funnel (No. 2)
10. Swirl separatory funnel No. 1 and drain any additional lower (aqueous) layer that separates into separatory funnel No. 2. Save the top (ethyl acetate) layer in separatory funnel No. 1.
11. Add 25 mL of water-saturated ethyl acetate to separatory funnel No. 2. Swirl the funnel for 30 seconds. Stopper the funnel; invert and vent through the stopcock. Shake the funnel horizontally for a few seconds; invert and vent through the stopcock. Continue to shake the funnel vigorously for 30 seconds, venting at least 2 times.
12. After the layers separate, discard the lower (aqueous) layer as completely as possible. Swirl the funnel and discard any additional aqueous layer that separates, taking care not to lose any of the ethyl acetate layer.
13. Transfer the contents of separatory funnel No. 2 (ethyl acetate layer) into funnel No. 1 (which contains the first ethyl acetate layer).

Back-Extraction of CD-2

1. Add 50 mL of 1.0 N sulfuric acid to separatory funnel No. 2 and swirl, rinsing the inside walls of the funnel. Save the funnel contents for step 3 below.
2. Gently swirl separatory funnel No. 1 and discard as completely as possible any lower (aqueous) layer that separates, taking care not to lose any of the ethyl acetate layer.
3. Transfer the contents of separatory funnel No. 2 into funnel No. 1.
4. Swirl the funnel for 30 seconds. Stopper the funnel; invert and vent through the stopcock. Shake the separatory funnel horizontally for a few seconds; invert and vent through the stopcock. Continue to shake vigorously for 30 seconds, venting 2 times.
5. Transfer the lower (acid) layer from separatory funnel No. 1 to a 250-mL beaker without losing any of the top layer.
6. Swirl separatory funnel No. 1 and transfer, as completely as possible, any additional lower (acid) layer that separates to the beaker.

Potentiometric Titration of CD-2

1. Add 5 drops of ferroin indicator to the 250-mL beaker.

   Note: Do not omit the ferroin, it aids the definition of the end point.

2. If using a Metrohm E536 Potentiograph autotitrator, use the following settings:

E536 Potentiograph:	Control Settings
Cut-off:	OFF
Autocontrol:	OFF
Feeding Time:	15 min/100% volume
Selector Switch:	mV, pH
Measuring Span:	750 mV
Changeover Switch:	400 mm/100% volume
Buret Size:	20 mL
Reference Electrode:	Double-Junction
Indicator Electrode:	Platinum Inlay/Disc

3. Place the beaker on the Metrohm titrator stand. Place the electrodes in the beaker.

   Note: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.

4. Titrate the solution with standardized 0.05 N sulfato cerate through the inflection.
5. Determine the end point using the concentric arcs technique. (Refer to Method XIE, Potentiometric Titrations, or any subsequent revisions.)
6. Record the end point as mL A.
7. Add 50 mL of 1.0 N sulfuric acid to a second 250-mL beaker containing a magnetic stir bar.
8. Add 5 drops of ferroin indicator.
9. This is the blank. This determination only needs to be performed once if a series of analyses will be performed.

   Note: This is the blank. This determination only needs to be performed once if a series of analyses will be performed.

Calculations

$$\text{CD-2, g/L} = \frac{(\text{N cerate})(\text{mL cerate})(\text{eq wt CD-2})(1000)}{(\text{mL sample}) \times (1000)} =$$

$$\frac{(\text{N cerate})(\text{mL cerate})(107.4)(1000)}{(25.0)(1000)} =$$

$$4.296(\text{N cerate})(\text{mL cerate})$$

where:

mL cerate = mL A – mL B

N cerate = Normality of standardized cerate

1000 = conversion factor meq to eq in the numerator and mL to L in the denominator

Potentiometric Determination of Ferricyanide in Process ECP-2 Ferricyanide Bleach ECP-00021/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	SR-27 SR-27R	—	—

INTRODUCTION

Excess iodide ions and a zinc reagent are added to the bleach sample. The ferricyanide reacts with the iodide to produce an equivalent amount of iodine. The iodine is titrated with standard sodium thiosulfate, using either an automatic titrator to record a potentiometric end point, or it is titrated manually using starch indicator to detect the end point visually. The potentiometric titration is recommended over the visual end point titration. However, for those unable to use an automatic titrator, the visual titrimetric technique is included. Judging end points with a visual color change can differ from person to person. The potentiometric method overcomes this problem because the end point is detected potentiometrically and displayed graphically by the titrator.

For the potentiometric measurement, a Metrohm Potentiograph, Model E536 or equivalent should be used. The potentiometric titration requires a platinum indicator electrode and a double-junction reference electrode.

The reaction of ferricyanide and iodide is quantitative as long as zinc ions are present in excess. Any ferrocyanide present in the bleach, as well as the ferrocyanide produced by the reduction of ferricyanide, is precipitated as zinc ferrocyanide. See reactions 1-3, below.

Persulfate ions and some other oxidizing agents will also oxidize iodide. Thus, if present, they will be measured as ferricyanide by this method.

$$2[Fe(CN)_6]^{3-} + 2I^- \rightarrow 2[Fe(CN)_6]^{4-} + I_2 \quad \text{(reaction 1)}$$

$$2[Fe(CN)_6]^{4-} + 2K^+ + 3Zn^{2+} \rightarrow K_2Zn_3[Fe(CN)_6]_2 \quad \text{(reaction 2)}$$

$$2\ S_2O_3^{2-} + I_2 \rightarrow (S_4O_6)^{2-} + 2I^- \quad \text{(reaction 3)}$$

Use of this method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Note: Separate statistics presented for potentiometric and visual titration methods.

Potentiometric Titrations

Repeatability Standard Deviation ($1s_r$) & 95 Percent Confidence Estimate (not including bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development (this procedure was performed by both potentiometric and visual end point detection):

1. A “fresh” ferricyanide bleach prepared with all components at their respective “working tank” aim concentrations.
2. A “seasoned” ferricyanide bleach analyzed potentiometrically as received at 32.636 g/L.
3. The same “seasoned” solution as in number 2, above, reanalyzed after making an analytically weighed, standard addition of 9.751 g/L $K_3Fe(CN)_6$.

$K_3Fe(CN)_6$ (Potentiometrically)				
Sample	**Mean (g/L $K_3Fe(CN)_6$)**	**N**	**Repeatability Standard Deviation, $1S_r$ (g/L $K_3Fe(CN)_6$)**	**95 Percent Confidence Estimate (g/L $K_3Fe(CN)_6$)**
“Fresh” at “Aim” (30.004 g/L K3Fe(CN)6)	30.143	6	0.058	± 0.15
“Seasoned”, As Received	32.636	5	0.015	± 0.04
“Seasoned” with Standard Addition	42.290	5	0.117	± 0.30

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for “fresh” samples only. Bias is not determined for “seasoned” samples, since the component concentration level was not determined independently of the test method.

A statistically significant high bias of (+0.139 g/L) for K3Fe(CN)6 was found for a Process ECP-2 “fresh” tank developer sample. However, the bias was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 99.0 percent for Process ECP-2 was not statistically different from 100 percent.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Three ferricyanide bleach samples were analyzed by four analysts, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A "fresh" tank solution prepared at 30.000 g/L $K_3Fe(CN)_6$.
2. A "seasoned" ferricyanide bleach sample analyzed at 32.582 g/L $K_3Fe(CN)_6$.
3. The same "seasoned" solution, as in number 2, above, analyzed in the same manner, after making a standard addition of 9.751 g/L $K_3Fe(CN)_6$.

$K_3Fe(CN)_6$ (Potentiometrically)				
Sample	**Mean (g/L $K_3Fe(CN)_6$)**	**N**	**Reproducibility Standard Deviation, $1S_c$ (g/L $K_3Fe(CN)_6$)**	**95 Percent Confidence Estimate (g/L $K_3Fe(CN)_6$)**
"Fresh" at "Aim" (30.000 g/L $K_3Fe(CN)_6$)	30.445	16	0.094	± 0.20
"Seasoned", As Received	32.582	16	0.081	± 0.17
"Seasoned" with Standard Addition	42.200	16	0.146	± 0.31

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independently of the test method.

A statistically significant high bias of (+0.445 g/L) for K3Fe(CN)6 was found for a Process ECP-2 "fresh" tank developer sample. However, the bias was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. Statistically, the recovery of 98.6 percent for Process ECP-2 was significantly different from 100 percent, but was judged not to be practically significant.

Visual Titration

Repeatability Standard Deviation ($1s_r$) & 95 Percent Confidence Estimate (not including bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development (this procedure was performed by both potentiometric and visual end point detection):

1. A "fresh" ferricyanide bleach prepared with all components at their respective "working tank" aim concentrations.
2. A "seasoned" ferricyanide bleach analyzed as received at 32.504 g/L.
3. The same "seasoned" solution as in number 2, above, reanalyzed after making an analytically weighed, standard addition of 9.751 g/L $K_3Fe(CN)_6$.

$K_3Fe(CN)_6$ (Visually)				
Sample	**Mean (g/L $K_3Fe(CN)_6$)**	**N**	**Repeatability Standard Deviation, $1S_r$ (g/L $K_3Fe(CN)_6$)**	**95 Percent Confidence Estimate (g/L $K_3Fe(CN)_6$)**
"Fresh" at "Aim" (30.004 g/L $K_3Fe(CN)_6$)	30.187	6	0.019	± 0.05
"Seasoned", As Received	32.504	5	0.013	± 0.03
"Seasoned" with Standard Addition	42.084	5	0.055	± 0.14

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independently of the test method.

A statistically significant high bias of (+0.183 g/L) for K3Fe(CN)6 was found for a Process ECP-2 "fresh" tank developer sample. However, the bias was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. Statistically, the recovery of 98.2 percent for Process ECP-2 was significantly different from 100 percent, but was judged not to be practically significant.

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Three ferricyanide bleach samples were analyzed by four analysts, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A “fresh” ferricyanide bleach prepared with all components at their respective “working tank” aim concentrations.
2. A “seasoned” ferricyanide bleach sample analyzed at 32.441 g/L $K_3Fe(CN)_6$.
3. The same “seasoned” solution, as in number 2, above, analyzed in the same manner, after making a standard addition of 9.751 g/L $K_3Fe(CN)_6$.

$K_3Fe(CN)_6$ (Visually)				
Sample	**Mean (g/L $K_3Fe(CN)_6$)**	**N**	**Reproducibility Standard Deviation, $1S_c$ (g/L $K_3Fe(CN)_6$)**	**95 Percent Confidence Estimate (g/L $K_3Fe(CN)_6$)**
“Fresh” at “Aim” (30.000 g/L $K_3Fe(CN)_6$)	30.346	16	0.116	± 0.25
“Seasoned”, As Received	32.441	16	0.128	± 0.27
“Seasoned” with Standard Addition	42.043	16	0.140	± 0.30

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for “fresh” samples only. Bias is not determined for “seasoned” samples, since the component concentration level was not determined independently of the test method.

A statistically significant high bias of (+0.346 g/L) for K3Fe(CN)6 was found for a Process ECP-2 “fresh” tank developer sample. However, the bias was judged not to be practically significant.

Recovery

Recovery is used instead of bias for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. Statistically, the recovery of 98.5 percent for Process ECP-2 was significantly different from 100 percent, but was judged not to be practically significant.

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- Pipette, (25.0-mL)
- Tip-up pipettes, (20-mL and 25-mL)
- Beakers, (250-mL)
- METROHM 536 Titrator or equivalent with a DOSIMAT and a 20-mL burette
- Platinum indicator electrode, BECKMAN, Model 39273 or equivalent
- Double junction reference electrode, ORION Model 900200 or equivalent
  Filling solutions:
  ORION No. 900002 (inner chamber)
  ORION No. 900003 (outer chamber)
- Burette, (50-mL) / (visual method only)
- Magnetic stirrer / (visual method only)
- Magnetic stir bar / (visual method only)

REAGENTS

Use ACS Reagent Grade reagents unless otherwise specified.

- 0.6 N potassium iodide
- Zinc sulfate - 7.0 N sulfuric acid reagent
- Starch indicator
- Sodium thiosulfate, ($Na_2S_2O_3$), (0.1 N) standardized to 4 places past the decimal point
- Water, Type I Reagent – This method was developed, and the resulting statistical data were obtained using reagent water equivalent to purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Removal of the Interfering Constituents

1. Pipette 25.0 mL of sample into a 250-mL beaker.
2. Add 25 mL of 0.6 potassium iodide from a tip-up pipet.
3. Add 20 mL of zinc sulfate - 7.0 N sulfuric acid reagent from a tip-up pipet; mix thoroughly.

Titration with Sodium Thiosulfate

Note: The end-point of the titration step can be determined either potentiometrically (Step 1) or visually (Step 2)

1. *Potentiometric Titration*:
   a. Set the following parameters on the METROHM Titrator:

Titration mode	mV/pH
Horizontal chart span	250 mV
Autocontrol	OFF
Maximum titration speed	15 min/100% volume
Vertical chart span	400 mm/100% volume
Automatic titration stop (U%)	OFF
Indicator electrode	Platinum, BECKMAN, Model 39273 or equivalent
Reference electrode	Double-junction ORION, Model 900200 or equivalent

   b. Place the 250-mL beaker on the METROHM titrator stand and add a magnetic stir bar. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex. Titrate the solution with standardized 0.1 N sodium thiosulfate through the inflection.
   c. Determine the end point using concentric arcs (Refer to method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revisions.) If a microprocessor controlled titrator is used, the endpoint will be picked automatically.
2. *Visual Titration*:
   a. Place the 250-mL beaker (from the *Removal of the Interfering Constituents* procedure) on a magnetic stirrer after adding a magnetic stir bar. Turn the magnetic stirrer on and adjust the setting so that the solution stirs vigorously but without creating a vortex or splashing.
   b. Using a 50-mL burette, titrate the solution with standardized 0.1 N sodium thiosulfate to a light yellow color.
   c. Add 5 mL of starch indicator from a tip-up pipet, and continue the titration until the blue color just disappears.

CALCULATIONS

For $Na_3Fe(CN)_6$

$$g/L\ Na_3Fe(CN)_6 = \frac{(mL\ Na_2S_2O_3)\ (N\ Na_2S_2O_3)\ (eq\ wt\ Na_3Fe(CN)_6)\ (1000)}{(mL\ sample)\ (1000)}$$

For $K_3Fe(CN)_6$

$$g/L\ K_3Fe(CN)_6 = \frac{(mL\ Na_2S_2O_3)\ (N\ Na_2S_2O_3)\ (eq\ wt\ K_3Fe(CN)_6)\ (1000)}{(mL\ sample)\ (1000)}$$

Where:

$mL\ Na_2S_2O_3$ = volume of $Na_2S_2O_3$ in milliliters required to reach the equivalence point

N = normality of the $Na_2S_2O_3$ in milliequivalents per milliliter (meq/mL)

eq. wt = equivalent weight of ferricyanide in milligrams per milliequivalents [280.92 for $Na_3Fe(CN)_6$, 329.25 for $K_3Fe(CN)_6$]

1000 = factor to convert milligrams to grams of ferricyanide

mL sample = milliliters of sample pipetted in step 1 of *Removal of the Interfering Constituents*

1000 = factor to convert mLs of sample to Litres

If mL 0.1000 N $Na_2S_2O_3$ = 34.77

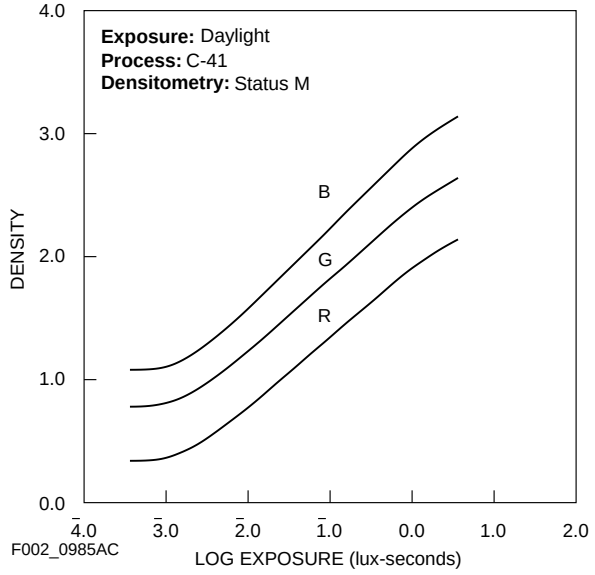
$$(g/L)\ Na_3Fe(CN)_6 = \frac{(34.77)\ (0.1000)\ (280.92)\ (1000)}{(25)\ (1000)}$$

$$(g/L)\ Na_3Fe(CN)_6 = 39.07$$

$$(g/L)\ K_3Fe(CN)_6 = \frac{(34.77)\ (0.1000)\ (329.25)\ (1000)}{(25)\ (1000)}$$

$$(g/L)\ K_3Fe(CN)_6 = 45.79$$

Figure 1 Typical Titration Curve, Ferricyanide in ECP-2D Ferricyanide Bleach



Potentiometric Determination of Ferrocyanide in Process ECP Ferricyanide Bleach and Ferrocyanide Stock Solutions

ECP-0023/01

INTRODUCTION

Ferrocyanide is determined by an oxidation titration with standardized sulfato cerate in an acid solution. The reaction is:

$$Ce^{+4} + Fe(CN)_6^{4-} \rightarrow Ce^{+3} + Fe(CN)_6^{3-}$$

The endpoint of the titration is detected potentiometrically. The electrodes used for the titration are a platinum indicator electrode and a double junction reference electrode. Results are reported in terms of potassium ferrocyanide trihydrate, $K_4Fe(CN)_6 \cdot 3H_2O$.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed three (3) replicates on each of the following solutions during methods development.

1. A “fresh” ferricyanide bleach prepared with all components at their respective “working tank” aim concentrations.
2. The same “fresh” solution as in number 1, above, reanalyzed after making an analytically weighed, standard addition of 2.9990 g/L $K_4Fe(CN)_6 \cdot 3H_2O$.
3. A “seasoned” ferricyanide bleach analyzed potentiometrically as received, at 3.0645 g/L $K_4Fe(CN)_6 \cdot 3H_2O$.
4. The same “seasoned” solution as in number 3, above, reanalyzed after making an analytically weighed, standard addition of 1.0034 g/L $K_4Fe(CN)_6 \cdot 3H_2O$.

$K_4Fe(CN)_6 \cdot 3H_2O$				
Sample	**Mean (g/L $K_4Fe(CN)_6 \cdot 3H_2O$)**	**N**	**Repeatability Standard Deviation, $1s_r$ (g/L $K_4Fe(CN)_6 \cdot 3H_2O$)**	**95 Percent Confidence Estimate g/L $K_4Fe(CN)_6 \cdot 3H_2O$)**
“Fresh”	0.097	3	0.0081	± 0.035
“Fresh” plus Standard Addition	3.075	3	0.0024	± 0.010
“Seasoned”, As Received	3.064	3	0.0142	± 0.061
“Seasoned” plus Standard Addition	4.040	3	0.0063	± 0.027

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. Instead, a recovery was calculated for the component in a fresh sample.

Statistically the recovery of 99.30 percent was significantly different from 100 percent, but was judged not to be practically significant.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically the recovery of 97.18 percent was significantly different from 100 percent, but was judged not to be practically significant.

REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed four ferricyanide bleach samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A fresh tank solution prepared at 30.000 g/L $K_3Fe(CN)_6$
2. The same "fresh" ferricyanide bleach sample as in number 1, above, analyzed in the same manner, after making a standard addition of 3.0038 g/L $K_4Fe(CN)_6 \cdot 3H_2O$.
3. A seasoned ferricyanide bleach sample analyzed, as received, at 3.0249 g/L $K_4Fe(CN)_6 \cdot 3H_2O$.
4. The same seasoned solution, as in number 3, above, analyzed in the same manner, after making a standard addition of 1.0012 g/L $K_4Fe(CN)_6 \cdot 3H_2O$.

$K_4Fe(CN)_6 \cdot 3H_2O$				
Sample	**Mean (g/L $K_4Fe(CN)_6 \cdot 3H_2O$)**	**N**	**Reproducibility Standard Deviation, $1s_c$ (g/L $K_4Fe(CN)_6 \cdot 3H_2O$)**	**95 Percent Confidence Estimate g/L $K_4Fe(CN)_6 \cdot 3H_2O$)**
"Fresh"	0.080	14	0.0083	± 0.018
"Fresh" plus Standard Addition	3.059	14	0.0205	± 0.044
"Seasoned", As Received	3.025	15	0.0879	± 0.189
"Seasoned" plus Standard Addition	4.012	16	0.0784	± 0.167

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. Instead, a recovery was calculated for the component in a fresh sample. Statistically, the recovery of 99.15 percent was significantly different from 100 percent, but was judged not to be practically different

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 98.55 percent was not statistically significantly different from 100 percent.

APPARATUS

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E288, and E969, unless otherwise stated.

- Pipette, (50.0-mL)
- Tip-up pipette, (50-mL)
- Beaker, (600-mL, 400-mL)
- METROHM 536 Titrator or equivalent with a DOSIMAT and a 20-mL burette
- Platinum indicator electrode, BECKMAN, Model 39273 or equivalent
- Double junction reference electrode, ORION Model 900200 or equivalent
- Filling solutions:
  - ORION No. 900002 (inner chamber)
  - ORION No. 900003 (outer chamber)

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 0.0500 N Sulfato Cerate
  (standardized to 4 decimal places)
- 7.0 N Sulfuric Acid
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Treatment of Sample

1. Pipet (wipe the pipet before leveling) the sample of ferricyanide bleach into a beaker according to the following table:

Expected Concentration of $K_4Fe(CN)_6 \cdot 3H_2O$ (g/L)	Beaker Size (mLs)	Sample (mLs)	Reagent Water (mLs)	7.oN H_2SO_4
Below 5	600	200.00	100	50
Between 5 and 10	600	100.00	200	50
Between 10 and 20	400	50.00	200	50
Between 20 and 40	400	25.00	200	50
Between 40 and 80	400	10.00	200	50
Between 80 and 200	400	5.00	200	50
Over 200	400	2.00	200	50

2. Add reagent water from a graduated cylinder according to the table in step 1.
3. Add 7.0 N sulfuric acid from a tip-up pipet according to the table in step 1. Mix thoroughly.

Potentiometric Titration of Sample

1. Titrate the solution with 0.0500 N sulfato cerate, using a METROHM Titrator or equivalent.
   a. Set the following parameters on the METROHM Titrator:

Titration mode	mV/pH
Horizontal chart span	500 mV
Autocontrol	OFF
Maximum titration speed	15 min/100% volume
Vertical chart span	400 mm/100% volume
Automatic titration stop (U%)	OFF
Indicator electrode	Platinum, BECKMAN, Model 39273 or equivalent
Reference electrode	Double-junction ORION, Model 900200 or equivalent

   b. Place the beaker on the METROHM titrator stand and add a magnetic stir bar. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex. Titrate the solution with standardized 0.0500 N sulfato cerate through the inflection.

   c. Determine the end point using concentric arcs (refer to Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revisions.) If a microprocessor controlled titrator is used, the endpoint will be picked automatically.

CALCULATIONS

For $K_4Fe(CN)_6 \cdot 3H_2O$;

$$\text{g/L } K_4Fe(CN)_6 \cdot 3H_2O = \frac{(\text{mL sulfato cerate})\ (\text{N sulfato cerate})\ (\text{eq. wt. } K_4Fe(CN)_6 \cdot 3H_2O)\ (1000)}{(\text{mL sample})\ (1000)}$$

where:

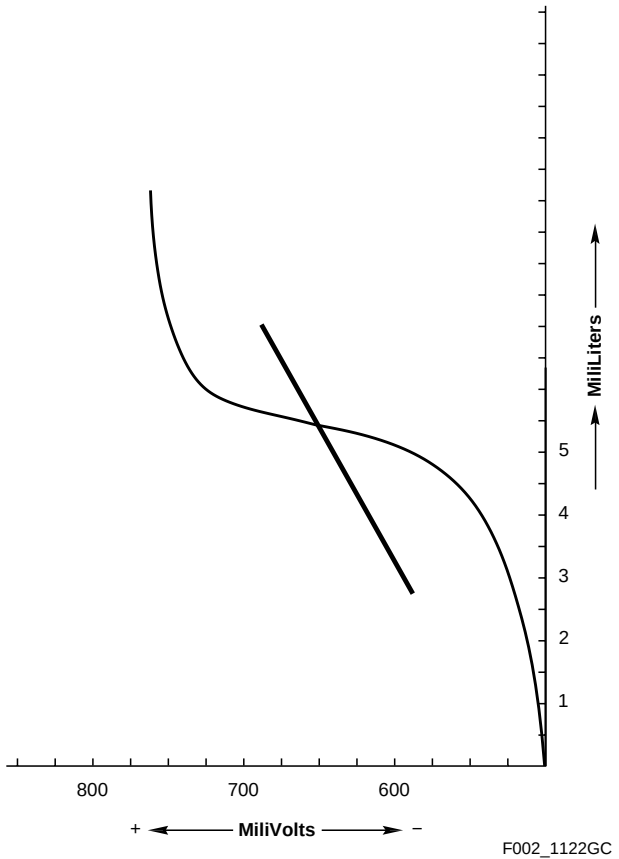
mL sulfato cerate	=	volume of sulfato cerate in milliliters required to reach the equivalence point
N	=	normality of sulfato cerate in milliequivalents per milliliter (meq/mL)
eq. wt.	=	equivalent weight of ferrocyanide in milligrams per milliequivalents [422.41 for $K_4Fe(CN)_6 \cdot 3H_2O$]
1000	=	factor to convert milligrams to grams of ferrocyanide
mL sample	=	milliliters of sample pipetted in step 1 of the *Treatment of Sample*
1000	=	factor to convert mLs of sample to liters

If mL 0.0500 N sulfato cerate = 16.41 mLs;

$$\text{g/L } K_4Fe(CN)_6 \cdot 3H_2O = \frac{(16.41\ (0.0500)\ (422.41)\ (1000)}{(50.0)\ (1000)}$$

$$\text{g/L } K_4Fe(CN)_6 \cdot 3H_2O = 6.93$$

Figure 2 S-shaped Curves



Spectrophotometric Determination of Ferrocyanide in Effluents

1122B

INTRODUCTION

The sample is diluted, if necessary, such that the ferrocyanide [$Fe(CN)_6^{-4}$] concentration falls within a range of 0.5 to 5 mg/L. A dilution of 25 mL of sample to 250 mL is sufficient for samples of as high as 100 mg/L sodium ferrocyanide [$Na_4Fe(CN)_6 \cdot 10\ H_2O$] concentration. In most cases, this is adequate. However, this method can be used for samples of sodium ferrocyanide concentrations as high as one g/L by making a second dilution of 25 mL to 250 mL.

After the dilution, the sample is made alkaline to dissolve ferrocyanide. The sample is then filtered to remove any insolubles. The filtrate is acidified and ferrous/ferric reagent added. After 15 minutes, the intensity of the blue color produced is measured at 700 nm using a spectrophotometer equipped with a tungsten lamp.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

This method was calibrated by preparing fixes containing known concentrations of sodium ferrocyanide, $Na_4Fe(CN)_6 \cdot 10\ H_2O$.

SPECIAL APPARATUS

- Spectrophotometer with a tungsten lamp
- 1-cm Silica Cell

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 2.5 N Sodium Hydroxide, NaOH
- Concentrated Hydrochloric Acid, HCl
- Ferrous/Ferric Reagent

PROCEDURE

1. Pipet (wipe the pipet before leveling) 25.0 mL of effluent sample (Solution A) into a 250-mL volumetric flask. Dilute to volume with distilled water; stopper and invert the flask several times to mix. (This is Solution B.)
2. Add, from a graduated cylinder, 100 mL of the diluted sample (Solution B) from Step 1 to a 250-mL conical flask, and make it alkaline by adding 10 drops of 2.5 N sodium hydroxide.
3. Mix thoroughly and filter the solution through Whatman 2V filter paper.
4. Make the filtrate acid by the dropwise addition of concentrated hydrochloric acid. (Use litmus paper as an indicator.)
5. Pipet (wipe) 40.0 mL of the filtrate into each of two 150-mL beakers. (One portion is read as a blank.)
6. For samples do:
   a. Add 2 drops of ferrous/ferric reagent; allow the beaker to stand for 15 minutes.
   b. If a blue color is apparent, rinse and fill a 1-cm silica cell with solution from the beaker. Measure the absorbance of the sample vs. air at 700 nm on a spectrophotometer equipped with a tungsten lamp.
   c. Record this reading as A_{700} sample.

   Note: If no blue color is produced by Solution B in Step 6a, repeat Steps 2 through 8 using the undiluted effluent sample (Solution A).
7. For blanks do:
   a. Allow the beaker to stand for 15 minutes.
   b. Measure the absorbance of the blank at 700 nm.
   c. Record this reading as A_{700} blank.

   Note: If the absorbance of Solution B at 700 nm after Step 7a is greater than 0.800, dilute again 25 mL of Solution B to 250 mL and repeat Steps 2 through 8 with this Solution (C).

Calculations

$Na_4Fe(CN)_6 \bullet 1O\ H_2O$, mg/L =

$$(\Delta A_{700})(22.6^{*})(2.28^{\dagger})(\text{dilution factor})$$

* 22.6 = factor used to convert absorbance at 700 nm to mg/L of $Fe(CN)_6^{-4}$

† 2.28 = factor used to convert mg/L $Fe(CN)_6^{-4}$ to mg/L $Na_4Fe(CN)_6 \bullet 1O\ H_2O$

where:

$$(\Delta A_{700}) = (\Delta A_{700}\ \text{sample} - \Delta A_{700}\ \text{blank})$$

Undiluted

$Na_4Fe(CN)_6 \bullet 1O\ H_2O$, mg/L =

$$(\Delta A_{700})(22.6)(2.28)(1) =$$

$$51.53(\Delta A_{700})$$

Diluted

Using Solution B

$Na_4Fe(CN)_6 \bullet 1O\ H_2O$, mg/L =

$$(\Delta A_{700})(22.6)(2.28)(10) =$$

$$515.3(\Delta A_{700})$$

Using Solution C

$Na_4Fe(CN)_6 \bullet 1O\ H_2O$, mg/L =

$$(\Delta A_{700})(22.6)(2.28)(100) =$$

$$5152.8(\Delta A_{700})$$

Hydroquinone in Sound Track Developer
ECP-2-407

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	SD-43b	—	—

INTRODUCTION
A phosphate buffer is added to the sample to control its pH. Then the hydroquinone (HQ) is extracted with ethyl acetate. Alcohol and sulfuric acid are added to the ethyl acetate layer to effect a single-phase system. This solution is then titrated with sulfato cerate. The end of the titration is detected by the change in color from orange or light green or colorless.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

SPECIAL APPARATUS
- 50-mL Buret (offset-tip)
- 5-mL Syringe

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS
Use ACS Reagent Grade reagents unless specified otherwise.
- Potassium Monohydrogen/Dihydrogen Phosphate Buffer, pH 7.9 at 27°C (80.6°F).
- Ethyl Acetate, water saturated
- 7.0 N Sulfuric Acid, H_2SO_4
- Ferroin Indicator
- Methyl Alcohol, CH_3OH
- 0.05 N Sulfato Cerate (standardized to 4 decimal places)

PROCEDURE
Extraction of Hydroquinone
1. Add 25 mL of potassium monohydrogen/dihydrogen phosphate buffer, pH 7.9, from a tip-up pipet, to a 250-mL separatory funnel No. 1.
2. Using a 5-mL syringe, add 2.00 mL of sample to funnel No. 1.
3. Add, from a tip-up pipes, 50 mL of water-saturated ethyl acetate to funnel No. 1.
4. Shake the separatory funnel briskly for 15 seconds; then allow the layers to separate (30 seconds or more).
5. Transfer as completely as possible the bottom (water) layer to separatory funnel No. 2 without losing any of the top layer containing HQ.
6. Add, from a tip-up pipet, 50 mL of water-saturated ethyl acetate to funnel No. 2.
7. Shake funnel No. 2 briskly for 15 seconds; then allow the layers to separate (30 seconds or more).
8. Discard the bottom layer. (A small amount of the bottom layer may be left in the funnel.)
9. Transfer the contents of funnel No. 2 to separatory funnel No. 1.
10. Add 10 m L of potassium monohydrogen /dihydrogen phosphate buffer, pH 7.9, from a tip-up pipet.
11. Shake briskly for 10 seconds and allow the layers to separate.
12. Discard as completely as possible the bottom layer without losing any of the top layer containing HQ.

Preparation of the Top Layer for Titration of HQ
1. Add, from a tip-up pipet, 50 mL of methyl alcohol and 50 mL of 7.0 N sulfuric acid to a 400-mL beaker.
2. Transfer the top layer to the 400-mL beaker.
3. Add three drops of Ferroin indicator.

Absorbance Measurements
1. Place the beaker on a magnetic stirrer and stir at a moderate rate. (Be careful to keep the sample from splashing.)
2. Immerse the tip of the buret into the sample, and titrate with standardized 0.05 N sulfato cerate at a moderate rate.
3. When near the end point, withdraw the tip of the buret from the solution, and reduce the rate of delivery to about three drops a second. Titrate to the *first light green color that persists for 15 seconds*.

Calculations
$$\text{HQ, g/L} = \frac{(\text{N cerate})(\text{mL cerate} - \text{blank})(\text{eq wt of HQ})(1000)}{(\text{mL sample})(1000)} =$$

$$\frac{(\text{N cerate})(\text{mL cerate} - 0.27)(55.0)(1000)}{(2.00)(1000)} =$$

$$27.5(\text{N cerate})(\text{mL cerate} - 0.27)$$

Titrimetric Determination of Hypo Index, Thiosulfate, and Sulfite in EASTMAN Color Films, Process ECP-2 Fixer

ECP-0002/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	F-35d/F-35dR	—	—

INTRODUCTION

This method describes the titrimetric determination of hypo index (total reductants), thiosulfate, and sulfite in EASTMAN Color Films, Process ECP-2, fixers. It is recommended that these determinations be carried out by a potentiometric titrimetric approach, using an auto-titrator. However, for those unable to use instrumentation, the manual titrimetric technique, using the visual starch indicator, is included.

For the potentiometric measurement, a *Metrohm* Potentiograph, Model E536 or equivalent should be used. The potentiometric titration requires a platinum indicator electrode and a double-junction reference electrode.

The **Hypo Index** (HI) or total reductants of a fixer is defined as the millilitres of 0.1 N iodine consumed by the thiosulfate and sulfite combined (reaction 1 & 2), in a specified volume of fixer. The fixer is added to an excess of iodine (liberated from the reaction of potassium iodate and potassium iodide under acidic conditions - reaction 3). The unreacted iodine is titrated either potentiometrically or visually with standardized sodium thiosulfate from the appropriate capacity burette. The difference between the blank titration and the sample titration represents the milliequivalents of iodine consumed by the sample. Dividing the milliequivalents of iodine by 0.1 meq/mL yields the HI of the sample. Hypo index is reported in the terms of HI(1), mL which is the millilitres of 0.1000 N I_2 consumed by 1.0 mL of sample.

$$2\ S_2O_3^{=} + I_2 \rightarrow 2I^{-} + S_4O_6^{=} \qquad \text{(reaction 1)}$$

$$HSO_3^{=} + I_2 + H2O \rightarrow SO_4^{=} + 2I^{-} + 3H^{+} \qquad \text{(reaction 2)}$$

$$IO_3^{-} + 5I^{-} + 6H^{+} \rightarrow 3I_2 + 3H_2O \qquad \text{(reaction 3)}$$

$$Na_2SO_3 + HCHO + H2O \rightarrow CH_3(OH)\ SO_3Na + NaOH \qquad \text{(reaction 4)}$$

The **thiosulfate** is determined potentiometrically by adding 6 percent formaldehyde to a second sample aliquot in reagent water. Under these conditions, the sulfite in the sample forms a formaldehyde bisulfite complex (reaction 4). This sample is then added to an excess of acidified iodine. The unreacted iodine is titrated either potentiometrically with standardized sodium thiosulfate from a 50-mL capacity burette. The difference between the blank titration and the sample titration represents the milliequivalents of iodine consumed by the thiosulfate in the sample. The thiosulfate is expressed as g/L thiosulfate ion ($S_2O_3^{=}$).

The **thiosulfate** is determined by the visual titration by adjusting the pH of a sample aliquot to 8.5. At this pH, the sulfite rapidly forms the stable sulfite - formaldehyde adduct. Upon acidification, which prevents the adduct from reacting with iodine, the thiosulfate from the sample is titrated with standardized iodine reagent to a starch end point.

The **sulfite** content is calculated by subtracting the milliequivalents of iodine consumed by the thiosulfate from the milliequivalents of iodine consumed by the thiosulfate and sulfite. The sulfite is reported as sodium sulfite.

Use of this method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions (this procedure was done by both potentiometric and visual end point detection):

a. A “fresh” EASTMAN Color Films, Process ECP-2, Fixer prepared with all components at their respective aim concentrations in a working tank.

b. A “seasoned” EASTMAN Color Films, Process ECP-2, Fixer analyzed as received at 94.650 g/L thiosulfate ion and 22.374 g/L sodium sulfite.

c. The same “seasoned” solution as in number b, above, reanalyzed after making standard additions of 28.055 g/L thiosulfate ion and 8.191 g/L sodium sulfite.

Reproducibility

Three EASTMAN Color Films, Process ECP-2, Fixer samples were analyzed by four analysts, each using different titration stations, on two different days. Each analyst analyzed each sample by both the potentiometric and the visual end point technique. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

a. a “fresh” tank solution prepared at 100.350 g/L thiosulfate ion and 23.624 g/L sodium sulfite.

b. an EASTMAN Color Films, Process ECP-2 “seasoned” tank fixer sample analyzed, as received, in the same manner as the “fresh” fixer.

c. the same (as in number b, above) EASTMAN Color Films, Process ECP-2 “seasoned” tank fixer sample reanalyzed in the same manner as the “fresh” fixer, after standard additions of thiosulfate and sulfite were made. The “seasoned” sample of EASTMAN Color Films, Process ECP-2 fixer, analyzed to be 75.823 g/L thiosulfate ion and 16.334 g/L sodium sulfite. Standard

additions of 23.168 g/L thiosulfate ion and 4.552 g/L sodium sulfite were made to that "seasoned" sample.

POTENTIOMETRIC TITRATION STATISTICS

Repeatability Standard Deviation, $1s_r$ & 95 Percent Confidence Estimate (not including bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test will include the mean value 95 percent of the time.

HYPO INDEX (1 mL)				
Samples (Process ECP-2 Fixer)	**Mean Level (mL 0.1 N I_2)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (mL 0.1 N I_2)**	**95 Percent Confidence Estimate (mL 0.1 N I_2)**
"Fresh" at "Aim"	9.86	5	0.063	± 0.17
"Seasoned", As Received	11.90	5	0.035	± 0.097
"Seasoned" with Standard Addition	14.99	5	0.12	± 0.33

THIOSULFATE ($S_2O_3^=$)				
Samples (Process ECP-2 Fixer)	**Mean Level (g/L $S_2O_3^=$)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (g/L $S_2O_3^=$)**	**95 Percent Confidence Estimate (g/L $S_2O_3^=$)**
"Fresh" at "Aim"	74.16	5	0.12	± 0.33
"Seasoned", As Received	94.09	5	0.45	± 1.2
"Seasoned" with Standard Addition	117.61	5	0.60	± 1.7

SULFITE ($SO_3^=$)				
Samples (Process ECP-2 Fixer)	**Mean Level (g/L Na_2SO_3)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (g/L Na_2SO_3)**	**95 Percent Confidence Estimate (g/L Na_2SO_3)**
"Fresh" at "Aim"	20.44	5	0.43	± 1.2
"Seasoned", As Received	22.37	5	0.29	± 0.80
"Seasoned" with Standard Addition	28.43	5	0.44	± 1.2

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independently of the test method.

Statistically significant biases were found for hypo index, thiosulfate, and sodium sulfite in a "fresh" tank Process ECP-2 Fixer sample (see table below). However, the individual biases for hypo index, thiosulfate, or sodium sulfite were judged not to be practically significant.

Analyte	Bias (Measurement Unit of Analyte)	Bias (%)
Hypo Index (mL 0.1 N I_2)	– 0.206	– 2.04%
Thiosulfate (g/L $S_2O_3^=$)	– 0.200	– 0.27%
Sodium Sulfite (Na_2SO_3)	– 0.590	– 2.81%

Recovery

Recovery is used instead of bias for "seasoned" samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the "seasoned" sample with a standard addition of the component minus the mean for the "seasoned" sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The table below shows whether or not a recovery is statistically or practically different from 100 percent.

Analyte	Recovery Value	Statistically Significant	Practically Significant
Hypo Index (1 mL)	81.0	Yes	No
Thiosulfate ($S_2O_3^=$)	83.8	Yes	No
Sodium Sulfite (Na_2SO_3)	73.9	Yes	No

Reproducibility

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The customer standard deviation is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

HYPO INDEX (1.0 mL)				
Samples (Process ECP-2 Fixer)	**Mean Level (mL 0.1 N I_2)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (mL 0.1 N I_2)**	**95 Percent Confidence Estimate (mL 0.1 N I_2)**
"Fresh" at "Aim"	12.59	16	0.17	± 0.36
"Seasoned", As Received	9.35	16	0.17	± 0.36
"Seasoned" with Standard Addition	11.75	16	0.13	± 0.29

THIOSULFATE ($S_2O_3^=$)				
Samples (Process ECP-2 Fixer)	**Mean Level (g/L $S_2O_3^=$)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (g/L $S_2O_3^=$)**	**95 Percent Confidence Estimate (g/L $S_2O_3^=$)**
"Fresh" at "Aim"	99.29	16	0.60	± 1.3
"Seasoned", As Received	75.82	16	0.58	± 1.2
"Seasoned" with Standard Addition	95.77	16	0.47	± 1.0

SULFITE (Na_2SO_3)				
Samples (Process ECP-2 Fixer)	**Mean Level (g/L Na_2SO_3)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (g/L Na_2SO_3)**	**95 Percent Confidence Estimate (g/L Na_2SO_3)**
"Fresh" at "Aim"	23.55	16	0.89	± 1.9
"Seasoned", As Received	16.33	16	1.02	± 2.2
"Seasoned" with Standard Addition	20.29	16	0.84	± 1.8

VISUAL TITRATION STATISTICS

Repeatability Standard Deviation, $1s_r$

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

HYPO INDEX (3.0 mL)				
Samples (Process ECP-2 Fixer)	**Mean Level (mL 0.1 N I_2)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (mL 0.1 N I_2)**	**95 Percent Confidence Estimate (mL 0.1 N I_2)**
"Fresh" at "Aim"	29.69	5	0.12	± 0.33
"Seasoned", As Received	35.48	5	0.066	± 0.18
"Seasoned" with Standard Addition	44.57	5	0.045	± 0.12

THIOSULFATE ($S_2O_3^=$)				
Samples (Process ECP-2 Fixer)	**Mean Level (g/L $S_2O_3^=$)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (g/L $S_2O_3^=$)**	**95 Percent Confidence Estimate (g/L $S_2O_3^=$)**
"Fresh" at "Aim"	76.54	5	0.17	± 0.48
"Seasoned", As Received	95.76	5	0.13	± 0.36
"Seasoned" with Standard Addition	119.12	5	0.17	± 0.47

SULFITE (Na_2SO_3)				
Samples (Process ECP-2 Fixer)	**Mean Level (g/L Na_2SO_3)**	**(N)**	**Repeatability Standard Deviation, $1S_r$ (g/L Na_2SO_3)**	**95 Percent Confidence Estimate (g/L Na_2SO_3)**
"Fresh" at "Aim"	19.36	5	0.27	± 0.75
"Seasoned", As Received	20.71	5	0.093	± 0.26
"Seasoned" with Standard Addition	26.67	5	0.10	± 0.28

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only. Bias is not determined for "seasoned" samples, since the component concentration level was not determined independently of the test method.

Statistically significant biases were found for hypo index, thiosulfate, and sodium sulfite for a "fresh" tank Process ECP-2 Fixer sample. However, the individual biases for hypo index, thiosulfate, or sodium sulfite were judged not to be practically significant.

Analyte	Bias (Measurement Unit of Analyte)	Bias (%)
Hypo Index (mL 0.1 N I_2)	–0.950	–3.10%
Thiosulfate (g/L $S_2O_3^=$)	–0.222	–0.29%
Sodium Sulfite (Na_2SO_3)	–1.861	–8.77%

Recovery

Recovery is used instead of bias for "seasoned" samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the "seasoned" sample with a standard addition of the component minus the mean for the "seasoned" sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The table below show whether or not a recovery is statistically or practically significant from 100 percent.

VISUAL RECOVERY			
Analyte	**Recovery Value**	**Statistically Significant**	**Practically Significant**
Hypo Index (1 mL)	79.7%	Yes	No
Thiosulfate ($S_2O_3^=$)	83.2%	Yes	No
Sodium Sulfite (Na_2SO_3)	72.7%	Yes	No

Reproducibility (Customer Standard Deviation), $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

HYPO INDEX (1.0 mL)				
Samples (Process ECP-2 Fixer)	**Mean Level (mL 0.1 N I_2)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (mL 0.1 N I_2)**	**95 Percent Confidence Estimate (mL 0.1 N I_2)**
"Fresh" at "Aim"	12.53	16	0.16	± 0.34
"Seasoned", As Received	9.34	16	0.084	± 0.18
"Seasoned" with Standard Addition	11.71	16	0.11	± 0.23

THIOSULFATE ($S_2O_3^=$)				
Samples (Process ECP-2 Fixer)	**Mean Level (g/L $S_2O_3^=$)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (g/L $S_2O_3^=$)**	**95 Percent Confidence Estimate (g/L $S_2O_3^=$)**
"Fresh" at "Aim"	100.25	16	0.47	± 1.0
"Seasoned", As Received	76.74	16	0.45	± 0.95
"Seasoned" with Standard Addition	97.05	16	0.62	± 1.3

SULFITE (Na_2SO_3)				
Samples (Process ECP-2 Fixer)	**Mean Level (g/L Na_2SO_3)**	**(N)**	**Reproducibility Standard Deviation, $1S_c$ (g/L Na_2SO_3)**	**95 Percent Confidence Estimate (g/L Na_2SO_3)**
"Fresh" at "Aim"	22.61	16	1.04	± 2.2
"Seasoned", As Received	15.74	16	0.56	± 1.2
"Seasoned" with Standard Addition	19.24	16	0.85	± 1.8

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

For Potentiometric Titration:

- *Metrohm Potentiograph,* Model E536 or equivalent titrator
- *Metrohm* Model 665 *Dosimat* with a 50-mL burette size (no substitution)
- Electrodes:

Indicator electrode	=	Platinum inlay (i.e., *Beckman* Model 39273 or equivalent)
Reference electrode	=	Double-junction (i.e., *Orion* 900200 or equivalent) (10% KNO_3 outer filling solution)

For Visual Titration:

- Burette, Class A, 50 mL capacity, *Teflon stopcock*
- Magnetic Stirrer

REAGENTS

Use ACS Reagent Grade reagents unless otherwise specified.

- Potassium Iodate, KIO_3 (0.1 N), - standardized to four decimal places
- Acetic Acid (2.0 N), CH_3COOH
- Potassium Iodide (0.6 M), KI
- Sodium Thiosulfate (0.1 N), $Na_2S_2O_3$ - standardized to four decimal places
- Formaldehyde (6%), pH 3.9
- Starch Indicator
- Phenolphthalein Indicator
- Sodium Hydroxide (1.0 N), NaOH
- Sulfuric Acid (1.0 N), H_2SO_4
- Iodine (0.1 N), I_2 - standardized to four decimal places
- Water, Type I Reagent – This method was developed, and the resulting statistical data were obtained using reagent water equivalent to or purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

For Potentiometric Titration

A. Hypo Index (HI) or Total Reductants

1. To a 400-mL beaker with a magnetic stir-bar, add 100 mL reagent water.
2. Pipette 40.0 mL (use a 20-mL pipette, twice) of standardized 0.1 N potassium iodate into the 400-mL beaker.
3. While stirring, add 10 mL of 2.0 N acetic acid and 25 mL of 0.6 M potassium iodide (KI) to the 400-mL beaker.
4. With continued stirring, immediately pipette 1.0 mL of sample *near the surface of the liquid*. Rinse the sides of the beaker with reagent water.
5. Titrate with standardized 0.1 N sodium thiosulfate on an E536 *Metrohm* Potentiograph or equivalent titrator. If using an E536, titrate the solution from step 4, using the following parameters:

Rate	=	10 min/100% vol
Auto Control	=	OFF
Mode	=	mV/pH
Range	=	500 mV
Burette Size	=	50 mL
Indicator Electrode	=	Platinum inlay or platinum wire (i.e., *Beckman* Model 39273)
Reference Electrode	=	Double-junction reference (i.e., *Orion* Model 90-02)

6. Determine the volume of 0.1 N sodium thiosulfate at the end point using concentric arcs (see Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or subsequent revision).
7. Run a blank (do steps 1–6, but omit the addition of the sample in step 4).

B. Thiosulfate Determination

1. Sample Pretreatment:
   a. To a 250-mL beaker with a magnetic stir-bar, add 75 mL of reagent water.
   b. Pipette 2.0 mL of sample into the 250-mL beaker.
   c. Add 5 mL of 6% formaldehyde (pH 3.9) to the beaker.
   d. Start stirring the contents of the 250-mL beaker, set and start a timer for 2 minutes of stirring.
2. Titration of Sample:
   a. Into a 400-mL beaker with a magnetic stir-bar, pipette 40.0 mL of standardized 0.1 N potassium iodate while the timer from step 1.d. is running.
   b. While stirring, add 10 mL of 2.0 N acetic acid to the 400-mL beaker (continue stirring through step 2e.).
   c. When the timer goes off, add 25 mL of 0.6 M KI to the 400-mL beaker.
   d. Immediately after the 0.6 M KI has been added, add the solution in the 250-mL beaker, from step 1, *Sample Pretreatment:*, to the 400-mL beaker.
   e. Rinse the 250-mL beaker three times with reagent water and add the rinses to the 400-mL beaker.
   f. Titrate the contents of the 400-mL beaker with standardized 0.1 N sodium thiosulfate on an E536 Metrohm Potentiograph or equivalent titrator. If using a Metrohm E536, titrate the solution from step 2e. using the parameters found in step 5 of the Hypo Index (HI) or Total Reductants procedure.
   g. Determine the volume of 0.1 N sodium thiosulfate at the end point using concentric arcs (see Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revision.
3. Run a blank, following all the steps in 1 and 2 above, except omit the addition of sample in step 1b.

C. Sulfite

1. Sulfite is a calculated value and requires no additional measurement.

For Visual Titration

A. Hypo Index (HI) or Total Reductants

Treatment and Titration of Sample:

1. Pipette (wipe before leveling) 40.0 mL of standardized 0.1 N potassium iodate solution into a 250-mL conical flask containing a magnetic stir bar.
2. Add 10 mL of 2.0 N acetic acid solution from a tip-up (or equivalent) pipette.
3. Stir the solution with a magnetic stirrer and add 25 mL of 0.6 M potassium iodide solution from a tip-up pipette.
4. Immediately pipette (wipe) 1.0 mL of the fixer sample into the 250-mL flask while the solution is stirring (hold the tip of the pipette against the wall of the flask and as close to the surface of the stirring solution as possible while the sample is draining but do not immerse the tip of the pipette in the stirring solution).
5. Titrate with standardized 0.1 N sodium thiosulfate solution to a light yellow color.
6. Add 5 mL of the starch indicator, from a tip-up pipette and continue the titration until the blue color just disappears for 15 seconds.
7. Run a blank (do steps 1–6, but omit the addition of the sample in step 4).

B. Thiosulfate (Hypo)

1. Treatment of the Sample:
   a. Pipette 2.0 mL of the fixer sample into a 250-mL conical flask containing a magnetic stir bar.
   b. Add 5 mL of formalin from a tip-up pipette.
   c. Add 3 or 4 drops of phenolphthalein indicator to the flask.
      - If the solution is pink, titrate with 1.0 N sulfuric acid to colorless.
      - If the solution is colorless, titrate with 1.0 N sodium hydroxide to the first light pink color.
   d. Let the solution stand for 2 minutes.
   e. Add 10 mL of 2.0 N acetic acid from a tip-up pipette.
2. Titration with Iodine:
   a. Add, from a tip-up pipette, 5 mL of the starch indicator to the conical flask.
   b. Titrate with standardized 0.1 N iodine solution to the first distinct blue color that persists for 15 seconds.

C. Sulfite

1. Sulfite is a calculated value and requires no additional measurement.

CALCULATIONS

For Potentiometric Titration

A. Hypo Index (HI) or Total Reductants:

$$\text{HI (1), mL} = \frac{(\text{mL Blank A} - \text{mL Sample A})\ (\text{N } Na_2S_2O_3)}{0.1000\ \text{N } Na_2S_2O_3}$$

Where:

HI (1), mL = mL of 0.1000 N I_2 consumed by 1.0 mL sample

mL Blank A = millilitres of titrant at the end point of the blank titration of potentiometric Procedure A.

mL Sample A = millilitres of titrant at the end point of the sample titration of potentiometric Procedure A.

N $Na_2S_2O_3$ = normality of the titrant (meq/mL)

0.1000 = nominal value for the normality of the titrant, in meq/mL

B. Thiosulfate ($S_2O_3^{=}$):

$$\text{g/L } S_2O_3^{=} = \frac{(\text{mL Blank B} - \text{mL Sample B})(\text{N } Na_2S_2O_3)(112.13)(1000)}{\text{sample size } (1000)}$$

Where:

mL Blank B = millilitres of titrant at the end point of the blank titration of potentiometric Procedure B

mL Sample B = millilitres of titrant at the end point of the sample titration of potentiometric Procedure B.

N $Na_2S_2O_3$ = normality of the titrant (meq/mL)

112.13 = equivalent weight of thiosulfate expressed in mg/meq

1000 = conversion factor of milligrams to grams

sample size = sample size used in potentiometric Procedure B (2.0 mL)

1000 = conversion factor of millilitres to litres

C. Sodium Sulfite (Na_2SO_3):

$$\text{mL Blank A} - \text{mL Sample A} = \text{D mL A}$$

$$\text{mL Blank B} - \text{mL Sample B} = \text{D mL B}$$

$$\text{g/L } Na_2SO_3 = \frac{[(\text{D mL A})(2.0) - (\text{D mL B})](\text{N } Na_2S_2O_3)(63.02)(1000)}{\text{sample size } (1000)}$$

Where:

N $Na_2S_2O_3$ = normality of the titrant

2.0 = conversion of hypo index to 2.0 mL sample size

63.02 = equivalent weight of sodium sulfite in mg/meq

1000 = conversion factor of milligrams to grams

sample size = sample size used in potentiometric Procedure B (2.0 mL)

1000 = conversion factor of millilitres to litres

Examples:

Titration		mL 0.1 N $Na_2S_2O_3$ Titrant
Blank A	=	40.50
Sample A	=	21.85
Blank B	=	40.55
Sample B	=	19.80

Hypo Index (HI) or Total Reductants:

$$\text{HI (1), mL} = \frac{(40.50 - 21.85)(0.0989)}{0.1000}$$

$$= 18.4 \text{ mL } 0.1000 \text{ N } I_2$$

Thiosulfate ($S_2O_3^{=}$):

$$\text{g/L } S_2O_3^{=} = \frac{(40.55 - 19.80)(0.0989)(112.13)(1000)}{(2.0)(1000)}$$

$$= 57.5 \text{ g/L}$$

Sodium Sulfite (Na_2SO_3):

$$\text{g/L } Na_2SO_3 = \frac{[(40.50 - 21.85)(2.0) - (40.55 - 19.80)](0.0989)(63.02)(1000)}{(2.0)(1000)}$$

$$= 51.4 \text{ g/L}$$

For Visual Titration

A. Hypo Index (HI) or Total Reductants:

$$\text{HI (1), mL} = \frac{(\text{mL Blank A} - \text{mL Sample A})\ (\text{N } Na_2S_2O_3)}{0.1000\ \text{N } Na_2S_2O_3}$$

Where:

HI (1), mL = mL of 0.1000 N I_2 consumed by 1.0 mL sample

mL Blank A = millilitres of titrant at the end point of the blank visual titration, Procedure A.

mL Sample A = millilitres of titrant at the end point of the sample visual titration, Procedure A.

N $Na_2S_2O_3$ = normality of the titrant (meq/mL)

0.1000 = nominal value for the normality of the titrant, in meq/mL

B. Thiosulfate ($S_2O_3^{=}$):

$$\text{g/L } S_2O_3^{=} = \frac{(\text{mL } I_2)(\text{N } I_2)[\text{eq. wt. } S_2O_3^{=}](1000)}{(\text{mL Sample size})(1000)}$$

Where:

mL I_2 = millilitres of iodine titrant measured at the visual end point

N I_2 = normality of the iodine titrant (meq/mL)

[eq. wt. $S_2O_3^{=}$] = equivalent weight of thiosulfate expressed in mg/meq (112.13)

1000 = conversion factor of milligrams to grams

Sample size = sample size used in Procedure B (2.0 mL)

1000 = conversion factors of milliliters to liters

C. Sodium Sulfite (Na_2SO_3):

$$\text{g/L } Na_2SO_3 = \frac{[(\text{HI})(\text{N* } I_2)(3)] - [(\text{mL } I_2)(\text{N } I_2)](\text{eq. wt. } S_2O_3^{=})(1000)}{(\text{mL Sample size})(1000)}$$

Where:

HI = mL of 0.1000 N I2 consumed by 1.0 mL sample

N* I_2 = nominal 0.1000 normality of iodine used in the Hypo Index calculation (meq/mL)

3 = conversion of Hypo Index to a 3.0 mL sample size

mL I_2 = millilitres of iodine titrant measured at the visual end point, Procedure B

N I_2 = normality of the iodine titrant (meq/mL) used in Procedure B, visual end point

eq. wt. $S_2O_3^{=}$ = equivalent weight of thiosulfate expressed in mg/meq (112.13)

mL Sample = sample size used in Procedure B, visual end point

1000 = conversion factors for milligrams to grams and milliliters to liters

Potentiometric Determination of Potassium Iodide in ECP-2 Persulfate Bleach Process Fixing Bath

ECP-0022/1

INTRODUCTION

The potassium iodide concentration of an Eastman Color Films, Process ECP-2 Persulfate Bleach Process Fixing Bath sample is determined by potentiometric titration with silver nitrate solution. The sample is first treated with sodium sulfide to remove any silver present and heated with alkaline hydrogen peroxide to destroy the thiosulfate and sulfite ions. See Figure 1 for a typical titration curve.

Use of this method requires handling potentially hazardous chemicals. Material Safety Data Sheets (MSDS) should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

A. Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, the analyst who developed this method performed five (5) replicates on each of the following solutions:

1. A "fresh" Fixing Bath prepared with all components at their respective aim "working tank" concentrations (0.502 g/L Potassium Iodide).
2. A "seasoned" Fixer Bath analyzed, as received, 0.542 g/L Potassium Iodide.
3. The same "seasoned" solution as in number 2, above, reanalyzed after making a standard addition of 0.151 g/L Potassium Iodide.

Sample	Mean (g/L KI)	N	Repeatability Standard Deviation, $1s_r$ (g/L KI)	95 Percent Confidence Estimate (g/L KI)
"Fresh," at "Aim" (0.502 g/L KI)	0.501	5	0.0046	± 0.013
"Seasoned" as Received	0.542	5	0.0031	± 0.009
"Seasoned" with Standard Addition	0.691	5	0.0015	± 0.004

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A statistically insignificant negative bias for KI of (-0.001 g/L) was found for a "fresh" tank Fixer Bath sample.

Recovery

Recovery is used instead of bias for "seasoned" samples. It is defined as the calculated mean for the "seasoned" sample with a standard addition of the component minus the mean for the "seasoned" sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 98.68 percent is statistically different from 100 percent. This was judged not to be practically significant.

B. REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed three Fixer Bath samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A "fresh" tank solution prepared at 0.5018 g/L KI.
2. A "seasoned" Fixer Bath sample analyzed, "as received", at 0.535 g/L KI.
3. The same "seasoned" solution, as in number 2, above, analyzed in the same manner, after making a standard addition of 0.151 g/L KI.

Potassium Ferrocyanide, trihydrate				
Sample	**Mean (g/L KI)**	**N**	**Reproducibility Standard Deviation, $1s_c$ (g/L KI)**	**95 Percent Confidence Estimate (g/L KI)**
"Fresh," at "Aim" (0.5018 g/L KI)	0.524	16	0.0208	± 0.44
"Seasoned" as Received	0.535	16	0.0200	± 0.43
"Seasoned" with Standard Addition	0.683	16	0.0289	± 0.62

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for "fresh" samples only.

A statistically significant positive bias for KI of (0.022 g/L) was found for a "fresh" tank Fixer Bath sample. This bias was judged not to be practically significant.

Recovery

Recovery is used instead of bias for "seasoned" samples. It is defined as the calculated mean for the "seasoned" sample with a standard addition of the component minus the mean for the "seasoned" sample, divided by the actual amount of the standard addition. It is expressed as a percentage. The recovery of 98.01 percent is statistically different from 100 percent. This was judged not to be practically significant.

APPARATUS

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- 15-mL, 5-mL, 25-mL pipettes
- Beakers, 600-mL and 100-mL
- 10-mL graduated cylinder
- Conical Flask, 125-mL
- Whatman 2V fluted filter paper, 15cm
- ORION double-junction reference electrode 900200 or equivalent with (10 percent KNO_3 outer filling solution)
- Silver billet indicator electrode BECKMAN Model 39261 or equivalent
- Automatic titrator with stirrer, METROHM E536 with an E665 Dosimat (20-mL burette) or equivalent.

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- Potassium Iodide, KI
- 6 N Sodium Hydroxide, NaOH
- 0.8 M Sodium Sulfide, Na_2S
- 30 percent Hydrogen Peroxide
- Glacial Acetic Acid
- 0.005 N Silver Nitrate, $AgNO_3$, standardized to four decimal places
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

A. Treatment of the Sample

1. Pipette (wipe the pipette before leveling) 15.0 mL of the sample into a 125-mL conical flask.
2. Pipette (wipe the pipette before leveling) 25.0-mL of 6 N sodium hydroxide into the flask.
3. Pipette (wipe the pipette before leveling) 5.0-mL of 0.8 M sodium sulfide into the flask.
4. Heat to boiling to coagulate the precipitate, cool and filter through a 15 cm Whatman 2V fluted filter paper into a dry 100-mL beaker. Discard the precipitate.
5. Pipette (wipe the pipette before leveling) 25.0 mL of the filtrate into a 600-mL beaker.
6. Add approximately 100 mL of reagent water. The solution must not be hot. Cautiously add 10.0 mL of 30 percent hydrogen peroxide.

Caution

Wear rubber gloves and safety glasses. If any reagent is spilled, flush with large quantities of water.

7. Boil to approximately half volume, using glass beads to prevent bumping. Cool to room temperature.
8. Add approximately 200 mL of reagent water and acidify with 6 mL of glacial acetic acid from a graduated cylinder.

B. Titration

1. Place the 600-mL beaker on the METROHM titrator stand and add a magnetic stir bar. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the silver electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex.
2. Titrate the sample, through the first break, on an automatic titrator with standardized 0.005 N silver nitrate. Use a silver billet as the indicator electrode and a double junction reference electrode. If using a METROHM E536 titration system, the following settings should be used:

Horizontal chart span	=	500 mV
Maximum titration speed (min/100% volume)	=	20
Stop (U%)	=	OFF
Vertical chart span (mm/100% volume)	=	400
Auto control	=	OFF
Titration mode	=	mV/pH
Titration “breaks” from	=	right to left

3. Determine the end point using concentric arcs (refer to Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revisions.)

C. Calculation:

$$KI, g/L = \frac{(mL\ AgNO_3)\ (N\ AgNO_3)\ (millieq.\ wt.\ KI)}{0.00833\ L\ Sample}$$

Where:

$N\ AgNO_3$ = Normality of $N\ AgNO_3$ in meq/mL

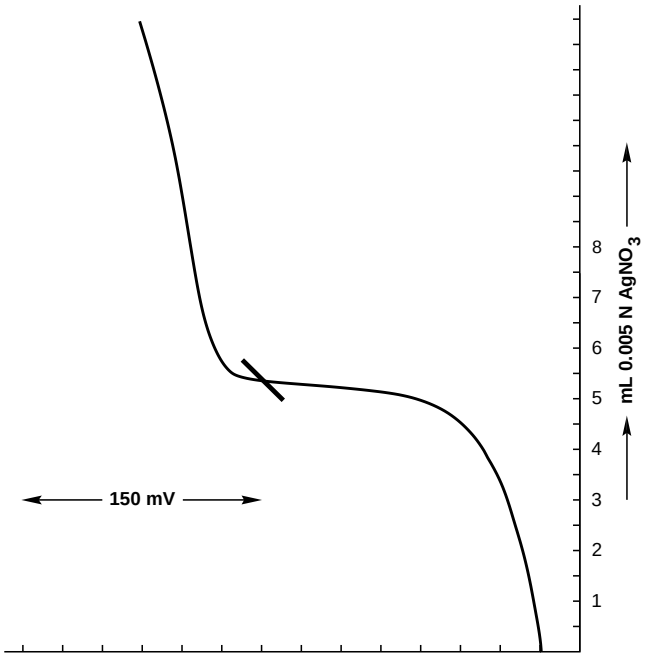
milliequivalent wt = 0.16601 g/meq KI

Example:

$$KI, g/L = \frac{(5.77\ mL\ AgNO_3)\ (0.0050\ N\ AgNO_3)\ (0.16601)}{0.00833\ L\ Sample}$$

$$= 0.57$$

Figure 1 Example Potassium Iodide Titration Curve of ECP-2 Fixer Bath



F002_1145GC

Potentiometric Determination of Kodak PBA-1 in Eastman Color Print -2 Bleach Accelerator ECP-0027-01

INTRODUCTION

Strong base is added to the sample to hydrolyze the KODAK persulfate bleach accelerator PBA-1 to a titratable mercaptan. The PBA-1 content is measured by means of a potentiometric titration with silver nitrate titrant using a silver/silver sulfide indicator electrode and a double junction reference electrode. This analysis is performed with an automatic titrator.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development.

1. A “fresh” Accelerator tank solution prepared with all components at their respective “working tank” aim concentrations.
2. A “seasoned” Accelerator tank solution analyzed as received, at 3.87 g/L PBA-1.
3. The same “seasoned” solution as in number 2, above, reanalyzed after making an analytically weighed, standard addition of 1.1794 g/L PBA-1.

PBA-1				
Sample	**Mean (g/L PBA-1)**	**N**	**Repeatability Standard Deviation, $1s_r$ (g/L PBA-1)**	**95 Percent Confidence Estimate (g/L PBA-1)**
“Fresh” (prepared at 3.31 g/L)	3.38	5	0.023	± 0.06
“Seasoned” As Received	3.87	5	0.011	± 0.03
“Seasoned” plus Standard Addition	5.11	5	0.008	± 0.02

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. Instead, a recovery was calculated for the component in a fresh sample.

A bias of 0.07 g/L PBA-1 was found to be statistically significant at the 95 percent confidence level, however it was judged not to be practically significant

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically the recovery of 105.14 percent was significantly different from 100 percent at the 95 percent confidence level, but was judged not to be practically significant.

REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

The Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed four Accelerator tank samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A "fresh" Accelerator tank solution prepared with all components at their respective "working tank" aim concentrations.
2. A "seasoned" Accelerator tank solution analyzed as received as 3.55 g/L PBA-1.
3. The same "seasoned" solution, as in number 2, above, analyzed in the same manner, after making a standard addition of 1.2327 g/L PBA-1.

PBA-1				
Sample	**Mean (g/L PBA-1)**	**N**	**Reproducibility Standard Deviation, $1s_c$ (g/L PBA-1)**	**95 Percent Confidence Estimate (g/L PBA-1)**
"Fresh" (prepared at 3.31 g/L)	3.31	16	0.104	± 0.22
"Seasoned" As Received	3.55	16	0.022	± 0.05
"Seasoned" plus Standard Addition	4.81	16	0.040	± 0.09

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method.

No statistically significant bias was found at the 95 percent confidence level.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically, the recovery of 102.21 percent was significantly different from 100 percent at the 95 percent confidence level, however it was judged not to be practically significant.

APPARATUS

- Metrohm E536 Autotitrator or equivalent
- Orion Silver-Silver Sulfide Electrode, Catalog No. 941600 or equivalent (Note: DO NOT use a silver billet or bar electrode as prepared in SLM-1295)
- Orion Double Junction Reference Electrode, Catalog No. 90-02-00 or equivalent
- Pipet (50.0 mL)
- Tip-up pipet (10 mL)
- Graduated Cylinder (250 mL)

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E288, and E969, unless otherwise stated.

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 10 N Sodium Hydroxide, NaOH
- 0.0500 N Silver Nitrate, $AgNO_3$ (standardized to four decimal places)
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

A. Preparation of Sample

1. Pipet (wipe the pipet before leveling) 50.00 mL of sample into a 400 mL beaker containing a magnetic stir bar.
2. Using a tip-up pipet, add 10 mL of 10 N sodium hydroxide to the beaker containing the sample.

Caution

Caustic, avoid contact with skin and eyes. In case of contact, flush with water.

3. Place the beaker on a magnetic stirrer and set a timer for 3 minutes.
4. After the solution has stirred for 3 minutes, add 250 mL of reagent water to the beaker from a graduated cylinder.

B. Titration of Sample

1. Titrate the solution with 0.0500 N silver nitrate, using a METROHM E536 Titrator or equivalent.

Caution

Silver nitrate is poisonous, causes burns, and stains skin. Avoid contact.

a. Set the following parameters on the METROHM E536Titrator:

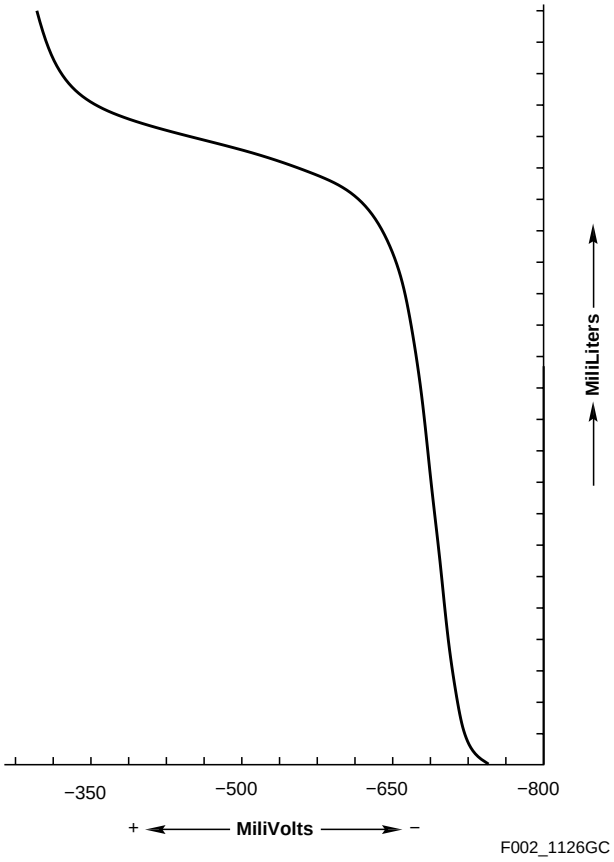
Potentiograph E536 Control	Setting
Titration mode	mV/pH
Horizontal chart span	750 mV
Auto Control	8
min/100% volume	20
MV x 100	-1
mV /pH	100%
°C	Auto
Indicator electrode	Silver/silver sulfide
Reference electrode	Model 900200 or equivalent

Dosimat 655Control	Setting
Buret Size	20 mL
Mode Switch	Mode 1

b. Place the beaker on the METROHM titrator stand and add a magnetic stir bar. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex. Titrate the solution with standardized 0.0500 N silver nitrate through the inflection.

c. Determine the end point using concentric arcs (refer to Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revisions.) If a microprocessor controlled titrator is used, the endpoint will be picked automatically. A typical titration curve is shown in Figure 1.

Figure 2 S-shaped Curves



CALCULATIONS

$$\text{g/L PBA-1} = \frac{(\text{mLs } AgNO_3)\ (\text{N } AgNO_3)\ (\text{eq. wt. of PBA-1})}{\text{mL sample}}$$

Where:

eq. wt. of PBA-1 = 220.2eq. wt. of PBA-1g/equivalent

If mL 0.0499 N silver nitrate = 15.24 mLs

$$\text{g/L PBA-1} = \frac{(15.24)\ (0.0499)\ (220.2)}{\text{mL sample}}$$

g/L PBA-1 = 3.35

Titrimetric Determination of Persulfate in ECP-2 Persulfate Bleach

ECP-0026/1

INTRODUCTION

This method is based upon the oxidation of ferrous ion by persulfate in an acid solution at room temperature. A known excess of ferrous ion is added to the sample and the residual ferrous ion is titrated with standardized sulfato cerate. A blank determination should be run daily because ferrous solutions are slowly oxidized by air during use.

Use of this method requires handling potentially hazardous chemicals. Material Safety Data Sheets (MSDS) should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development.

1. A "fresh" Persulfate bleach tank solution prepared with all components at their respective "working tank" aim concentrations.
2. A "seasoned" Persulfate bleach tank solution analyzed as received, at 30.30 g/L $Na_2S_2O_8$.
3. The same "seasoned" solution as in number 2, above, reanalyzed after making an analytically weighed, standard addition of 8.6150 g/L $Na_2S_2O_8$.

$Na_2S_2O_8$				
Sample	**Mean g/L $Na_2S_2O_8$**	**N**	**Repeatability Standard Deviation, $1s_r$ g/L $Na_2S_2O_8$**	**95 Percent Confidence Estimate g/L $Na_2S_2O_8$**
"Fresh" (prepared at 33.13 g/L)	32.26	5	0.049	± 0.14
"Seasoned" as Received	30.30	5	0.139	± 0.39
"Seasoned" plus Standard Addition	38.51	5	0.065	± 0.18

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A bias of – 0.87 g/L $Na_2S_2O_8$ was found to be statistically significant at the 95 percent confidence level, however it was judged not to be practically significant.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically the recovery of 95.30 percent was significantly different from 100 percent at the 95 percent confidence level, but it was judged not to be practically significant.

REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed four Persulfate bleach tank samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A "fresh" Persulfate bleach tank solution prepared with all components at their respective "working tank" aim concentrations.
2. A "seasoned" Persulfate bleach tank solution analyzed as received, at 27.19 g/L $Na_2S_2O_8$.
3. The same "seasoned" solution as in number 2, above, analyzed in the same manner, after making a standard addition of 8.6330 g/L $Na_2S_2O_8$.

Potassium Ferrocyanide, trihydrate				
Sample	**Mean g/L $Na_2S_2O_8$**	**N**	**Reproducibility Standard Deviation, $1s_c$ g/L $Na_2S_2O_8$**	**95 Percent Confidence Estimate g/L $Na_2S_2O_8$**
"Fresh" (prepared at 33.01 g/L)	32.61	16	0.352	± 0.75
"Seasoned" as Received	29.17	16	0.360	± 0.77
"Seasoned" plus Standard Addition	37.33	16	0.403	± 0.86

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A bias of – 0.40 g/L $Na_2S_2O_8$ was found to be statistically significant at the 95 percent confidence level, however it was judged not to be practically significant.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically, the recovery of 94.52 percent was significantly different from 100% at the 95 percent confidence level, however it was judged not to be practically significant.

APPARATUS

- Conical Flask with stopper (250-mL)
- 2 Tip-up pipettes (50-mL, 15-mL)
- Pipet (5-mL, 10-mL)

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 7.0 N sulfuric acid
- 0.25 N ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$
- 0.0500 N sulfato cerate (standardized to four decimal place
- Ferroin indicator solution
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

Determination of Persulfate

1. Pipet (wipe the pipet before leveling) 5.00 mL of sample into a 250 mL conical flask containing a magnetic stir bar.
2. Add 50 mL of reagent water from a tip-up pipet.
3. Add 15 mL of 7.0 N sulfuric acid from a tip-up pipet.

Caution

Acid, avoid contact with skin and eyes. In case of contact, flush with water.

4. Pipet (wipe the pipet before leveling) 10.0 mL of 0.25 N ferrous ammonium sulfate into the flask. Using a squeeze bottle, wash down the sides of the flask with reagent water.
5. Swirl the solution to mix, stopper the flask and let it stand for 3 minutes.

   Note: Longer standing times do not adversely affect the titration providing the solution is protected from air.
6. Add 4 drops of ferroin indicator and titrate with 0.0500 N sulfato cerate to the first light cyan color.
7. Record the end point as mL A.

Determination of Reagent Blank

Note: A reagent blank should be run at least once per day because the 0.25 N ferrous ammonium sulfate will slowly change with usage.

1. Add 50 mL of reagent water, with a tip up pipet, to a 250 mL conical flask containing a magnetic stir bar.
2. Repeat steps 3 through 6 of Section A.
3. Record the end point as mL B.

CALCULATIONS

For Sodium Persulfate, g/L

$$\text{g/L } Na_2S_2O_8 = \frac{(\text{mLs B - mLs A})\ (\text{N cerate})\ (\text{eq wt } Na_2S_2O_8)}{\text{mL Sample}}$$

Where:

mLs B = volume of sulfato cerate in milliliters required to reach the equivalence point without the addition of sample (Blank)

mLs A = volume of sulfato cerate in milliliters required to reach the equivalence point with the addition of sample

N cerate = normality of the sulfato cerate in milliequivalents per milliliter (meq/mL)

eq wt $Na_2S_2O_8$ = equivalent weight of sodium persulfate in milligrams per milliequivalent (119.05 mg/meq)

mL Sample = volume of sample pipetted in step 1 of part A of procedure

If mL 0.0497 N sulfato cerate = 32.85 mLs

mLs Blank = 49.90 mLs

$$\text{g/L } Na_2S_2O_8 = \frac{(49.90 - 32.85)\ (0.0497)\ (119.05}{5.00}$$

g/L $Na_2S_2O_8$ = 20.18

Determination of the pH of the Eastman Color Print-2 Stop Bath
ECP-2-890

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	SB-14	—	—

INTRODUCTION
Exposure of the electrodes to the low pH of the stop bath causes improper electrode response when the same electrodes are used to measure the pH of more alkaline solutions. A separate set of electrodes should be used for measurement of stop bath pH.

Sulfuric acid, 0.25 N, (pH 0.95 ± 0.05) is used as a reference solution in measuring stop bath pH. The electrodes and meter are first standardized with potassium acid phthalate buffer (pH 4.010 at 27°C). The pH of the 0.25 N sulfuric acid is then measured. If the pH value for the 0.25 N sulfuric acid is 0.95 ± 0.05, the meter is adjusted to the nominal value of 0.95 and the pH of the stop bath is measured. Stop bath pH is measured at 27 ± 5°C.

SPECIAL APPARATUS
- Corning Model 12 Research pH Meter or equivalent
- Corning No. 476024 Glass Electrode or Leeds and Northrup No, 117169 Glass Electrode
- Beckman Fiber Junction Calomel Electrode, No. 39170 (filled with 3.5 N potassium chloride)

REAGENTS
Use reagents that are ACS Reagent Grade unless specified otherwise.
- Potassium Acid Phthalate Buffer, 0.05 M
- Sulfuric Acid, 0.25 N

PROCEDURE
1. Follow the *Standardization of pH Meter - Low pH Range* procedure in Method ULM-191-2, *pH Measurement of Photographic Processing Solutions*, (or any subsequent pH method) for preparation of the meter.
2. Rinse the electrode assembly with distilled water and immerse the electrodes in potassium acid phthalate buffer. Set a timer for two minutes. At the end of the two minutes standardize the meter at pH 4.010.
3. Rinse the electrode assembly with distilled water and lower the electrodes into 0.25 N sulfuric acid solution in a 150-mL beaker. Set a timer for two minutes. At the end of two minutes the pH should be 0.95 ± 0.05.
   a. If the pH of the 0.25 N sulfuric acid is 0.95 ± 0.05, adjust the meter to the nominal value of 0.95 and proceed to step 4.
   b. If the pH is not 0.95, repeat the procedure using another glass electrode.
4. Rinse the electrodes and lower the assembly into the stop bath solution. Set a timer for two minutes. At the end of two minutes record the pH of the stop bath. If another stop bath pH measurement is to be made, repeat the procedure.

Determination of the pH of Processed Photographic Emulsions

ECP-2-806

INTRODUCTION

pH is a measure of the effective hydrogen ion concentration in an aqueous solution. In this method, a sample of an emulsion is cut into catalpa and is shaken with water. The pH of the solution is then measured with a pair of electrodes and a pH meter. The bulb of the glass electrode is entirely immersed in the solution during measurement.

The method is not valid for lacquered emulsions because most lacquers prevent the water from becoming equilibrated with the surface of the emulsion. Any method employed for removal of the lacquer may change the original pH value of the emulsion.

RELIABILITY

It is expected that 95 percent of all individual pH measurements on the name portion of processed emulsion will be within the range of ± 0.08 pH unit.

SPECIAL APPARATUS

- Corning Model 12 Research pH Meter or equivalent
- Corning No. 476024 Glass Electrode or Leeds and Northrup No, 117169 Glass Electrode
- CORNING No. 476002, reference, ceramic junction, calomel
- Beaker, 30-mL
- Test tube, 150 mm
- New cork stoppers

REAGENTS

Use reagents that are ACS Reagent Grade unless specified otherwise.

- Potassium Acid Phthalate Buffer, 0.05 Molar
- Borax Buffer, 0.01 Molar
- Distilled Water, 27°C

PROCEDURE

Note: Measurements must be made in a well-ventilated room where the atmosphere is free of volatile gases which will form acids or bases in solution. Examples are chlorine, hydrogen chloride, sulfur dioxide, and ammonia.

Preparation of the Meter and Electrodes

1. Follow the *Standardization of pH Meter - High pH Range* procedure in Method ULM-191-2, *pH Measurement of Photographic Processing Solutions*, (or any subsequent pH method) for preparation of the meter.
    a. Adjust the temperature of the buffers and the water.
    b. Adjust the meter.
    c. Standardize the meter with potassium acid phthalate buffer.
    d. Cross-check the electrodes with borax buffer.
2. Fasten the electrodes together as follows: Place a rubber band around the electrodes so that they touch or are very close together with the tips in a horizontal plane. (The rubber band should be above the level of any sample or buffer.)

Preparation of the Sample

Note: Be certain that the film sample is not contaminated in any manner. Thin cloth gloves should be worn while preparing the sample.

1. Cut the film as follows:
    a. For **35 mm film samples**, cut two 5-inch pieces of film and carefully remove the perforations from both sides. Cut the 5-inch pieces in half the long way.
    b. For **16 mm film samples**, carefully remove the perforations from one side of the film.
2. Arrange the pieces in a stack such that support sides are face-to-face and emulsion sides are face-to-face. Emulsion sides should face outward on each end of the stack.

Shaking the Sample with Water

1. Set a timer for 2-½ minutes
2. Add 10 mL of temperature - equilibrated (27°C) distilled water to a 150 mm test tube from a tip up pipet.
3. Add the stack of film strips; immediately stopper with a *clean* cork (not a rubber stopper).
4. Start the timer and shake the test tube vigorously for 2-½ minutes. Shake test tube in a horizontal position.
5. After 2-½ minutes, pour the water into a 30-mL beaker and place the beaker in the water bath.

Note: Do not allow the sample to remain in the test tube after it has been shaken. Proceed directly to the pH measurement.

Determination of the Sample pH

1. *Rinse the electrodes* with distilled water and dry them with cleansing tissue.
2. Immerse the electrodes into the sample beaker while it remains in the water bath.
3. Determine the pH after the electrodes have been in the sample beaker for two minutes.
4. Remove the sample and rinse the electrodes with distilled water. Place them in potassium acid phthalate buffer.
5. Repeat the cross-check after the third sample measurement. Then place the electrodes in the potassium acid phthalate buffer for storage, or restandardize them if more determinations are to be made.

Note: No more than 20 minutes should elapse between any standardization and final cross-check.

Potentiometric Determination of Silver in Process ECP-2 Fixing Baths

ECP-0024-01

INTRODUCTION

The sample containing silver is titrated potentiometrically with standardized sodium sulfide using a silver billet/double junction electrode pair. The sample is made alkaline to prevent the decomposition of sodium thiosulfate, which occurs in acid solutions. Ethylenedinitrilotetraacetic acid (EDTA) is added to minimize interference of other metal ions. The EDTA reagent does not prevent interference from zinc ions. Gelatin is added to prevent the coagulation of the silver sulfide that is formed. This prevents the coagulated silver sulfide from occluding the silver ions.

Changes in the volume of sample and of sodium hydroxide/EDTA reagent affect the silver results. If a small amount of sample is used, the sample volume must be adjusted to about 300 mL with 1.0 M sodium thiosulfate.

Use of this method requires handling potentially hazardous chemicals. Material Safety Data Sheets (MSDS) should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

A. Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed three (3) replicates on each of the following solutions during methods development.

1. A “fresh” fixing tank prepared with all components at their respective “working tank” aim concentrations.
2. The same “fresh” solution as in number 1, above, reanalyzed after making an analytically weighed, standard addition of 1.0745 g/L Ag.
3. A “seasoned” fixing tank analyzed potentiometrically as received, at 0.1547 g/L Ag.
4. The same “seasoned” solution as in number 3, above, reanalyzed after making an analytically weighed, standard addition of 0.0537 g/L Ag.

Ag				
Sample	**Mean (g/L Ag)**	**N**	**Repeatability Standard Deviation, $1s_r$ (g/L Ag)**	**95 Percent Confidence Estimate (g/L Ag)**
“Fresh”	0.0080	3	0.00346	± 0.0149
“Fresh” plus Standard Addition	1.1006	3	0.00294	± 0.0127
“Seasoned”, As Received	0.1547	3	0.00167	± 0.0072
“Seasoned” plus Standard Addition	0.2088	3	0.00184	± 0.0079

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. Instead, a recovery was calculated for the component in a fresh sample.

Statistically the recovery of 101.68 percent was significantly different from 100 percent at the 95 percent confidence level, but judged to be not practically significant.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically the recovery of 103.63 percent* was not significantly different from 100 percent at the 95 percent confidence level.

* Note: Recovery was calculated by accounting for a 1 percent error from dilution of 1 liter of seasoned fixer by a 10.00 mL aliquot of silver nitrate.

$$\text{Example: } \frac{(0.2088) - (0.1547 \times 0.99)}{0.0537} \times 100 = 103.63\%$$

B. REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed four fixing bath samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A "fresh" fixing tank prepared with all components at their respective "working tank" aim concentrations.
2. The same "fresh" fixing tank sample as in 1 above, analyzed in the same manner, after making a standard addition of 0.5372 g/L Ag.
3. A "seasoned" tank solution analyzed as received as 3.6301 g/L Ag.
4. The same "seasoned" solution, as in number 3, above, analyzed in the same manner, after making a standard addition of 1.0044 g/L Ag.

Ag				
Sample	**Mean (g/L Ag)**	**N**	**Reproducibility Standard Deviation, $1s_c$ (g/L Ag**	**95 Percent Confidence Estimate (g/L Ag)**
"Fresh"	0.0338	16	0.03073	± 0.0628
"Fresh" plus Standard Addition	0.5863	16	0.00833	± 0.0170
"Seasoned", As Received	3.6301	16	0.01504	± 0.0307
"Seasoned" plus Standard Addition	4.5015	16	0.02787	± 0.0569

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. Instead, a recovery was calculated for the component in a fresh sample. Statistically, the recovery of 102.85 percent was not significantly different from 100 percent at the 95 percent confidence level.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage. Statistically the recovery of 104.84 percent* was significantly different from 100 percent at the 95 percent confidence level, but judged not to be practically significant.
* Note: Recovery was calculated by accounting for a 5 percent error from dilution of 2 liters of seasoned fixer by a 100.00 mL aliquot of silver nitrate.

$$\text{Example: } \frac{(4.5015) - (3.6301 \times 0.95)}{1.0044} \times 100 = 104.84\%$$

APPARATUS

- METROHM 536 Titrator or equivalent with a DOSIMAT and a 50-mL burette
- Beaker (600-mL)
- Tip-up pipette (50-mL, 10-mL)
- Graduated Cylinder (500-mL, 250-mL)
- Pipet (50-mL, 100-mL)
- Indicator electrode, Silver Billet, BECKMAN, Model 39261 or equivalent
- Double junction reference electrode, ORION Model 900200 or equivalent
- Filling solutions:
  - ORION No. 900002 (inner chamber filling solution)
  - ORION No. 900003 (outer chamber filling solution)

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E288, and E969, unless otherwise stated.

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 0.1 M Sodium Thiosulfate, $Na_2S_20_3$
- 70.1 N Sodium Hydroxide/Ethylenedinitrilotetraacetic Acid (EDTA) reagent, 1 N NaOH/EDTA
- 4 g/L Gelatin
- 0.06 N Sodium Sulfide, Na_2S (standardized to 4 decimal places)
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

A. Treatment of Sample

1. Pipet (wipe the pipet before leveling) the sample of fix solution into a 600 mL beaker according to the following table:

Note: Fresh solutions will have less than 1.0 g/L silver, for seasoned samples a 50 mL sample size may be used to determine approximate level of silver in sample.

Silver Concentration g/L	Sample, mL	1.0 M Sodium Thiosulfate, mL
Less than 1	300*	0
1 to 3	100.0	200
More than 3	50.0	250

* Use a graduated cylinder.

2. From a 250-mL graduated cylinder, add to the 600-mL beaker the amount of 1.0 M sodium thiosulfate indicated in the table.
3. Add 100 mL of 1 N NaOH/EDTA reagent from a 50-mL tip-up pipet.
4. Add 10 mL of 4 g/L gelatin from a tip-up pipet.

B. Potentiometric Titration of Sample

1. Titrate the solution with 0.0600 N sodium sulfide, using a METROHM E536 Titrator or equivalent.
   a. Set the following parameters on the METROHM E536 Titrator:

Titration mode	mV/pH
Horizontal chart span	750 mV
Autocontrol	OFF
Maximum titration speed	15 min/100% volume
Vertical chart span	400 mm/100% volume
Automatic titration stop (U%)	OFF
Indicator electrode	Silver Billet BECKMAN, Model 39261 or equivalent
Reference electrode	Double-junction ORION, Model 900200 or equivalent

   b. Place the beaker on the METROHM titrator stand and add a magnetic stir bar. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex. Titrate the solution with standardized 0.0600 N sodium sulfide through the inflection.

Note: Avoid unnecessary exposure of the standardized sodium sulfide to air. The reagent should be standardized each week. Discard all unused reagent remaining in any open bottles at the end of each day (60 mL reagent bottles are suggested for storage of 0.06 N sodium sulfide).

c. Determine the end point using concentric arcs (refer to Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revisions.) If a microprocessor controlled titrator is used, the endpoint will be picked automatically.

CALCULATIONS

For Silver, g/L;

$$\text{g/l Ag} = \frac{(\text{mL } Na_2S)\ (\text{N } Na_2S)\ (\text{eq wt Ag})\ (1000)}{(\text{mL sample})\ (1000)}$$

Where:		
mL Na_2S	=	volume of sodium sulfide in milliliters required to reach the equivalence point
N Na_2S	=	normality of the sodium sulfide in milliequivalents per milliliter (meq/mL)
eq. wt. Ag	=	equivalent weight of silver in milligrams per milliequivalents [107.88 for Ag]
1000	=	factor to convert milligrams to grams of Ag
mL sample	=	milliliters of sample pipetted in step 1 of part A of procedure
1000	=	factor to convert mLs of sample to Liters

For samples containing less than 1 g/L silver:

$$\text{g/l Ag} = \frac{(\text{mL } Na_2S)\ (\text{N } Na_2S)\ (107.88)\ (1000)}{(300)\ (1000)}$$

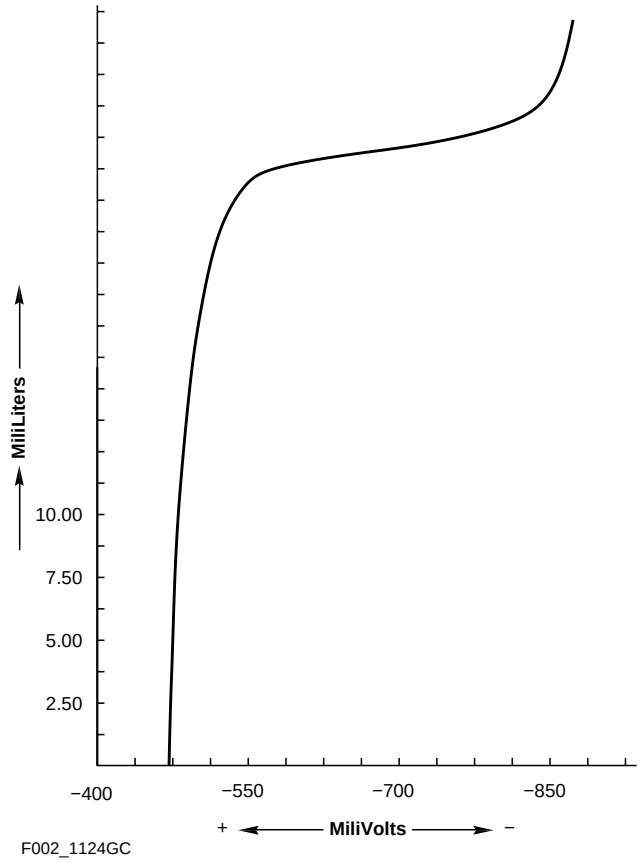
For samples containing 1 to 3 g/L silver:

$$\text{g/l Ag} = \frac{(\text{mL } Na_2S)\ (\text{N } Na_2S)\ (107.88)\ (1000)}{(100.00)\ (1000)}$$

For samples containing more than 3 g/L silver:

$$\text{g/l Ag} = \frac{(\text{mL } Na_2S)\ (\text{N } Na_2S)\ (107.88)\ (1000)}{(50.00)\ (1000)}$$

Figure 1 S-shaped Curve



Determination of Sodium Metabisulfite in Process ECP-2 Accelerator Tank

ECP-0025/01

INTRODUCTION

The concentration of sodium metabisulfite ($Na_2S_2O_5$) in an ECP-2 bleach accelerator sample is determined by a manual or potentiometric titration using an iodine (I_3^-) titrant. In the method an excess of iodine is added to the sample. Sodium metabisulfite and Kodak persulfate bleach accelerator, PBA-1, present in the sample react with a portion of the iodine. The iodine that did not react with sodium metabisulfite and PBA-1 is then titrated with standardized sodium thiosulfate, using manual (starch indicator) or potentiometric endpoint detection.

In order to determine the sodium metabisulfite concentration, the contribution of PBA-1 in the titration must be accounted for. This is done by subtracting a factor in the calculation of sodium metabisulfite concentration. The factor is calculated based on the PBA-1 concentration as determined by method *ECP-0027-01* and it's iodimetric equivalent weight.

The measured level of sodium metabisulfite in the sample may be lower than the amount added during mixing. This is due to either a reaction of PBA-1 and sodium metabisulfite that can result in a lower equilibrium concentration of sodium metabisulfite, or aerial oxidation of sodium metabisulfite.

Use of this method requires handling potentially hazardous chemicals. Material Safety Data Sheets (MSDS) should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

Note: Separate statistics presented for potentiometric and visual titration methods.

I. Potentiometric Titrations

A. Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed three (3) replicates on each of the following solutions during methods development.

1. A “fresh” Accelerator tank solution prepared with all components at their respective “working tank” aim concentrations.
2. The same “fresh” solution as in number 1, above, reanalyzed after making an analytically weighed, standard addition of 0.8080 g/L $Na_2S_2O_5$ (assay 99.04 percent).
3. A “seasoned” Accelerator tank solution analyzed as received, at 2.2536 g/L $Na_2S_2O_5$.
4. The same “seasoned” solution as in number 3, above, reanalyzed after making an analytically weighed, standard addition of 0.7036 g/L $Na_2S_2O_5$ (assay 99.04 percent).

$Na_2S_2O_5$				
Sample	**Mean (g/L $Na_2S_2O_5$)**	**N**	**Repeatability Standard Deviation, $1s_r$ (g/L $Na_2S_2O_5$)**	**95 Percent Confidence Estimate (g/L $Na_2S_2O_5$)**
“Fresh”	2.39	3	0.038	± 0.16
“Fresh” plus Standard Addition	3.24	3	0.066	± 0.29
“Seasoned”, As Received	2.18	2	0.008	± 0.11
“Seasoned” plus Standard Addition	2.83	3	0.000	± 0.00

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. An equilibrium is established between sodium metabisulfite and PBA-1 that effectively lowers the concentration of sodium metabisulfite in freshly mixed solutions. Therefore bias is estimated for fresh solutions by spiking a known amount of sodium metabisulfite to a fresh mix that has been allowed to sit overnight, and the recovery is then calculated.

The recovery of 106.28 percent was not statistically significantly different from 100 percent at the 95 percent confidence level.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

The recovery of 93.23 percent was statistically significantly different from 100 percent at the 95 percent confidence level, but was judged not to be practically significant.

B. REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed four Accelerator tank samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A "fresh" Accelerator tank solution prepared with all components at their respective "working tank" aim concentrations.
2. The same "fresh" solution as in number 1, above, reanalyzed in the same manner, after making a standard addition of 1.2038 g/L $Na_2S_2O_5$ (assay 99.04 percent).
3. A "seasoned" Accelerator tank solution analyzed as received as 2.2705 g/L $Na_2S_2O_5$.
4. The same "seasoned" solution, as in number 3, above, analyzed in the same manner, after making a standard addition of 1.0296 g/L $Na_2S_2O_5$ (assay 99.04 percent).

$Na_2S_2O_5$				
Sample	**Mean (g/L $Na_2S_2O_5$)**	**N**	**Reproducibility Standard Deviation, $1s_c$ (g/L $Na_2S_2O_5$)**	**95 Percent Confidence Estimate (g/L $Na_2S_2O_5$)**
"Fresh"	2.10	16	0.115	± 0.24
"Fresh" plus Standard Addition	3.17	16	0.087	± 0.19
"Seasoned", As Received	2.27	16	0.111	± 0.24
"Seasoned" plus Standard Addition	3.30	15	0.128	± 0.27

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. An equilibrium is established between sodium metabisulfite and PBA-1 that effectively lowers the concentration of sodium metabisulfite in freshly mixed solutions. Therefore bias is estimated for fresh solutions by spiking a known amount of sodium metabisulfite to a fresh mix that has been allowed to sit overnight, and the recovery is then calculated.

The recovery of 88.59 percent was statistically significantly different from 100 percent at the 95 percent confidence level, but was judged not to be practically significant.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

The recovery of 100.05 percent was not statistically significantly different from 100 percent at the 95 percent confidence level.

II. Visual Endpoint Titrations

A. Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed three (3) replicates on each of the following solutions during methods development.

1. A "fresh" Accelerator tank solution prepared with all components at their respective "working tank" aim concentrations.
2. The same "fresh" solution as in number 1, above, reanalyzed after making an analytically weighed, standard addition of 0.6552 g/L $Na_2S_2O_5$ (assay 99.04 percent).
3. A "seasoned" Accelerator tank solution analyzed as received, at 1.9093 g/L $Na_2S_2O_5$.
4. The same "seasoned" solution as in number 3, above, reanalyzed after making an analytically weighed, standard addition of 0.6106 g/L $Na_2S_2O_5$ (assay 99.04 percent).

$Na_2S_2O_5$				
Sample	**Mean (g/L $Na_2S_2O_5$)**	**N**	**Repeatability Standard Deviation, $1s_r$ (g/L $Na_2S_2O_5$)**	**95 Percent Confidence Estimate (g/L $Na_2S_2O_5$)**
"Fresh"	2.08	5	0.018	± 0.05
"Fresh" plus Standard Addition	2.69	5	0.024	± 0.07
"Seasoned", As Received	1.91	3	0.017	± 0.07
"Seasoned" plus Standard Addition	2.53	3	0.010	± 0.04

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. An equilibrium is established between sodium metabisulfite and PBA-1 that effectively lowers the concentration of sodium metabisulfite in freshly mixed solutions. Therefore bias is estimated for fresh solutions by spiking a known amount of sodium metabisulfite to a fresh mix that has been allowed to sit overnight, and the recovery is then calculated.

The recovery of 94.57 percent was statistically significantly different from 100 percent at the 95 percent confidence level, but was judged not to be practically significant.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

The recovery of 101.86 percent was not statistically significantly different from 100 percent at the 95 percent confidence level.

B. REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed four Accelerator tank samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A "fresh" Accelerator tank solution prepared with all components at their respective "working tank" aim concentrations.
2. The same "fresh" solution as in number 1, above, reanalyzed in the same manner, after making a standard addition of 0.5448 g/L $Na_2S_2O_5$ (assay 99.04 percent).
3. A "seasoned" Accelerator tank solution analyzed as received as 2.6286 g/L $Na_2S_2O_5$.
4. The same "seasoned" solution, as in number 3, above, analyzed in the same manner, after making a standard addition of 0.7360 g/L $Na_2S_2O_5$ (assay 99.04 percent).

$Na_2S_2O_5$				
Sample	**Mean (g/L $Na_2S_2O_5$)**	**N**	**Reproducibility Standard Deviation, $1s_r$ (g/L $Na_2S_2O_5$)**	**95 Percent Confidence Estimate (g/L $Na_2S_2O_5$)**
"Fresh"	1.96	16	0.162	± 0.35
"Fresh" plus Standard Addition	2.43	16	0.136	± 0.29
"Seasoned", As Received	2.63	16	0.186	± 0.40
"Seasoned" plus Standard Addition	3.33	16	0.173	± 0.37

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias was not determined for this sample because the component concentration level was not determined independently of the test method. An equilibrium is established between sodium metabisulfite and PBA-1 that effectively lowers the concentration of sodium metabisulfite in freshly mixed solutions. Therefore bias is estimated for fresh solutions by spiking a known amount of sodium metabisulfite to a fresh mix that has been allowed to sit overnight, and the recovery is then calculated.

The recovery of 86.03 percent was not statistically significantly different from 100 percent at the 95 percent confidence level.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

The recovery of 95.84 percent was not statistically significantly different from 100 percent at the 95 percent confidence level.

APPARATUS

- METROHM 536 Titrator or equivalent with a DOSIMAT and a 50-mL burette
- Beaker (250-mL
- 2 Tip-up pipettes (25-mL)
- Pipet (10.0 mL, 50.0-mL)
- Platinum indicator electrode, BECKMAN Model 39273 or equivalent
- Double junction reference electrode, ORION Model 900200 or equivalent
- Filling solutions:
  - ORION No. 900002 (inner chamber filling solution)
  - ORION No. 900003 (outer chamber filling solution)

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E288, and E969, unless otherwise stated.

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 0.1 N Sodium Thiosulfate, $Na_2S_20_3$ (standardized to 4 decimal places)
- 7.0 N Sulfuric Acid
- 0.6 M Potassium Iodide
- 0.1 N Potassium Iodate, (standardized to 4 decimal places)
- Starch Indicator (visual mode only)
- Water, Type I Reagent - This method was developed using reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

A. Treatment of Sample

Note: Titration endpoint may be determined potentiometrically or visually.

1. Pipet (wipe the pipet before leveling) 50.0 mL of 0.1000 N potassium iodate into a 250 mL beaker containing a magnetic stir bar.
2. Add 25 mL of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 25 mL of 0.6 M potassium iodide from a tip-up pipet.
4. Pipet (wipe the pipet before leveling) 10.0 mL of sample into the beaker while stirring.
5. Titrate with 0.1000 N sodium thiosulfate. (See section B for potentiometric and section C for visual)
6. Repeat steps A1 through A5 above, using 40.0 mLs of 0.1000 N potassium iodate and omitting addition of 10.0 mL sample, and titrate with 0.1000 N sodium thiosulfate and record endpoint as mLs Blank.

B. Potentiometric Titration of Sample

1. Titrate the solution with 0.1000 N sodium thiosulfate, using a METROHM E536 Titrator or equivalent.
   a. Set the following parameters on the METROHM E536 Titrator:

Titration mode	mV/pH
Horizontal chart span	500 mV
Autocontrol	OFF
Maximum titration speed	15 min/100% volume
Vertical chart span	400 mm/100% volume
Automatic titration stop (U%)	OFF
Indicator electrode	Platinum, BECKMAN, Model 39273 or equivalent
Reference electrode	Double-junction ORION, Model 900200 or equivalent

   b. Place the beaker on the METROHM titrator stand and add a magnetic stir bar. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.) Set the stirrer speed to stir rapidly without splashing or creating a vortex. Titrate the solution with standardized 0.1000 N sodium thiosulfate through the inflection.
   c. Determine the end point using concentric arcs (refer to Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revisions.) If a microprocessor controlled titrator is used, the endpoint will be picked automatically.

C. Visual Titration of Sample

1. Titrate the solution with 0.1000 N sodium thiosulfate to a yellow color. Then add approximately 5 mL of starch indicator solution and continue the titration until the blue color disappears.

CALCULATIONS

For Sodium metabisulfite, g/L;

g/L $Na_2S_2O_5$ = [4.753 ((mLs Blank x 1.25) - (mLs $Na_2S_2O_3$) (N $Na_2S_2O_3$)
- [0.216 (Kodak ECP-2 persulfate bleach accelerator, PBA-1, g/L

where:

mLs Blank = volume of sodium thiosulfate in milliliters required to reach the equivalence point without the addition of sample

mL $Na_2S_2O_3$ = volume of sodium thiosulfate in milliliters required to reach the equivalence point with sample

N $Na_2S_2O_3$ = normality of the sodium thiosulfate in milliequivalents per milliliter (meq/mL)

BA-1, g/L = grams per liter of PBA-1 in Accelerator tank as measured by method *ECP-0027-01*

4.753 = equivalent weight of sodium metabisulfite divided by the sample size

0.216 = equivalent weight of PBA-1 divided by sample size

If mL 0.1008 N $Na_2S_2O_3$ = 37.85 mLs

mLs Blank = 39.87 mLs

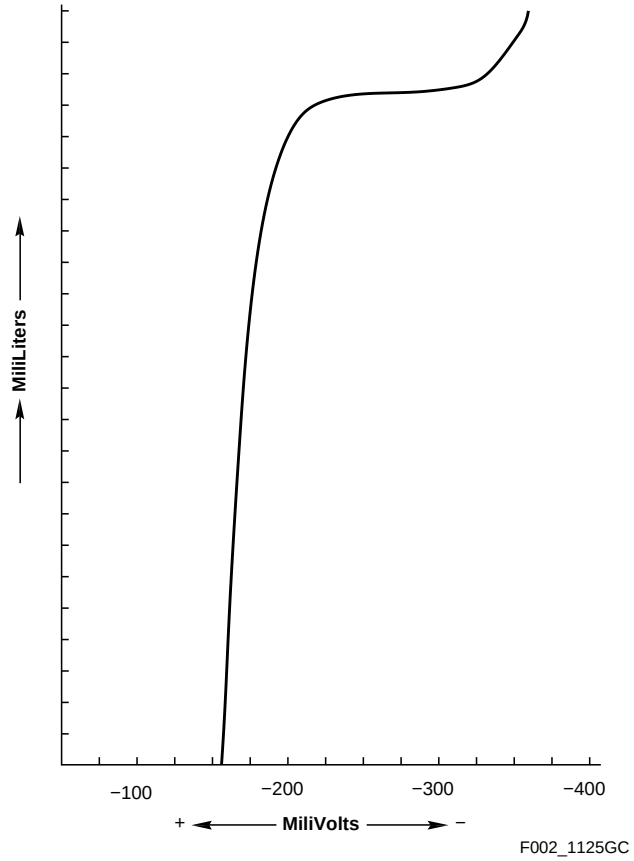
PBA-1 = 3.45 g/L

g/L $Na_2S_2O_5$ = [4.753 ((39.87 x 1.25) - 37.85) (0.1008] - 0.216 (3.45)

= 5.740 - 0.745

g/L $Na_2S_2O_5$ = 4.995

Figure 2 S-shaped Curve



F002_1125GC

Viscosity Determination of Sound-Track Developer
ECP-2-99

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	SD-43b	—	—

INTRODUCTION

The viscosity of the sound-track developer is critical to proper sound-track-developer coating and bead width. The following procedure will help ensure the developer is mixed correctly and consistently from batch to batch.

Check the viscosity by measuring the discharge time from a standard volumetric or transfer pipet. Always measure the solution at the same temperature, preferably near the actual application temperature. Use the same pipet for all measurements, or select and set aside several pipets having the same discharge time.

Establish an acceptable discharge range (control limits) using solutions that applicate satisfactorily.

SPECIAL APPARATUS

- 10-mL Volumetric Pipet, Class A, Kimax
- Stopwatch or equivalent timer

PROCEDURE

1. Bring the developer solution to measuring temperature.
2. Season the pipet with solution.
3. Draw the solution into the pipet above the calibration mark.
4. Time the discharge from the time the solution passes the mark, until the stream first breaks.
5. Compare the discharge time to your control limits to accept or reject the developer.

Titrimetric Determination Of Benzyl Alcohol In Reversal Color Developers
ECR-1603E

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	DR-150/151	DR-150

INTRODUCTION
The benzyl alcohol in the alkaline developer is oxidized to benzoic acid with a solution of permanganate at room temperature. The excess permanganate is reduced with hydroxylamine sulfate in an acid solution and nitrogen is bubbled through the treated sample to provide mixing. The benzoic acid is extracted into butyl acetate which is then washed with a saturated sodium chloride solution. Methanol is added to the butyl acetate extract, and the single phase is titrated with standardized sodium hydroxide.

Critical steps in the procedure are the bubbling with nitrogen and the separations. Violent bubbling with foaming may result in loss of sample. Because of this, a pipet is preferable to a gas dispersion tube. It is also possible to use a drawn-out glass tube. If the layers are drawn off too rapidly and/or too soon after the shaking, they will be contaminated and high results will occur. Any transfer of the aqueous phase will also falsely increase the answer.

The butyl acetate should be used in an ignition-free environment. Locally acceptable practices should be used when discarding waste butyl acetate.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY
Four standard mixes, containing 3.50, 4.00, 5.00, and 6.00 mL/L benzyl alcohol, were analyzed in duplicate by four analysts. The 95 percent confidence limits for an individual determination, based on these data, are ± 0.20 mL/L benzyl alcohol.

Crossover data determined on seasoned tank samples, between the previous version of this procedure (chloroform as the extractant), and this procedure using butyl acetate, indicates no significant differences.

SPECIAL APPARATUS
- Gas pressure regulator and reducing valve

Note: The flowmeter should measure 0 to 15 L/min. The regulator must be constructed to withstand a pressure of 3000 pounds per square inch.

- Nitrogen cylinder (water-pumped nitrogen)

Note: "High purity" water-pumped nitrogen is not required but can be used. Oil-pumped nitrogen (left-hand threaded cylinder) cannot be used with the recommended regulator valve (right-hand thread) but can be used if a left-hand threaded regulator valve is available.

- Exhaust hood

Note: All pipets and volumetric glassware should be "Class A" as defined by NIST (National Institute of Standards and Technology, formerly National Bureau of Standards).

REAGENTS
All reagents are ACS Reagent Grade unless specified otherwise.
- 0.41 M Potassium Permanganate, $KMnO_4$
- 2.5 M Hydroxylamine Sulfate, $(NH_2OH)_2 \cdot H_2SO_4$
- 18 N Sulfuric Acid, H_2SO_4
- Butyl Acetate, Reagent Grade
- Sodium Chloride NaCl, Saturated solution
- Methyl Alcohol containing Thymol blue
- 0.1 N Sodium Hydroxide, NaOH (standardized to 4 decimal places)

PROCEDURE

Sample Treatments

1. Adjust the sample to room temperature.
2. Pipet 20.0 mL of sample (at room temperature) into a 500-mL separatory funnel.
3. Insert a long-stem funnel into the separatory funnel.

   Note: The funnel prevents the potassium permanganate from adhering to the stopper of the separatory funnel when it is added in the next step.
4. Add 40 mL of 0.41 M potassium permanganate using a 20-mL tip-up pipet.
5. Swirl the separatory funnel vigorously for 15 seconds, but avoid splashing the liquid high on the sides.
6. Let the funnel stand for five minutes (set a timer).
7. Add 5 mL of 18 N sulfuric acid from a tip-up pipet, and swirl the funnel to mix.
8. Add 10 mL of 2.5 M hydroxylamine sulfate from a tip-up pipet.

Caution

Make certain that the funnel is not pointing at anyone because there may be considerable foaming.

9. Swirl the separatory funnel until all of the MnO_2 (brown precipitate) disappears.

   Note: The MnO_2 on the sides of the separatory funnel can be removed by carefully tipping the funnel on its side.
10. Bubble nitrogen through the solution vigorously, but without splashing, for five minutes (set a timer). Use a pipet as a bubbling tube.

    Note:

    a. Comply with the Safety Precautions for Use of Gas Cylinders included with this method.

    b. If nitrogen is not available, clean compressed air may be substituted.

Extraction

Warning

FLAMMABLE. CAUSES EYE IRRITATION. Keep away from heat, sparks and flame. Avoid breathing vapor. Avoid contact with eyes and skin. Keep container closed. Use with adequate ventilation. Avoid prolonged or repeated contact with skin.

1. Add 50 mL of butyl acetate from a tip-up pipet, washing down the pipet used for the nitrogen bubbling.
2. Stopper and shake the funnel vigorously for one minute (set a timer) venting the funnel occasionally through the stopper.
3. Let the funnel stand for five minutes (set a timer). Swirl the funnel gently so that any of the aqueous layer remaining in the butyl acetate layer will separate completely.
4. Slowly drain and discard approximately three-quarters of the lower (aqueous) layer; swirl the funnel and allow to separate; then discard the lower (aqueous) layer completely.
5. Add, from a tip-up pipet, 5 mL of saturated sodium chloride solution into the 500-mL separatory funnel containing the butyl acetate layer.
6. Stopper and shake the funnel for 30 seconds.
7. Allow the layers to separate for three minutes (use a timer). Then slowly drain and discard the lower (aqueous) layer, allowing $\frac{1}{4}$ inch of the lower layer to remain in the funnel. Swirl the funnel and allow the layers to separate.
8. After the layers have separated, completely drain and discard any remaining lower (aqueous) layer, being careful not to lose any of the top (butyl acetate) layer.

   Note: Also discard any emulsion layer that may refuse to separate.
9. Drain the butyl acetate layer into a dry 250-mL conical flask equipped with a magnetic stirring bar.

Titration

1. Using a tip-up pipet, rinse down the sides of the flask with 50 mL of methyl alcohol containing thymol blue.
2. Using a 25-mL buret, titrate with standardized 0.1 N sodium hydroxide to the first persistent yellow-green color. Approach the end point dropwise. Read the buret to the nearest hundredth (0.01 mL).

   Note: Use locally acceptable procedures for disposal of waste butyl acetate.

Calculation:

Benzyl alcohol, mL/L = 5.50(N NaOH)(mL N NaOH) – 1.04

Potentiometric Determination of Bromide in Reversal Color Developers

ECR-930E

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	DR-150/151*	DR-150

* This procedure was developed for a process other than VNF-1 and RVNP, that did not contain sodium thiocyanate. Thiocyanate is a well known interferent to halide determinations when using a silver ion titration, due to co-precipitation. A significant high bias may be found when applying this procedure to determine bromide in developers containing thiocyanate.

INTRODUCTION

This method contains two separate procedures for analysis of bromide. Procedure A is used for the analysis of fresh tank and replenisher solutions. Procedure B is used for the analysis of seasoned tank solutions. Analysis of seasoned tank solutions using Procedure A will result in erroneously high results—as much as 0.3 g/L This effect is dependent upon seasoning; aging is not a factor. Acetone is added in Procedure A to eliminate interference.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

Procedure A—The sample is acidified and acetone added. It is then titrated potentiometrically with silver nitrate.

Procedure B—Bromide enrichment by selective precipitation is utilized. All of the bromide is precipitated as silver bromide along with minor amounts of other silver salts, by the addition of a small excess of silver to an acidified sample of seasoned developer. The silver salts are filtered and developed by a silver-halide developer, releasing soluble bromide. The sample is filtered again, the filtrate is acidified, and then the treated sample is titrated potentiometrically with silver nitrate.

As an aid in selecting the proper inflection point and detecting instrument trouble or analytical errors, a set of standard titration curves of all developers should be kept on file. Such curves can be compared with the general shape and relative position of any routine titration curve. Figure 1 includes typical titration curves as an aid in determining the increment size to use in the region of the end point and the expected potential change in millivolts.

RELIABILITY

Procedure A—The 95 percent confidence limits for an individual analysis of a fresh tank sample are estimated to be slightly less than ± 0.05 g/L sodium bromide.

Procedure B—This procedure was specifically designed for current mix formulations and variance due to seasoning. Any change in mix formulation, especially in bromide concentration, may necessitate recalibration.

Four seasoned samples in the appropriate bromide concentration range were analyzed by three analysts. Based on the 12 data points obtained, the 95 percent confidence limits for an individual determination are ± 0.05 g/L sodium bromide.

SPECIAL APPARATUS

- Reference Electrode, Double Junction, Orion No.900200 or equivalent
- Indicator Electrode, Silver Billet, Beckman No. 39261 or equivalent
- Millipore Filter apparatus (Millipore Corp., Bedford, Mass. 01730, Catalog No. XX1004700)
- Millipore Filter membrane (0.45 micron porosity 47 mm, Catalog No. HAWP-04700
- Exhaust Hood

Note: Use pipets and volumetric glassware meeting the “Class A” definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- Acetone, $(CH_3)_2CO$
- 1.0 M Ammonium Nitrate, NH_4NO_3
- Celite
- Silver Halide Developer
- 0.05 N Silver Nitrate, $AgNO_3$ (standardized to 4 decimal places)
- 18 N Sulfuric Acid, H_2SO_4

PROCEDURE A

For Fresh Tank and Replenisher

Note: Prepare the double junction/silver billet electrode pair and calibrate the electrode-instrument system according to the instructions given in Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revision.

Sample Treatment

(Perform in an Exhaust Hood)

1. Pipet the sample, wipe the pipet before leveling, into the beaker indicated below.

Solution	Sample Size	Beaker Size
Fresh Tank	100.0 mL	600 mL
Replenisher	200.0 mL	800 mL

2. Stir the sample moderately on a magnetic stirrer, and add very slowly from a tip-up pipet, 50 mL of 18 N sulfuric acid.

Warning

ACID. Avoid contact with skin and eyes. In case of contact, flush with water.

3. From a graduated cylinder add Acetone to the solution in the beaker as it stirs.

Solution	Acetone
Fresh Tank	250 mL
Replenisher	300 mL

Warning

EXTREMELY FLAMMABLE. Keep away from heat, sparks and flame. Keep container closed. Use with adequate ventilation. Avoid prolonged or repeated contact with skin.

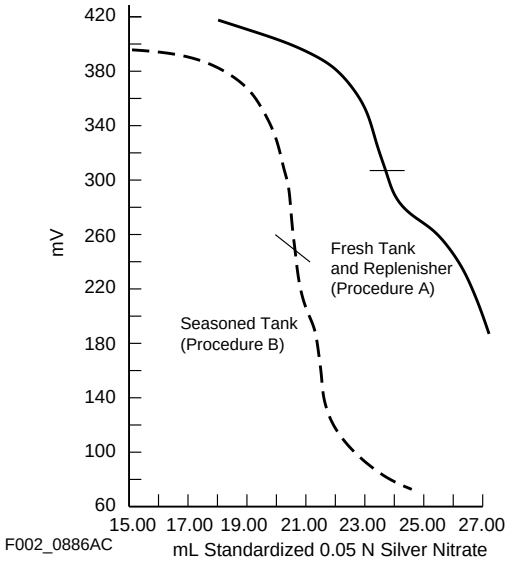
Titration

1. Using a 25-mL buret, titrate the sample potentiometrically, according to Method ULM-0003-01, with standardized 0.05 N silver nitrate.

   Note: The titration may be performed most rapidly in the beginning where the potential change is the smallest. Refer to Figure 1 to determine the increment size to use in the region of the end point and the expected potential change in millivolts.

2. Determine the end point using the concentric arcs method. (Refer to Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revisions.)

Figure 1 Typical Bromide Titration Curve in Reversal Color Developer



Calculations

NaBr, g/L =

$$\frac{(\text{N } AgNO_3)(\text{mL } AgNO_3) \times (\text{eq. wt. NaBr}) \times (1000)}{(\text{mL sample}) \times (1000)} =$$

Fresh Tank—100-mL sample

$$\frac{(\text{N } AgNO_3)(\text{mL } AgNO_3) \times (102.91) \times (1000)}{(100) \times (1000)} =$$

$$1.029(\text{mL } AgNO_3)(\text{N } AgNO_3)$$

Replenisher—200-mL sample

$$\frac{(\text{N } AgNO_3)(\text{mL } AgNO_3) \times (102.91) \times (1000)}{(200) \times (1000)} =$$

$$0.515(\text{mL } AgNO_3)(\text{N } AgNO_3)$$

PROCEDURE B

For Seasoned Tank

Note: Prepare the double junction/silver billet electrode pair and calibrate the electrode-instrument system according to the instructions given in Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revision.

Sample Treatment

(Bromide Enrichment)

1. Pipet, wipe before leveling, 100.0 mL of sample into a 250-mL Phillips beaker. Stir moderately on a magnetic stirrer in an exhaust hood.
2. While stirring add very slowly, from a tip-up pipet, 50 mL of 18 N sulfuric acid to the Phillips beaker.

Warning

ACID. Avoid contact with skin and eyes. In case of contact, flush with water.

3. Add approximately 0.2 grams of Celite to the Phillips beaker. (One level scoop from a Coors No. 04 porcelain spatula is approximately 0.2 grams.)
4. Add, from a graduated cylinder, 23 mL of standardized 0.05 N silver nitrate to the solution as it stirs. Immediately set a timer for five minutes and continue to stir during that period.
5. As the solution stirs, assemble a Millipore filter holder and filter membrane (type HAWP—0.45 micron porosity, 47 mm) on a 250-mL filter flask.
6. At the end of the five-minute stirring period, connect the aspirator hose and filter the solution through the Millipore apparatus, retaining the stirring bar in the Phillips beaker by means of another may-bar outside the beaker. When filtering is completed, disconnect the aspirator hose.
7. Rinse the sides of the Phillips beaker with 25 mL of 1.0 M ammonium nitrate from a tip-up pipet. Retaining the stirring bar in the Phillips beaker, rinse the sides of the Millipore funnel by pouring the solution through a long, thin-stemmed glass funnel. Reconnect the aspirator hose and filter the solution into the 250-mL filter flask. Disconnect the aspirator hose when the filtering is completed. Save both the long-stemmed funnel and the Phillips beaker.
8. Remove the 250-mL filter flask from the Millipore filter apparatus and discard the filtrate. Do not disassemble the Millipore filter apparatus.
9. Rinse the inside and outside of the stem only of the Millipore funnel with distilled water from a wash bottle, and place the filter apparatus on a clean 250-mL filter flask.

Silver Development

1. Add, from a graduated cylinder, 25 mL of silver-halide developer to the 250-mL Phillips beaker.

Note: Do not expose the silver-halide developer to air any longer than necessary When not in use, store the silver-halide developer in a cool, dark place. A developer that has turned brown should not be used. The developer is still usable if it has a light tan color.

2. Swirl the Phillips beaker and immediately rinse the sides of the Millipore funnel (with no applied suction) by pouring the developer through the long-stemmed funnel. Set a timer for five minutes and allow the developer to remain in the Millipore funnel for that period. At one-minute intervals, swirl the Millipore funnel for several seconds.
3. During the five-minute period, add from a tip-up pipet, 25 mL of distilled water to the 250-mL Phillips beaker.
4. At the end of the five-minute period, connect the aspirator hose and filter the solution into the clean 250-mL filter flask. (Care must be taken to prevent loss of the filtrate through the aspirator hose.) With the aspirator hose still connected, rinse the sides of the Millipore funnel with the solution in the Phillips beaker by pouring the solution through the long-stemmed funnel. Disconnect the aspirator hose when the filtration is completed.
5. Quantitatively transfer the solution in the 250-mL filter flask into a 400-mL beaker using a maximum of 100 mL of distilled water.
6. Stir the solution moderately on a magnetic stirrer in an exhaust hood.
7. Add carefully from a tip-up pipet, 50 mL of 18 N sulfuric acid to the beaker.

Warning

ACID. Avoid contact with skin and eyes. In case of contact, flush with water.

Titration

1. Using a 25-mL buret, titrate the sample potentiometrically, according to Method ULM-0003-01, with standardized 0.05 N silver nitrate.

   Note: The titration may be performed most rapidly in the beginning where the potential change is the smallest. Refer to Figure 1 to determine the increment size to use in the region of the end point and the expected potential change in millivolts.

2. Determine the end point using the concentric arcs method. (Refer to Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revisions.)

Calculations

Seasoned Tank—100-mL sample

NaBr, g/L =

$$\frac{(\text{N } AgNO_3)(\text{mL } AgNO_3) \times (\text{eq. wt. NaBr}) \times (1000)}{(\text{mL sample}) \times (1000)} =$$

$$1.029(\text{mL } AgNO_3)(\text{N } AgNO_3)$$

Potentiometric Determination of Bromide in Reversal First Developer

D94-0001/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	DR-100/101	DR-150

INTRODUCTION

This method describes the potentiometric determination of bromide contained in a KODAK Reversal First Developer, D-94. The solution is acidified and titrated with a standard solution of silver nitrate. Since this solution also contains thiocyanate, which will titrate with silver nitrate, high bromide numbers due to coprecipitation may result. To overcome this problem, the bromide content is obtained by subtracting the amount of thiocyanate present in the sample, as determined by method *D94-0003/1*.

Use of this method requires handling of potentially hazardous chemicals. Material Safety Data Sheets should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

Repeatability Standard Deviation, $1s_r$

Repeatability Standard Deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

One fresh KODAK Reversal First Developer, Process D-94 was analyzed by one analyst on one day using one titrator. The sample was analyzed five times. The fresh sample was prepared at aim level (6.989 g/L NaBr). A seasoned tank sample was analyzed in the same manner as the fresh sample. A standard addition of 2.171 g/L NaBr was made to this seasoned tank sample and the sample was analyzed in the same manner as the fresh and seasoned samples.

Sample	N	Repeatability Standard Deviation, $1S_r$
Fresh tank prepared at 6.989 g/L NaBr	5	0.16 g/L NaBr
Seasoned sample (mean = 4.370 g/L NaBr)	5	0.056 g/L NaBr
Seasoned sample + addition (mean = 6.542 g/L NaBr)	5	0.032 g/L NaBr

Bias

Bias is a statistically significant deviation of the mean from the known analyte level at the 95 percent confidence level. Bias is reported for fresh samples only, because the analyte level in the seasoned samples was not determined by an independent test method. Bias is based on the information obtained in the repeatability study described in the *Repeatability Standard Deviation, $1s_r$* section above.

A statistically significant low bias was found at the fresh tank aim level. However, this bias was not practically significant.

Recovery

Recovery is defined as a measure of the method's ability to predict the amount of analyte in a seasoned sample, containing a standard addition of the analyte. The percent recovery is based on the information obtained during the repeatability study described in the *Repeatability Standard Deviation, $1s_r$* section.

$$\text{Recovery} = \frac{(\overline{X}(\text{seas + known addition}) - \overline{X}(\text{season})) \cdot 100}{\text{known addition}}$$

The recovery of the standard addition was not statistically different from 100 percent.

Customer Standard Deviation, $1s_c$

The customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

One fresh KODAK Reversal First Developer, Process D-94 was analyzed by four analysts on two separate days using two titrators. The samples were analyzed four times on each day. The fresh sample was prepared at aim level (7.002 g/L NaBr). A seasoned sample of KODAK Reversal First Developer, Process D-94 analyzed to be 4.419 g/L NaBr, was tested in the same manner as the fresh sample above.

Sample	N	Customer Standard Deviation, $1S_c$
Fresh tank prepared at 7.002 g/L NaBr	32	0.079 g/L NaBr
Seasoned sample (mean = 4.419 g/L NaBr)	32	0.073 g/L NaBr

95 Percent Confidence Estimate (not including bias)

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean component concentration level 95 percent of the time. It is not adjusted for method bias.

Sample	95 Percent Confidence Estimate
Fresh prepared at 7.002 g/L NaBr	± 0.16 NaBr
Seasoned (mean = 4.419 g/L NaBr)	± 0.15 NaBr

APPARATUS

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- 5-mL pipette
- 250-mL beaker
- ORION double-junction reference electrode 900200 or equivalent:
  Filling Solutions:
  - ORION No. 900002 (inner chamber)
  - ORION No. 900003 (outer chamber)
- Silver billet indicator electrode, BECKMAN Model #39261 or equivalent
- METROHM Potentiograph, Model E536 with a 20-mL burette, or equivalent

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise stated.

- 0.05 N Silver nitrate, $AgNO_3$, standardized to 4 places past the decimal point.
- Water, Type I Reagent —This method was developed using reagent water equivalent to or purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.
- 7N Sulfuric acid, H_2SO_4

PROCEDURE

1. Pipet 5.0 mL of sample into a 250-mL beaker containing 100 mL of reagent water and a TEFLON coated stirring bar.
2. Slowly add 25 mL 7.0 N sulfuric acid and stir the solution moderately without creating a vortex.
3. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the silver billet electrode.) Titrate the solution through two breaks with standardized 0.05 N $AgNO_3$. Use the following parameters, if using a METROHM E536:

   Measuring span = 500 mV

   Maximum titration rate (min/100% vol) = 10

   Cut-off (%U) = OFF

   Paper drive (mm/100% vol) = 400

   Auto-control = OFF

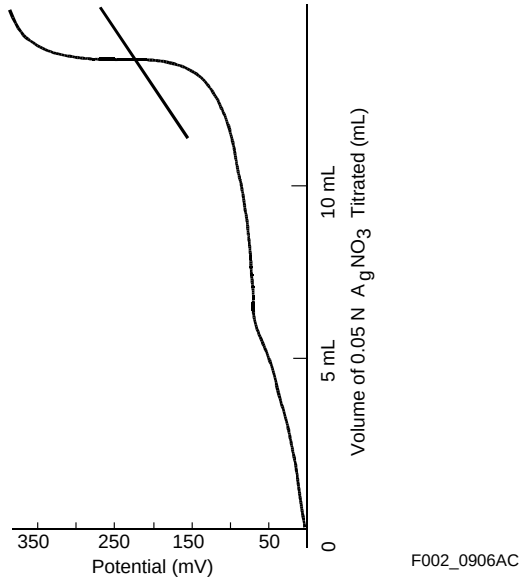
   Selector switch = mV/pH

   Buret size = 20 mL

   Counter voltage = 0

   Zero-point shift = right margin
4. Determine the end point using the concentric arcs method. See Figure 1. (Refer to Universal Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions* or any subsequent revisions.)

Figure 1 Typical Titration Curve for Bromide in Kodak Reversal First Developer



CALCULATIONS

mL $AgNO_3$ that would be consumed by the thiocyanate, as measured by Method *D94-0003/1*:

$$\text{NaSCN, g/L} = \frac{(\text{mL } AgNO_3)(\text{N } AgNO_3)(\text{eq. wt. NaSCN})(1000)}{(\text{mL sample})(1000)}$$

where:

N $AgNO_3$	=	Normality of $AgNO_3$ in meq./mL
eq. wt.	=	81.08 mg/meq
mL sample	=	5.0 mL
1000	=	factor to convert mg to g in the numerator and mL to L in the denominator

Solve the equation for mL $AgNO_3$

$$5.97 \text{ g/L NaSCN} = \frac{(\text{mL } AgNO_3)(0.0491 \text{ N } AgNO_3)(81.08)(1000)}{(5.0)(1000)}$$

$$\text{mL } AgNO_3 = 7.50$$

g/L NaBr

$$\text{NaBr, g/L} = \frac{[(\text{mL } AgNO_3 \text{ titrated}) - (\text{mL } AgNO_3 \text{ from thiocyanate})](\text{N } AgNO_3)(\text{eq. wt.})(1000)}{(\text{mL sample})(1000)}$$

where:

mL $AgNO_3$ titrated	=	Total mL $AgNO_3$ consumed by both Br^- and SCN^-
mL $AgNO_3$ from thiocyanate	=	Calculated mL of mL $AgNO_3$ from analyzed amount of sodium thiocyanate
N $AgNO_3$	=	Normality of $AgNO_3$ in meq./mL
eq. wt.	=	102.91 mg/meq
mL sample	=	5.0
1000	=	factor to convert mg to g in the numerator and mL to L in the denominator

Example:

$$\text{NaBr, g/L} = \frac{[(14.2 \text{ mL } AgNO_3) - (7.50 \text{ mL } AgNO_3)](0.0491 \text{ N } AgNO_3)(102.91)(1000)}{(5.0)(1000)}$$

$$\text{NaBr, g/L} = 6.8 \text{ g/L}$$

Titrimetric Determination of Buffer Capacity of Persulfate Bleach

ECR-754A

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	SR-45	SR-45

INTRODUCTION

This method determines the buffer capacity of persulfate bleach in terms of volume of 85 percent phosphoric acid. The sample is adjusted to pH 1.60 with hydrochloric acid and titrated to pH 2.80 with standard sodium hydroxide. The volume of sodium hydroxide used is then related to a volume of 85 percent phosphoric acid necessary to maintain the desired buffer capacity.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

Based on 16 determinations by four analysts, the 95 percent confidence limits for an individual determination are ± 0.33 mL/L 85 percent phosphoric acid.

SPECIAL APPARATUS

- pH Meter
- Reference Electrode, Ceramic Junction, Calomel, Corning No. 476002, Beckman No. 38423 or equivalent (Filled with 3.5 M potassium chloride solution)
- Indicator Electrode, glass (pH), Rugged Bulb, Corning No. 476024 or equivalent
- 25-mL Buret

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 1 N Sodium Hydroxide, NaOH (standardized to 4 decimal places)
- 3.0 N Hydrochloric Acid, HCl

PROCEDURE

Meter Preparation

1. Follow Method ULM-191-2, *pH Measurement of Photographic Processing Solutions*, to prepare the pH meter for making measurements below pH 9.

Titration

1. Pipet (wipe the pipet before leveling) 100.0 mL of sample into a 250-mL beaker containing a magnetic stirring bar.
2. Immerse the electrode assembly in the sample solution and stir without splashing.
3. Adjust the pH of the sample to approximately pH 1.5, using 3.0 N hydrochloric acid.
4. Add, from a pipet or buret, standardized 1 N sodium hydroxide to attain a pH of exactly 1.60. (This volume does not have to be measured.)

Caution

Stir the solution rapidly without splashing. Do not rinse the sides of the beaker with distilled water because dilution will affect the results.

5. Using a 25-mL buret, titrate the sample to exactly pH 2.80 with standardized 1 N sodium hydroxide. Record the volume of titrant used.

   Note: If the titration exceeds pH 2.80, discard the sample and repeat the analysis.

6. Remove the sample and rinse the electrode assembly with distilled water. If rinsing does not completely remove sample deposits, wipe the assembly with a cleansing tissue and rerinse. Replace the assembly in pH 4.01 potassium acid phthalate buffer for storage.

Calculations

$$\text{Buffer Capacity, mL/L} = 1.415(\text{N NaOH})(\text{mL NaOH}) - 4.52$$

Potentiometric Determination of *Kodak* Color Developing Agent, CD-3 In Reversal Color Developers

ECR-125F

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	DR-150/151	DR-150

INTRODUCTION

The KODAK Developing Agent, CD-3, is extracted into a butyl acetate solvent layer from a sample of developer. The CD-3 in the solvent layer is then extracted with dilute sulfuric acid and titrated with sulfato cerate.

A surfactant (polystyrene sulfonate) is added to minimize the formation of emulsion layers during the extraction of developing agent. Occasionally a narrow emulsion layer is present. If the layer is not transferred to (or with) the sulfuric acid, no significant error is introduced. Our experience shows that by using polystrene sulfonate we have slightly better precision and fewer emulsion problems with seasoned samples.

An exhaust hood is recommended when using butyl acetate but is not an absolute necessity. Impervious Extraction gloves, safety glasses, and observance of local safety regulations are necessary.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

The 95 percent confidence limits for an individual determination are ± 0.17 g/L for fresh solutions. The limits are based on 9 data points using standard mixes containing from 9.00 to 13.00 g/L CD-3.

An empirical calculation is used for the procedure. The procedure is about 5.O percent low from weighed amounts of CD-3 in fresh solutions. The empirical calculation was derived from a 2 variable linear regression of the data. An empirical calculation was used to compensate for the bias from weighed amounts of assayed CD-3 when a stoichiometric calculation is used. When standard additions of 1 g/L CD-3 were made to seasoned samples, the average recovery was 96.3 percent.

SPECIAL APPARATUS

- pH Meter or Automatic Titrator
- Reference Electrode, Double Junction, Orion No. 900200 or equivalent
- Indicator Electrode, Platinum Inlay/Disc, Beckman No. 39273 or equivalent
- Exhaust Hood

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 0.10 M Acidified Ferric Nitrate
- 0.1% Polystyrene Sulfonate
- Butyl Acetate, $CH_3COO(CH_2)_3CH_3$, technical grade
- Ferroin Indicator
- 1.0 N Sulfuric Acid, H_2SO_4
- 0.05N Sulfato Cerate, $(NH_4)_2Ce(NO_3)_6$, standardized to 4 decimal places

PROCEDURE

Extraction

1. Pipet (wipe the pipes before leveling) 25.O mL of tank or replenisher sample into a 250-mL separatory funnel No. 1.
2. Add 2 mL of 0.1% polystyrene sulfonate from a tip-up pipes and mix by gently swirling the funnel for 10 seconds.
3. Add, from a tip-up pipes, 25 mL of butyl acetate. Stopper and shake separatory funnel No. 1 for a few seconds, then vent through the stopper. Continue to shake vigorously for 30 seconds, venting occasionally.
4. Allow enough time for complete separation of the phases.

   Note: It may take longer for complete separation of the phases in highly seasoned samples.
5. Transfer as completely as possible the lower (aqueous) layer to another 250-mL separatory funnel, No. 2, without losing any of the top layer containing the developing agent.
6. Swirl separatory funnel No. 1 and drain any additional lower (aqueous) layer that separates into separatory funnel No. 2.

   Note: Save the top (butyl acetate) layer in separatory funnel No. 1.

7. Add, from a tip-up pipes, 25 mL of butyl acetate to separatory funnel No. 2; stopper and shake the funnel for a few seconds, then vent through the stopper. Continue to shake vigorously for 30 seconds, venting occasionally.
8. Allow enough time for complete separation of the phases.

   Note: It may take longer for complete separation of the phases in highly seasoned samples.
9. Discard as completely as possible the lower (aqueous) layer from separatory funnel No. 2 without losing any of the top (butyl acetate) layer.
10. Transfer the contents of separatory funnel No. 2 (butyl acetate layer) into funnel No. 1.

Back-Extraction

1. Add, from a tip-up pipes, 100 mL of 1.0 N sulfuric acid to separatory funnel No. 2 and swirl, rinsing the inside walls of the funnel. Save for Step 3.
2. Gently swirl separatory funnel No. 1 and discard as completely as possible any lower (aqueous) layer that separates, being careful not to lose any of the butyl acetate layer.
3. Transfer the contents of separatory funnel No. 2 into funnel No. 1.
4. Stopper separatory funnel No. 1 and shake vigorously for 30 seconds, venting occasionally through the stopper.
5. Allow enough time for complete separation of the phases.

   Note: It may take longer for complete separation of the phases in highly seasoned samples.
6. Transfer the lower (acid) layer from separatory funnel No. 1 to a 250-mL beaker without losing any of the top layer.
7. Swirl separatory funnel No. 1 and transfer as completely as possible any additional lower (acid) layer that separates to the beaker.

   Note: The end point of the titration can be determined either potentiometrically or visually.

Potentiometric Titration

1. Add 5 mL 0.10 M acidified ferric nitrate to the sample.
2. Titrate the sample potentiometrically with standardized 0.05 N sulfato cerate using an automatic titrator with at least a 20-mL buret capacity See Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revision.

   Note: Use a one mL/min titration speed with a chart span of approximately 1000 mV. (Appropriate settings for individual titrators should be determined experimentally for the best inflection point.)
3. Determine the end point by means of the concentric arcs technique. Record this as mL A. See Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revision.
4. Add 100 mL of 1.0 N sulfuric acid to a second 250-mL beaker. Repeat Step 2 above. Record this as mL B. (This is your blank and only needs to be determined once for any batch of samples.)
5. mLA-mLB =

   mL standardized 0.05 N sulfato cerate titrated

Manual (Visual) Titration

1. Stir the solution vigorously, without splashing, on a magnetic stirrer and add 5 drops of ferroin indicator.
2. Titrate the solution with standardized 0.05 N sulfato cerate to the first green color that persists for 15 seconds. Add the titrant dropwise when within an estimated two mL of the end point, allowing sufficient time for complete mixing before making another addition. Record the end point as mL A.
3. Add 100 mL of 1.0 N sulfuric acid to a second 250-mL beaker with 5 drops of ferroin indicator. Repeat Step 2 above, but record the end point as the first light blue color that persists for 15 seconds. Record this as mL B. (This is your blank and only needs to be determined once for any batch of samples.)
4. mLA-mLB =

   mL standardized 0.05 N sulfato cerate titrated

Calculations

$$\text{CD-3, g/L} = \frac{(\text{N cerate})(\text{mL cerate})(\text{eq. wt. CD-3})(1000)}{(\text{mL sample})(1000)} + 0.49 =$$

$$\frac{(\text{N cerate})(\text{mL cerate})(218.0)(1000)}{(25.0\ \text{mL})(1000)} + 0.49 =$$

$$8.72(\text{N cerate})(\text{mL cerate}) + 0.49$$

Spectrophotometric Determination of Citrazinic Acid in Reversal Color Developers
ECR-1611D

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	DR-150/151	DR-150

INTRODUCTION
Citrazinic acid is determined by measuring the absorbance of its sodium salt solution on a spectrophotometer at 345 nm. Since the decomposition products of the developer also absorb at this wavelength and vary with solution use and air exposure, the citrazinic acid must first be separated from the rest of the mix. Citrazinic acid has very low solubility in an acidic solution, but can be dissolved by forming the sodium salt. Therefore, it can be separated from the mix by acid precipitation and filtration. The precipitate is then dissolved and measured in an alkaline solution.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY
The calibration curve was prepared by analyzing several standard laboratory mixes containing varying known amounts of specially purified citrazinic acid and constant amounts of the other constituents. The absorbance values, determined by following the analytical procedure, were plotted against the corresponding concentrations of citrazinic acid. The best straight line was determined from the data.

The individual results obtained by this method have 95 percent confidence limits of ± 0.08 g/L. These limits are based upon 35 individual analyses of standard laboratory mixes.

SPECIAL APPARATUS
- Fritted Pyrex Disc Buchner Funnel, 40 mm dia. fine porosity
- Spectrophotometer with a hydrogen lamp
- 1-cm Silica Cell

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS
Use ACS Reagent Grade reagents unless specified otherwise.
- Celite filter-aid
- 7.0 N Sulfuric Acid, H_2SO_4
- 0.10 N Sulfuric Acid, H_2SO_4
- 0.10 N Sodium Hydroxide, NaOH

PROCEDURE
Precipitation
1. Using a No. 4 Coors porcelain spoon, add four scoops of Celite to a 150-mL beaker.
2. Pipet (wipe the pipet before leveling) 20.0 mL of sample into the beaker.
3. Add 2 mL of 7.0 N sulfuric acid from a tip-up pipet. Swirl the beaker to mix the Celite, sample, and acid thoroughly.
4. Allow ten minutes for complete precipitation.

Filtration
1. Prepare an aspirator-filter assembly Use a 250- or 500-mL filtering flask and a fine-porosity, 40-mm fritted-glass Buchner funnel.
2. After ten minutes have elapsed, filter the reacted sample.
3. Rinse the beaker, then the funnel, with two 10 mL portions of 0.10 N sulfuric acid from a tip-up pipet. Retain the beaker.
4. Disconnect the aspirator-filter assembly. Discard the filtrate and rinse the inside of the flask three times with distilled water.

Salt Formation
1. Mount the funnel in the filtering flask. Add, from a tip-up pipet, 20 mL of 0.10 N sodium hydroxide to the beaker, and then transfer the solution to the funnel. Retain the beaker.
2. Mix the contents of the funnel by gently swirling the funnel for one minute.
3. Apply suction and filter the dissolved precipitate.
4. Rinse the beaker, then the funnel with four 15 mL portions of distilled water from a tip-up pipet.
5. Quantitatively transfer the filtrate to a l00-mL volumetric flask. Dilute to volume with distilled water. Stopper and invert 6 to 12 times.
6. Pipet 10.00 mL of the dilution into a 250-mL volumetric flask. Dilute to volume with distilled water. Stopper and invert 6 to 12 times.

Absorbance Measurement

Measure the absorbance of the dilution with the spectrophotometer at 345 nm (A34s). Use the hydrogen lamp. See instructions given in Method ULM-0001/1, *Instructions for Performance Checks of Ultraviolet-Visible Spectrophotometers and Quartz Cells*.

Calculations

$$\text{Citrazinic acid, g/L} = 2.53(A_{345}) + 0.09$$

Titrimetric Determination of Citrazinic Acid in Reversal Color Developers

ECR-1612

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	DR-150/151	DR-150

PRINCIPLE

The citrazinic acid is removed from solution by precipitation with acid. Celite is added to aid the precipitation by acting as a collecting agent. A known excess of sodium hydroxide is added, and a portion of it reacts with an equivalent amount of the precipitate. The excess hydroxide is then titrated with sulfuric acid.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

The calibration equations were calculated by the method of least squares from the data obtained by three analysts who analyzed four laboratory standard mixes of each developer. The range of calibration for developers is from 1.00 to 2.00 g/L citrazinic acid. Based on 12 analyses, the 95 percent confidence limits for an individual determination are ± 0.07 g/L citrazinic acid in the developers.

SPECIAL APPARATUS

- Millipore filter holder, Pyrex, Catalog No. XX 1004700, Millipore Corp., Bedford, Mass. 01730
- 984H Ultra filter, glass paper 4.25 cm, H. Reeve Angel & Co., Inc., 9 Bridewell Place, Clifton, N. J.

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- Celite filter-aid
- 7.0 N Sulfuric Acid, H_2SO_4
- Foamex
- 0.10 N Sodium Hydroxide, NaOH (standardized to 4 decimal places)
- Meta Cresol Purple indicator
- 0.10 N Sulfuric Acid, H_2SO_4 (standardized to 4 decimal places)

PROCEDURE

Precipitation

1. Add 3 to 4 g of Celite to a 400-mL beaker.
2. Pipet 100.0 mL of sample into the beaker.
3. Add 10 mL of 7.0 N sulfuric acid from a tip-up pipet.
4. Stir on a magnetic stirrer for 15 minutes.

Filtration

1. Prepare a filtration setup using a Millipore filter holder and a 500-mL filtering flask. Place the glass-fiber filter paper in the filter holder.
2. After 15 minutes have elapsed, apply full suction. Transfer the mixture onto the filter paper using a glass rod; filter the solution. (The precipitate will be easier to wash if it does not collect on the holder.) Retain the stirring bar in the beaker by placing a second bar on the outside of the beaker.
3. Rinse the beaker, stirring bar, and glass rod with two 10 mL portions of distilled water. Transfer each rinse to the Millipore holder.
4. Disconnect the aspirator filter assembly and discard the filtrate. Rinse the flask and the tip of the Millipore holder three times with distilled water. Discard the rinses.

Salt Formation

1. Add one drop of Foamex to the flask. Reassemble the apparatus, but do not apply suction.
2. Pipet 50.0 mL of standardized sodium hydroxide into the beaker. Swirl the beaker to dissolve any citranzinic acid that may still be in the beaker.
3. Cautiously transfer the sodium hydroxide to the Millipore holder.

   Note: Do not rinse the beaker; the strength of hydoxide must not be reduced at this time. See Step 6 below.
4. Swirl the Millipore holder for one minute.

   Note: The Celite and citrazinic acid material must become suspended during the swirling action.
5. Apply suction and filter the solution.
6. Rinse the beaker with distilled water, and cautiously transfer the rinses to the holder. All solid material must be transferred to the holder.
7. Cautiously rinse the holder and the Celite with at least two 20 mL portions of distilled water.
8. Disconnect the suction line, and quantitatively transfer the filtrate to a 400-mL beaker.

Titration

1. Add six drops of meta cresol purple indicator to the beaker.
2. While stirring on a magnetic stirrer, titrate the solution with standardized 0.1 N sulfuric acid to the first clear *yellow*.
3. Determine the acid-base blank by pipetting 50.0 mL of standardized 0.1 N sodium hydroxide into a 150-mL beaker. Proceed by repeating Steps 1 and 2.

Calculations

Subtract the buret reading recorded in Step 2 of the Titration procedure above from the reading in Step 3 of the Titration procedure above. Substitute the difference, (ΔmL) in the following equation:

$$\Delta mL = mL\ Acid_{blk} - mL\ Acid_{spl}$$

$$\text{Citrazinic acid, g/L} = 0.0831(\Delta mL) + 0.01$$

Potentiometric Determination of Ethylenediamine in Reversal Color Developers

ECR-617B

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	DR-150/151	DR-150

INTRODUCTION

A sample of the developer is first acidified to a given pH. Formalin is then added to react with the ethylenediamine to release hydronium ions (H3O+) as shown.

$$H_3N(CH_2)_2NH_3^+ + CH_2O \rightarrow H_2N(CH_2)_2NH_2 + H_3O^+$$

The hydronium ions that are released are then titrated with base to give an indirect measure of ethylenediamine.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

The calibration curve was calculated from the 40 results obtained by two analysts who analyzed standard laboratory mixes for the reversal processes. The mixes contained from 1.50 to 3.40 g/L ethylenediamine. The volumes of base required in the titrations were used to calculate, by the method of least squares, the best straight line for the universal calibration curve. The equation for this line is found under Calculations. The 95 percent confidence limits for an individual determination are ± 0.04 g/L of ethylenediamine.

SPECIAL APPARATUS

- pH Meter
- Reference Electrode, Ceramic Junction, Calomel, Corning No. 476002, Beckman No. 38423 or equivalent (Filled with 3.5 M potassium chloride solution)
- Indicator Electrode, glass (pH), Rugged Bulb, Corning No. 476024 or equivalent

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- Foamex
- 1.0 N Sulfuric Acid, H_2SO_4
- 0.1 N Sodium Hydroxide, NaOH (standardized to 4 decimal places)
- 37.5 percent Formaldehyde solution, pH 3.9

PROCEDURE

Meter Preparation

1. Follow Method ULM-191-2, *pH Measurement of Photographic Processing Solutions* (or any subsequent pH method) for making pH measurements below 9.

Titration

1. Pipet 50.0 mL of sample into a 250-mL beaker.
2. Immerse the electrode assembly in the sample and add sufficient distilled water to cover the tips of the electrodes.
3. Add 1 drop of Foamex, and stir the solution with a magnetic stirrer.
4. Add, from a squeeze bottle or buret, 1.0 N sulfuric acid to attain a pH equal to or slightly less than 3.8. (This volume does not have to be measured.)
5. Adjust the solution to pH 3.90 with standardized 0.1 N sodium hydroxide from a squeeze bottle or an eyedropper.
6. Add 25 mL of 37.5 percent formaldehyde solution, pH 3.9, from a tip-up pipet.
7. Titrate to pH 3.90 with standardized 0.1 N sodium hydroxide.

Calculation

$$\text{Ethylenediamine, g/L} = 1.16(\text{N NaOH})(\text{mL NaOH}) + 0.26$$

Titrimetric Determination of Ferricyanide and Persulfate in Ferricyanide Bleach

ECR-1113D

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	SR-40	—

PRINCIPLE

Zinc sulfate is added to a sample of ferricyanide bleach to precipitate the ferricyanide and ferrocyanide. The persulfate remains in solution. The mixture is then centrifuged and the supernatant liquid is decanted.

The combined zinc ferricyanide and ferrocyanide precipitate is dispersed in acid and excess potassium iodide. Iodide equivalent to the amount of ferricyanide present is oxidized to iodine. A titration of the liberated iodine with standard sodium thiosulfate gives an indirect measure of the ferricyanide content. This ferricyanide determination is valid in the presence of persulfate and other oxidizing agents. Although sodium ferricyanide is usually purchased as a hydrate, it is reported here as anhydrous sodium ferricyanide, $Na_3Fe(CN)_6$.

The persulfate remaining in the decanted supernatant liquid is determined by treatment with a known excess of ferrous ion. The unoxidized ferrous ion is titrated in an acid solution with standardized 0.01 N sulfato cerate using Ferroin indicator.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

SPECIAL APPARATUS

- Centrifuge, with head to accommodate 50-mL centrifuge tubes
- 50-mL Centrifuge Tubes, glass- or rubber-stoppered

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 7.0 N Sulfuric Acid, H_2SO_4
- 50 g/L Zinc Sulfate, $ZnSO_4$
- Potassium iodide, KI
- 0.1 N Sodium Thiosulfate, $Na_2S_2O_3$ (standardized to 4 decimal places)
- Starch Indicator
- 0.10 N Ferrous Ammonium Sulfate, $Fe(NH_4)_2(SO_4)_2$
- Ferroin Indicator
- 0.01 Sulfato Cerate (standardized to 4 decimal places)

Note: The concentration of the ferrous ammonium sulfate must be determined daily since its strength decreases because of aerial oxidation.

PROCEDURE

Separation from Persulfate

1. Pipet (wipe the pipes before leveling) 5.00 mL of sample into a 50-mL centrifuge tube.
2. Add 3 mL of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 20 mL of 50 g/L zinc sulfate from a tip-up pipet.
4. Stopper the tube and shake it vigorously for 15 seconds. Rinse the stopper with distilled water into the centrifuge tube.
5. Stopper the tube and centrifuge for two minutes.
6. Carefully decant the supernatant liquid into a 250-mL conical flask. (Do not pour the solution too slowly since this promotes a greater loss of precipitate.
7. Add from a tip-up pipes 20-mL of distilled water to the precipitate.
8. Stopper and shake the tube until the precipitate has completely broken up. Shake for an additional 10 seconds. Rinse the stopper with distilled water into the centrifuge tube.
9. Stopper the tube and centrifuge for two minutes.
10. Carefully decant the rinse into the conical flask containing the previously decanted liquid. (Do not pour the solution too slowly since this promotes a greater loss of precipitate.) Save the decanted liquid for the section *Persulfate Determination.*

Ferricyanide Determination

1. Add from a tip-up pipes 5 mL of 7.0 N sulfuric acid to the precipitate remaining after Step 10 of the *Separation from Persulfate* section above.
2. Add 6 g of potassium iodide crystals.
3. Stopper the tube and shake it until the precipitate is completely dispersed.
4. Quantitatively transfer the mixture into a 250-mL conical flask, using distilled water from a wash bottle
5. Rinse the stopper and sides of the centrifuge tube with distilled water and add the rinses to the flask.
6. Add distilled water to the 250-mL conical flask to attain an approximate volume of 125 mL.
7. Titrate with standardized 0.1 N sodium thiosulfate to a *light yellow* color.
8. Add 5 mL of starch indicator and continue the titration until the *blue* color just disappears. Any precipitate present does not interfere.

Calculations

$Na_3Fe(CN)_6$, g/L =

$$\frac{(\text{N } Na_2S_2O_3)(\text{mL } Na_2S_2O_3)[\text{eq wt } Na_3Fe(CN)_6](1000)}{(\text{mL sample})(l000)} =$$

$$\frac{(\text{N } Na_2S_2O_3)(\text{mL } Na_2S_2O_3)[280.6](1000)}{(5.00)(l000)} =$$

$$56.12(\text{N } Na_2S_20_3)(\text{mL } Na_2S_2O_3)$$

Persulfate Determination

1. Pipet (wipe the pipet before leveling) 4.00 mL of 0.10 N ferrous ammonium sulfate into the 250-mL conical flask containing the decanted liquid from Step 10 of the *Separation from Persulfate* section.
2. Swirl the flask and allow it to stand for one minute.
3. Add 10 mL of 7.0 N sulfuric acid from a tip-up pipet.
4. Add four drops of Ferroin indicator to the flask.
5. Titrate with standardized 0.01 N sulfato cerate to the first *blue* color that persists for 15 seconds. The volume of sulfato cerate required is “B” in the calculations below.

   Note: If the volume of titrant required for the decanted liquid is 5 mL or less, repeat the *Separation from Persulfate* section and this section, pipetting 10.0 mL of 0.10 N ferrous ammonium sulfate.
6. Once daily, determine the strength of the ferrous ammonium sulfate using approximately 20 mL of distilled water in place of the decanted liquid. Repeat Steps 1 through 5 of this section as you did with the decanted liquid. The volume of sulfato cerate required is “A” in the calculations below.

Calculations

Potassium Persulfate

$K_2S_2O_8$, g/L =

$$\frac{(\text{N sulfato cerate})(A - B)(\text{eq wt } K_2S_2O_8)(1000)}{(\text{mL sample})(l000)} =$$

$$\frac{(\text{N sulfato cerate})(A - B)(135)(1000)}{(5.00)(l000)} =$$

$$27(\text{N sulfato cerate})(A - B)$$

Ammonium Persulfate

$(NH_4)_2S_2O_8$, g/L =

$$\frac{(\text{N sulfato cerate})(A - B)[\text{eq wt } (NH_4)_2S_2O_8](1000)}{(\text{mL sample})(l000)} =$$

$$\frac{(\text{N sulfato cerate})(A - B)(114)(1000)}{(5.00)(l000)} =$$

$$22.8(\text{N sulfato cerate})(A - B)$$

Iodometric Determination of Ferricyanide in Ferricyanide Bleach

ECR-1100G

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	SR-40	—

PRINCIPLE

Excess iodide ions and a zinc reagent are added to the bleach sample. The ferricyanide reacts with the iodide to produce an equivalent amount of iodine. The iodine is titrated with standard sodium thiosulfate. The reaction of ferricyanide and iodide is quantitative as long as zinc ions are present in excess. Any ferrocyanide present in the bleach, as well as the ferrocyanide produced by the reduction of ferricyanide, is precipitated as zinc ferrocyanide. Carbowax is not separated out of the sample in this method, and if present in your solution, may interfere with the iodine end point.

Persulfate ions and some other oxidizing agents will also oxidize iodide. Thus, if present, they will be measured as ferricyanide by this method.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 0.60 M Potassium iodide, KI
- Zinc Sulfate/7.0 N Sulfuric Acid Reagent
- 0.1 N Sodium Thiosulfate, $Na_2S_2O_3$ (standardized to 4 decimal places)
- Starch Indicator

PROCEDURE

Removal of Interfering Constituents

1. Pipet (wipe the pipet before leveling) the indicated sample size into a 250-mL conical flask.

Process	Sample Size
VNF-1/LC	5.00 mL

2. Add 25 mL of 0.60 M potassium iodide from a tip-up pipet.
3. Add 20 mL of zinc sulfate/7.0 N sulfuric acid reagent from a tip-up pipet; mix thoroughly.

Titration

1. Titrate with standardized 0.1 N sodium thiosulfate to a light yellow color.
2. Add 5 mL of starch indicator from a tip-up pipes, and continue the titration until the blue color just disappears.

Calculations

VNF-1/LC (5-mL sample)

$K_3Fe(CN)_6$, g/L =

$$\frac{(N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)[eq\ wt\ K_3Fe(CN)_6](1000)}{(mL\ sample)(1000)} =$$

$$\frac{(N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)(329.25)(1000)}{(5.00)(1000)} =$$

$$65.85(N\ Na_2S_20_3)(mL\ Na_2S_2O_3)$$

$Na_3Fe(CN)_6$, g/L =

$$\frac{(N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)[eq\ wt\ Na_3Fe(CN)_6](1000)}{(mL\ sample)(1000)} =$$

$$\frac{(N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)(280.92)(1000)}{(5.00)(1000)} =$$

$$56.18(N\ Na_2S_20_3)(mL\ Na_2S_2O_3)$$

Potentiometric Determination of Ferrocyanide in Ferricyanide Bleach and Ferrocyanide Stock Solutions

ECR-1102C

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	SR-40	—

PRINCIPLE

Ferrocyanide is oxidized in an acid solution by sulfato cerate. This reaction is:

$$Ce^{+4} + Fe(CN)_6^{-4} \rightarrow Ce^{+3} + Fe(CN)_6^{-3}$$

The sample is titrated potentiometrically. The progress of the titration is followed by measuring the potential of a platinum electrode against a double junction reference electrode. Results are reported in terms of sodium ferrocyanide decahydrate.

The record or plotted curve will "break" in a direction opposite that found in a bromide titration.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

This method is based on stoichiometry. The 95 percent confidence limits for a single determination are expected to be ± 3 percent.

SPECIAL APPARATUS

- Automatic Titrator or pH Meter
- Reference Electrode, Double Junction, Orion No. 900200 or equivalent
- Indicator Electrode, Platinum Inlay/Disc, Beckman No. 39273 or equivalent

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 7.0 N Sulfuric Acid, H_2SO_4
- 0.05 N Sulfato Cerate (standardized to 4 decimal places)

PROCEDURE

Sample Treatment

1. Pipet (wipe the pipet before leveling) the sample of ferricyanide bleach into a beaker according to the following table.

Concentration of Ferrocyanide (g/L)	Sample Size (mL)	Sample (mL)	Distilled Water (mL)	7.0 N Acid (mL)
Below 5	600	200.0	100	50
Between 5 and 10	600	100.0	200	50
Between 10 and 20	400	50.0	200	50
Between 20 and 40	400	25.0	200	50
Between 40 and 80	400	10.0	200	50
Between 80 and 200	400	5.00	200	50
Over 200	400	2.00	200	50

2. Add distilled water from a graduated cylinder according to the table above.
3. Add 7.0 N sulfuric acid from a tip-up pipet according to the table above. Mix thoroughly.

Potentiometric Titration

1. Titrate the solution with standardized 0.05 N sulfato cerate, using an automatic titrator of pH meter. See *Potentiometric Titrations for Photoprocessing Solutions*, Method ULM-0003-01, or any subsequent revision.

Calculation

$Na_4Fe(CN)_6 \cdot H_2O$, g/L =

$$\frac{(\text{N cerate})(\text{mL cerate})(\text{eq wt } Na_4Fe(CN)_6 \cdot 10H_2O)(1000)}{(\text{mL sample})(1000)} =$$

$$\frac{(\text{N cerate})(\text{mL cerate})(484.1)(1000)}{(\text{mL sample})(1000)} =$$

$$\frac{484.1(\text{N cerate})(\text{mL cerate})}{(\text{mL sample})} =$$

Iodometric Determination of Formalin in Stabilizer

ECR-1803G

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	–	S-1c	S-16	S-16

INTRODUCTION

In this method the sample is added to an excess of hypoiodite, formed by acidifying standard potassium iodate, adding an excess of potassium iodide, and making the solution alkaline. Part of the hypoiodite is reduced by the formaldehyde in the sample, and the unreduced part is converted to iodine by acidifying the solution. The iodine is then titrated with sodium thiosulfate using starch indicator. KODAK Stabilizer Additive does not interfere in these reactions.

Formalin is a solution of formaldehyde in water. The formulas for processing solutions are based on formalin which is 37.5 percent formaldehyde by weight and with a specific gravity of 1.095. The percent by weight and the specific gravity enter into the calculations for this determination. The specific gravity varies slightly depending on the concentration of methyl alcohol present as an antifreeze and preservative.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

RELIABILITY

The equation for determining the formalin content should be checked by preparing several standard laboratory mixes containing the particular strength of the formalin stock solution used in the processing solution. Normally the results obtained are slightly below the amount added to the mix.

The results obtained on standard mixes should be within 5 percent of the mix value. If this is not the case, the concentration and the specific gravity of the formalin stock solution must be determined. The concentration can be found by using the ANSI test procedure, ANSI PH4.152-198O(R1987).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 0.1 N Potassium Iodate, KIO_3 (standardized to 4 decimal places)
- 7.0 N Sulfuric Acid, H_2SO_4
- 0.60 M Potassium Iodide, KI
- 2.5 N Sodium Hydroxide, NaOH
- 0.1 N Sodium Thiosulfate, $Na_2S_2O_3$ (standardized to 4 decimal places)
- Starch Indicator

PROCEDURE

Sample Treatment

1. Pipet (wipe the pipet before leveling) 50.0 mL of standardized 0.1 N potassium iodate into a 250-mL glass-stoppered conical flask.
2. Add 5 mL of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 25 mL of 0.60 M potassium iodide from a tip-up pipet. Swirl to mix.
4. Pipet (wipe the pipet before leveling) the indicated volume of stabilizer into the flask:

Process	Formula	Sample Size
ECP-2D	S-1c	10.00 mL
VNF-1/LC	S-16	20.0 mL
RVNP	S-16	20.0 mL

5. Add 25 mL of 2.5 N sodium hydroxide from a tip-up pipet.
6. Stopper the flask, swirl the contents, and allow it to stand approximately one minute.
7. At the end of one minute, add 10 mL of 7.0 N sulfuric acid from a tip-up pipet.

Titration

1. Titrate immediately with standardized 0.1 N sodium thiosulfate to a light yellow color.
2. Add 5 mL of starch indicator from a tip-up pipet and continue the titration to the disappearance of the blue color.
3. Record the mL of standardized 0.1 sodium thiosulfate used.

Calculation

Formalin, mL/L =

$$\frac{(\text{N } KIO_3)(\text{mL } KIO_3) - (\text{N } Na_2S_2O_3)(\text{mL } Na_2S_2O_3)(\text{eq wt } CH_2O)(1000)(100)}{(\text{mL sample})(\%\ CH_2O \text{ by wt})(\text{sp gr of } CH_2O)(l000)} =$$

ECP-2D Stabilizer S-1c

$$\frac{(\text{N } KIO_3)(50.0) - (\text{N } Na_2S_2O_3)(\text{mL } Na_2S_2O_3)(15.015)(1000)(100)}{(10.0)(37.5)(1.095)(l000)} =$$

$$3.66[(\text{N } KIO_3)(50.0) - (\text{N } Na_2S_2O_3)(\text{mL } Na_2S_2O_3)]$$

VNF-1/LC and RNVP Stabilizer S-16

$$\frac{(\text{N } KIO_3)(50.0) - (\text{N } Na_2S_2O_3)(\text{mL } Na_2S_2O_3)(15.015)(1000)(100)}{(20.0)(37.5)(1.095)(l000)} =$$

$$1.828[(\text{N } KIO_3)(50.0) - (\text{N } Na_2S_2O_3)(\text{mL } Na_2S_2O_3)]$$

Spectrophotometric Determination of Hydroquinone and Phenidone in First Developers
ECR-440B

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	DR-100/101	DR-105

INTRODUCTION
Hydroquinone and Phenidone (1-phenyl-3-pryazolidinone) are spectrophotometrically determined simultaneously. They are extracted into water-saturated ethyl acetate. Aliquots of the extract are diluted and measured on a spectrophotometer. The concentration of the two components is determined by solving two three-variable linear regression equations which were derived for fresh samples of known composition.

Prior to being water-saturated, the ethyl acetate should be checked for ultraviolet absorbance. If the absorbance of a 1-cm silica cell filled with ethyl acetate exceeds 0.150 (measured against an air blank at 295 and 315 nm), the ethyl acetate is not suitable for use. Reagent ACS, spectro grade ethyl acetate, is recommended for use in this analysis, but it must be checked and it must meet the indicated absorbance criteria. Any grade ethyl acetate that meets the indicated absorbance criteria may be used. Locally acceptable practices should be used when discarding waste ethyl acetate.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY
Five first developer laboratory standard mixes were prepared containing the following combinations of hydroquinone and Phenidone.

Hydroquinone, g/L	Phenidone, g/L
3.00	0.200
3.00	0.200
5.00	0.400
7.50	0.200
7.50	0.600

They were analyzed by seven analysts in two laboratories for a total of 35 data points for each component. The 95 percent confidence limits for an individual determination of a fresh tank or replenisher sample are:

± 0.12 g/L Hydroquinone and
± 0.02 g/L Phenidone

SPECIAL APPARATUS
- Spectrophotometer with UV lamp
- 1-cm Silica Cell

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS
Use ACS Reagent Grade reagents unless specified otherwise.
- Glacial Acetic Acid, CH_3COOH, Reagent ACS
- Ethyl Acetate, Reagent ACS, Spectro-grade, water saturated
- 1.0 N Sulfuric Acid, H_2SO_4

Note: Prior to being water-saturated, the ethyl acetate should be checked for ultraviolet absorbances. If the absorbance of a 1-cm silica cell filled with ethyl acetate exceeds 0.150 when measured against an air blank at 295 and 315 nm, it is not suitable for use.

PROCEDURE

Extraction

1. Pipet, wipe before leveling, 25.0 mL of sample into a 250-mL separatory funnel.
2. Add, from a tip-up pipet, 4 mL of glacial acetic acid to the funnel.
3. Swirl the unstoppered funnel to allow the rapidly forming gases to escape.
4. Pipet (wipe) 50.0 mL of water-saturated ethyl acetate into the separatory funnel; stopper and shake the funnel for a few seconds, then vent through the stopper, continue to shake vigorously, venting occasionally, for 30 seconds.
5. Allow the phases to separate; do not remove the stopper.

Acidic Dilution

1. Add approximately 200 mL of distilled water to a 250-mL volumetric flask and add, by tip-up pipes, 25 mL of 1.0 N sulfuric acid to the flask.
2. Add approximately 20 mL of distilled water to a 50-mL volumetric flask and add, by tip-up pipet, 5 mL of 1.0 N sulfuric acid to the flask.
3. Remove the stopper from the separatory funnel and pipet (wipe) 2.00 mL of the upper (ethyl acetate) layer into both the 250-mL and 50-mL volumetric flasks.
4. Swirl both volumetric flasks until the ethyl acetate is completely dissolved.
5. Dilute both volumetric flasks to volume with distilled water; stopper the flasks and mix the contents by inverting 6 to 10 times.

Absorbance Measurements

1. Rinse and fill a clean 1-cm silica cell with the solution in the 250-mL volumetric flask. Measure the absorbance of the solution in the cell versus air on a spectrophotometer at 288 nm; record as A_{288}.
2. Discard the solution in the 1-cm silica cell and rinse with at least 6 portions of the solution in the 50-mL volumetric flask, and then fill the cell. Measure the absorbance of the solution in the cell versus air on a spectrophotometer at 250 nm; record as A_{250}.

Calculations

Hydroquinone, g/L =

$$12.01(A_{288}) - 0.117\ (A_{250}) - 0.59$$

Phenidone, g/L =

$$1.35(A_{250}) - 0.35\ (A_{288}) - 0.091$$

Titrimetric Determination of Hypo Index, Sulfite, Bisulfite, and Thiosulfate Content of Fixers
ECR-1308J

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	F-36	F-38

PRINCIPLE

The Hypo Index (HI) of a fixer is defined as the millilitres of standardized 0.1 N iodine consumed by the sulfite, bisulfite, and thiosulfate in a specified volume of the fixer. H.I. is determined (Part I) by adding the sample to an excess of iodine (formed by acidifying potassium iodate and adding potassium iodide) and titrating the remaining iodine with standard sodium thiosulfate. The difference between the mL of standardized 0.1 N potassium iodate added originally and the mL of standardized 0.1 N sodium thiosulfate used in the titration is, therefore, the Hypo Index of the sample.

Ferrocyanide interferes in the determination of both Hypo Index and sulfite in fixers. Zinc sulfate is added to remove the ferrocyanide.

The theoretical consumption of iodine by sulfite, bisulfite, and thiosulfate is a close approximation of the actual consumption (see Table 1) The "theoretical" Hypo Index is calculated from a consideration of the equivalent weights of ammonium thiosulfate, sodium sulfite, sodium bisulfite, and sodium thiosulfate pentahydrate. Photographic-grade ammonium thiosulfate is supplied as a waster solution having an assay of 57.0 to 61.0 percent and containing a maximum of 0.7 percent sulfite (ANSI PH4.252-1987 or revision). Photographic-grade sodium sulfite is usually less than 100 percent pure with a minimum assay of 97.0 percent (ANSI PH4.275-1987 or revision). Photographic-grade sodium bisulfite is a mixture of sodium sulfite, sodium metabisulfite and water. Its purity, as determined by an iodine titration and expressed as sodium bisulfite, is approximately 107.5 percent with a minimum assay of 105 percent. If it were pure sodium metabisulfite, it would assay 110 percent (ANSI PH4.276-1987) as sodium bisulfite. Photographic-grade sodium thiosulfate has an assay of 99.0 to 101.0 percent as sodium thiosulfate pentahydrate (ANSI PH4.250-1987 or revision).

In order to determine only the thiosulfate content (Part II), a separate sample is adjusted to pH 8.5. Formaldehyde solution, 37.5 percent, is then added to form a complex with the sulfite. At this pH the complex forms rapidly. The solution is then made acid to prevent the complex from reacting with iodine, which is subsequently used to titrate the thiosulfate.

The sulfite content is calculated (Part III) by subtracting the volume of iodine consumed by the thiosulfate from the volume of iodine consumed by the sum of sulfite, bisulfite, and thiosulfate (the Hypo Index).

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

All pipets and volumetric glassware should be "Class A" as defined by NIST (National Institute of Standards and Technology, formerly National Bureau of Standards).

REAGENTS

Use reagents that are ACS Reagent Grade unless specified otherwise.

- 0.1 N Potassium Iodate, KIO_3, (standardized to four decimal places)
- 2.0 N Acetic Acid, CH_3COOH
- 50 g/L Zinc Sulfate. $ZnSO_4$
- 0.60 M Potassium Iodide, KI
- 0.1 N Sodium Thiosulfate, $Na_2S_2O_3$ (standardized to four decimal places)
- Starch Indicator
- 37.5% Formaldehyde Solution, CH_2O
- Phenolphthalein Indicator
- 1.0 N Sodium Hydroxide, NaOH
- 0.1 N Iodine, I_2 (standardized to four decimal places)

PROCEDURE

Hypo Index

(Total Bisulfite, Sulfite, and Thiosulfate)

Sample Treatment

1. Pipet (wipe the pipet before leveling) 50.0 mL of standardized 0.1 N potassium iodate into a 250-mL conical flask.
2. Add 10 mL of 2.0 N acetic acid from a tip-up pipet.
3. Add 5 mL of 50 g/L zinc sulfate from a tip-up pipet.
4. Stir the solution with a magnetic stirrer and add 25 mL of 0.60 M potassium iodide from a tip-up pipet.
5. Immediately pipet (wipe) 3.00 mL of fixer into the 250-mL flask while the solution is stirring.

Titration

1. Titrate with standardized 0.1 N sodium thiosulfate to a *light yellow* color.
2. Add 5 mL of starch indicator from a tip-up pipet and continue the titration until the *blue* color disappears.

Calculation:

Hypo Index (3 mL sample) = (50.00 – mL $Na_2S_2O_3$)

Note: Always specify the sample size when reporting results.

Thiosulfate (Hypo)

Sample Treatment

1. Pipet 3.00 mL of sample into a 250-mL conical flask.
2. Add 5 mL of 37.5 percent formaldehyde solution from a tip-up pipet.
3. Add three to four drops of phenolphthalein indicator.
   a. If the solution is *pink*, titrate with 1.0 N sulfuric acid to colorless.
   b. If the solution is *colorless*, titrate with 1.0 N sodium hydroxide to the first *light pink* color.
4. Let the solution stand for two minutes.
5. Add 10 mL of 2.0 N acetic acid from a tip-up pipet.
6. Add 5 mL of 50 g/L zinc sulfate from a tip-up pipet.

Titration

1. Add, from a tip-up pipet, 5 mL of starch indicator to the sample.
2. Titrate with standarized 0.1N iodine to the first distinct *blue* color.

Calculations:

1. Sodium Thiosulfate:

$Na_2S_2O_3 \cdot 5\ H_2O$, g/L =

$$\frac{(N\ I_2)(mL\ I_2)(eq\ wt\ (Na_2S_2O_3 \cdot 5\ H_2O)(1000)}{(mL\ sample)(1000)} =$$

$$\frac{(N\ I_2)(mL\ I_2)(248.19)(1000)}{(3.00)(1000)} =$$

$82.73\ (N\ I_2)(mL\ I_2)$

2. Ammonium Thiosulfate:

$(NH_4)_2S_2O_3$ [58.6%], mL/L* =

* The average of nine typical lots of ammonium thiosulfate stock solution tested was 58.6% as ammonium thiosulfate and contained 0.7% as ammonium sulfite, the sp gr = 0.5688.

$$\frac{(N\ I_2)(mL\ I_2)[eq\ wt\ (NH_4)_2S_2O_3](10^3)(10^2)}{(mL\ sample)[\%(NH_4)_2S_2O_3][sp\ gr\ (NH_4)_2S_2O_3](10^3)} =$$

$$\frac{(N\ I_2)(mL\ I_2)[63.8](1000)(100)}{(3.00)[58.6][0.5688](1000)} =$$

$63.8\ (N\ I_2)(mL\ I_2)$

Bisulfate and Sulfite (as Na_2SO_3)

$Na_2S_2O_3$, g/L = 2.10 [(H.I.) – (mL I_2 for hypo)]

Table 1 Reducing Capacity of Fixer Constituents

(mL of standardized 0.1 N Iodine Consumed by 1.00 g or mL of Constituent)		
Constituent	**Theoretical**	**By Experiment**
Ammonium thiosulfate solution, mL	53.1	53.5*
Sodium sulfite, g	159	156†
Sodium bisulfite, g	192	207‡
Sodium thiosulfate	40.3	40.3§

* Using a sample of solution having an assay of 58.5 percent and containing 0.86 percent ammonium sulfite (ANSI PH4.252-1987). Ammonium thiosulfate and ammonium sulfite contributed to theoretical value to the extent of 52.1 and 0.98 respectively, and to the experimental value by 52.1 and 1.4 respectively.
† Using photographic grade sodium sulfite which has a minimum assay of 97.0 percent as sodium sulfite (ANSI PH4.275-1987).
‡ Using sodium bisulfite which assayed 107.5 percent as sodium bisulfite (ANSI PH4.276-1987).
§ Using photographic-grade sodium thiosulfate crystalline which has an assay between 99.0 and 101.0 percent as sodium thiosulfate pentahydrate (ANSI PH4.250-1987

Table 2 Contribution of Constituents to Hypo Index of a Process ECP-2 Fixer

Replenisher	Constituent	Mix Value	mL 0.1 N I_2 Consumed Theoretical
Fresh	Ammonium thiosulfate*	170.0 mL	27.1
	Sodium sulfite	16.0 g	7.6
	Sodium bisulfite	5.8 g (3 mL sample)	3.3 38.0

* 58.6 Percent solution.

Potentiometric Determination of Iodide in Reversal Color Developers

ECR-925A

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	DR-150/151*	DR-150

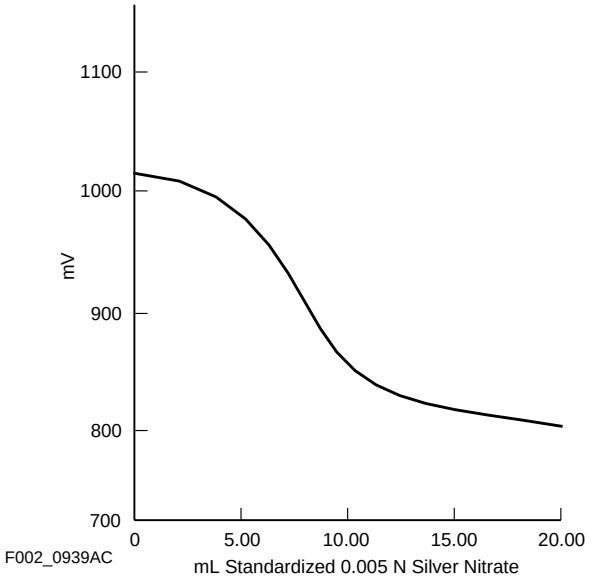
* This method was developed for a process other than VNF-1 and RVNP that did not contain sodium thiocyanate. Thiocyanate is a well-known interferent to halide determinations when using a silver ion titration, due to co-precipitation. A significant high bias could exist when applying this procedure to determine bromide in developers containing thiocyanate.

PRINCIPLE

A sample of developer is made highly alkaline to prevent the formation of an emulsion during the extraction of CD-3 and RA-1 with chloroform. After the extraction, the aqueous phase is acidified with glacial acetic acid. The solution is then titrated potentiometrically with a silver nitrate solution using silver billet and double junction electrodes. The inflection point is determined by applying the concentric arcs technique.

The addition of sodium chloride alters the shape of the potentiometric curve such that the end point determined by this technique is slightly beyond the actual inflection point. However, the concentric arcs technique is used because it produces more reliable results than other techniques for determining the location of the end point. The difference between the determined end point and the actual inflection point is fairly constant and is calibrated out. See Figure 1 for a typical titration curve.

Figure 1 Typical Iodide Titration Curve in Reversal Color Developers



This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

This method uses chloroform-a highly toxic solvent and suspected carcinogen. The following strict precautions must be observed when using chloroform:

1. *An exhaust (fume) hood must be used that provides 100-ft/min minimum average air face velocity*. The greatest laboratory hazard presented by chloroform is through inhalation. The odor threshold of chloroform (50 ppm) is much higher than its threshold limit value (TLV) of 2 ppm. Therefore, since there is no odor warning, toxic levels can be present without an analyst's awareness.
2. *Impervious gloves should be worn when handling chloroform*. Chloroform can cause defatting, and subsequent cracking of the skin. In addition, this defatting can make the skin more susceptible to dermatitis from other sources.
3. *Eye protection, in the form of safety glasses or goggle must be worn by the analyst*. Chloroform vapors can cause irritation of the eye—especially to the conjunctiva (the eye's membrane covering). Splashing of the liquid into the eye can be painful. If it occurs despite precautions, wash the eye immediately and seek medical attention.
4. *Keep chloroform away from heat and open flames*. Although not a flammable substance, chloroform may break down to phosgene ($COCl_2$), which further decomposes to hydrochloric acid and carbon monoxide after inhalation into the body.
5. *Local regulations must be adhered to regarding the use and/or disposal of chloroform*. Regulations concerning chloroform use may vary from one locality to another. It is the responsibility of the laboratory supervisor to be aware of, and follow, these regulations.

RELIABILITY

Three standard reversal color developer mixes containing 20, 50 and 80 mg/L of potassium iodide were analyzed in duplicate by two analysts. For the first analysis of each mix the analyst added RA-1, equivalent to 56 mg/L, to the sample before treatment. The second analysis was performed after a 168 mg/L RA-1 addition. The RA-1 was added just prior to the analyses because of its tendency to decompose in developer solutions during storage. The procedure was repeated the next day using three color developer mixes from another color reversal process.

The least mean square line and 95 percent confidence limits for individual results are based on these data. The 95 percent confidence limits are ± 1.71 mg/L of KI.

SPECIAL APPARATUS

- pH Meter
- Reference Electrode, Double Junction, Orion No. 900200 or equivalent [Filling solutions: Sat. Silver Chloride soln. or Orion No. 900002 (inner chamber) and 10 percent potassium nitrate, or Orion No. 900003 (outer chamber)]
- Indicator Electrode, Silver Billet, Beckman No. 39261 or equivalent

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 10 N Sodium Hydroxide, NaOH
- Chloroform, $CHCl_3$, reagent-grade
- Acetic Acid, Glacial, CH_3COOH, Reagent ACS
- Sodium Chloride, NaCl
- 0.005 N Silver Nitrate, $AgNO_3$ (standardized to 5 decimal places)

PROCEDURE

Extraction

1. Add 250 mL of developer, from a graduated cylinder, to a 500-mL separatory funnel.
2. Add 25 mL of 10 N sodium hydroxide from a tip-up pipet.
3. Add 100 mL of chloroform from a tip-up pipet.

Warning

DANGER! Suspected carcinogen. **WARNING!** Harmful if inhaled. Can cause embryo-fetal injury Avoid breathing vapor. Keep container closed. Use with adequate ventilation. Avoid prolonged or repeated contact with skin.

4. Stopper and shake the funnel a few times; then vent through the stopper. Continue to shake the funnel for 30 seconds, venting occasionally.
5. Discard the lower (chloroform) layer and any emulsion present at the interface.

   Note: Waste chloroform should be disposed of according to locally acceptable practices.
6. Repeat Steps 3, 4, and 5 twice.

Titration

Note: Prepare the electrode pair and calibrate the electrode-instrument system according to the instructions given in Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revision.

1. Drain the remaining (aqueous) layer into a 400-mL beaker.
2. While stirring on a magnetic mixer, add 35 mL of glacial acetic acid from a tip-up pipet.
3. Add and dissolve 10 g of sodium chloride.
4. Titrate the sample with standardized 0.005 N silver nitrate using a 25-mL buret. See instructions for potentiometric titrations in Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions.*
5. Determine the end point using the concentric arcs technique from Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions.*

Calculation

$$KI, mg/L = 708(N\ AgNO_3)(mL\ AgNO_3) - 3.43$$

Potentiometric Determination of Potassium Iodide in First Developers

ECR-929C

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	DR-100/101	DR-150

PRINCIPLE

A potentiometric titration of iodide can be done successfully only in a limited range of iodide to bromide and iodide to thiocyanate ratios. If the bromide and thiocyanate concentrations are considerably higher than the iodide concentration, poor titration curves result due to small potential changes and co-precipitation. The ratios in VNF-1 and RVNP first developers are unfavorable, being in excess of 1000:1. Through a precipitation enrichment process, these ratios can be improved.

The iodide is precipitated with silver nitrate over a five-minute period. Only a small amount of bromide precipitates under experimental conditions. The precipitate is collected on a filter and washed. The iodide is then solubilized in a hydroquinone silver-halide developer. It is filtered twice to remove the silver metal generated during development that can interfere with the analysis. The iodide in the filtrate is titrated potentiometrically with silver nitrate.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

All calibration mixes were made to current specifications. Any considerable change in salt content, particularly bromide, may necessitate recalibration. Four standard mixes containing 5.00, 10.00, 15.00, and 20.00 mg/L potassium iodide, respectively, were analyzed by three analysts in two laboratories. The 95 percent confidence limits were determined to be ± 0.6 mg/L potassium iodide. The iodide additions to the calibration mixes were made with a potassium iodide stock solution that was assayed to be 1.00 g/L potassium iodide.

SPECIAL APPARATUS

- pH Meter
- Reference Electrode, Double Junction, Orion No. 900200 or equivalent
- Indicator Electrode, Silver Billet, Beckman No. 39261 or equivalent
- Millipore Filter apparatus
- Millipore Filter membrane, 0.45 micron porosity

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 18 N Sulfuric Acid, H_2SO_4
- Celite filter aid
- 0.001 N Silver Nitrate, $AgNO_3$ (standardized to 5 decimal places)
- 1.0 M Ammonium Nitrate, NH_4NO_3
- Silver Halide Developer

PROCEDURE

Apparatus Preparation

1. Avoidance of contamination is essential. All glassware should be cleaned with sulfuric-dichromate cleaning solution prior to use.
2. A double junction/silver billet electrode pair should be used for the potentiometric titrations. The electrode pair may be stored in distilled water when not in use.

Silver Iodide Precipitation

1. Pipet, wipe the pipet before leveling, 200.0 mL of sample into a 1-litre conical flask.
2. Set the 1-litre conical flask in an exhaust hood and stir moderately on a magnetic stirrer.
3. While stirring add very slowly, from a tip-up pipet, 50 mL of 18 N sulfuric acid to the conical flask.

Caution

ACID. Avoid contact with skin and eyes. In case of contact, flush with water.

Note: Do not add Foamex to control the foaming action.

4. Add approximately 0.3 to 0.4 grams of Celite to the flask. (Two scoops from a Coors No. 2 porcelain spoon is about 0.3 to 0.4 grams.)
5. Add, from a graduated cylinder, 50 mL of standardized 0.001 N silver nitrate to the solution as it stirs. Immediately set a timer for five minutes and continue to stir for that period.
6. As the solution stirs, assemble a Millipore filter holder and filter membrane (type HAWP 0.45 micron porosity) on a 500-mL filter flask.
7. At the end of the five-minute stirring period, connect the aspirator hose and filter the solution through the Millipore apparatus, retaining the stirring bar in the conical flask by means of another mag-bar outside the flask. Do not discard the conical flask. When filtering is completed, disconnect the aspirator hose.
8. Rinse the sides of the original 1-litre conical flask with 25 mL of 1.0 M ammonium nitrate from a tip-up pipet. Retaining the stirring bar in the conical flask, rinse the sides of the Millipore funnel by pouring the solution through a long, thin-stemmed glass funnel. Reconnect the aspirator hose and filter the solution into the 500-mL filter flask. Disconnect the aspirator hose when the filtering is completed. Save both the long-stemmed funnel and the 1-litre conical flask.
9. Only rinse the inside and outside of the stem of the Millipore funnel with distilled water from a squeeze bottle. Do not disassemble the filter holder and membrane. Discard the filtrate and place the filter holder and membrane on a clean 250-mL filter flask.

Silver Iodide Development

1. Add, from a graduated cylinder, 20 mL of silver-halide developer to the original 1-litre flask.

   Note: Do not expose the silver-halide developer to air any longer than necessary. When not in use, store the silver-halide developer in a cool, dark place. A developer that has turned brown should not be used. The developer is still usable if it has a light tan color.
2. Swirl the conical flask and immediately rinse the sides of the Millipore funnel (with no applied suction) by pouring the developer through the long-stemmed funnel. Set a timer for five minutes and allow the developer to stay in the Millipore funnel for that period. At one-minute intervals, swirl the Millipore funnel for several seconds.
3. During the five-minute waiting period, add, from a tip-up pipet, 50 mL of distilled water to the 1-litre conical flask and swirl.
4. At the end of the five-minute waiting period, connect the aspirator hose to the Millipore filter apparatus and filter the solution into the clean 250-mL filter flask. (Care must be taken to prevent loss of the filtrate through the aspirator hose.) Disconnect the aspirator hose when the filtration is completed.
5. Swirl the 1-litre conical flask and wash the sides of the Millipore funnel by pouring the solution from the flask through the long-stemmed funnel. Connect the aspirator hose and filter the solution. Disconnect the aspirator hose when the filtration is completed.
6. Assemble a Millipore filter holder and filter membrane (type HAWP 0.45 micron porosity) on a 250-mL filter flask.
7. Quantitatively transfer the filtrate from Step 5 into the Millipore apparatus set up in Step 6. Connect the aspirator hose and filter the solution. Disconnect the aspirator hose when the filtration is completed.
8. Quantitatively transfer the filtrate into a 250-mL beaker.
9. Slowly add 50 mL of 18 N sulfuric acid to the beaker from a tip-up pipes or graduated cylinder.

Caution

ACID. Avoid contact with skin and eyes. In case of contact flush with water.

Titration

Note: For preparation of the electrode pair, refer to *Apparatus Preparation* at the beginning of the procedure.

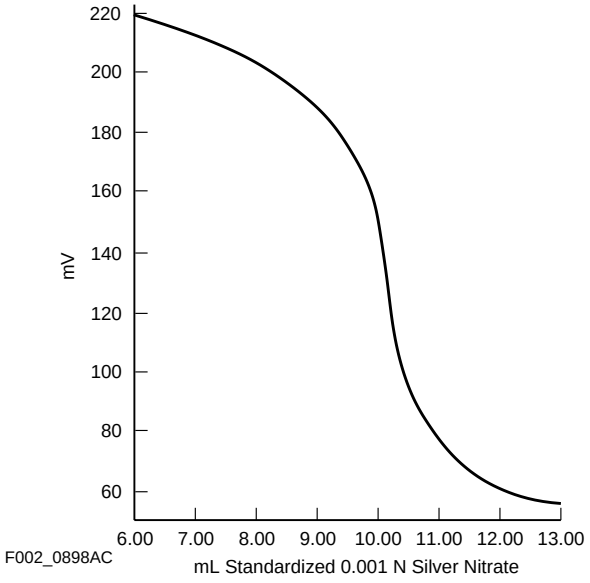
1. Stir the solution moderately on a magnetic stirrer.
2. Equilibrate an electrode pair by immersing them into the solution and waiting several minutes for the meter to settle down.
3. Titrate potentiometrically with standardized 0.001 N silver nitrate using a 50R-mL buret.

Note: Because of the relatively low iodide level, the system may take several minutes to equilibrate between additions, particularly at or near the end point. Taking potential readings at specific intervals, such as three minutes, in the vicinity of the end point, will result in uniform results. This is generally only necessary near the end point. Faster equilibration times at the beginning and end of the titration do not require a time interval quite as long. A potential change of less than 5 mV over a three-minute period can generally be regarded as a sign of equilibrium conditions.

These titrations may be done on automatic titrators equipped with controls for slow titration speeds. In any case, results from automated titrations should be checked against those from manual titrations prior to using an automatic titrator routinely. Refer to Figure 1 for a typical titration curve.

4. Determine the inflection point using the Concentric Arcs from Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revision.

Figure 1 Typical Iodide Titration Curve in Reversal First Developers



Calculation

Potassium Iodide, mg/L =

$$878(\text{N } AgNO_3)(\text{mL } AgNO_3) + 0.52$$

Titrimetric Determination of Persulfate in Persulfate Bleach

ECR-1125B

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	SR-45	SR-45

INTRODUCTION

This method is based upon the oxidation of ferrous ion by persulfate in an acid solution at room temperature. A known excess of ferrous ion is added to the sample and the residual ferrous ion is titrated with standardized sulfato cerate. A blank determination should be run daily because ferrous solutions are slowly oxidized by air during use.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

RELIABILITY

The 95 percent confidence limits for an individual determination are expected to be ± 0.24 g/L of total oxidizing compounds reported as potassium persulfate.

REAGENTS

Use reagents that are ACS Reagent Grade unless specified otherwise.

- 7.0 N Sulfuric Acid, H_2SO_4
- 0.25 N Ferrous Ammonium Sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$
- 0.05 N Sulfato Cerate (standardized to 4 decimal places)
- Ferroin Indicator

PROCEDURE

Persulfate Determination

1. Pipet (wipe the pipet before leveling) the indicated sample size into a 250-mL conical flask equipped with a magnetic stir bar.

Process	Sample Size
VNF-1/LC	1.00 mL
RVNP	1.00 mL

2. Add 50 mL of distilled water from a tip-up pipet.

Warning

ACID. Avoid contact with skin and eyes. In case of contact, flush with water.

3. Add 15 mL of 7.0 N sulfuric acid from a tip-up pipet.
4. Pipet 10.0 mL of 0.25 N ferrous ammonium sulfate into the flask. Using a squeeze bottle, wash down the sides of the flask with distilled water.
5. Swirl the solution to mix, stopper the flask and let it stand for 3 minutes.

   Note: Longer standing times do not adversely affect the titration providing the solution is protected from air.

6. Add 4 drops of Ferroin indicator and from a 50-mL buret, titrate with standardized 0.05 N sulfato cerate to the first *light* cyan color.
7. Record the end point as mL A.

Reagent Blank Determination

Note: A reagent blank should be run at least once per day because the 0.25 N ferrous ammonium sulfate will slowly change with usage.

1. Add 50 mL of distilled water, with a tip-up pipet, to a 250-mL conical flask equipped with a magnetic stir bar.
2. Repeat Steps 3 through 6 of the *Persulfate Determination* section.
3. Record the end point as mL B.

Calculations

Note: Total oxidizing compounds can be reported as potassium, ammonium, or sodium persulfate, g/L.

1. Potassium Persulfate:

   VNF-1/RVNP

   $K_2S_2O_8$, g/L = 6.75(mL B – mL A)

2. Ammonium Persulfate:

   VNF-1/RVNP

   $(NH_4)_2S_2O_8$, g/L = 5.70(mL B – mL A)

3. Sodium Persulfate:

   VNF-1/RVNP

   $Na_2S_2O_8$, g/L = 5.95(mL B – mL A)

Spectrophotometric Determination of Kodak Reversal Agent in Reversal Color Developer
ECR-0001-1

INTRODUCTION

KODAK Reversal Agent, reducing agent Tertiary Butylamine Borane (RA-1), reduces molybdophosphoric acid to molybdenum blue. Since the intensity of the molybdenum blue is affected by KODAK Anti-Calcium No. 4, several milliliters of the sequestrant are added to the reaction mixture to saturate the system. The absorbance of the molybdenum blue formed is measured at 725 nm.

The molybdenum blue color is both temperature and time dependent, however it was determined that the temperature effect is not practically significant when reagents are at room temperature (20°C - 25°C). Time dependence effect is minimized using a specified procedure time of five minutes.

Use of this method requires handling potentially hazardous chemicals. Material Safety Data Sheets (MSDS) should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

A. Repeatability Standard Deviation, $1s_r$ and 95 Percent Confidence Estimate (not including Bias)

Repeatability standard deviation is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample, with one instrument, within one day).

The 95 percent confidence estimate (calculated using the repeatability standard deviation) around a single test result will include the mean value 95 percent of the time.

To obtain the repeatability data, a single skilled analyst performed five (5) replicates on each of the following solutions during methods development.

1. A “fresh” Reversal Color Developer tank prepared with all components at their respective “working tank” aim concentrations.
2. A “seasoned” Reversal Color Developer tank analyzed spectrophotometrically as received, at 113.3 mg/L RA-1.
3. The same “seasoned” solution as in number 2, above, reanalyzed after making an analytically weighed, standard addition of 33.0 mg/L RA-1.

RA-1				
Sample	**Mean (mg/L RA-1)**	**N**	**Repeatability Standard Deviation, $1s_r$ (mg/L RA-1)**	**95 Percent Confidence Estimate (mg/L RA-1)**
“Fresh” (prepared at 82.2 mg/L)	83.0	5	1.48	± 4.1
“Seasoned” as Received	113.3	5	3.25	± 9.0
“Seasoned” plus Standard Addition	139.3	5	0.84	± 2.3

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A bias of 0.8 mg/L RA-1 was found not to be statistically significant at the 95 percent confidence level.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

Statistically, the recovery of 78.79 percent was significantly different from 100 percent at the 95 percent confidence level, but was judged not to be practically significant.

B. REPRODUCIBILITY

Customer Standard Deviation, $1s_c$ & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Four analysts analyzed three Reversal Color Developer tank samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A "fresh" Reversal Color Developer tank prepared with all components at their respective "working tank" aim concentrations.
2. A "seasoned" tank solution analyzed as received as 28.4 mg/L RA-1.
3. The same "seasoned" solution, as in number 2, above, analyzed in the same manner, after making a standard addition of 18.0 mg/L RA-1.

RA-1				
Sample	**Mean (mg/L RA-1)**	**N**	**Reproducibility Standard Deviation, $1s_c$ (mg/L RA-1)**	**95 Percent Confidence Estimate (mg/L RA-1)**
"Fresh" (prepared at 82.0 mg/L)	79.2	14	3.51	± 7.6
"Seasoned" as Received	28.4	14	3.34	± 7.2
"Seasoned" plus Standard Addition	40.1	14	3.89	± 8.4

Bias

Bias is a statistically significant deviation of the mean from the known mix level at a 95 percent confidence level. It is determined for fresh samples only. Bias is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A bias of –2.8 mg/L RA-1 was found to be statistically significant at the 95 percent confidence level, however it was judged not to be practically significant.

Recovery

Recovery is used for seasoned samples, since the component concentration level was not determined independently of the test method. It is defined as the calculated mean for the seasoned sample with a standard addition of the component minus the mean for the seasoned sample, divided by the actual amount of the standard addition. It is expressed as a percentage.

The recovery of 65.00 percent was statistically significantly different from 100 percent at the 95 percent confidence level, but was judged not to be practically significant due to rapid oxidation of RA-1 during the two day study.

APPARATUS

- Spectrophotometer with a tungsten lamp
- 1-cm Silica Cell

All volumetric glassware should meet all Class A specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- KODAK Anti-Calcium, No. 4
- Molybdenum Reagent
- 1.0 N Sulfuric Acid, H_2SO_4

PROCEDURE

A. Treatment of Sample

1. Add, from a tip-up Pipet, 5 mL of KODAK Anti-Calcium No. 4 to a 100 mL volumetric flask containing a magnetic stir bar. (Allow 15 seconds for the tip-up pipet to drain.)
2. Start stirring moderately. Pipet (wipe the pipet before leveling) 3.00 mL of Color Developer solution into the flask.
3. Set, but do not start, a timer for five minutes.
4. Add, from a tip-up pipet, 10 mL of molybdenum reagent to the flask. Immediately start the timer.
5. To the flask, add, from a graduated cylinder, 80 mL of 1.0 N sulfuric acid that is at room temperature (20.0°C - 24.0°C).
6. Remove the stirring bar and dilute the solution to its final 100.0 mL volume with 1.0 N sulfuric acid.
7. Stopper the flask and invert it five times to complete mixing.

B Absorbance Measurement

1. Zero the spectrophotometer vs. air.
2. After four minutes have elapsed, rinse and fill a 1-cm silica cell with the molybdenum blue solution (Step A.7, above).
3. Place the cell in the sample compartment of the spectrophotometer and measure the solution absorbance at 725-nm (AR) at exactly five minutes after the addition of the molybdenum reagent in Step A.4, above. Record the absorbance.

Note: Do not place the cell in the spectrophotometer for longer than one minute.

CALCULATIONS

$y = mx + b$

Definition of the equation is found in the Regression section of Appendix A.

$$\text{mg/L RA-1} = m\,(A_{725}) + b$$

Where:

m = slope of the calibration line [(mg/L) RA-1 / $ABU_{@725}$]

A_{725} = Absorbance of sample at 725 nm

b = the intercept of the calibration line with the y-axis (mg/L RA-1)

Each laboratory should establish its own regression equation based on a set of calibration standards. Appendix A explains this calibration procedure. The regression equation may be different for each spectrophotometer. A typical regression equation line for the effluent is described by the following equation:

$$\text{mg/L RA-1} = 143.3\,(A_{725}) - 4.355$$

Example:

$A_{725} = 0.847$

$\text{mg/L RA-1} = 143.3\,(0.847) - 4.355$

$= 117.0$

APPENDIX A

Calibration of Spectrophotometer RA-1 in Reversal Color Developer

This Appendix should be used to establish the initial calibration equation, whenever the instrument has been adjusted, or to recheck the calibration (at least every six months)

A. Preparation of Standards

A stock standard solution without RA-1 is prepared by dissolving the remaining required constituents of a Reversal Color Developer in a 1 liter volumetric flask and diluting to the mark with reagent water at room temperature.

1. The stock standard solution is added to a 100 mL volumetric flask and labeled 0.0 mg/L RA-1.
2. Two mg of RA-1 is weighed to the nearest 0.1 mg and added to a 100 mL volumetric flask and diluted to volume with the stock standard solution. Stopper the flask and invert six times to insure proper mixing. This flask is labeled 2 mg/L RA-1.
3. Five mg of RA-1 is weighed to the nearest 0.1 mg and added to a second 100 mL volumetric flask and diluted to volume with the stock standard solution. Stopper the flask and invert six times to insure proper mixing. This flask is labeled 5 mg/L RA-1.
4. Seven mg of RA-1 is weighed to the nearest 0.1 mg and added to a second 100 mL volumetric flask and diluted to volume with the stock standard solution. Stopper the flask and invert six times to insure proper mixing. This flask is labeled 7 mg/L RA-1.
5. Ten mg of RA-1 is weighed to the nearest 0.1 mg and added to a second 100 mL volumetric flask and diluted to volume with the stock standard solution. Stopper the flask and invert six times to insure proper mixing. This flask is labeled 10 mg/L RA-1.

B. Analysis of Standards

1. Run each sample by the method described in the preceding Procedure.
2. Table of Data gathered from Analysis of Standards

RA-1 Standard (mg/L)	Abs_{725}	Abs_{725}
0.0	0.050	0.055
2.4	0.182	0.179
4.9	0.379	0.365
7.0	0.499	0.503
10.9	0.817	0.792

C. Regression

1. This data was processed by a least squares linear regression to develop the line represented by equation, $y = mx + b$:

Where:

y = mg/L RA-1

m = slope of the line or the relation between absorbance and concentration determined during calibration [(mg/L)/absorbance]

x = absorbance of sample at 725 nm

b = the intercept of the calibration line with the y-axis (in mg/L RA-1)

2. The equation generated using the above data was:

$$\text{RA-1, mg/L} = 143.3\ (ABS_{@725\ nm}) - 4.355$$

3. The calibration equation was done in the following manner on a (SHIMADZU Model UV 160 U) spectrophotometer. Five fresh solutions were prepared (see Step #1 of *A. Preparation of Standards*). Each solution was analyzed twice to create a linear regression, based on 10 data points, for each spectrophotometer being used. Each laboratory should calibrate their spectrophotometer, otherwise an unknown bias may exist.

APPENDIX B

Effect of Temperature in Spectrophotometric Determination of RA-1 in Reversal Color Developer

A. Preparation of Standards

A stock standard solution was prepared by dissolving the required constituents of a Reversal Color Developer in a 1 liter volumetric flask and diluting to the mark with reagent water at room temperature.

1. Five 250 mL beakers were each filled with approximately 200 mL of 1.0 N sulfuric acid.
2. Each beaker was maintained at the following temperatures:

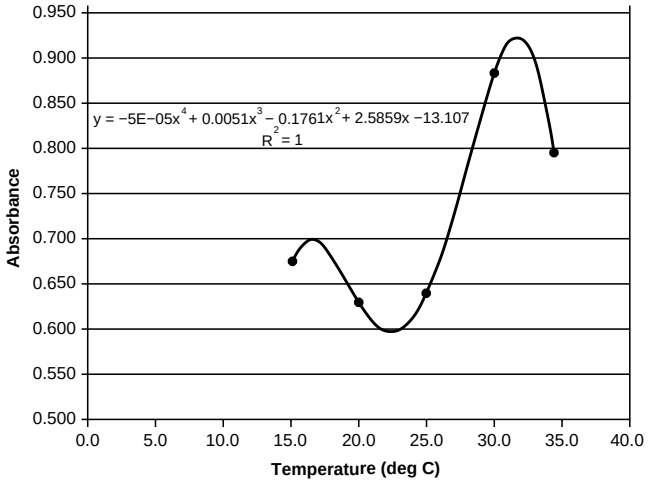
Beaker	Temperature (°C)
1	15.1
2	20.8
3	24.8
4	30.0
5	34.5

B. Analysis of Standards

1. A sample of the stock standard solution was analyzed by the method described in the preceding Procedure using the 1.0 N sulfuric acid from Beaker 1 in step 1 of *,A. Preparation of Standards*.
2. This procedure was repeated four times using the remaining four beakers of temperature controlled 1.0 N sulfuric acid.
3. Table of Data gathered from Analysis of Standards.

Beaker	Abs_{725}	RA-1 (mg/L)
1	0.676	92.52
2	0.616	83.92
3	0.630	85.92
4	0.875	121.03
5	0.797	109.86

4. Graph of Temperature Dependence for RA-1 in Reversal Color Developer Determination.



F002_1127AC

Potentiometric Determination of Silver in Fixing Baths

1208E

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	F-36	F-38

INTRODUCTION

The sample is made alkaline to prevent the decomposition of sodium thiosulfate, which occurs in acid solutions. Ethylenedinitrilo tetraacetic acid (EDTA) is added to minimize interference of other metal ions. The EDTA reagent does not prevent interference from zinc ions. Gelatin is added to prevent the coagulation of the silver sulfide that is formed. This prevents the coagulated silver sulfide from occluding the silver ions.

The sample containing silver is titrated potentiometrically with standardized sodium sulfide using a silver billet/double junction electrode pair. Changes in the volume of sample and of sodium hydroxide/EDTA reagent affect the silver results. If a small amount of sample is used, the sample volume must be adjusted to about 300 mL with 1.0 M sodium thiosulfate.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

Four fixing baths containing 0.100 to 1.00 g/L silver (Ag) were analyzed by two analysts. The 95 percent confidence limits for an individual determination are ± 0.01 g/L silver.

SPECIAL APPARATUS

- pH Meter or Automatic Titrator
- Reference Electrode, Double Junction, Orion No. 900200 or equivalent (filled with 10 percent potassium nitrate bridge solution in outer chamber)
- Indicator Electrode, Silver Billet, Beckman No. 39261 or equivalent

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 1.0 M Sodium Thiosulfate, $Na_2S_2O_3$
- 1 N Sodium Hydroxide/Ethylenedinitrilo Tetraacetic Acid (EDTA) Reagent, 1 N NaOH/EDTA
- 4 g/L Gelatin
- 0.06 N Sodium Sulfide, Na_2S (standardized to 4 decimal places)

PROCEDURE

Sample Treatment

1. Pipet (wipe the pipet before leveling) sample into a 600-mL beaker according to the table below.
2. From a 250-mL graduated cylinder, add to the 600-mL beaker the amount of 1.0 M sodium thiosulfate indicated in the table.

Silver Concentration g/L	Sample, mL	1.0 M Sodium Thiosulfate, mL
Less than 1	300*	0
1 to 3	100.0	200
More than 3	50.0	250

* Use a graduated cylinder.

3. Add 100 mL of 1 N NaOH/EDTA reagent from a 50-mL tip-up pipet.
4. Add 10 mL of 4 g/L gelatin from a tip-up pipet.

Titration

Titrate the sample with standardized 0.06 N sodium sulfide using a silver billet/double junction electrode pair. For instructions, see Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, (or subsequent revision).

Note: Avoid unnecessary exposure of the standardized sodium sulfide to air. The reagent should be standardized each week. Discard all unused reagent remaining in any open bottles at the end of each day (60 mL reagent bottles are suggested for storage of 0.06 N sodium sulfide).

Calculation

Silver, g/L =

$$\frac{(N\ Na_2S)(mL\ Na_2S)(eq\ wt\ Ag)(1000)}{(mL\ sample)(1000)} =$$

For samples containing less than 1 g/L silver

$$\frac{(N\ Na_2S)(mL\ Na_2S)(107.88)(1000)}{(300)(1000)} =$$

$0.360(N\ Na_2S)(mL\ Na_2S)$

For samples containing 1 to 3 g/L silver

$$\frac{(N\ Na_2S)(mL\ Na_2S)(107.88)(1000)}{(100)(1000)} =$$

$1.08(N\ Na_2S)(mL\ Na_2S)$

For samples containing more than 3 g/L silver

$$\frac{(N\ Na_2S)(mL\ Na_2S)(107.88)(1000)}{(50)(1000)} =$$

$2.16(N\ Na_2S)(mL\ Na_2S)$

Potentiometric Determination of Sodium Chloride in Persulfate Bleach

ECR-937

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formula	—	—	SR-45	SR-45

INTRODUCTION

The sodium Chloride content of a potassium persulfate bleach is analyzed by direct titration with standardized silver nitrate solution. The portentiometric titration is done manually with a pH meter or on an automatic titrator. The results follow the indicated stoichiometry completely.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

RELIABILITY

Four standard mixes of fresh persulfate bleach were analyzed by two analysts in two laboratories. The mixes contained 5.00, 10.00, 15.00, and 20.00 g/L of sodium Chloride respectively, and 30.00 g/Lof potassium persulfate. The 95 percent confidence limits for a single determination are ± 0.11 g/L sodium chloride.

SPECIAL APPARATUS

- PH Meter
- Reference Electrode, Double Junction, Orion No. 900200 or equivalent
- Orion Double Junction Reference Electrode, Catalog No. 90-02-00 or equivalent
- Indicator Electrode, Silver Billet, Beckman No. 39261 or equivalent)

Note: Use pipets and volumetric glassware meeting the "Class A" definition by NIST (National Institute of Standards and Technology, formerly National Bureau of Standards).

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 7.0 N Sulfuric Acid, H_2SO_4
- 0.05 N Silver Nitrate, $AgNO_3$ (standardized to four decimal places)

PROCEDURE

Sample Treatment

1. Pipet, wipe before leveling, 5.00 mL of sample into a 250-mL beaker containing a magnetic stirring bar.
2. Add 10 mL of 7.0 N sulfuric acid from a tip-up pipet.
3. Add approximately 150 mL of distilled water to the beaker. Stir moderately on a magnetic stirrer.

Titration

1. Titrate the sample potentiometrically using standardized 0.05 N silver nitrate following Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions,* or any subsequent revision.
2. Determine the end point using the concentric arcs technique, Method ULM-0003-01.

CALCULATIONS

$$\text{NaCl, g.L} = \frac{(\text{N } AgNO_3)(\text{mL } AgNO_3)(\text{eq wt NaCl})(1000)}{(\text{mL sample})(1000)}$$

$$= \frac{(\text{N } AgNO_3)(\text{mL } AgNO_3)(58.45)(1000)}{(50)(1000)}$$

$$= 11.69\ (\text{N } AgNO_3)(\text{mL } AgNO_3)$$

Iodometric Determination of Total Sulfite in Reversal Color Developers Containing KODAK Reversal Agent, RA-1

ECR-1303

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	DR-150/151	DR-150

INTRODUCTION

KODAK Reversal Agent, RA-1 contributes a positive interference to the iodometric determination of the total sulfite in a color developer. The effect of this interference can be corrected if the concentration of RA-1 is known. The iodometric titration and known reversal agent concentration can then be used to calculate the real concentration of sodium sulfite in the sample.

PRINCIPLE

For the iodometric titration, the developer sample is added to an excess of iodine, formed by acidifying standard potassium iodate solution and adding potassium iodide. Part of the iodine is reduced to iodide by the sulfite in the sample; the remaining iodine is measured by titrating it with standard sodium thiosulfate using starch indicator. Since the quantity of sulfite is equivalent to the quantity of reduced iodine and since the quantity of sodium thiosulfate used in the titration is equivalent to the quantity of remaining iodine, the difference between the total iodine and the volume of sodium thiosulfate is a measure of the sodium sulfite concentration.

In developers containing RA-1, some iodine is also reduced by the reversal agent and this will erroneously be calculated as sulfite unless a correction is made. The RA-1 is analyzed using Method *ECR-0001-1* (or subsequent revision).

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST).

RELIABILITY

Photographic-grade sodium sulfite (Na_2SO_3) is usually less than 100 percent pure (minimum assay is 98.5 percent). Photographic-grade sodium bisulfite ($NaHSO_3$) is a mixture of sodium bisulfite, sodium metabisulfite ($Na_2S_2O_5$), and water. Its purity, as determined by an iodine titration and expressed as sodium bisulfite, is approximately 107.5 percent. If it were pure sodium metabisulfite it would assay 110 percent as sodium bisulfite. One gram of photographic-grade sodium bisulfite is equivalent to 1.30 grams of sodium sulfite (100 percent).

Correction equations were calculated from ten analyses of sodium sulfite in color developer with RA-1 concentrations ranging from 0 to 125 mg/L. The 95 percent confidence limits are essentially the same for developers with or without RA-1. The 95 percent confidence limits for an individual determination are ± 0.05 g/L sodium sulfite.

Reagents

Use ACS Reagent Grade reagents unless otherwise specified.

- 0.1 N Potassium Iodate, KIO_3 (standardized to 4 decimal places)
- 7.0 N Sulfuric Acid, H_2SO_4
- 0.60 M Potassium Iodide, KI
- 0.1 N Sodium Thiosulfate, $Na_2S_20_3$ (standardized to 4 decimal places)
- Starch Indicator

PROCEDURE

Sample Treatment

1. Pipet, wipe the pipet before leveling, 50.0 mL of standardized 0.1 N potassium iodate into a 250-mL Erlenmeyer flask.
2. Add 25 mL of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 25 mL of 0.60 M potassium iodide from a tip-up pipet.
4. Pipet (wipe) 25.0 mL of sample into the flask.

Titration

1. Titrate with standardized 0.1 N sodium thiosulfate to a *light yellow color*. Then, add 5 mL of starch indicator from a tip-up pipet and continue the titration until the *blue color* disappears.
2. Analyze for RA-1 using Method *ECR-0001-1* (or subsequent revision).

Calculations

1. Calculate the apparent total sulfite concentration using the following equation:

Apparent Total Na_2SO_3, g/L =

$$\frac{[(N\ KIO_3)(mL\ KIO_3) - (N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)](eq\ wt\ Na_2SO_3)(1000)}{(mL\ sample)(1000)} =$$

$$\frac{[(N\ KIO_3)(50.0) - (N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)](63.02)(1000)}{(1.00)(1000)} =$$

$$2.521[(N\ KIO_3)(50.0) - (N\ Na_2S_2O_3)(mL\ Na_2S_2O_3)]$$

2. Correct the apparent sulfite concentration for RA-1 using the following equation:

Total Na_2SO_3, g/L =

(Apparent Na_2SO_3, g/L) – [0.0034 (RA-1, mg/L) – 0.001)]

Titrimetric Determination of Total Alkalinity of a Processing Solution

ECR-702J

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	—	—	DR-100/101 DR-150/151	DR-105 DR-150

INTRODUCTION

A critical appraisal of the pH, specific gravity, and total alkalinity of a developer mix is useful in detecting incorrect amounts of the inorganic constituents and certain of the organic constituents.

PRINCIPLE

The total alkalinity (T. Alk.) of a processing solution is defined as the millilitres of standardized 0.1 N sulfuric acid required to adjust a specified volume of processing solution to pH 4.3. That pH was selected because most salts derived from weak acids show an inflection point in their titration curves near pH 4.3.

Samples that are colored (and some colorless samples) when titrated visually do not give a clear end point, thus causing excessive variability. For this reason, potentiometric titrations are recommended. Complete titration curves need not be plotted routinely.

A pH meter can be used with glass and calomel electrodes. The instrument is standardized at the nominal temperature at which pH measurements are obtained. The temperature is usually 25°C (77°F).

Table 2, *Contribution of Constituents to Total Alkalinity of a Typical Replenisher Solution*, shows the contribution of each constituent to the total alkalinity of two developers. The T. Alk. of the negative developer is mainly a measure of the sodium carbonate content. The T. Alk. of the print developers is primarily a measure of the carbonate but also indicates a significant contribution from the sulfite.

The sample size is so chosen that the total volume of sulfuric acid consumed falls between 25 and 45 mL. The sample sizes must be specified with all total alkalinity analyses.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS's are available from your chemical supplier.

SPECIAL APPARATUS

- pH Meter or Automatic Titrator
- Calomel reference electrode filled with 3.5 N KCl, CORNING Model 476002, or equivalent
- pH Indicator electrode, CORNING Model 476024, or equivalent

Note: Use pipets and volumetric glassware meeting the "Class A" definition by the National Institute of Standards and Technology (NIST)

REAGENTS

Use ACS Reagent Grade reagents unless specified otherwise.

- 0.1 N Sulfuric Acid, H_2SO_4
  (standardized to four decimal places)

PROCEDURE

Preparation of the Meter

Follow Method ULM-191-2, *pH Measurement of Photographic Processing Solutions* (or any subsequent pH method), for making pH measurements below pH 9

Titration of the Sample and Reporting Results

1. Pipet the sample volume indicated below into a 150-mL beaker containing 50 mL of distilled water. The water should be approximately the same temperature as the buffer used in the cross-check

Process	Formula	Sample Size
VNF-1/LC	DR-100/101 DR-150/151	4.00 mL 10.0 mL
RVNP	DR-105 DR-150	4.00 mL 10.0 mL

2. Place the electrode assembly and stirrer in the solution, turn on the stirrer.
3. Titrate to a pH of 4.3 with standardized 0.1 N sulfuric acid, allowing the needle of the pH scale to equilibrate as the acid is slowly added. When the region of pH 5 is reached, add the titrant in 0.l0-mL increments, allowing the needle in the pH meter to equilibrate after each addition.
4. Report the mL of acid required to reach a pH of 4.3.

   Note: This is, by definition, the total alkalinity. Always indicate the sample size when reporting the results.
5. Remove the sample and rinse the electrode assembly with distilled water. If rinsing does not completely remove sample deposits, wipe the assembly with a cleansing tissue and rerinse. Replace in pH 4.01 potassium acid phthalate buffer.

Approximate Calculation of Total Alkalinity

The approximate total alkalinity of a fresh mix can be calculated from the mix formula and the alkalinity factor *of each constituent. Table 1, *Alkalinity of Processing Chemicals*, lists the various constituents and their alkalinity factors.

The numerical value of the total alkalinity of 1 litre of a processing solution is calculated by summing the amounts of acid that will bring each of the constituents, considering the concentrations used in the solution, to approximately pH 4.3. The sum for 1 litre of solution is then corrected for the sample size normally used in the analysis by using the following equation

$$\text{T. Alk. for the specified sample size} = \frac{[\text{mL, proposed sample size}][\text{mL, std 0.1 N } H_2SO_4 \text{ for 1 litre}]}{1000}$$

* The alkalinity factor equals the experimentally determined amount of acid required to adjust 1 g of a chemical to pH 4.3.

Table 1 Alkalinity of Processing Chemicals

Constituent	Formula	Mole Wt.	Eq. Wt.	Alkalinity Factor by Experiment
Acetic Acid	CH_3COOH	60	60	–170.4*
Ammonium Thiosulfate, 58% Solution	$(NH_4)_2S_2O_3$	148	—	2.4
Anti-Calcium, No. 4, KODAK	—	—	—	3.4
Anti-Fog, No. 9, EASTMAN	—	—	—	0
Benzyl Alcohol	$C_6H_5CH_2OH$	108	—	0
Borax, 5-hydrate	$Na_2B_4O_7 \cdot H_2O$	291	146	70.0
Citrazinic Acid	$C_6H_5NO_4$	—	—	–150.0†
Color Developing Agent, CD-2, KODAK	—	—	—	0.7
Color Developing Agent, CD-3, KODAK	—	—	—	–44.0†
Ethylenediamine (98% by wt)	$NH_2CH_2CH_2NH_2$	—	—	290.0
Quadrofos	—	—	—	24
Sodium Bicarbonate	$NaHCO_3$	84	42	120
Sodium Bromide	NaBr	103	—	0
Sodium Carbonate, Anhydrous	Na_2CO_3	106	53	189‡
Sodium Carbonate, 1-hydrate	$Na_2CO_3 \cdot H_2O$	124	62	163
Sodium Hydroxide	NaOH	40	40	250‡
Sodium Phosphate, Dibasic, 2-hydrate	$Na_2HPO_4 \cdot 2H_2O$	178	—	76.2
Sodium Phosphate, Tribasic, 12-hydrate	$Na_2PO_4 \cdot 12H_2O$	380	127	60.4
Sodium Sulfate	Na_2SO_4	140	—	0
Sodium Sulfite	Na_2SO_3	126	126	76
Sodium Thiocyanate	Na_2CNS	81	81	5.3
Sodium Thiosulfate, 5-hydrate,	$Na_2S_2O_3 \cdot 5H_2O$	248	—	0
Sulfuric Acid (Conc.)	H_2SO_4	98	49	–360

* The mL of standardized 0.1 N sulfuric acid required to adjust 1.00 g (or 1.00 mL) of chemical to pH 4.3.
† These chemicals make a negative contribution to the T. Alk.; i.e., they have a pH less than 4.3.
‡ 1000/(eq wt)(N Acid) = Calculated alkalinity contribution

Table 2 Contribution of Constituents to Total Alkalinity of a Typical Replenisher Solution

Constituent	Concentration	Alkalinity Factor	Contribution	
			mL	%
ECN-2 SD-49R				
Anti-Calcium, No. 4	2.7 mL/L	3.4	9	0.2
Na_2SO_3	2.5 g/L	76	190	4.0
Anti-Fog, No. 9	0.30 g/L	0	0	0
NaBr	0.80 g/L	0	0	0
Na_2CO_3	25.0 g/L	189	4725	99.4
$NaHCO_3$	0.6 g/L	120	72	1.5
CD-3	5.5 g/L	–44	–242	–5.1
Total for 1 L			4754	100.0
T. Alk. for 5-mL sample = (5)(4754)/1000 = 23.8				

Constituent	Concentration	Alkalinity Factor	Contribution	
			mL	%
ECP-2D SD-50R				
Anti-Calcium, No.4	1.4 mL/L	3.4	5	0.1
Na_2SO_3	4.50 g/L	76	342	8.8
CD-2	6.00 g/L	0.7	4.2	0
Na_2CO_3	18.0 g/L	189	3402	87.2
NaBr	1.60 g/L	0	0	0
NaOH	0.60 g/L	250	150	3.9
Total for 1 L			3903	100.0
T. Alk. for 10-mL sample = (10)(3903)/1000 = 39.0				

Determination of Sulfite in KODAK Reversal First Developer, Process D-94/D-95

D94-0002/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP	B/W Reversal
Formulas	—	—	—	—	D94/D95R/D95

INTRODUCTION

This method is used to determine sulfite concentration in a sample of KODAK Reversal First Developer, Process D-94 and KODAK Reversal Redeveloper, Process D-95. The sulfite content is determined by reacting the sample with excess iodine (liberated from the reaction of potassium iodate and potassium iodide under acidic conditions). The unreacted iodine is titrated potentiometrically with standard sodium thiosulfate. The sulfite content is equivalent to the reacted iodine, which is the difference between the total iodine formed and the unreacted iodine titrated.

Use of this method requires handling of potentially hazardous chemicals. Material Safety Data Sheets should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

One fresh tank sample of KODAK Reversal First Developer, Process D-94 was analyzed by one analyst on one day using one titrator. The sample was analyzed five times. The fresh sample was prepared at aim level (39.189 g/L sodium sulfite). All seasoned tank samples were analyzed in the same manner as the fresh sample. A standard addition of 14.897 g/L sodium sulfite was made to this seasoned tank sample and the sample the was analyzed in the same manner as the fresh and seasoned samples.

Repeatability Standard Deviation, $1s_r$

This is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample with one instrument within a day).

Sample	(N)	Repeatability Standard Deviation, $1S_r$
Fresh Tank prepared at 39.189 g/L sodium sulfite	5	0.038 g/L Na_2SO_3
Seasoned (mean = 30.004 g/L Na_2SO_3)	5	0.53 g/L Na_2SO_3
Seasoned sample + addition (mean = 43.007 g/L Na_2SO_3)	5	0.18 g/L Na_2SO_3

Bias

Bias is a statistically significant deviation of the mean from the known analyte level at a 95 percent confidence level. Bias is reported for fresh samples only, because the analyte level in the seasoned samples was not determined by an independent test method. Bias is based on the information obtained in the repeatability study above. A statistically significant low bias was found at the fresh tank aim level. However, this bias was not practically significant.

Recovery

Recovery is defined as a measure of the method's ability to predict the amount of analyte in a seasoned sample, containing a standard addition of the analyte. The percent recovery is based on the information obtained in the repeatability study above.

$$\text{Recovery} = \frac{[\overline{X}(\text{seas + know addition}) - \overline{X}(\text{season}) \bullet 100]}{\text{known addition}}$$

The recovery of the standard addition was statistically different from 100 percent. This was judged not to be practically significant.

Reproducibility

One fresh tank sample of KODAK Reversal First Developer, Process D-94 was analyzed by four analysts on two separate days using two titrators. The samples were analyzed four times each day. The fresh sample was prepared at aim level (40.116 g/L Na_2SO_3). A seasoned sample of KODAK Reversal First Developer, Process D-94 analyzed to be 38.165 g/L Na_2SO_3, was tested in the same manner as the fresh tank sample above.

Customer Standard Deviation, $1s_c$

The Customer Standard Deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

Sample	(N)	Customer Standard Deviation, $1S_c$
Fresh prepared at 39.165 g/L Na_2SO_3	31	0.98 g/L Na_2SO_3
Seasoned (mean = 30.020 g/L Na_2SO_3)	32	0.57 g/L Na_2SO_3

95 Percent Confidence Estimate (not including bias)

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean value 95 percent of the time.

Sample	95 Percent Confidence Estimate
Fresh prepared at 40.116 g/L Na_2SO_3	± 1.99 g/L Na_2SO_3
Seasoned (mean = 30.020 g/L Na_2SO_3)	± 1.16 g/L Na_2SO_3

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- 3.0, 20.0-mL pipets
- 250-mL beakers
- Automatic titrator with stirrer, METROHM E536 or equivalent with a 50-mL buret
- ORION double-junction reference electrode 900200 or equivalent (10 percent KNO_3 outer filling solution)
- Platinum inlay electrode, BECKMAN #39273 or equivalent

REAGENTS

Use ACS Reagent Grade reagents unless otherwise specified.

- 0.1 N Potassium Iodate, KIO_3 (standardized to 4 decimal places)
- 0.6 M Potassium Iodide, KI
- 0.1 N Sodium Thiosulfate, $Na_2S_2O_3$ (standardized to 4 decimal places)
- 7 N Sulfuric Acid, H_2SO_4
- Water, Type I Reagent—This method was developed using reagent water equivalent to purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

1. Pipet 40.0 mL (pipet two 20.0 mL portions) of standardized 0.10 N potassium iodate into a 250-mL beaker containing 50 mL of reagent water and TEFLON-coated stirring bar.
2. While stirring, add 25 mL of 7.0 N sulfuric acid and 25 mL of 0.6 M potassium iodide.
3. While stirring, immediately pipet 3.0 mL of sample *near the surface* of the liquid. Rinse the sides of the beaker with reagent water.
4. Place the electrodes in the beaker. (NOTE: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the platinum electrode.) Titrate the solution potentiometrically with standardized 0.10 N sodium thiosulfate solution while stirring. Use the following parameters with a METROHM E536 Potentiograph:

Titration Rate:	15 min/100% volume
Auto Control:	OFF
Selector Switch:	mV/pH
Measuring Span:	500 mV
Buret Size:	50 mL
Paper Drive:	400mm/100% volume
Cut-off:	OFF
Counter Voltage:	0 mV
Zero-Point Shift:	left margin

5. Determine the volume, in mL, of 0.10 N sodium thiosulfate added to reach the end point using concentric arcs Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, (or subsequent revision). This is mL A.
6. Repeat Steps 1-5, pipetting 40.0 mL (pipet two 20.0 mL portions) of standardized 0.10 N potassium iodate and substituting reagent water for the sample. This is the blank (mL B).

CALCULATIONS

$$Na_2SO_3,\ g/L = \frac{(mL\ B - mL\ A) \times (N\ Na_2SO_3) \times (eq.\ wt.) \times (1000)}{(mL\ sample) \times (1000)}$$

$$= \frac{(mL\ B - mL\ A) \times (N\ Na_2SO_3) \times (63.02) \times (1000)}{(3) \times (1000)}$$

Where:

mL A	=	mL of Na_2SO_3 consumed by sample
mL B	=	mL of Na_2SO_3 consumed by blank
N Na_2SO_3	=	Normality of Na_2SO_3 in milleq./mL used for titration
eq. wt. Na_2SO_3	=	63.02 mg/meq
mL sample	=	3.0 mL
1000	=	factor to convert mg to g in the numerator and mL to L in the denominator

Example:

$$Na_2SO_3,\ g/L = \frac{(40.32 - 21.98) \times (0.0996\ N\ Na_2SO_3) \times (63.02) \times (1000)}{(3)(1000)}$$

$$= 38.4\ g/L\ Na_2SO_3$$

Colorimetric Determination of Thiocyanate in KODAK Reversal First Developer, Process D-94

D94-0003/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP	B/W Reversal
Formulas	—	—	—	—	D94/D95R

INTRODUCTION

This method describes the spectrophotometric determination of thiocyanate contained in a KODAK Reversal First Developer, D-94 between 3.0 and 12.0 g/L NaSCN calculated as 100 percent salt. An aliquot of the sample is reacted with acidified ferric nitrate reagent to produce a red-colored ferri-thiocyanate complex. The absorbance of this solution is measured at 460 nm on a spectrophotometer. This absorbance value follows Beer's Law to yield a linear relationship with thiocyanate concentration which can be represented by the linear regression equation displayed in the Calculation section.

Use of this method requires handling of potentially hazardous chemicals. Material Safety Data Sheets should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PRECISION AND BIAS

Repeatability

One fresh KODAK Reversal First Developer, Process D-94 tank sample was analyzed by one analyst on one day using one spectrophotometer. The sample was analyzed three times. The fresh sample was prepared at aim level (6.046 g/L NaSCN as 100 percent salt). A seasoned tank sample was analyzed in the same manner as the fresh sample. A standard addition of 2.309 g/L, NaSCN was made to this seasoned tank sample and the sample was analyzed in the same manner as the fresh and seasoned samples. This sample was analyzed five times.

Repeatability Standard Deviation, $1s_r$

This is an estimate of the variability one trained analyst should be able to obtain under favorable conditions (analyzing a sample with one instrument within a day).

Sample	(N)	Repeatability Standard Deviation, $1S_r$
Fresh Tank (prepared at 6.046 g/L NaSCN)	3	0.011 g/L NaSCN as 100% salt
Seasoned sample (mean = 9.223 g/L NaSCN as 100% salt)	3	0.15 g/L NaSCN as 100% salt
Seasoned sample + addition (mean = 11.568 g/L NaSCN as 100% salt)	5	0.033 g/L NaBr as 100% salt

Bias

Bias is a statistically significant deviation of the mean from the known analyte level at a 95 percent confidence level. Bias is reported for fresh samples only, because the analyte level in the seasoned samples was not determined by an independent test method. Bias is based on the information obtained in the repeatability study above.

A statistically significant low bias was found at the fresh tank aim level. However, this bias was not practically significant.

Recovery

Recovery is defined as a measure of the method's ability to predict the amount of analyte in a seasoned sample, containing a standard addition of the analyte. The percent recovery is based on the information obtained in the repeatability study described the *Repeatability Standard Deviation, $1s_r$* section above.

$$\text{Recovery} = \frac{[\overline{X}(\text{seas + know addition}) - \overline{X}(\text{season})] \cdot 100}{\text{known addition}}$$

The recovery of the standard addition was not statistically different from 100 percent.

Reproducibility

One fresh tank sample of KODAK Reversal First Developer, Process D-94 was analyzed by four analysts on two separate days using one spectrophotometer. The sample was analyzed four times each day. The fresh sample was prepared at aim level (6.003 g/L NaSCN as 100 percent salt). A seasoned sample of KODAK Reversal First Developer, Process D-94 analyzed to be 5.972 g/L NaSCN as 100 percent salt, was tested in the same manner as the fresh tank sample above. One set of data was not used to calculate the statistics. The data was rejected due to a possible dilution error.

Customer Standard Deviation, $1s_c$

The Customer Standard Deviation ($1s_c$) is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services laboratory, where any trained analyst could test the sample using any instrument on any day.

Sample	(N)	Customer Standard Deviation, $1S_c$
Fresh tank (prepared at 6.003 g/L NaSCN as 100% salt)	24	0.060 g/L NaSCN as 100% salt
Seasoned (mean = 5.972 g/L NaSCN as 100% salt)	24	0.048 g/L NaSCN as 100% salt

95 Percent Confidence Estimate (not including bias)
The 95 percent confidence estimate (calculated using the Customer Standard Deviation) around a single test result will include the mean value 95 percent of the time. It is not adjusted for the method bias.

Sample	95 Percent Confidence Estimate
Fresh (prepared at 6.003 g/L NaSCN as 100% salt)	± 0.12 g/L NaSCN as 100% salt
Seasoned (mean = 5.97 g/L NaSCN as 100% salt)	± 0.10 g/L NaSCN as 100% salt

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- 1-cm silica cells
- Spectrophotometer, equipped with a visible light source (i.e., SHIMADZU Model UV 160 U or equivalent)
- 5, 10-mL pipets
- 100, 250-mL volumetric flasks

REAGENTS

Use ACS Reagent Grade reagents unless otherwise specified.

- 0.10 M Acidified Ferric Nitrate

Warning

Acidified ferric nitrate is very corrosive to eyes, skin, and metals.

- Water, Type I Reagent—This method was developed using reagent water equivalent to purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

PROCEDURE

1. Pipet 10.0 mL of sample into a 100-mL volumetric flask. Dilute to volume with reagent water and mix thoroughly.
2. Set a timer for two minutes, but do not start.
3. Pipet 5.0 mL of the solution from step 1 into a 250-mL volumetric flask. Dilute to volume with 0.10 M acidified ferric nitrate and mix thoroughly.
4. Start timer and allow the solution to sand for two minutes.
5. Set the spectrophotometer wavelength to 460 nm. Fill two clean 1-cm silica cells with 0.10 M acidified ferric nitrate. Place one cell in the sample beam, and the other in the reference beam. Either adjust the balance (zero control) until the spectrophotometer reads 0.000 absorbance or use the instrument autozero, if so equipped.
6. After two minutes has elapsed, rinse the cell from the sample beam several times and fill with the solution from step 3. Rinse the outer faces of the cell with reagent water and carefully dry with a tissue. Determine the absorbance at 460 nm vs the 0.10 M acidified ferric nitrate blank.

CALCULATIONS

$$y = mx + b$$

Definition of the equation is found in the *Regression* section of Appendix A:

$$\text{NaSCN, g/L as 100\% salt} = m(\text{ABS}) + b$$

Where:

m = slope of the calibration line (g/L NaSCN/ABU @ 460 nm)

ABS = Absorbance of sample vs 0.10 acidified ferric nitrate blank

b = the intercept of the calibration line with the y-axis (g/L NaSCN)

Each laboratory should establish its own regression equation based on a set of calibration standards. *APPENDIX A* explains this calibration procedure. The regression equation may be different for each spectrophotometer. A typical regression equation line for the developer is described by the following equation:

$$\text{NaSCN, g/L as 100\% salt} = 9.65\,(\text{ABS}) - 0.07$$

Example Calculation

$$\text{NaSCN, g/L as 100\% salt} = 9.65\,(0.630) - 0.07$$

$$= 6.01 \text{ g/L NaSCN}$$

APPENDIX A

Calibration of Spectrophotometer for Sodium Thiocyanate

This Appendix should be used to establish the initial calibration equation, whenever the instrument has been adjusted, or to recheck the calibration (at least every six months).

Preparation of Standards

A litre of fresh KODAK Reversal First Developer, Process D-94 should be made containing all the constituents of the mix at aim tank concentrations, except the sodium thiocyanate. This solution will be referred to as the Minus Mix.

1. For the sodium thiocyanate standards in D-94 Reversal First Developer, weigh out 0.30, 0.60, 0.90, and 1.2 g portions of assayed (assay procedure appears as *APPENDIX B*) sodium thiocyanate to the nearest 0.0001 g.
2. Quantitatively transfer each portion of sodium thiocyanate to 100-mL volumetric flasks, respectively labeled with the corresponding weight, washing the weigh boat with fresh D-94 Reversal First Developer Minus Mix. Swirl the flasks to dissolve the sodium thiocyanate.
3. When the sodium thiocyanate has dissolved, fill each volumetric to the mark with the fresh Minus Mix. Invert each flask, 6-10 times, to thoroughly mix the solutions.

Analysis of Standards

1. Run each sample in (at least) duplicate by the method described in the preceding Procedure.
2. Table of Data gathered from Analysis of Standards:

Standard (g/L NaSCN as 100% salt)	ABS @ 460 rim
3.018	0.317
3.018	0 319
3.018	0.319
6.046	0.627
6.046	0.627
6.046	0.629
9.036	0.941
9.036	0.944
9.036	0.942
12.032	1.256
12.032	1.243
12.032	1.254

Regression

1. This data was processed by a least squares linear regression to develop the line represented by equation, $y = mx + b$:

   Where:

   y = g/L sodium thiocyanate as 100% salt

   m = slope of the line or the relation between absorbance and concentration determined during calibration [(g/L)/absorbance]

   x = net absorbance of the sample at 460 nm

   b = the intercept of the calibration line with the y-axis (in g/L sodium thiocyanate as 100% salt)

2. The equation generated using the above data was:

   NaSCN, g/L as 100% salt = 9.65 (ABS @ 460 nm) – 0.07

3. The calibration equation was done in the following manner on a (SHIMADZU Model UV 160 U) spectrophotometer. Four fresh Reversal First Developer, Process D-94 solutions were prepared (see step 1 of Preparation of Standards). Each solution was analyzed in triplicate to create a separate linear regression, based on 12 data points, for each spectrophotometer being used. The average standard deviation (1s) for the linear regression was 0.012 g/L NaSCN as 100 percent salt, corresponding to a 95 percent confidence estimate of ± 0.026 g/L NaSCN as 100 percent salt. Each laboratory should calibrate their spectrophotometer, otherwise an unknown bias may exist.

APPENDIX B

Assay of Sodium Thiocyanate

This method was obtained from: Reagent Chemicals American Chemical Society Specifications; Eighth Edition; American Chemical Society: Washington, DC, 1993.

Reagents

Use ACS Reagent Grade reagents unless otherwise specified.

- 0.1 N Silver Nitrate

Caution

Observe safety precautions for handling concentrated acids. Wear eye protection and impervious gloves. Use caution and always add acid slowly to water. Corrosive to skin, metals, and clothing. Avoid contact with liquid and vapor. Use in an exhaust hood.

- Nitric Acid
- Ferric Ammonium Sulfate Indicator Solution

Procedure

1. Weigh 6.0 g of sodium thiocyanate to the nearest 0.0001 g.
2. Quantitatively transfer to a 1000-mL volumetric flask containing 100 mL reagent water. Swirl the flask to dissolve the sodium thiocyanate.
3. Dilute to the mark with reagent water and stir to mix.
4. Pipet 50.0 mL of the sodium thiocyanate solution into a 250-mL glass stoppered conical flask.
5. Pipet, while agitating, 50.0 mL of standardized 0.1 N silver nitrate.

Caution

Observe safety precautions for handling concentrated acids. Wear eye protection and impervious gloves. Use caution and always add acid slowly to water. Corrosive to skin, metals, and clothing. Avoid contact with liquid and vapor. Use in an exhaust hood

6. Add 3 mL nitric acid and 2 mL ferric ammonium sulfate indicator solution.
7. Titrate the excess silver nitrate with standardized 0.1 N ammonium thiocyanate solution. The end point is the first permanent orange color that cannot be removed upon stirring.

Calculations

$$\% \text{ NaSCN} = \frac{[(50.0 \times \text{N } AgNO_3) - (\text{mL} \times \text{N } NH_4SCN)](81.07)(1000)(100)}{(\text{Sample wt (g)})(50)(1000)}$$

Where:

50.0	=	mL of silver nitrate
N $AgNO_3$	=	normality of silver nitrate in meq/mL
mL	=	mL of NH_4SCN titrated
N NH_4SCN	=	normality of NH_4SCN in meq/mL
81.07	=	eq. wt. of NaSCN in mg/meq
50	=	aliquot of sample taken
1000	=	dilution volume in mL (in numerator)
100	=	factor to convert to %
Sample wt	=	amount of sample weighed out in grams
1000	=	factor to convert mg to g (in denominator)

Example:

$$\% \text{ NaSCN} = \frac{[(50.0 \times 0.0991 \text{ N } AgNO_3) - (13.2 \times 0.0985 \text{ N } NH_4SCN)](81.07)(1000)(100)}{(6.0018)(50)(1000)}$$

$$= \frac{[(4.955 - 1.3002)](81.07)(1000)(100)}{(6.0018)(50)(1000)}$$

$$= 98.7\%$$

To correct weighed amounts of sodium thiocyanate used to prepare standards:

$$\frac{(\text{g of sodium thiocyanate reagent})(\text{assay value determined})}{(\text{theoretical assay} = 100\%)}$$

$$\frac{(0.6046 \text{ g of sodium thiocyanate reagent})(98.7)}{100}$$

$$= 0.5967 \text{ g of sodium thiocyanate corrected for assay}$$

Analysis Order for Photographic Processing Solutions

ULM-0006-1

INTRODUCTION

Certain components of photographic processing solutions tend to degrade with time. It is important that some analyses of these photographic processing solutions be performed prior to others. The analysis order is basically the same for all color developers, first developers, bleaches and fixers. The actual order will depend on specific components present in the photographic processing solutions. Prior to the start of analysis, when the sample is originally collected, it is important to minimize unnecessary air space in the sample bottle. If the bottle is plastic, it should be "squeezed" off to facilitate this,otherwise, nitrogen can be blown into the head space above the solution to prevent oxidation. Similar protection from air should be taken whenever the sample bottle is opened.

ANALYSIS ORDER

The following gives the recommended analysis order for various photographic processing solutions. The recommended order has been broken down by solution type into K-14 color developers, other color developers, first developers, bleaches/bleach-fixes, fixers, and ferri-type bleaches. The analysis order is listed in descending order. If the sample volume submitted for testing is insufficient to perform all requested tests; pH should be perfrmed first, with care taken to minimize effects of oxidation, then the destructive tests are performed in the order listed. Order of analysis within brackets may be arbitrary.

K-14 Color Developers

Analysis Order	Components			
	Cyan	Magenta	Yellow	
Do First	Sulfite	Sulfite	Sulfite	1
	BD-98	NA	BD-89	
	C-16	M-38/CZA	Y-55	
	CD-4	CD-3	CD-6	
	AF-2	HS-104	AF-2	2
	NA	SCN	NA	
	pH	pH	pH	
	Density	Density	Density	
Do Last	Halides	Halides	Halides	

Other Color Developers

Analysis Order	Components*	
Do First	Sulfite	1
	BD-98	
	HAS	
	Color Developing Agent	
	Citrazinic Acid	2
	Benzyl Alcohol	
	Stain Reducing Agent	
	Carbonate	
	pH	
	Density	
Do Last	Halides	

* All components may not be found in all Developers.

First Developers

Analysis Order	Components	
Do First	Sulfite	1
	Developing Agent	
	Thiocyanate	2
	Total Alkalinity	
	pH	
	Density	
Do Last	Halides	

Bleach/Bleach-Fix

Analysis Order	Components				
	Bleaches			**Bleach-Fix**	
Do First	Ferrous		1	Ferrous	
	Iron (total)			Hypo Index	1
	EDTA (free)			Hypo	
	pH		2	Sulfite	
	Density			Iron (total)	
	Metals			EDTA (free)	
				pH	2
				Density	
Do Last				Metals	

Fixers

Analysis Order	Components*	
Do First	Hypo Index	
	Hypo	1
	Sulfite	
	pH	
	Density	
	Metals	2
	pH	
Do Last	Halides	

* All components may not be found in all Developers.

Ferri-Type Bleaches

Analysis Order	Components*	
Do First	Ferrocyanide	
	Ferricyanide	1
	pH	
	Density	2
Do Last	Halides	

* All components may not be found in all Developers.

Procedure for Electroplating a Silver-Silver Iodide Electrode

900

INTRODUCTION

Current development work for the determination of potassium iodide in developers showed a problem when the silver electrodes were cleaned to brightness. Subsequent titrations after cleaning yielded low answers due to aerial oxidation of the electrode when used for a silver nitrate titration of potassium iodide. The problem is more pronounced at low levels of iodide (0.25-2.00 mg/L KI). The electroplating procedure should be used whenever an electrode is first used for a silver nitrate titration of iodide, regardless of the iodide level. The electrode should not be recleaned and replated between titrations but simply rinsed with distilled water and wiped dry. It can be stored dry or in distilled or deionized water

APPARATUS

- Silver Bar or Silver Billet Electrode
- Dry Cell, 3-6 volts (e.g. Burgess No. 5156, 22 ½ volt)

REAGENTS

For instructions on the preparation of the required analytical reagents see Module 4, *Reagent Preparation Procedures*.

- 50 mg/L Potassium Iodide
- Aluminum Wire, 20 gauge, Reagent Grade.

PROCEDURE

1. Thoroughly clean a silver electrode with an abrasive cloth or household cleanser. Rinse well with distilled water and wipe dry.

   Note: If powdered cleanser has been used, make sure any adhering cleanser is removed from the electrode. If it is allowed to remain, it will prevent even plating.

2. Prepare a 50 mg/L potassium iodide solution by dissolving 50 mg of reagent grade potassium iodide in distilled water and diluting to one litre.

3. Add about 300 mL of the 50 mg/L potassium iodide solution to a 400-mL beaker. Enough solution should be added to completely cover the silver metal section of the electrode, while it is being held about one inch from the bottom of the beaker. Do not immerse the electrode yet.

4. Connect a 6-inch piece of reagent grade aluminum wire to the –3 volt terminal of a dry cell. Immerse about 2 inches of the wire into the solution in the 400-mL beaker.

5. Connect the electrode lead to the positive terminal of the dry cell.

6. While stirring gently, immerse the electrode in the potassium iodide solution for approximately three minutes. After three minutes, remove the electrode from the solution and rub dry with a tissue.

7. Repeat step 6 *six times.*

   Note: There should now be a smooth even coating of silver iodide on the electrode. If bare spots are apparent, the electrode should be recleaned and replated according to this procedure.

8. When satisfactorily plated, the electrode needs only to be rinsed well with distilled water and wiped dry between titrations. It can be stored dry or in distilled or deionized water.

The Selection, Care, and Use of Volumetric Glassware and Weighing Equipment

ULM-0005/1

Introduction

This document outlines the various glassware and weighing equipment required to accurately perform the procedures for analyzing photoprocessing chemistry defined in methods. Most require measurement of liquids with a tolerance of ± 0.1 mLs and weights of 0.001 g.

VOLUMETRIC MEASURING EQUIPMENT

The standard unit of volume in the metric system is the litre. It is defined as the volume occupied by the mass of one kilogram of water at its temperature of maximum density and under normal atmospheric pressure. Volumetric glassware is calibrated in terms of litres (L) or millilitres (mL). A volumetric determination can be no better than the equipment and technique used in performing it. Table 1 at the end of this document summarizes the various glassware and gives information on the specifications of each type.

Selection And Tolerances

The volumetric glassware used must have adequate accuracy to avoid introducing a significant error to the analytical result. If a volume of solution is critical in an analytical procedure, pipets, burets, or volumetric flasks of high accuracy must be used. Other steps may require the measurement of only an approximate volume, thus either a graduated cylinder or a "tip-up pipet" may be used.

The National Institute of Standards and Technology (formerly National Bureau of Standards) Circular 602 specifies tolerances for volumetric glassware that meet the most precise requirements of the analytical procedures used in the control of photographic processing. This equipment is designated in Federal Specification DD-V-581 as "Class A." Glassware certified to meet these specifications are available from most manufacturers of laboratory glassware. The required tolerances are given in Table 1.

Care of Volumetric Glassware

1. Cleaning Solutions

   A piece of glass apparatus is not sufficiently clean unless its surface is uniformly wetted by reagent water*. Grease prevents the glass walls from being uniformly wetted, causing drainage to be uneven and delivery not precise. To keep volumetric glassware scrupulously clean and free from grease, three types of cleaning solutions are recommended. These solutions are used undiluted and may be re-used until no longer effective. Do not draw any of these cleaning solutions into pipets or burets by mouth. Use a rubber bulb.

   a. Types

      Detergent—Most detergents are very effective for most cleaning problems encountered.

      Sulfuric Dichromate—A solution of sodium or potassium dichromate in concentrated sulfuric acid (H_2SO_4) is most effective against grease. It is also the most dangerous because of its strong acid, oxidizing, and dehydrating properties. Add about 30 grams of sodium dichromate to one litre of concentrated sulfuric acid. Technical grade dichromate and acid are satisfactory, and the exact concentration of sodium dichromate is not important. After stirring the mixture a few minutes, decant the clear liquid from any sediment that may clog buret or pipet tips during cleaning. The solution will become green as it loses its usefulness as an oxidizing and cleansing agent and should be discarded.

      Acid-Alcohol—A solution of one volume of 3 N hydrochloric acid (HCl) added to one volume of practical or reagent-grade methyl alcohol is effective in removing cyan stains and in cleaning spectrophotometer cells.

Caution

Do not mix this solution in a closed container. The heat produced may cause a dangerous increase in pressure.

   b. Safety

      When mixing and handling the sulfuric dichromate or acid-alcohol cleaning solutions, wear rubber gloves and safety goggles and observe the other safety precautions for handling concentrated acids. Never add water to sulfuric-dichromate solution in a container because excessive heat and steam are likely to spatter the hot acid. If acid is spilled on the skin or clothing or splashed into the eyes, flush the affected parts with a large amount of water. The water will dilute the acid and wash it away. Seek medical treatment immediately.

2. Cleaning and Storing Glassware

   To use a cleaning solution, the glassware should first be rinsed well with water, then immersed in or filled with the cleaning solution for a few minutes. The cleaning solutions are best stored and used in polyethylene containers. Pipet jars, being tubular, are excellent for soaking and storing pipets and burets. After treatment with a cleaning solution, the glassware should be thoroughly rinsed inside and out with reagent water. For reasons of economy, ordinary tap water may be used for the preliminary rinsing, reserving the reagent water for the final rinsing. If

* Water, Type I Reagent - Reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

water droplets adhere to the inside walls of the glassware after one minute of draining, it is not sufficiently clean. Only an unbroken film of water should remain. Burets and pipets should drain in a vertical position. Volumetric flasks are inverted with the bottom at a slight angle from the horizontal, so that drops on the bottom will drain away. If burets and pipets are clean, they generally do not have to be dried before being used with standard solutions. The slight amount of water which remains after rinsing and draining is removed by rinsing two or three times with small amounts of the solution to be used, allowing the buret or pipet to drain completely between rinses. If it is necessary to have volumetric vessels dry, a gentle stream of clean air can be used. Acetone should not be used as a drying agent because of the likelihood of trace amounts left in glassware causing unwanted absorption in ultraviolet methods of analysis.

Use of Volumetric Glassware

1. General Instructions

   a. Effects of Temperature on Glassware and Solutions:

   Glassware—The temperature at which volumetric vessels are calibrated is 20°C (68°F). For the greatest precision and accuracy, all measurements should be made at this temperature. Since this condition may not be practicable, it is important to consider the magnitude of the errors introduced into volumetric procedures by using standard solutions at temperatures other than 20°C (68°F). The change in *capacity* of glass volumetric apparatus with temperature is, at the most, only 1 part in 10,000 for each 5°C change in temperature in the region of 20°C. This source of error generally may be disregarded.

   Solutions—Whereas the change in capacity of glassware with temperature generally may be disregarded, it is not to be confused with the change in volume of a solution with temperature. The effect of temperature on volume is shown in Table 2. To attain accuracy of approximately 0.1 percent it is necessary that the solution be at 20 ± 2°C (68 ± 3.6°F) when measured.

   The change in concentration of standard solutions is also affected by temperature. It may become of such magnitude as to introduce appreciable errors. In general, the more concentrated the solution the more serious the change. The coefficient of expansion of dilute aqueous solutions of different electrolytes is practically the same for similar concentrations and hence, the values given in Table 2 serve as a general index of their behavior.

   b. Meniscus

   In the use of graduated cylinders, pipets, burets, and flasks, the lowest point of the meniscus should be taken as the reading. See Figures 1 and 2. Opaque solutions, however, must be measured by reading at the top of the meniscus. Another special case is the determination of specific gravity. The top of the meniscus is read because the hydrometer is calibrated on that basis.

Figure 1
Reading the Meniscus on a Pipet or Volumetric Flask

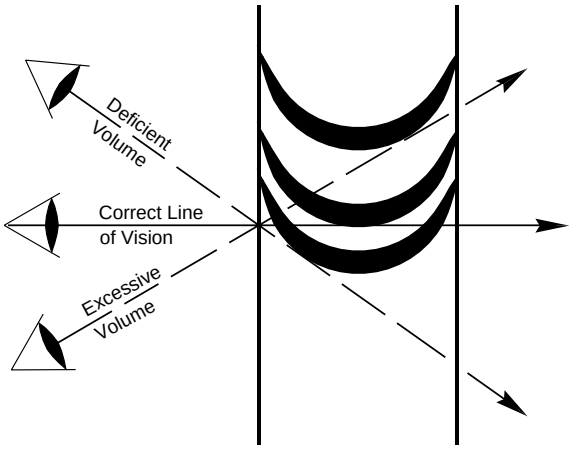


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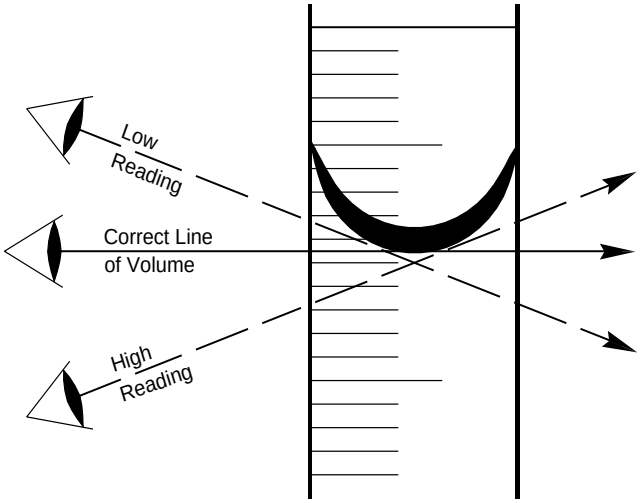
Figure 2 Reading the Meniscus on a Buret



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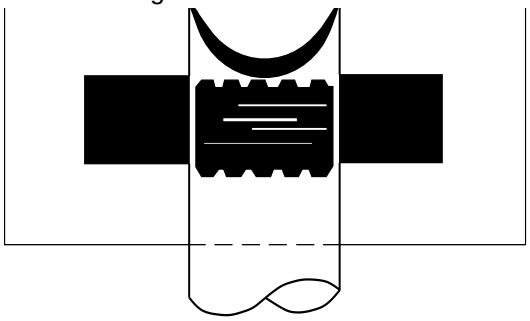
In observing the lowest point on the meniscus it is very important that the line of vision be in the same horizontal plane as the bottom of the meniscus. This is easily ascertained if the graduations on the glassware extend at least halfway around the tube. The eye is correctly positioned when both front and back portions of the graduation coincide (Figures 1 and 2). The meniscus may be seen more clearly if a small white card with a rectangular black patch is held behind the meniscus. Raise or lower the card until the bottom of the meniscus is clearly outlined (Figure 3).

Figure 3 Outlining the Meniscus



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2. Pipets

   Pipet specifications are established on the basis of a pipet's ability to deliver (TD) a known volume of distilled water (20°C [68°F]) within the specified tolerances. Pipets meeting the volume shown in Table 1 have been used successfully. The pipets conforming to these requirements are defined as "Class A." However, experience has shown that some pipets marked "Class A" do not meet delivery time specifications. Other pipets having shorter delivery time than "Class A" meet "Class A" volume tolerances. Pipets meeting "Class A" volume tolerances but not meeting delivery time requirements may be used for analytical purposes as long as the analyst understands and practices the following instructions on the use of pipets:

   a. Cleanliness

      Use a clean pipet. The pipet does not have to be dry, but must be perfectly clean and free from grease so that drops of the solution will not adhere to the walls, causing the pipet to deliver less than the rated volume. Any contaminant may affect the results.

   b. Perfect Tip

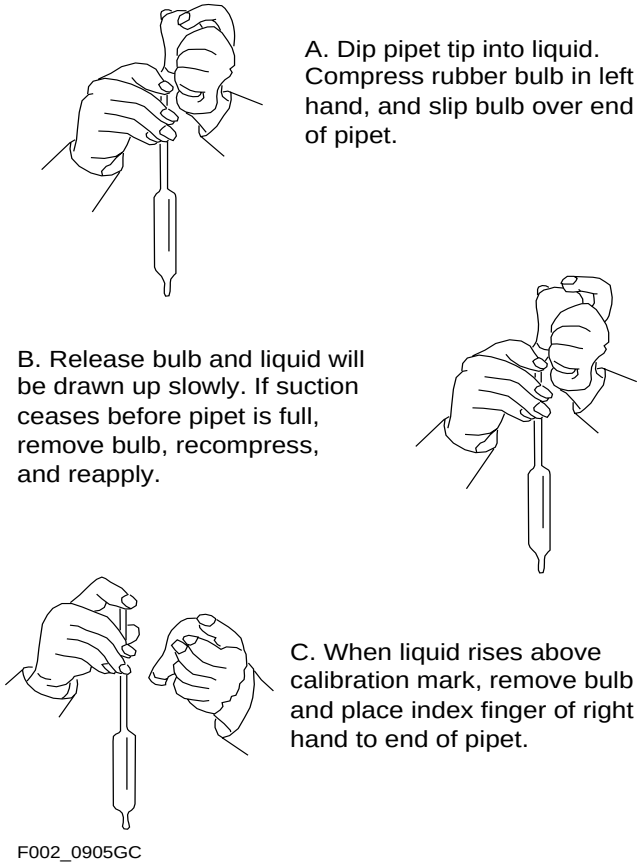
      Use a pipet with a perfect tip. A pipet with a broken or chipped tip must be discarded since it will deliver a volume other than the rated volume when the tip is touched against the wall of the receiving vessel.

   c. Rinsing (or Seasoning)

      With one hand holding the pipet and the other hand holding a rubber bulb, squeeze the bulb, place it over the upper end of the pipet and release slowly. Draw a small portion of the solution into the pipet, i.e., about 20 percent of the volume of the pipet, then remove the bulb and cap the pipet with the forefinger. See Figure 4. Place the pipet in a horizontal position, and rotate it, permitting the solution to wet the walls to a point about two inches above the calibration mark. Do not permit the top of the mouthpiece to become contaminated with solution, which in turn may contaminate the bulb. Discharge the solution through the tip, and repeat the rinsing with another portion of the solution.

      Note: If the solution being pipeted is a standardized reagent, the reagent is drawn into the pipet from a clean beaker which was rinsed once with reagent. To prevent contamination of the reagent, the pipet should not be placed into the stock bottle.

Figure 4 How to Use a Rubber Bulb for Pipeting



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d. Filling

Using a bulb, draw the solution into the pipet to a point about one inch above the calibration mark, then remove the bulb and cap the pipes with the forefinger.

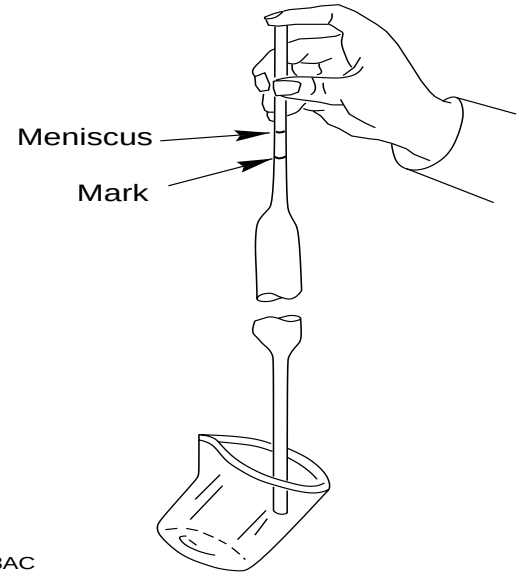
e. Wiping Outside

Before adjusting the liquid level to the mark, wipe off the drops adhering to the outside with a paper cleansing tissue. This prevents droplets on the outside from draining into the receiving vessel and affecting the results.

f. Lowering Meniscus to Mark

Hold the pipet in a vertical position at eye level over a waste container. Touch the tip of the pipet against the wall of the container. Hold the waste container at approximately a 30° angle so that the out-flowing liquid makes continuous contact with the container. Carefully lower the meniscus to the mark. See Figure 5.

Figure 5 Lowering Meniscus to the Mark



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g. Movement of Pipet to Receiving Vessel

Carefully move pipet to the receiving vessel, avoiding rapid vertical motion which might dispense part of the solution prior to reaching the receiving vessel.

h. Delivery

Keeping the pipet in a vertical position, place the tip against the wall of the receiving vessel (at approximately a 30° angle) just above the surface of the liquid, then remove the forefinger. Allow to drain at a vertical position until the continuous outflow ceases, then remove the pipet. A small amount of the solution will, and should, remain in the tip of the pipet. Do not blow it out.

i. Cleaning

If, after usage, a pipet has a film of liquid in it, not droplets of liquid, it may be reused immediately with the same solution without being cleaned in a cleaning solution. Merely rinse it with the solution to be pipeted. It is not necessary to rinse it with reagent water just prior to rinsing with the sample to be pipeted. However, if droplets of liquid are adhering to the inner surface of the pipes or if it is colored, it should be rinsed with a cleaning solution, then rinsed inside and out with reagent water for approximately five seconds. If drops of water remain in the pipet, it is contaminated and must be treated again with cleaning solution. Store pipets in racks in a vertical position. Pipets must be recleaned immediately before use if allowed to stand more than an hour under ordinary conditions of air-contamination.

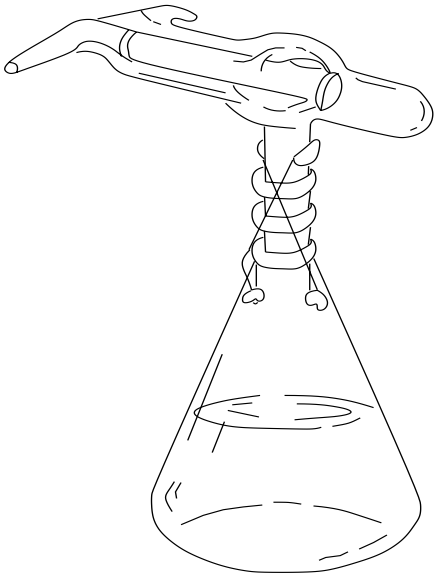
3. Micropipets

Micropipets are used in methods where precise samples, 1.00 mL or less, are required. They are usually equipped with disposable tips. Follow the manufacturer's instructions for care and use of the micropipet and any additional instructions that may be included in the method.

4. Graduated Cylinders and Tip-up Pipets

   In many cases the volume of a solution to be used in an analytical method need be only an approximation of the specified volume. For example, the method may prescribe 20 mL of a reagent whereas only slightly more than 15 mL would suffice. In these cases, graduated cylinders or "tip-up" pipets are used. Graduated cylinders are calibrated to delivery (TD) or to contain (TC). See Table 1 for tolerances. "Tip-up" pipets require less time for operation and are. therefore, preferable. Portable "tip-up" pipets, shown in Figure 6, are available in different sizes. They have the accuracy of a graduated cylinder. They may be purchased with either standard taper, ground glass, male joints, or for use with rubber stoppers. It is suggested that Erlenmeyer flasks of 250-, 500-, or l000-mL capacity be selected with the ground glass joint to match. The restraining wires as shown in Figure 6 need not be used.

Figure 6 Tip-up Pipet



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5. Burets

   Burets are graduated to deliver variable known volumes of liquids. Methods are generally developed to employ 30 to 50 mL of solution as measured from a buret. For such purposes, a 50-mL capacity buret is used. In those cases in which 10 to 20 mL of solution are measured from a buret, a 15 or 25 mL buret is used. Class A burets are required. See Table 1 for tolerances. Analysts should understand and apply the following specific instructions for the use of burets.

   a. Cleanliness

      Use a clean buret. The buret does not have to be dry before rinsing it with the solution to be used. If the buret is not perfectly clean, drops of the solution will adhere to the wall and the buret will deliver less than the indicated volume. Furthermore, the contaminants may affect the results.

   b. Perfect Tip

      Use a buret with a good tip. A buret with a broken tip may deliver a volume other than the rated volume when the tip is touched against the wall of the receiving vessel. A buret with a broken or chipped tip sometimes can be fire-polished and salvaged.

   c. Stopcock Seal

      Use a buret which will hold a constant reading for at least 5 minutes. If the stopcock seal is defective, the solution will leak and thus lower the buret reading. Teflon stopcocks do not require grease, and are preferred.

   d. Rinsing

      Rinse the entire inner surface of the buret two or three times with portions of the solution to be used.

   e. Lowering Meniscus to the Zero Mark

      Fill the buret well above the zero mark. With the buret zero mark at eye level, lower the meniscus to the zero mark. Allow a minute or two for drainage, then make the initial reading, or readjust the buret precisely to the zero mark. During the waiting period, check for leaks and make certain that air bubbles are expelled either at the top or from the tip. After the meniscus has been adjusted, remove the final drop by touching the tip with the wall of a waste-solution beaker which is kept under the buret *except* during titration. One-second contact is adequate.

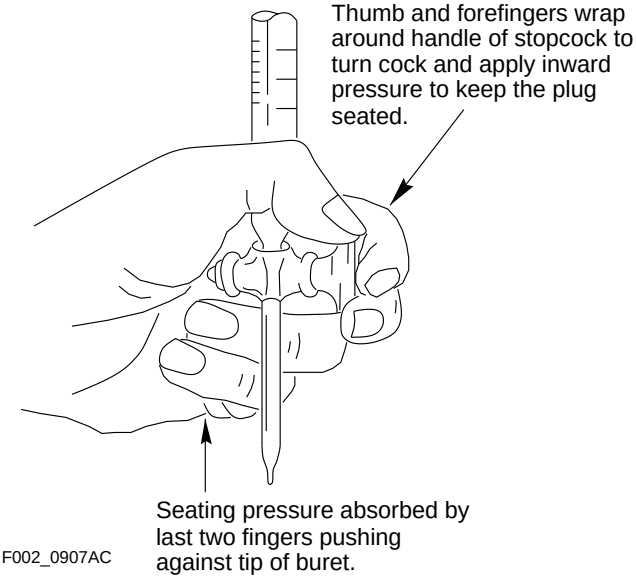
   f. Position

      The buret should be clamped in a vertical position during the readings and while the solution is being titrated.

g. Titration

After the initial reading is made and the final drop removed, the standard solution is added to the titration vessel with constant swirling. See Figure 7 for the proper way to turn a stopcock. As the end point is approached, the rate of addition is decreased, until finally the titrant is added dropwise or as split drops. At this point, tilt the vessel and remove each drop by touching the tip with the wall of the vessel at a level just above the surface of the liquid. Tilt the vessel slightly more to rinse in the drop. Generally the end point is defined as a specified color change that persists for at least 15 seconds. When the end point has been reached, there should be no final drop to remove. If an end point is not sharp, or if it is unfamiliar, it may be difficult to decide when the end point has been reached. Then after a drop, record the buret reading, add another drop, and note the change produced in the indicator. Continue this procedure until the specified color change has occurred.

Figure 7 How to Turn a Stopcock



h. Drainage Error

Unless the titration to the end point has been slow and gradual, wait 30 seconds before taking the final reading of the meniscus, so that the effect of further drainage will be negligible. Read meniscus at eye level.

i. Cleaning Buret

Clean the buret with cleaning solution. Prevent the concentrated cleaning solution from coming into contact with the stopcock lubricant. A convenient way to clean burets without removing any of the stopcock lubricant is to invert them in a pipet jar containing enough cleaning solution to fill the buret to the stopcock. After a few minutes, rinse inside and out with tap water, then rinse three times with small quantities of reagent water. Store in a vertical position.

j. Capping

Capping the buret with an inverted test tube will aid in preventing evaporation of the solution and contamination by dust. If the solution is not alkaline and does not contain fluorides or phosphates in acid solution, it is generally safe to allow the solution to stand in the buret. A full buret will stay clean longer than a dry or partially filled buret.

k. Greasing Stopcock (glass stopcocks)

If the stopcock sticks or leaks, remove the old lubricant by wiping with a cloth, using methanol or acetone if desired. Replace with fresh “Lubriseal”. Apply only a thin film since too much lubricant may plug the hole. Unless the parts of the stopcock are dry before lubricating and sealing the plug, the seal may be defective. Teflon stopcocks are not to be greased.

l. Offset Tip

A buret with an offset tip is useful when titrating with a potentiometer or when the apparatus is crowded into a small space.

m. Plugged Tip

Occasionally a buret tip becomes plugged with a small amount of lubricant. The plug can be expelled in the following manner: Open the stopcock so that the pressure of the liquid column is on the plugged tip. Insert the tip in a beaker of warm water. If this treatment does not dissolve the plug, it will be necessary to disassemble the stopcock and thoroughly clean the buret with cleaning solution, after which the stopcock must be relubricated. In certain instances the use of a thin wire probe (pipet probe), or buret wire, is a satisfactory means of unplugging buret tips.

6. Microburets

   Microburets equipped with 1.00-, 5.00-, or l0.00-mL syringes are used in some methods where microtitrations are performed. Follow the manufacturer's instructions for care and use of the microburet and any additional instructions that may be included in the method.

7. Volumetric Flasks

   Volumetric flasks are generally graduated “to contain” (TC) known volumes of solutions and should never be used “to deliver” (TD) known volumes unless they have been so calibrated. Volumetric flasks are used to make up solutions to a given volume. Use Class A flasks. See Table 1 for tolerances.

   Analysts should understand and practice the following instructions for the use of volumetric flasks.

   a. Safety

      Volumetric flasks are fragile, and when shaken, should be held at both the neck and bottom. A flask should never be shaken when held at the neck only. When inserting a stopper, hold at the neck rather than at the bottom.

   b. Cleanliness

      Use a clean flask. It usually does not have to be dry, but it must be clean. Rinse the entire interior of the flask two or three times with distilled water prior to use.

   c. Diluting to Volume

      Add the solution to be diluted to the flask, and add distilled water or specified diluent to bring to volume. While raising the meniscus to the graduation mark, hold the mark at eye level and add the last few drops from a wash bottle or from a small pipet. Stopper and invert 6 to 12 times to assure homogeneity. Care should be taken when making the initial inversion. Some solutions have a tendency to effervesce, and loss of the solution may result if the stopper is not held firmly in place. If such is the characteristic of the solution being mixed, a momentary removal of the stopper (flask in an upright position) prior to the second inversion will release the gas pressure formed and avoid possible loss.

   d. Cleaning and Storing

      Clean the flask with Alconox or a similar cleaning solution. It is not necessary to fill the volumetric flask with cleaning solution. If a generous portion is placed in the flask and the flask is stoppered, cleaning will be accomplished if the flask is shaken and inverted several times so as to keep the walls moistened with cleaning solution. After a thorough rinse inside and out with tap water, rinse 3 times with small quantities of reagent water. Store in an inverted position with the bottom slightly inclined. If the bottom is horizontal, the flask may not drain completely.

WEIGHING EQUIPMENT

The internationally accepted unit of mass is embodied in a platinum-iridium cylinder maintained at the International Bureau of Weights and Measures at Sevres, France. The mass of this cylinder is 1 kg exactly, by definition.

Selection

When making analytical reagents or standard laboratory mixes, it is necessary to weigh the various constituents. Thus, it is evident that the weighing operation is of fundamental importance. When weighing a sample to a specified weight, the tolerance is ± 1 unit in the last decimal place to the right. For example, 15.0 grams is understood to mean 15 g ± 0.1 g and 15.000 grams is understood to mean ± 0.001 gram. The type of balance used for weighings (analytical, torsion) is immaterial provided that the accuracy of the balance (given in its specifications) is commensurate with the demand of the weighing operation. Take advantage (if reagent expiration date permits) of preparing large volumes of reagents, as this will permit the use of balances accurate to fewer decimal places and still give a satisfactorily small percentage error.

Care and Use of the Analytical Balance

1. Weighing Area

   If possible, keep the balance in a room separate from the laboratory. Keep the balance at a reasonably constant temperature and out of direct sunlight and air currents. Level the balance and place it upon a solid support to protect it from vibration.

2. Protection of Knife Edges

   To prevent injury to the agate knife edges and planes when the balance is not in use, raise the beam and the pan supports. Leave nothing on the pans and keep the door of the case closed. When weighing, raise the beam and arrest the pans before placing any object on the pans. To test for equilibrium lower the beam and then release the pans. Before removing any object or weight from the pans, raise the beam to arrest the pans.

3. Protection of Pans

   Never weigh chemicals directly on the pans since they may injure the pans. Never weigh chemicals on paper in an analytical balance. Use weighing bottles, watch glasses, or aluminum laboratory dishes as containers for weighing. The aluminum dishes are used and then discarded.

Caution

Sodium hydroxide should not be weighed in an aluminum dish.

4. Temperature

   Weigh objects at room temperature. Differences in temperature will cause air currents which lead to errors in weighing.

5. Rest Point

   Determine the zero rest point at each sitting.

6. Maximum Load

   Do not overload the balance. Refer to manufacturer's literature for maximum capacity.

7. Cleanliness

   Keep the balance clean. If any chemical is spilled, clean it up at once. Do not use liquids for cleaning the pans. Use a balance brush.

Care and Use of the Weights

Handle Class S weights only with forceps, preferably bone-tipped. To counterbalance an object, try the large weights first and then the smaller in systematic order. Always use the least number of weights possible, for example, a 3-gram weight in preference to a 1- and a 2-gram weight. To avoid oscillation, place large weights in the center of the pan. Use great care to avoid dropping weights. Always double-check the result of a weighing by adding the values implied by the empty compartments in the box of weights and then record immediately in a notebook.

References

1. *Standard Specification for Laboratory Glass Graduated Burets;* American Society for Testing and Materials: ASTM Designation E 287-94, Philadelphia, PA, March 1994.
2. *Standard Specification for Laboratory Glass Volumetric Flasks;* American Society for Testing and Materials: ASTM Designation E 288-94, Philadelphia, PA, April 1994.
3. *Standard Specification for Glass Volumetric (Transfer) Pipets;* American Society for Testing and Materials: ASTM Designation E 969-95, Philadelphia, PA, December 1995.
4. *Standard Specification for Glass Measuring Pipets;* American Society for Testing and Materials: ASTM Designation E 1293-94, Philadelphia, PA, April 1994.
5. *Standard Specification for Laboratory Weights and Precision Mass Standards;* American Society for Testing and Materials: ASTM Designation E 617-91, Philadelphia, PA, October 1991.

Table 1 Required Tolerance for Volumetric Glassware

Capacity, mL	Delivery Time*	Tolerance of Glassware, mL			
		Pipets Class A or Equiv. TD†	Graduated Cylinder TD†	Burets (Class A) TD†	Volumetric Flasks (Class A) TC‡
1	10	± 0.006	± 0.1		± 0.01
2	10	0.006			0.015
3	10	0.01			0.015
4	10	0.01			
5	15	0.01			0.02
10	15	0.02	0.1	± 0.02	0.02
15	15	0.03			
20	25	0.03			
25	25	0.03	0.3	0.03	0.03
50	30	0.05	0.4	0.05	0.05
100	40	0.08	0.6	0.10	0.08
200	50	0.10	1.4		0.10
250			1.4		0.12
500			2.6		0.15
1000			5.0		0.3
2000			10.0		0.5
4000			50.0		

* Minimum delivery time for Class A serialized and non-serialized (maximum delivery time 60 sec).
† Calibrated to deliver.
‡ Calibrated to contain.

Table 2 Effect of Temperature on Solution Volume

Solution Composition	Volumes (mL) Occupied at*				
	59°F	68°F	77°F	86°F	95°F
	15°C	20°C	25°C	30°C	35°C
1.0 N HCl	996.7	1000.0	1001.3	1002.8	1004.7
0.1 N HCl	997.1	1000.0	1001.2	1002.6	1003.8
Water	999.1	1000.0	1001.1	1002.5	1004.2

* References: Fales and Kenney, *Inorganic Quantitative Analysis* (1940).

pH Measurement of Photographic Processing Solutions

ULM-191-2

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	All	All	All	All

SCOPE AND SIGNIFICANCE

This procedure measures pH over the range 1-14 in working strength and concentrates of photographic processing solutions, and in raw chemicals used in the manufacture of photoprocessing solutions.

SUMMARY OF METHOD

A two-point calibration is used for measuring pH, utilizing either high or low pH-range buffer pairs, with nominal values of pH 7 and 10, or pH 7 and 4, respectively. These buffer solutions are assigned values as measured against National Institute of Standards and Technology (NIST) buffers. Buffers of pH values 11.43 and 3.63 at 25°C are used as measurement controls* and to verify system accuracy. All sample solutions and buffers are equilibrated at 25°C before measurement of pH, and stirred during meter calibration and measurement.

DEFINITIONS

With regard to buffers used in this method, prepared by a vendor or certified by NIST (e.g., Radiometer Copenhagen), the term reference applies to those buffers prepared by a vendor using NIST procedures with NIST materials. Values for NIST buffers will change only if a new lot of standard reference material is used. *Calibrating buffers* are used to prepare the meter for pH measurement of samples. *Standardization* is the process through which a pH value will be assigned to a calibrating buffer using reference buffers. *Control buffers* are used to monitor day-to-day performance of the pH measurement system and to indicate the need for process control.

PRECISION AND BIAS

Two separate precision studies were performed on photoprocessing concentrates and working strength processing solutions using the CORNING 476024 pH electrode. In each study, the pH data was collected by three trained analysts over a period of two days on three different pH meters using six different pH electrodes and three different reference electrodes.

Triplicate determinations were performed (three determinations per sample, per day) by each analyst. Thus, as many components of variability as possible were entered into the study to obtain a true estimate of the customer standard deviation.†

Concentrated Processing Solutions

Five processing solutions (one acidic and four basic) were analyzed in triplicate on two days. The pooled customer standard deviation (1s) for processing solutions with a pH value below 10 is 0.007 pH units with a 95 percent confidence estimate of ± 0.015 pH units. The pooled customer standard deviation (1s) for solutions with a pH value greater than 10 is 0.013 pH units with a 95 percent confidence estimate of ± 0.027 pH units.

Working Strength Processing Solutions

Seven processing solutions (two acidic and five basic) were analyzed in triplicate on two days. The pooled customer standard deviation (1s) for processing solutions with a pH value below 10 is 0.005 pH units with a 95 percent confidence estimate of ± 0.010 pH units. The pooled customer standard deviation (1s) for solutions with a pH value greater than 10 is 0.011 pH units with a 95 percent confidence estimate of ± 0.023 pH units.

SAFETY PRECAUTIONS

Normal safety precautions and safe handling practices should be observed. If the preservative DEARCIDE 702 is used in preparation of the potassium hydrogen tartrate buffer, appropriate care should be used. Material Safety Data Sheets, which can be obtained from the chemical supplier, should be consulted prior to handling the DEARCIDE.

SOURCES OF ERROR

1. Covering or capping sample solutions and buffers during temperature equilibration to 25°C reduces aerial oxidation and prevents dilution, evaporation, or contamination of solutions.
2. Using either NIST or calibrating buffers that are contaminated or expired may prevent meter calibration within the specified buffer tolerances.
3. A change in temperature of 1°C produces a change of 0.015 – 0.020 pH unit in carbonate-buffered developers of pH 10. For photoprocessing solutions of higher pH that are not as well buffered, this variation with temperature can be 0.03 pH unit per °C or greater. Because of this effect, careful control of temperature is essential to precise and accurate measurement of pH. The section on *Temperature Equilibration* describes requirements for temperature control.
4. Stirring is required during both meter calibration and sample pH measurement for the best precision, in measurements on the NIST phthalate buffer (pH 4), 95 percent confidence limits for a single analyst were

* These values represent the mean values obtained by Kodak Rochester site laboratories using commercially prepared control buffers described in *APPENDIX D*.

† This is an estimate of the variability a customer could expect when submitting a sample to any laboratory where any analyst could test the sample using any instrument on any day. The customer standard deviation (1s) incorporates all laboratory variables associated with pH measurement.

± 0.023 pH without stirring the buffers and test sample, and ± 0.007 pH with stirring (based on ten measurements by each method, recalibrating the meter between measurements). Suggestions for adding stirring capability to existing water baths appear in the section on *Stirring*.

5. Clogging of reference electrode junctions occurs quite readily in photoprocessing solutions due to the high ionic strengths and complicated matrices. Reference electrodes can be tested in several ways for proper performance. Suggestions appear in *APPENDIX C*. Reference electrodes with ceramic frit or plug-type junctions gave good response when new, but should be checked regularly for electrolyte flow, based on the frequency of measurements made. Sleeve-type junction reference electrodes gave the best accuracy and precision. However, due to the high flow rate of filling solution, close attention is required from the analyst to ensure that the electrode has adequate filling solution and that the electrolyte is not allowed to drain completely into the sample to be measured. This is necessary both for proper performance of the electrode and to avoid sample contamination.
6. In meter calibration, slope may be determined by adjusting a manual slope control or reading a slope value calculated by the meter. Historically, 95 percent of Nernstian electrode response has been used as the cut-off point for continued use of electrodes for pH measurements. We now use 8 slope criterion for electrode use based on a 4 percent window that starts at the maximum new electrode slope (for the model of pH electrode being used) to determine if an electrode can be used to measure the pH of a sample. Therefore, for a pH electrode which typically has a slope of 102 percent when new, such as CORNING 476024, the appropriate slope range would be 98-102 percent. Outside of this range, the analyst may be unable to calibrate the meter within the buffer tolerances specified in the method.

APPARATUS

pH Meter

The pH meter selected must be capable of two-point calibrations with either an adjustable slope control, or read-out of slope values available. Readability to 0.001 pH unit and accuracy of at least ± 0.002 are required. Using two meters (Section a. below), or a meter with dual channel electrode inputs (Section b. below), is more convenient for maintaining separate electrode pairs for high and low-range pH measurements.

a. Single channel meter (only one pair of electrode inputs) e.g., CORNING 255, FISHER ACCUMET 925, or equivalent.

b. Dual channel meter (two electrode pairs can be used; the meter retains calibration information about each pair) e.g., ORION EA 940 or equivalent.

Electrodes

Reference electrodes are rinsed and filled with 3.5 M KCl rather than saturated KCl solution*. There is less crystallization inside the electrodes and in the reference junction with the lower salt concentration.

Because of the effect of the complex matrices of photoprocessing solutions on the glass membranes of pH electrodes, a significant difference has been observed between different manufacturers' pH sensing glasses. CORNING Rugged Bulb pH Electrode 476024 serves as the Kodak standard for processing solutions. This electrode has improved lifetime compared to the CORNING 476281 and performs better in alkaline solutions. Investigations of other manufacturers' electrodes continue in order to identify pH glass electrodes with increased lifetimes and improved precision.

Note: Presently, there is no standardization among pH electrode manufacturers of pH sensing glasses nor internal fill solutions. Thus, if one chooses to use electrodes other than those recommended in this method, one *must* verify that no bias exists between measurements made with the recommended CORNING pair of electrodes and the electrodes under investigation.

Theoretically, there is no reason that combination electrodes cannot be used for this method, and they are being tested for their precision relative to a standard pair of electrodes. A reference and glass pH electrode pair are easier to maintain and troubleshoot.

Recommended Reference Electrodes

- CORNING 476002, reference, ceramic junction, calomel (VWR, CAT No. 34106-749)

  This reference electrode, 476002, should be used with the 476024 pH electrode as the internal fill solutions of this reference electrode are matched to this pH electrode.

Note: With growing environmental concerns, many electrode manufacturers are moving toward the elimination of calomel electrodes. Presently, a Ag/AgCl reference electrode matched to the 476024 pH electrode is not available, but the manufacturer has indicated that it plans to offer this electrode as an alternative if it plans to phase out production of calomel electrodes.

- CORNING 476360, reference, reverse sleeve, Ag/AgCl (VWR CAT No. 34108-201)
- Other electrodes can be tested for suitability by following procedures in *APPENDIX C*.

Glass pH Electrodes

- CORNING 476024, glass, rugged bulb (US Standard Connector)
  (VWR, CAT No. 34106 568)

* See R.G. Bates, *Determination of pH, Theory and Practice*; John Wiley and Sons: New York (1973) pp. 311-312.

Temperature Equilibration

All samples and buffer solutions must be equilibrated to 25°C prior to the measurement. Water baths used for equilibrating samples should allow circulation around the sample container, and be controlled such that the sample temperature can be maintained to within ± 0.25°C. A digital thermometer is recommended for water temperature measurement to eliminate reading error. Any thermometer used for verifying the accuracy of water bath temperature should be calibrated against a NIST traceable thermometer or other standard on a yearly basis or in accordance with standard laboratory operating procedures. Circulating rather than static constant-temperature water baths are recommended since they provide shorter equilibration times and more uniform temperature.

Stirring

For viscous samples or where a smaller stirrer (in immersible dimensions) is necessary, TROEMER Model 700 (or equivalent), submersible magnetic stirrer with isolated power supply, is recommended. A paddle or propeller-type stirrer can be used to stir the solutions directly if adequate rinsing of paddle or propeller is provided. Magnetic stirrers are available which may be immersed in water baths and are driven by air or water. This type of stirrer was tested to determine if water bath temperature would be affected by the water circulating in the tubing to and from the stirrer. In a 28-litre circulating bath, no change in bath temperature due to flow-water temperature was observed.

Stirring speed is difficult to judge without some point of reference; the intention in stirring is to present a more uniform sample to the electrode pair while avoiding excessive oxidation during the course of the measurement, so a moderate stirring rate is recommended. Avoid vigorous stirring, where a large amount of air will be drawn into the solution.

Glassware

Volumetric glassware should meet all "Class A" specifications, as defined by the American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

REAGENTS AND MATERIALS

All buffer values given here are nominal; all values used in pH measurements are either based on current NIST lot number values or are assigned after meter standardization with NIST buffers. Preparation instructions for all reagents listed appear in *APPENDIX A*. All reference buffers of NIST formulation may, be purchased from Radiometer-America (see *APPENDIX D* for ordering information).

If pH measurements below pH 3 will be made regularly, substitution of a buffer prepared from NIST Standard Reference Material 189, potassium tetroxalate, may be made for reagent in Section *8* below, the low pH control buffer. The tetroxalate buffer has a nominal pH value of 1.679 at 20°C. Preparation instructions are available from NIST.

1. pH 4 phthalate reference buffer: NIST chemicals and preparation requirements, *pH 4 Phthalate Reference Buffer* in *APPENDIX A*, or purchase from vendor (see *APPENDIX D*).
2. pH 4 phthalate calibrating buffer: Prepare from reagent grade chemicals, *pH 4 Phthalate Calibrating Buffer* in *APPENDIX A*, or purchase from vendor (see *APPENDIX D*).
3. pH 7 equimolar phosphate reference buffer: NIST chemicals and preparation requirements, *pH 7 Equimolar Phosphate Reference Buffer* in *APPENDIX A*, or purchase from vendor (see *APPENDIX D*).
4. pH 7 equimolar phosphate calibrating buffer: Prepare from reagent grade chemicals, *pH 7 Equimolar Phosphate Calibrating Buffer* in *APPENDIX A*, or purchase from vendor (see *APPENDIX D*).
5. pH 9 borate reference buffer: NIST chemicals and preparation requirements, *pH 9 Borate Reference Buffer* in *APPENDIX A*, or purchase from vendor (see *APPENDIX D*).
6. pH 10 carbonate calibrating buffer: Prepare from reagent grade chemicals, *pH 10 Carbonate Calibrating Buffer* in *APPENDIX A*, or purchase from vendor (see *APPENDIX D*).
7. pH 11.43 phosphate high pH control buffer: Prepare from reagent grade chemicals, *pH 11.43 Phosphate High pH Control Buffer* in *APPENDIX A*, or purchase from vendor (see *APPENDIX D*).
8. pH 3.63 tartrate low pH control buffer: Prepare from reagent grade chemicals, *pH 3.63 Tartrate Low pH Control Buffer* in *APPENDIX A*, or purchase from vendor (see *APPENDIX D*).
9. Reference electrode filling and storage solution, 3.5 M KCl: Prepare from reagent grade chemicals, *Reference Electrode Filling and Storage Solution, 3.5 M KCl* in *APPENDIX A*.
10. Storage buffer, 0.1 M KCl in pH 7 buffer: Prepare from reagent grade chemicals, *Storage Buffer, 0.1 M KCl In pH 7 Buffer* in *APPENDIX A*).
11. Water, Type I Reagent—This method was developed at Kodak, using reagent water equivalent to or purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.

For calibrating buffers, other formulations than those given in *Preparation of Calibrating Buffers* in *APPENDIX A* may be used, if desired, since values will be assigned from NIST buffers.

CALIBRATION

Standardization of buffer solutions is described in *APPENDIX B*. Buffers used for meter calibration should be changed at least once per day (8-hour shift). The replacement frequency should be based on the number of samples measured. If it becomes difficult to maintain the specified buffer tolerances, buffers should be replaced with fresh aliquots. Covering the buffer containers that are used in the water bath aids in preventing contamination, dilution, evaporation, or oxidation of buffer solutions and is strongly recommended.

For pH measurements in the range of 7-14 pH units, the 11.43 phosphate buffer will be used as a control. Values obtained from measurement of the pH of the 11.43 phosphate buffer with a calibrated meter will be used to determine the day-to-day variability of the pH measurement system.

For the pH range 1-7, an NIST reference buffer of potassium hydrogen tartrate of pH 3.63 will be used as a control. This value differs slightly from that stated by NIST, but appears more representative of the mean value achievable in a typical laboratory.

The control buffers should be measured at least once per 8-hour shift. Individual laboratories should decide how these control buffers can best be utilized in their operation.

Calibration of Meter

For all meters, set the temperature compensator to be 25°C. Either adjust the manual control to this value or input the value if using a microprocessor-controlled meter.

Note: Use of an automatic temperature compensator on a pH meter only ensures that the meter corrects the Nernst equation for the actual temperature of the sample (i.e., calibrates the pH-millivolt scale of the meter). It does not correct that temperature to 25°C, the specified temperature for this method. To obtain pH values on photoprocessing solutions equivalent to those given in product specifications, the pH must be measured at 25°C.

For microprocessor-controlled pH meters, two-point calibration procedures often involve the input of the assigned buffer values through a keypad, or through use of a pre-set soft key, labeled “CAL 1" or “CAL 2." Many of these meters automatically go to a stand-by mode; for those using older meters, the meter should always be put on stand-by when moving the electrodes in or out of a solution.

High-range pH Measurements (pH 7-14)

1. Rinse electrodes with reagent water and blot excess water from the tips of the electrodes (and any protective assemblies that are being used) with a soft tissue, taking care not to rub the tissue against the electrode membrane surface (rubbing produces static which in turn will affect the reading). It should be sufficient to hold a tissue near the surface of the electrode and allow the water to be drawn into it.

   Immerse the electrodes in pH 7 calibrating buffer stirred with either a TEFLON-coated stir bar and magnetic stirrer, or a paddle-type stirrer that has been rinsed with reagent water.

2. Wait 2 minutes for electrodes to equilibrate and meter reading to stabilize. At the end of the 2 minutes, if the meter does not display the assigned value for the pH 7 buffer (determined as in *APPENDIX B*), either adjust the calibrate control or set the meter to the assigned buffer value.

3. Rinse electrodes with reagent water, blot as in step 1, and immerse electrodes in pH 10 calibrating buffer (stirred as in step 1).

4. Wait 2 minutes for electrodes to equilibrate and meter reading to stabilize. At the end of the 2 minutes, if the meter does not display the assigned value for the pH 10 buffer, either adjust the slope control or set the meter to the assigned buffer value.

5. Repeat steps 1–4 until the meter displays the assigned buffer values ± 0.003* pH units. Read the final slope value obtained and record.

   Note: If slope value is not within 98–102 percent of optimum electrode response, go back to step 1, and redo the calibration. If slope is still out of range, try another glass electrode.

6. This step must be performed at least once per 8-hour shift. Rinse electrodes with reagent water, blot as in step 1, and immerse electrodes in pH 11.43 phosphate control buffer (stirred as in step 1). Wait 2 minutes for electrodes to equilibrate and meter reading to stabilize. Read the pH value to the nearest 0.001 pH unit and plot the value on the high-range control chart. Initially, the limits will be set at ± 0.03 pH units from the mean. Once enough readings are collected (minimum of 40 data points), new control limits can be calculated. Figure 1, *pH 11.4 High Control @ 25°C*, shows a sample control chart.

* Buffer tolerances of ± 0.003 pH were used in determining the estimate of the precision of this procedure given in *PRECISION AND BIAS*. Based on time available for analysis and precision requirements, a practical range of ± 0.005 pH may be used.

Low-range pH Measurements (pH 1-7)

1. Rinse electrodes with reagent water and blot excess water from the tips of the electrodes (and any protective assemblies that are being used) with a soft tissue, taking care not to rub the tissue against the electrode membrane surface (rubbing produces static which in turn will affect the reading). It should be sufficient to hold a tissue near the surface of the electrode and allow the water to be drawn into it.

   Immerse the electrodes in pH 7 calibrating buffer stirred with either a TEFLON-coated stir bar and magnetic stirrer, or a paddle-type stirrer that has been rinsed with reagent water.

2. Wait 2 minutes for electrodes to equilibrate and meter reading to stabilize. At the end of the 2 minutes, if the meter does not display the assigned value for the pH 7 buffer (determined as in *APPENDIX B*), either adjust the calibrate control or set the meter to the assigned buffer value.

3. Rinse electrodes with reagent water, blot as in step 1, and immerse electrodes in pH 4 calibrating buffer (stirred as in step 1).

4. Wait 2 minutes for electrodes to equilibrate and meter reading to stabilize. At the end of the 2 minutes, if the meter does not display the assigned value for the pH 10 buffer, either adjust the slope control or set the meter to the assigned buffer value.

5. Repeat steps 1–4 until the meter displays the assigned buffer values ± 0.003* pH units. Read the final slope value obtained and record.

Note: If slope value is not within 98–102 percent of optimum electrode response, go back to step 1, and redo the calibration. If slope is still out of range, try another glass electrode.

6. This step must be performed at least once per 8-hour shift. Rinse electrodes with reagent waters and immerse in a stirred pH 3.63 tartrate control buffer. Wait 2 minutes for electrodes to equilibrate and meter reading to stabilize. Read the pH value to the nearest 0.001 pH unit and plot the value on the low-range control chart. Initially, these limits sill be set at ± 0.020 pH units from the mean. Once 40 data points are collected, new control limits can be calculated.

SAMPLE PREPARATION

No sample preparation is required other than equilibration to 25°C in a water bath prior to measuring pH. A sample size of 80-120 mL is adequate. An 8-ounce (250-mL) wide-mouth jar can be used as a sample container allowing the sample to be capped and providing adequate space for the electrode pair and any stirring apparatus.

PROCEDURE

After calibration of the meter for the desired pH range, as in the *CALIBRATION* section, and temperature equilibration of the sample in a water bath, as in the *SAMPLE PREPARATION* section, pH of the sample may be determined.

1. Verify that the sample temperature is 25 ± 0.25°C.
2. Rinse electrodes with reagent water, blot as in Step 1 of the *High-range pH Measurements (pH 7-14)* procedure, and immerse electrodes in the stirred sample to be measured.
3. Wait 2 minutes for electrodes to equilibrate and meter reading to stabilize. Read the pH value to 0.001 pH unit and report to the nearest 0.01 pH unit.
4. Recalibrate the meter between each sample measurement, if possible. If multiple measurements before recalibration are desired, a maximum of three measurements are recommended to maintain the precision stated in the method. Experience has shown that for seasoned samples, measuring a larger number of samples without recalibration increases the variability of the system and may lead to difficulty in keeping buffer values within the specified tolerances. Samples spanning a large range in pH (i.e., 7.5 and 12), in most cases require recalibration between each sample.

   Regardless of the total number of samples measured, if measuring more than one sample, the meter should be calibrated after the final sample is run to ensure that no malfunction occurred at some point during the process. If the specified buffer tolerances cannot be met, those samples run since the last calibration should be retested.

CALCULATIONS

Each laboratory should chart, for each meter in use, the pH values of the phosphate and tartrate control buffers obtained during meter calibration, and calculate and plot the moving range for each buffer. In addition to providing information with regard to the current status of the pH measurement system, systems in separate laboratories that are capable of maintaining control on these buffers should be able to obtain similar mean pH values on photoprocessing solutions.

Individual laboratories may wish to determine the mean value on a given batch of control buffer from 5-6 aliquots and use this value as the initial aim value.

REPORT

The sample pH value should be reported to the nearest 0.01 pH unit, and the temperature of measurement, 25°C.

* Buffer tolerances of ± 0.003 pH were used in determining the estimate of the precision of this procedure given in *PRECISION AND BIAS*. Based on time available for analysis and precision requirements, a practical range of ± 0.005 pH may be used.

APPENDIX A

Preparation of Reagent Solutions

Preparation of NIST Reference Buffers

NIST reference materials are available from the Office of Standard Reference Materials, National Institute of Standards and Technology, Gaithersburg, MD 20899, 301-975-6776.

All NIST buffers should be prepared with reagent grade water with a conductance less than 2 x 10^{-6} ohm^{-1} cm^{-1}. Each lot of reference material issued has an associated lower-case letter following the material number, ex. 185*g*. Because different lots may exhibit different pH values, the certificate which comes with each lot from NIST should be retained for reference. The letters given here are for the current lots. The uncertainty of the pH of NIST Standard Reference Materials (SRM) described here is estimated not to exceed ± 0.005 pH unit at the current measurement temperature. NIST buffers prepared as described here can be used for up to four weeks, except for pH 7 (two weeks).

1. pH 4 Phthalate Reference Buffer

   Reference: National Institute of Standards and Technology Certificate, Standard Reference Materials Number: 185.

   For SRM 185, lot g, pH @ 25°C = 4.006

   Standard Reference Material 185*f*, potassium hydrogen phthalate ($KHC_8H_4O_4$), should be dried for 2 hours at 110°C and cooled to room temperature in a desiccator. For 1 L of buffer, add 10.120 g of SRM 185*g* to a 1-L volumetric flask containing 500 mL of reagent water. Dissolve the salt, fill to the mark with reagent water at 25°C, and mix thoroughly by shaking. The water used in the preparation of this buffer need not be protected from atmospheric oxygen, but should be protected against evaporation and contamination by molds.

2. pH 7 Equimolar Phosphate Reference Buffer

   Reference: National Institute of Standards and Technology Certificate, Standard Reference Materials Numbers: 186I and II

   For SRM 186I and 186II, lot e, pH @ 25°C = 6.863

   Standard Reference Materials 186I*e*, potassium dihydrogen phosphate (KH_2PO_4), and 186II*e*, disodium hydrogen phosphate (Na_2HPO_4), should be dried for 2 hours at 110°C and cooled to room temperature in a desiccator. For 1 L of buffer, add 3.387 g of SRM 186I*e* and 3.533 g of 186II*e* to a 1-L volumetric flask containing 500 mL of reagent carbon dioxide-free water. Dissolve the salts, fill to the mark with water at 25°C, and mix thoroughly by shaking. All water used in the preparation of this buffer should be carbon dioxide-free; boil reagent water for 10 minutes and cool in a vessel guarded by a CO_2 absorbent tube (e.g., ASCARITE II or soda lime). "U"-shaped tubes reduce the possibility of buffer contamination from the absorbent. Store the prepared buffer under a CO_2 absorbent tube. Keep the tube in place except when removing aliquots of buffer.

3. pH 9 Borate Reference Buffer

   Reference: National Institute of Standards and Technology Certificate, Standard Reference Materials Number: 187.

   For SRM 187, lot C, ph @ 25°C = 9.180

   Standard Reference Material 187*c*, sodium tetraborate decahydrate (borax, $Na_2B_4O_7 \cdot 10\ H_2O$) should *not* be dried before use. Gently crush any large lumps of salt. For 1 L of buffer, add 3.800 g of the borax (SRM 187*c*) to a 1-L volumetric flask containing 500 mL of reagent carbon dioxide-free water. Dissolve the salt, and fill to the mark with water at 25°C, and mix thoroughly by shaking. All water used in the preparation of this buffer should be carbon dioxide-free; boil reagent water for 10 minutes and cool in a vessel guarded by a CO_2 absorbent tube (e.g., ASCARITE II or soda lime). "U"-shaped tubes reduce the possibility of buffer contamination from the absorbent. Store the prepared buffer under a CO_2 absorbent tube, Keep the tube in place except when removing aliquots of buffer.

Preparation of Calibrating Buffers

Calibrating buffers may be purchased, or are prepared with reagent grade chemicals and reagent water. While it is not necessary for these buffers to use carbon dioxide-free water for preparation, for the pH 10 buffer, bottles should be kept sealed after preparation.

1. pH 4 Phthalate Calibrating Buffer

   Prepare as in *pH 4 Phthalate Reference Buffer* with reagent grade potassium hydrogen phthalate (drying of the salt is not necessary), using 10.1 g of salt per litre of buffer.

2. pH 7 Equimolar Phosphate Calibrating Buffer

   Prepare as in *pH 7 Equimolar Phosphate Reference Buffer*, using 3.5 g of reagent grade disodium hydrogen phosphate and 3.4 g of reagent grade potassium dihydrogen phosphate per litre of buffer (drying of the salts is not necessary). This buffer is stable for up to 6 months unless mold appears or a large pH change is noted during standardization.

3. pH 10 Carbonate Calibrating Buffer

   For 1 litre of buffer, add 2.1 g of reagent grade sodium bicarbonate ($NaHCO_3$) and 2.6 g of reagent grade sodium carbonate (Na_2CO_3) (drying of the sodium carbonate is not necessary) to a 1-L volumetric flask containing 500 mL of reagent water. Dissolve the salt and fill to the mark with reagent water.

Preparation of Control Buffers

1. pH 11.43 Phosphate High pH Control Buffer

   To prepare one litre of phosphate control buffer, boil 1300 mL of reagent water for 10 minutes. Cool the water in a vessel guarded by carbon dioxide absorbent (e.g., ASCARITE II or soda lime). (Store the prepared buffer under the same absorbent tube, keeping the tube in place except when removing aliquots of buffer.)

   Add 43.20 g of reagent grade tripotassium phosphate ($K_3PO_4 \cdot nH_2O$), and 31.70 g of reagent grade dipotassium hydrogen phosphate (K_2HPO_4, also known as potassium phosphate, dibasic powder) to a 1-L volumetric flask containing 600 mL of boiled and cooled reagent water. Add a magnetic stir bar and stir until dissolved. Remove the stir bar and dilute to volume with more boiled and cooled reagent water. Mix thoroughly.

   This buffer has replaced the previously suggested glycerinate control buffer (pH 11.40) as the phosphate buffer has shown greater long-term stability.

Note: Environmental (a), microbiological challenge (b), and aeration (c) studies were performed on this buffer to ensure that it was a stable, suitable choice for a high control buffer:

   a. After 11 days in environmental chambers held at 20°F and 120°F, pH differences of not more than 0.005 pH units from the original pH value were observed.

   b. Samples of phosphate control with and without a biocide (PROXEML®) were spiked with various strains of bacteria and fungi (including an alkaline-tolerant bacterium). Bacterial and fungal counts after 6 and 29 days at room temperature indicate that the high pH of the buffer alone does a good job of killing bacteria and inhibiting fungal growth.

   c. Continuous bubbling of air into a sample of phosphate buffer for 30 minutes resulted in a decrease of only 0.02 pH units.

2. pH 3.63 Tartrate Low pH Control Buffer

   Reference: National Institute of Standards and Technology Certificates, Standard Reference Materials Number: 188.

   Standard Reference Material 188, potassium hydrogen tartrate ($KHC_4H_4O_6$), need not be dried before use. For 1 L of buffer, add 1.878 g of SRM 188 to a 1-L volumetric flask containing 500 mL of reagent water. Dissolve the salt, and fill to the mark with reagent water at 25°C, and mix thoroughly by shaking. The water used in the preparation of this buffer need not be free of dissolved oxygen, but solutions of tartrate are *extremely* susceptible to mold growth with an accompanying change in pH of the solution. In order to use this buffer as a reference solution without preparing it fresh each day, a biocide must be added. 0.3 mL DEARCIDE 702 (KAN 441629) should be added to each litre of buffer prepared. This amount will permit use of the solution for the same time period as the other NIST buffers; solutions prepared in this manner were found to be stable for the indicated period of time. Solutions prepared with water from a high-purity cartridge-type water system (for example, the MILLI-Q system, MILLPORE CORPORATION) were stable without addition of DEARCIDE, and did not exhibit mold growth, possibly due to the filtering stages which remove organic contaminants from the water.

Reference Electrode Filling and Storage Solution, 3.5 M KCl

For calomel electrodes: For 1 L of 3.5 M solution, add 261 g KCl to a 2-L beaker containing 400 mL of reagent water. Dissolve the salt, heating if necessary, transfer the solution to a 1-L volumetric flask and bring to volume with reagent water, and mix thoroughly.

For silver/silver chloride electrodes: To prepare 1 L of 3.5 M KCl solution. add 261 g of reagent grade KCl to a 2-L beaker containing 400 mL of reagent water. Add a magnetic stir bar and place on a magnetic stir plate. Stir until dissolved (heating or use of an ultrasonic bath may be necessary). Add 10 mL of 0.05 M silver nitrate ($AgNO_3$) and stir to aid equilibration. Transfer the cooled solution to a l-L volumetric flask and bring to volume with reagent water. Mix thoroughly.

Storage Buffer, 0.1 M KCl in pH 7 Buffer

For 1 L of storage buffer, add 7.5 g KCl to a 1-L volumetric flask containing 400 mL of pH 7 buffer. Dissolve the salt, bring to volume with pH 7 buffer, and mix thoroughly.

APPENDIX B

Standardization of Calibrating Buffer Solutions

Kodak has evaluated the performance of several commercially prepared calibrating buffers. It is our recommendation that calibrating buffers be assigned a pH value versus a primary buffer standard such as NIST buffers, since the pH of the buffers may vary from container to container and from lot to lot. These commercially prepared primary buffer standards can be purchased from Radiometer, Copenhagen (see *APPENDIX D*).

A recent study in Kodak laboratories compared the differences in pH between photoprocessing solutions measured using the values assigned to the calibrating buffers versus NIST primary standards (6.988 and 10.020) [method a] and those measured using the value quoted on the label of the commercial calibrating buffer (simply 7.00 and 10.00) [method b]. The following table displays the average difference obtained by subtracting the method a pH values from the method b pH values.

pH of solution measured	Average difference in pH
9.66	0.02
10.65	0.03
12.14	0.04

The data in the table above clearly indicate the importance of referencing all calibrating buffers against primary NIST standards. The practice of using the pH values printed on the container of calibrating buffer (e.g., 7.00 and 10.00), in place of those values obtained by referencing against NIST buffers, should be avoided as it contributes a significant source of variability to the measurement. And this added variability is approximately one-half of the pH specification of some photographic developers.

Standardization of pH Meter - High pH Range

1. Bring NIST reference buffers, pH 7 and 9, and calibrating buffers, pH 7 and 10 (to be standardized), to temperature equilibrium at 25°C.
2. Rinse electrodes with reagent water and blot excess water from the tips of the electrodes (and any protective assemblies that are being used) with a soft tissue, taking care not to rub the tissue against the electrode membrane surface (rubbing produces static which in turn will affect the reading). It should be sufficient to hold a tissue near the surface of the electrode and allow the water to be drawn into it.

   Immerse the electrodes in pH 7 calibrating buffer stirred with either a TEFLON-coated stir bar and magnetic stirrer, or a paddle-type stirrer that has been rinsed with reagent water.
3. Wait 2 minutes for electrodes to equilibrate and meter reading to stabilize. At the end of the 2 minutes, if the meter does not read the value, ± 0.003 pH units, determined by NIST for the lot of SRM used for this buffer (e.g., 6.863), either adjust the calibrate control or set the meter to the proper buffer value.
4. Rinse electrodes with reagent water, blot as in step 1, and immerse electrodes in NIST pH 9 reference buffer (stirred as in step 1).
5. Wait 2 minutes for electrodes to equilibrate and meter reading to stabilize. At the end of the 2 minutes, if the meter does not display the value, ± 0.003 pH units, determined by NIST for the lot of SRM used for the buffer (e.g., 9.180), either adjust the calibrate control, or set the meter to the assigned buffer value.
6. Repeat steps 1–5 until the meter displays the assigned buffer values ± 0.003 pH units. Read the final slope value obtained and record.

Note: If slope value is not within 98–102 percent of optimum electrode response, go back to step 1, and redo the calibration. If slope is still out of range, try another glass electrode.

Proceed to the *Standardization of Calibrating Buffers - High pH Range* procedure.

Standardization of pH Meter - Low pH Range

1. Bring NIST reference buffers pH 7 and 4, and calibrating buffer pH 4 (to be standardized) to temperature equilibrium at 25°C.
2. Rinse electrodes with reagent water and blot excess water from the tips of the electrodes (and any protective assemblies that are being used) with a soft tissue, taking care not to rub the tissue against the electrode membrane surface (rubbing produces static which in turn will affect the reading). It should be sufficient to hold a tissue near the surface of the electrode and allow the water to be drawn into it.

   Immerse the electrodes in NIST pH 7 calibrating buffer stirred with either a TEFLON-coated stir bar and magnetic stirrer, or a paddle-type stirrer that has been rinsed with reagent water.
3. Wait 2 minutes for electrodes to equilibrate and meter reading to stabilize. At the end of the 2 minutes, if the meter does not read the value, ± 0.003 pH units, determined by NIST for the lot of SRM used for this buffer (e.g., 6.863), either adjust the calibrate control or set the meter to the proper buffer value.
4. Rinse electrodes with reagent water, blot as in step 1, and immerse electrodes in NIST pH 4 reference buffer (stirred as in step 1).
5. Wait 2 minutes for electrodes to equilibrate and meter reading to stabilize. At the end of the 2 minutes, if the meter does not display the value, ± 0.003 pH units, determined by NIST for the lot of SRM used for the buffer (e.g., 4.006), either adjust the calibrate control, or set the meter to the assigned buffer value.
6. Repeat steps 1–5 until the meter displays the assigned buffer values ± 0.003 pH units. Read the final slope value obtained and record.

Note: If slope value is not within 98–102 percent of optimum electrode response, go back to step 1, and redo the calibration. If slope is still out of range, try another glass electrode.

Proceed to the *Standardization of Calibrating Buffers - Low pH Range* procedure.

Standardization of Calibrating Buffers - High pH Range

1. For high pH range calibrating buffers (pH 7 or 10), use the meter standardized as in *Standardization of pH Meter - High pH Range* and measure the pH of the calibrating buffer (pH 7 or 10) to the nearest 0.001 pH unit.
2. Repeat the meter standardization procedure, *Standardization of pH Meter - High pH Range*, and measure the calibrating buffer (pH 7 or 10) again.
3. If the two values obtained in steps 1 and 2 are within 0.005 pH units of each other, the values may be averaged. If the values differ by 0.005 pH units or more, disregard the data, and repeat the meter calibration (*Standardization of pH Meter - High pH Range*) and measurements (in steps 1–2 of this procedure) using fresh aliquots of the NIST reference buffers and calibrating buffers.
4. Average the two values (from steps 1 and 2 of this procedure) and use the mean value as the standardization value for the calibrating buffer.
5. Repeat this procedure once per week; (see *Frequency of Standardization of Calibrating Buffers*).

Standardization of Calibrating Buffers - Low pH Range

1. For low pH range calibrating buffers (pH 4), use the meter standardized as in *Standardization of pH Meter - Low pH Range* and measure the pH of the calibrating buffer (pH 4) to the nearest 0.001 pH unit.
2. Repeat the meter standardization procedure, *Standardization of pH Meter - Low pH Range*, and measure the calibrating buffer (pH 4) again.
3. If the two values obtained in steps 1 and 2 are within 0.005 pH units of each other, the values may be averaged. If the values differ by 0.005 pH units or more, disregard the data, and repeat the meter calibration (*Standardization of pH Meter - Low pH Range*) and measurements (in steps 1-2 of this procedure) using fresh aliquots of the NIST reference buffers and calibrating buffers.
4. Average the two values (from steps 1 and 2 of this procedure) and use the mean value as the standardization value for the calibrating buffer.
5. Repeat this procedure once per week; (see *Frequency of Standardization of Calibrating Buffers*).

Frequency of Standardization of Calibrating Buffers

In the past, weekly standardization was recommended for all calibrating buffers. A recent Kodak laboratory study indicated that the frequency of standardization of 20-L cubes of calibrating buffer can be reduced to once per two months provided *all* of the following laboratory practices are strictly adhered to:

1. Calibrating buffers recommended in *APPENDIX D* should be used. The vendors of these buffers have taken adequate precautions to protect against biological growth (biocides), aerial oxidation (self-collapsible polyethylene cubes), and light degradation (cubes contained in cardboard boxes during use). Thus, use of commercial buffers other than those specified in *APPENDIX D*, still requires the weekly standardization.

   Cubes of buffer should be allowed to drain by themselves, i.e., air should not be introduced to speed draining.
2. Three measurements should be performed instead of two (as in *Standardization of Calibrating Buffers - High pH Range* and *Standardization of Calibrating Buffers - Low pH Range*) and the average of the three measurements should be taken.
3. The recommended control buffers should be measured daily so that any changes in calibrating buffers can be detected.
4. Freshly opened commercially prepared (Radiometer) NIST reference buffers or freshly prepared NIST reference buffers (from SRM) should be used. After the standardization procedure is completed, remaining reference buffers should be discarded.

APPENDIX C

Electrode Care

In general, manufacturer's recommendations for electrode care should be followed when possible. Studies performed in Kodak laboratories indicate that pH electrodes stored in distilled water require 1.5 to 2.5 times longer for equilibration in calibrating buffers than those electrodes stored in pH 7 buffer. Also, studies performed by the manufacturer of the 476024 pH electrode indicate that storage of the electrode in water accelerated degradation of the sensing glass (cations from the glass are removed by the water). Based on consultations with the technical staff at Ciba-Corning Diagnostics (manufacturer of the recommended electrodes), pH 7 buffer is recommended for glass electrode storage and 3.5 M KCl is recommended for reference electrode storage when the electrode pair is not in use; the electrode pair may be temporarily stored between measurements in a buffer consisting of 0.1 M KCl in pH 7 buffer (see *Storage Buffer, 0.1 M KCl in pH 7 Buffer*).

Glass Electrodes - Preconditioning/Rejuvenation

Preconditioning of glass pH electrodes should follow manufacturer's recommendations, but in general, a minimum soaking time of 2 hours in pH 7 buffer is recommended before use for pH measurement; overnight soaking is preferred.

If the electrode fails in the slope requirement, cannot achieve the assigned buffer values, or gives an unsatisfactory value in measurement of the control solution, place the glass electrode tip (detach the electrode lead from the pH meter during this process) in 1.0 M HCl, for 5 minutes. Then place the same electrode in 1.0 M NaOH for 5 minutes. Return the electrode to 1.0 M HCl for another 5 minutes. Rinse the electrode with distilled or demineralized water and soak in pH 7 buffer for 2 hours. Reconnect the electrode and try a calibration. If no improvement is noted, discard the electrode. More severe reconditioning procedures are not recommended due to both the toxicity of reagents required and the cost in analyst time versus the cost of electrode replacement. If an improvement is noted, but the electrode is still not reading the desired values, repeat the HCl/ NaOH/ HCl soak procedure one more time, and calibrate the meter with the treated electrode. If no further improvement is noted, discard the electrode.

Reference Electrode Care/Rejuvenation

For new reference electrodes, withdraw the filling solution and refill the electrode with 3.5 M KCl (calomel electrodes) or 3.5 M KCl saturated with AgCl (Ag/AgCl electrodes).

At the beginning of each shift/day, the KCl filling solution should be withdrawn and the electrode refilled with fresh 3.5 M KCl (calomel electrodes) or 3.6 M KCl saturated with AgCl (Ag/AgCl electrodes).

When poor performance of the pH measurement system is not improved with substitution of a new pH electrode, reference electrode junction clogging may be the problem, especially where inaccurate or unsteady readings are obtained. If there is a possibility the filling solution may have become contaminated, refill with fresh KCl and recheck the system. Frit-type junctions can be checked for flow by pressing just the tip of the reference electrode gently against a paper towel several times. A small wet spot will be visible if the junction is flowing.

For clogged calomel reference electrodes, warm (not above 50°C) a solution of 3.5 M KCl diluted 1 part to 9 with distilled water, and soak the electrode junction for 1/2 hour. Drain the electrolyte and replace with fresh 3.5 M KCl, and retest the electrode.

For Ag/AgCl reference electrodes, a 10-minute soak in 10 percent NH_4OH can remove precipitated AgCl from the junction. It is important that the electrode have filling solution present when trying this procedure. Higher concentrations of NH_4OH or longer periods of soaking should be avoided as in some types of Ag/AgCl reference electrodes damage to the reference element may occur.

As with glass electrodes, more severe procedures are not recommended as they are costly and, in many cases, do more to damage the electrode than to improve its performance.

Reference Electrode Accuracy Check

Liquid-junction potential error in reference electrodes can be assessed* by determining the pH of the NIST equimolar phosphate buffer (See *pH 7 Equimolar Phosphate Reference Buffer* in *APPENDIX A*) at two ionic strengths differing by a factor of 10. The meter is standardized with the NIST phosphate buffer (pH 7, full strength), and the NIST phthalate buffer (pH 4) as in *APPENDIX B.* Dilute 110 mL of the NIST phosphate buffer (pH 7) to 1 L with distilled water, and measure the pH of the diluted buffer. The meter reading should be 7.065 ± 0.010 pH units for a properly functioning reference junction.†

APPENDIX D

RECOMMENDED COMMERCIALLY PREPARED BUFFER SOLUTIONS AND THEIR SOURCES

NIST Reference Buffers

1. pH 1.68, 500 mL, Radiometer America Order No. 511M001
2. pH 4.01, 500 mL, Radiometer America Order No. 511M002 (European No. S1316)
3. pH 6.86, 500 mL, Radiometer America Order No. 511M003 (European No. S1346)
4. pH 9.18, 500 mL, Radiometer America Order No. 511M006 (European No. S1336)

In the U.S., above buffers are available from:

Radiometer America
810 Sharon Drive
Westlake, OH 44145
1-800-736-0600

In Europe, they are manufactured by and available from:

Radiometer A/S
Emdrupvjet 72
Copenhagen NV
Denmark

Calibrating Buffers

1. pH 4, 20-L cube, VWR Scientific, CAT No. 34170-155
2. pH 7, 20-L cube, VWR Scientific, CAT No. 34170-158

   VWR Scientific
   P.O. Box 483
   Bridgeport, NJ 08014
   800-932-5000
3. pH 10,20-L cube, Fisher Scientific, CAT No. SB-115-20

   Fisher Scientific Company
   50 Fadem Road
   Springfield, NJ 07081-3193
   800-766-7000

Control Buffers

1. pH 3.63, gallon, SPI CAT No. 1750

   Also available in 120-mL and quart volumes
2. pH 11.43, gallon, SPI CAT No. 6805

   Also available in 120-mL and quart volumes

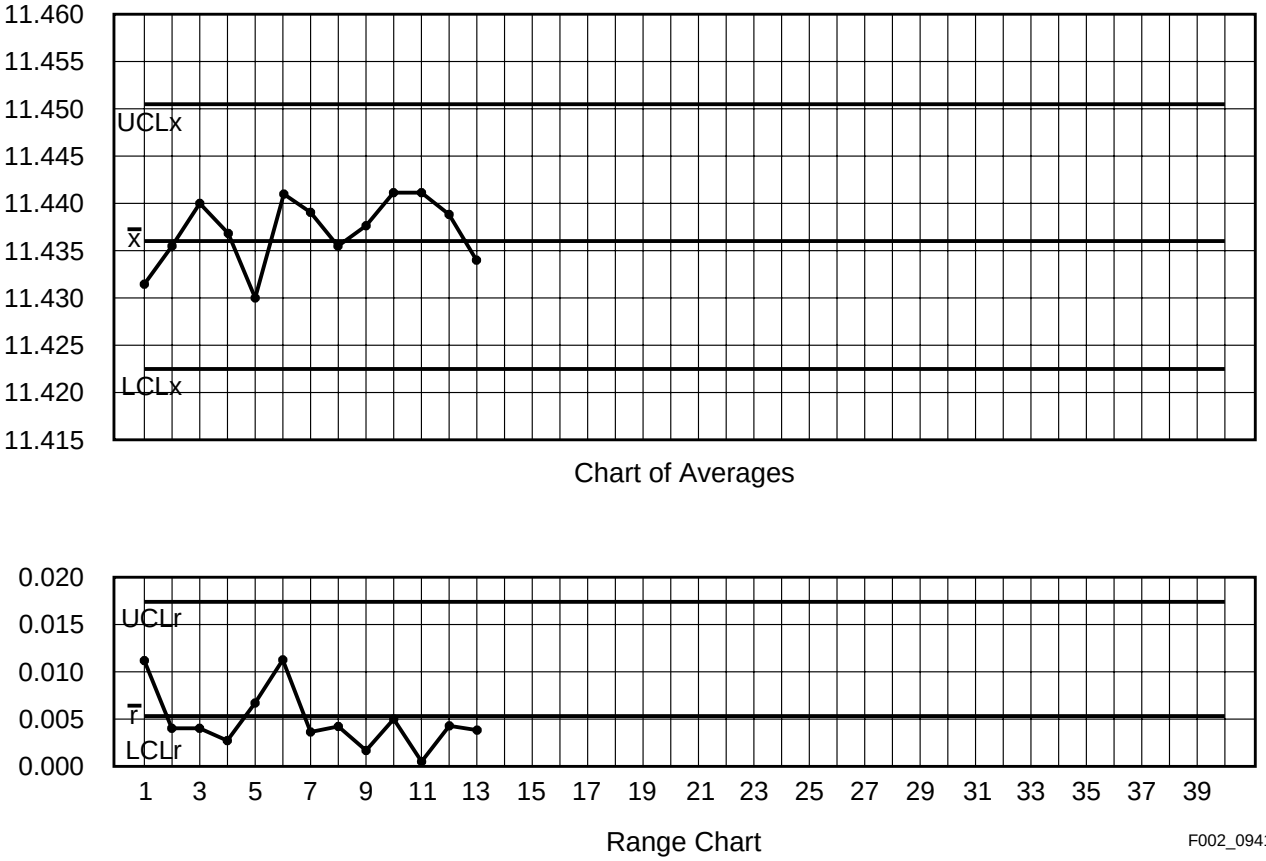
These control buffers are manufactured for Kodak by:

Solution Plus, Inc.
2275 Cassens Drive, Suite 147
Fenton, MO 63026
314-349-4922

* J.A. Illingsworth, *A Common Source of Error in pH Measurements*; Biochem. J. (1981) 195, 259.

† Additional methods for reference electrode evaluation can be found in: C.C. Westcott *pH Measurements*; Academic Press: New York (1978) pp. 65-70.

Figure 1 pH 11.4 High Control @ 25°C



Individuals		Ranges	
UCLx	11.4504	UCLr	0.0172
X bar	11.4363	r bar	0.0053
LCLx	11.4223	LCLr	0.0000
Units: pH Historical Limits: n = 19			

Potentiometric Titrations for Photoprocessing Solutions

ULM-0003-01

INTRODUCTION

Titrations involve the addition of accurately known volumes of standardized titrant to a solution containing the sample. The concentration of the analyte(s) being determined by titration can be calculated based on the volume of titrant used to reach the endpoint (also referred to as the equivalence point or break) of the titration. The titration endpoint can be determined manually or potentiometrically. In a manual titration the endpoint is determined by use of a visual indicator that changes color when the endpoint of the titration has been reached. In a potentiometric titration the endpoint is determined by use of a pair of electrodes or a combination electrode. The endpoint occurs where there is a maximal rate of change of potential at the endpoint of the titration. In the portion of the curve corresponding to this large change in potential, there is a point at which the curve changes its direction of curvature. This point is an inflection point or break in the curve and ideally it occurs at the equivalence point of the titration. However, in certain cases, there may be a bias in the analysis, and the break may be slightly displaced from the true equivalence point. The analysis of known samples may indicate that the bias is large enough to require a correction.

The electrode pair for potentiometric titrations includes an indicator and reference electrode. The combination electrode contains the indicator and reference electrode configured in a single electrode. The electrodes for potentiometric titrations are chosen so that a change in potential of the titration solution, caused by titration of the analyte(s) of interest, is optimally detected. Potentiometric titrations are preferred to manual titrations, since they are more accurate and precise. They are also more easily adapted to automation, where automated titration systems can process larger volumes of samples with minimal analyst involvement.

Use of this method requires handling of potentially hazardous chemicals. Material Safety Data Sheets should be consulted for each chemical before use. These can be obtained from the chemical's supplier.

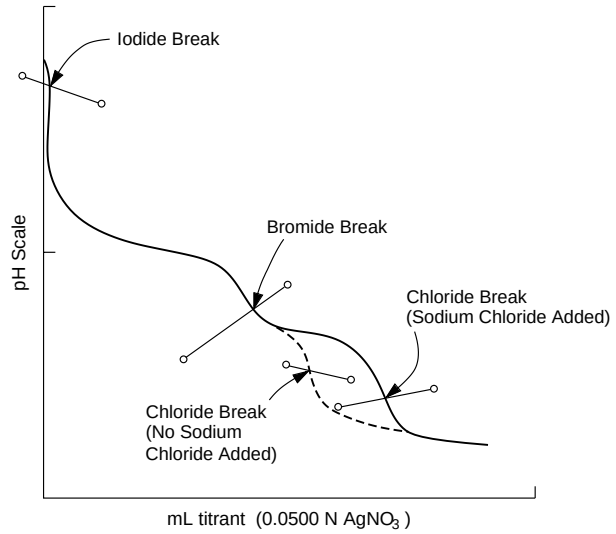
TYPES OF TITRATIONS

Types of potentiometric titrations for the determination of analytes in photoprocessing solutions include acid-base (total alkalinity and total acidity), redox (HI/HY and cerate), precipitation (halides), and complexometric (free EDTA and Antical #5). The specific titrimetric method, including which electrode(s) to use, can be found in individual analytical methods for each photographic process.

Since silver halide titrations are not explained in more detail in most methods, they will be discussed here. An Orion double junction electrode with an outer filling solution of potassium nitrate is used as the reference electrode for titrations of halides with silver nitrate. A silver electrode is used as the indicating electrode for halide titrations, because its potential is a function of the silver ion concentration in the titration solution. The potential between the electrodes is measured and recorded manually when a potentiometer or a pH meter is used; this is done automatically when an automatic titrator is used. These potential measurements are read on a millivolt scale.

Difficulties may occur when more than one halide is present in a solution. One of the difficulties in titrations with silver nitrate is in knowing which particular halide caused the inflection point on the curve. Where iodide, bromide and chloride are present the first break should be that of the iodide, because it has the lowest solubility. However, if little or no iodide is present in the sample, the first break will be that of the bromide, followed by a break for chloride. See Figure 1, *Typical Bromide Titration Curve*. When little chloride is present, the bromide and chloride in the sample may co-precipitate. If so, one break may easily be confused with the other. This situation is avoided in several bromide methods by the addition of more chloride to the sample before titration, to pull the chloride break away from the bromide break.

Figure 1 Typical Bromide Titration Curve



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TITRANT PREPARATION AND STANDARDIZATION

Titrant preparation and standardization methods can be found in *Processing KODAK Motion Picture Films, Module 4, Reagent Preparation Procedures.*

PREPARATION AND STORAGE OF ELECTRODES

Preparation of Indicator-Electrodes

1. Silver Bar or Silver Billet Electrodes

   a. Clean the silver electrode to brightness using Silver Polish, obtainable from Fisher Scientific Co. (catalog number 9-311-309), on a damp tissue. Rinse the electrode well with reagent water, Type 1. For a definition of reagent water, Type 1, see ASTM standard B 1193.

   b. Do an initial titration. This allows the electrode the opportunity to become equilibrated in the system in which it will be used. Discard the results from this initial titration.

   c. Rinse the silver electrode well with reagent water, Type I and wipe it with a tissue between subsequent titrations of similar samples (e.g. a silver electrode equilibrated in a bromide system may be used only for subsequent bromide titrations or until it no longer performs before recleaning to brightness).

   The silver electrode should be stored dry in air when not being used.

2. Electroplated Silver-Silver Iodide Electrode

   Follow instructions provided in Method 900, *Procedure for Electroplating a Silver-Silver Iodide Electrode*, or any subsequent revision.

   The silver iodide electrode should be stored dry in air when not being used.

3. Platinum Disc Electrode

   Whenever a deposit or coating collects on the disc, clean the disc using an aluminum oxide polishing strip, made by Moyco and obtainable from Orion, part number 301044-001. Thoroughly rinse the electrode with reagent water, Type 1.

   The platinum electrode should be stored dry in air when not being used.

4. Glass Electrodes

   See Method ULM-191-2, *pH Measurement of Photographic Processing Solutions*, (or any subsequent method for determining pH) for instructions on care and storage of glass indicator electrodes.

5. Ion specific electrodes (Copper, Silver Sulfide, Potassium Iodide, Calcium)

   Refer to the analytical procedure or manufacturers directions for proper electrode cleaning and storage.

Reference Electrodes

1. Calomel Electrodes for Use with a Glass Indicator Electrode

   See Method ULM-191-2, *pH Measurement of Photographic Processing Solutions*, (or any subsequent method for determining pH) for instructions on care and storage of calomel electrodes.

2. Calomel Electrodes for Use with Silver Bar or Billet and Platinum Disc Electrodes

   a. Remove the potassium chloride fill solution and substitute saturated potassium nitrate solution when titrating with silver nitrate.

   Note: Refer to the specific method when determining whether to use 3.5 N potassium chloride or saturated potassium nitrate solution in the calomel electrode, for titrations with titrants other than silver nitrate.

   b. There should be a few potassium nitrate crystals present in the calomel electrode after filling with saturated potassium nitrate solution. The electrode should be checked to ensure that the solution is flowing through the inverted sleeve or fiber tip, before using.

3. Ag/AgCl Double Junction Electrodes

   It is recommended that the manufacturers supplied solution be used for the inner chamber (AgCl) and that it be emptied and refilled weekly. The outer chamber should be filled with an appropriate solution for the analysis being carried out, usually a 10 percent potassium nitrate solution, which should be emptied and refilled daily.

   Ag/AgCl electrodes can be stored in reagent water, Type 1 for up to one week. For longer periods of time drain the electrode, rinse with water and store dry.

PERFORMANCE CHECK OF ELECTRODE / INSTRUMENT SYSTEM

Analysis of samples containing known amounts of the analyte being measured can be an effective way of determining whether the system will produce reliable results on samples containing unknown amounts of the same analyte.

BLANK DETERMINATION

Some test methods call for the determination of a blank (e.g. HI/HY and cerate titrations). The titration blank should be determined under the same conditions as the sample, including temperature, equipment parameters, and titration speed. The blank should include everything except the analyte being measured.

When measuring titration blanks for a potentiometric analysis, the blank value to be subtracted from the sample titration should correspond to the volume of titrant required to titrate the titration matrix (containing everything except the analyte of interest being measured). This volume

difference corresponds to the potential of the equivalence point of the sample or standard being measured.

DETERMINATION OF THE END POINT FOR POTENTIOMETRIC TITRATIONS

Microprocessor Controlled Titrators

Microprocessor controlled titrators are programmed to pick end points automatically using algorithms.

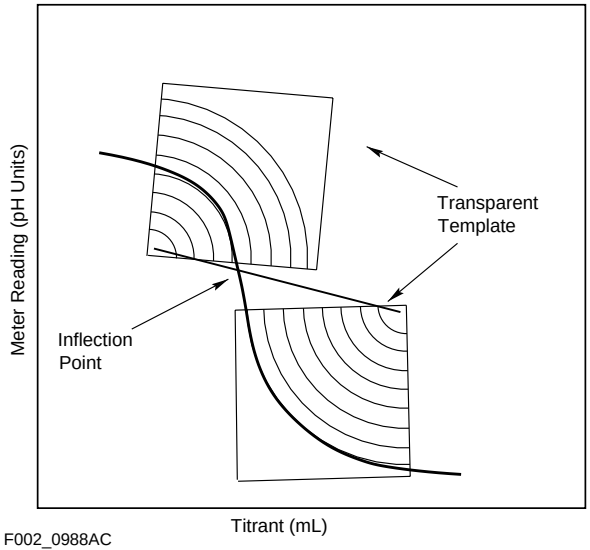
Concentric Arcs Method

One way of manually locating the endpoint of a titration curve is by using a concentric arcs template. This template is semi-rigid and transparent. A series of arcs is scribed upon it $\frac{1}{4}$-inch apart.

Locate the approximate position of the endpoint, which is in the part of the curve representing the greatest rate of potential change. Place the template on the curve on one side of the approximate endpoint, superimposing one of the arcs on the curve. Try different arcs to find the largest one that best fits the curve. Then make a dot on the graph through the small hole in the template.

Place the template on the curve on the other side of the approximate endpoint and repeat the procedure. The arc that best fits this part of the curve is not necessarily the same arc that best fit the first part of the curve. Draw a straight line between the two dots. The point where the straight line intersects the curve is the end point. See Figure 2, *Use of Concentric Arcs Template to Determine the End Point of a Potentiometric Titration*.

Figure 2 Use of Concentric Arcs Template to Determine the End Point of a Potentiometric Titration



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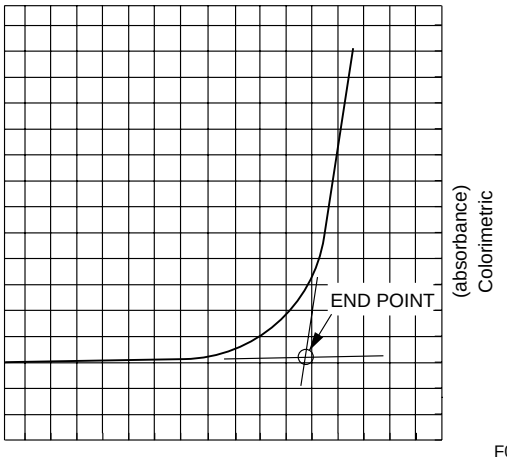
Colorimetric Endpoint Determination

Some titrations use color change end point detection instead of potentiometric (e.g. Antical #5 in RA-4 and free EDTA). Colorimetric endpoints should be determined using a Brinkmann 701 colorimeter, or equivalent, and optical probe at the optimal wavelength. Endpoints are best determined using a strip chart recorder and using the intersecting tangents method for determining the endpoint. See Figure 3, *Colorimetric – Intersecting Tangents*.

Figure 3 Colorimetric – Intersecting Tangents



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Directions:

1. Use a straight edge to draw a line tangential to the bottom half of the curve.
2. Draw another line tangential to the top half of the curve.
3. The endpoint is measured where the lines intersect.

TITRATION PROCEDURE

Preparation for Titration

Note: See the particular instrument (pH meter or automatic titrator) manual for specific operating instructions and appropriate settings.

1. Attach the appropriate electrode pair or combination electrode to the instrument according to the specific method. Electrodes with side caps (plugs) should be uncapped before use to allow appropriate "weeping" of fill solutions.

   Note: All titrations must be run with the indicator electrode in the indicator jack of the instrument and the reference electrode in the reference jack. Refer to the instructions included with specific combination electrodes used, as they do not all attach to the titrator in the same manner.

2. Fill the burette with the proper titrant, making sure the delivery tip has been "seasoned" (purged several times with small aliquots of fresh titrant). Rinse all excess titrant from the delivery tip with reagent water, Type 1 from a wash bottle into a "waste" beaker.

3. Prepare the sample with its necessary reagents as indicated in the specific method. Add a magnetic stir bar. Be sure to leave enough space at the bottom of the beaker so the magnetic stir bar does not damage the electrodes.

4. Stir the sample on a magnetic stirrer and immerse the electrodes and burette tip in the sample.

   Note: The titrant delivery tip should be placed so that the titrant flows past the reference electrode before the indicator electrode. Set the stirrer speed to stir rapidly without splashing or creating a vortex.

5. Add reagent water, Type 1, if necessary, to cover at least the lower $\frac{1}{2}$-inch of the electrodes. Keep the solution level below the electrode fill solution level to insure proper "weeping" of electrode fill solution.

6. Remove the delivery tip from the solution as soon as titration is complete to prevent contamination of titrant by sample solution diffusion.

Actual Titration

Note: Make the necessary instrument and recorder adjustments before starting the titration.

1. Manual Titration Using a pH Meter
   a. Add the titrant in 0.20-mL increments, unless otherwise indicated in the specific method. After each addition, wait until the needle stops moving and record burette and meter readings.
   b. Titrate until each succeeding 0.20 ml increment produces less change in the meter reading than the preceding addition. Make at least five more additions of titrant before ending the titration. Plot on graph paper, ml of titrant on the x axis versus millivolts on the y axis.

      Note: For bromide titrations, titrate until the chloride endpoint has been passed, unless more than 10 ml of titrant is required.

   c. Remove the electrode assembly from the beaker. Rinse the electrodes with reagent water, Type 1. If rinsing does not remove all deposits, gently blot the electrodes with a tissue and rinse them again. Place the electrodes in their appropriate storage media.
   d. Determine the endpoint by the *Concentric Arcs Method*.

2. Automatic Titration Using Recording Titrators and Microprocessor Controlled Titrators

   Note: Automatic titrators should be set to the parameters found in the specific method being performed.

   a. When using a recording titrator (such as a Metrohm E-536) turn the titrator drive on and allow the titration to proceed through the desired break(s). Turn the titrator drive off. Microprocessor controlled titrators have other operating directions, which can be found in the instrument manuals.
   b. Remove the titration beaker and rinse the delivery tip and electrodes. (if rinsing does not remove all deposits, gently blot the electrodes and delivery tip with a tissue and rinse them again.) Place the electrodes in their appropriate storage media.
   c. Microprocessor controlled titrators will automatically pick the endpoint(s). For recording titrators, determine the endpoint by the *Concentric Arcs Method*.

Determination of Residual Thiosulfate in Processed Black-and-White Films as Methylene Blue

ULM-0004/1

INTRODUCTION

This method is a modification of the procedure developed by Warburton and Przybylowicz for the determination of residual thiosulfate in processed black-and-white films. Thiosulfate is extracted from the processed film with a solution containing potassium phosphate and potassium iodide. The thiosulfate in the extract is reduced by borohydride to sulfide, which is then reacted with N,N-dimethyl-p-phenylenediamine in the presence of ferric ion. The product of this reaction, methylene blue, is measured spectrophotometrically.

Use of this method requires handling of potentially hazardous chemicals. Material Safety Data Sheets should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PERECISION AND BIAS

Six processed black-and-white film samples were each analyzed, in duplicate, by four analysts, on each of two different days using two different instruments. All results reported below are expressed as micrograms $S_2O_3^{=}/cm^2$.

Customer Standard Deviation, $1s_c$

The customer standard deviation is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services Laboratory, where any analyst could test the sample using any instrument on any day.

95 Percent Confidence Estimate

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean component concentration level 95 percent of the time.

Sample	n	Mean	$1S_c$	95% CE
TMG/RA-458	16	2.2	0.18	± 0.4
PFC/RA XO541	16	2.8	0.36	± 0.8
MRM-758	16	4.3	0.44	± 0.9
EHN-731	16	6.6	0.45	± 1.0
XRP-539	16	11.5	0.99	± 2.1
TMH/RA-443	16	13.8	0.54	± 1.2

Bias

Bias is a statistically significant deviation of the mean from the known analyte level at the 95 percent confidence level. Bias was not determined for this method, since the thiosulfate content of the samples was not known.

APPARATUS

All volumetric glassware should meet all "Class A" specifications, as defined by the American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- Film punch, with 1 cm^2 die calibrated to nearest 0.001 cm^2
- Scintillation vials, polyethylene, with screw caps, 20-mL
- Repeating dispenser, 10-mL, Oxford Model 1063 or equivalent
- Pipettor, 5-mL, VWR CAT No. 53499-605
- Repeating dispenser, adjustable, 1-mL capacity, EM Science Optifix, or equivalent (4 required)
- Spectrophotometer, visible wavelength
- Spectrophotometer cells, 1-cm

REAGENTS

All reagents used are ACS Reagent Grade unless otherwise stated.

- Water, Type I Reagent – This method was developed using reagent water equivalent to or purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.
- Extractant
- Borohydride Reagent
- Acetone
- Ferric Chloride Reagent
- N, N-Dimethyl-p-phenylenediamine Sulfate (NND) Reagent

PROCEDURE

Preparation for Analysis

1. Zero the spectrophotometer vs air at 665 nm.
2. Transfer some of the extractant to the reservoir for the 10-mL repeating dispenser. Transfer the borohydride reagent, acetone, ferric chloride reagent and NND reagent to separate reservoirs for the 1-mL repeating dispensers. Flush each reagent dispenser by dispensing and discarding at least 10 aliquots of reagent before the first determination of the day.

Extraction of Residual Thiosulfate

1. Inspect the film to be tested for streaking, spots, and fingerprints. Choose an area free from these defects, at least 1" from the sheet edge, for the sample.

   Note: It is recommended that the analyst wear clean, white cotton gloves when handling film samples.

2. Cut a 1-cm^2 piece of the film to be tested, using a calibrated punch, and place the film piece in a clean, dry 20-mL plastic scintillation vial.
3. Dispense 10.0 mL of extractant into the vial, using the 10-mL repeating dispenser.
4. Cap the vial and allow to stand for 10 minutes, swirling occasionally (once every 1-3 minutes).

Formation and Measurement of Methylene Blue

1. Transfer 5.0 mL of the film extract from step 4 of the *Extraction of Residual Thiosulfate* procedure, to another clean, dry 20-mL plastic scintillation vial with the 5-mL pipettor.

   Note: All of the following reagent additions are made without delay between additions.

2. Add 0.25 mL of borohydride reagent and mix the solution.
3. Add 0.50 mL acetone and mix the solution.
4. Add 0.25 mL ferric chloride reagent. DO NOT MIX THE SOLUTION.
5. Add 0.25 mL NND reagent and immediately cap the vial.
6. Shake the vial vigorously for 1 minute, then immediately proceed to the next step.
7. Using a small portion of the solution (maximum 1.5 mL), rinse a 1-cm spectrophotometer cell, then fill the cell with the remainder of the solution. Rinse the outer surface of the cell with deionized water and wipe dry with a tissue. Ensure that gas bubbles are absent from the cell. If necessary, tap the cell to dislodge gas bubbles adhering to the cell walls.
8. Immediately read the absorbance at 665 nm vs air. (The absorbance should be measured within 1 minute or low results may be obtained.)
9. Analyze a reagent blank by following steps 1 through 8 of this procedure, substituting extractant solution for the film extract in step 1.

CALCULATIONS

$$\text{Net A} = A_s - A_b$$

Where:

A_s = absorbance of the sample solution at 665 nm
A_b = absorbance of the blank solution at 665 nm

$$\text{Residual thiosulfate } (S_2O_3^{=}),\ \mu g/cm^2 = \frac{m(\text{net A}) + b}{\text{Area}}$$

Where:

m = the slope obtained from the calibration equation
b = the intercept obtained from the calibration equation
Area = actual area of die on film punch (cm^2)

The slope and intercept are obtained from a calibration equation derived according to *APPENDIX A*.

Note: Each laboratory should establish its own calibration equation based on analysis of standards. *APPENDIX A* details this calibration procedure. Due to differences among spectrophotometers, each equation may be different. A significant bias may occur from use of an equation which was not established on the spectrophotometer used for the test.

RESULTS

The results from this analysis should be reported to the nearest $\mu g/cm^2$.

APPENDIX A

Calibration Procedure

This appendix is used to establish the initial calibration, whenever equipment has been adjusted, or to recheck response every six months.

Preparation of Standards (prepare fresh daily)

1. Pipet 25.0 mL of standardized 0.1 N sodium thiosulfate into a 500-mL volumetric flask, dilute to volume with extractant, and mix. This is the first dilution.
2. Pipet 5.00 mL of the first dilution into a 250-mL volumetric flask, dilute to volume with extractant, and mix. This is the second dilution.
3. Referring to the table below, pipet the specified volumes of the second dilution into the corresponding volumetric flasks, dilute each to volume with extractant, and mix.

Volume of Second Dilution (mL)	Volumetric Flask (mL)	Approximate Concentration (μg/cm²)
1.00	200	0.56
2.00	100	2.2
2.00	50	4.5
4.00	50	9.0
7.00	50	15.7
10.0	50	22.4
15.0	50	33.6

Analysis of Standards

1. Analyze the standards by performing steps 1 through 8 of the *Formation and Measurement of Methylene Blue* procedure, substituting each standard for the film extract in step 1.
2. For the 0.0 μg/cm² standard, analyze a blank by performing step 9 of the *Formation and Measurement of Methylene Blue* procedure.
3. Repeat the analysis of each standard, including the blank, once.

Derivation of Calibration Equation

1. Calculate the actual concentrations of the standards, expressed as micrograms thiosulfate/cm² of film, as follows:

$$\mu g\ S_2O_3^{=})/cm^2 = \frac{N \times V1 \times 1121.3}{V2}$$

Where:

N = Normality of standardized $Na_2S_2O_3$, meq/mL
V1 = Volume of second dilution pipetted, mL
V2 = Volumetric flask size for standard, mL
1121.3 = 112.13 x 1000 x 0.001 x 10
112.13 = Formula weight of thiosulfate ($S_2O_3^{=}$) mg/meq
1000 = Factor to convert mg to μg
0.001 = Dilution factor, first and second dilutions (25 mL/500 mL x 5 mL/250 mL)
10 = Dilution factor, film extract (10 mL/1 cm²)

2. For each standard, calculate net absorbances as follows:

$$\text{Net A} = A_s - A_b$$

Where:

A_s = absorbance of the sample solution at 665 nm
A_b = absorbance of the blank solution at 665 nm

For the 0.0 μg/cm² standard (the blank), the net absorbance is 0.

3. Determine the calibration equation by least-squares linear regression of the μg/cm² thiosulfate and the corresponding net absorbance data obtained above. Include the data for the 0.0 μg/cm² standard. The regression equation should follow the form $y = m(x) + b$,

Where:

y = thiosulfate concentration in μg/cm²
m = slope of the calibration line (the relationship between thiosulfate concentration and absorbance at 665 nm)
x = Net A, the net absorbance at 665 nm
b = the intercept of the calibration line with the y (concentration) axis

Example Raw Data

μg $S_2O_3^=$/cm²	Absorbance	Net Absorbance
0 (blank)	0.0849	0
0 (blank)	0.0821	0
0.5561	0.1196	0.0361
0.5561	0.1205	0.0370
2.224	0.1895	0.1060
2.224	0.1823	0.0988
4.449	0.3000	0.2165
4.449	0.2986	0.2151
8.898	0.5175	0.4340
8.898	0.5088	0.4253
15.571	0.7841	0.7006
15.571	0.8007	0.7172
22.245	1.1138	1.0303
22.245	1.1058	1.0223
33.367	1.5542	1.4707
33.367	1.5661	1.4826

From the data above, a linear regression yields:

m (slope) = 22.467 μg $S_2O_3^=$/(cm² • net A)

b (intercept) = – 0.309 μg $S_2O_3^=$/cm²

μg $S_2O_3^=$/cm² = 22.467 (net A) – 0.309

Determination of Silver in Thiosulfate Fixing Baths
(A Non-Instrumental Method Using Thioacetamide)
1209D

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	F-34a	F-35b F-35c	F-36	F-38

PRINCIPLE

This technique is basted on the work of Bush, Zuehlke, and Ballard,* but no instrument is required. The silver in a fixing bath is titrated, in effect, by adding graduated amounts of a thioacetamide solution to samples of the bath that have been adjusted to a pH greater than 12. At this alkalinity, thioacetamide decomposes to sulfide which immediately precipitates a chemically equivalent amount of silver sulfide. The silver sulfide is filtered and the filtrate is tested for completeness of silver precipitation by adding more thioacetamide.

It is probable that this method will be used most frequently to determine the amount of silver in a fixing bath before and/or after the fixing bath has passed through the Kodak Chemical Recovery Cartridge and associated Kodak Circulating Unit. A fix which has passed through this silver recovery unfit contains moderate amounts of ferrous iron ion. This method assumes that every fixer contains Iron II ions and includes a step to remove their effect before the conventional silver determination.

The fixing solution must not have very much color, although some can be tolerated if a suitable blank is used.

The practical extremes of measuring silver concentration by this technique are presented as Procedures A and B. Procedures C and D illustrate very useful specific modifications.

Procedure A – *Rapid Determination of the Approximate Silver Concentration in Thiosulfate Fixing Baths*.

Procedure B – *Determination of Silver in Thiosulfate Fixing Baths*. (This is a more precise procedure making use of pipets and burets.)

Procedure C – *Determination of Silver in Thiosulfate Fixing Baths When Concentration of Silver is Less Than 0.5 Grams per Liter*.

Procedure D – Special Application of Procedure C for *Determination of Exhaustion of Kodak Chemical Recovery Cartridge*.

RELIABILITY

Eight fixing baths were prepared containing known amounts of silver and varying in pH from 4 to 10. Each contained some of the following items: conventional sequestering agents, sulfite (bisulfite), carbonate (bicarbonate), thiosulfate (sodium or ammonium), formaldehyde, acetate, borate, potassium alum, anti foaming agent, and citrate.

The fixers were analyzed using Procedure B. End points were determined to 0.05 g/L. Of 30 results in the range from 0.50 to 6.00 g/L all were within 0.10 g/L of the nominal value and there appeared to be no bias.

Ten acid hardening fixes were prepared to contain either 0.50 g or 5.00 g of silver and 0.1 to 10 g of Iron II ions. These were analyzed according to Procedure B and all results were within ± 0.2 g/L of the mix level.

SPECIAL APPARATUS

- 100-ml Glass-Stoppered Graduated Cylinder (VWR Scientific, catalog no. 24760-100)
- 10-ml Graduated Cylinder (VWR Scientific, catalog no. 24710-044)
- Filter Paper, Whatman No. 3 (12.5 cm diameter) (VWR Scientific, catalog no. 28456-101)
- Torsion Balance, sensitivity 0.01 g

REAGENTS

- 6.0 N Accelerator Reagent
- 0.00926 N Thioacetamide
- 0.1 M Potassium Ferricyanide
- 0.2 M Potassium Ferricyanide

* D. G. Bush, C. W. Zuehlke, and A. E. Ballard, Analytical Chemistry, 31, 1368 (1959).

PROCEDURE A

Rapid Determination of the Approximate Silver Concentration in Thiosulfate Fixing Baths

Note: Use the markings on the cylinders for all measurement.

Treatment of Sample

1. Obtain three 100-mL glass-stoppered graduated cylinders (labeled 2, 4, and 6). Add to each graduated cylinder 10 mL of fixing bath sample, 10 mL of 0.1 M potassium ferricyanide, and 10 mL of 6 N accelerator reagent. Swirl to mix. If the resulting color is:
   a. **Reddish-brown**, proceed to Step 2.
   b. **Black**, add 10 ml more of 0.1 M potassium ferricyanide and swirl to mix. Proceed to Step 2 if the resulting color is reddish-brown. If not, start over again, using a fresh sample and a 0.2 M potassium ferricyanide reagent.
2. Using a polyethylene squeeze bottle, add to the cylinders the following volumes of 0.00926 N thioacetamide:

Cylinder Identification	mL 0.0926 N Thioacetamide
2	20
4	40
6	60

3. Stopper and shake all cylinders vigorously for 5 seconds.
4. Filter approximately 20 ml of the contents of each cylinder through a Whatman No. 3 (12.5 cm diameter) filter paper and collect the filtrates in beakers containing approximately 5 mL of 0.00926 N thioacetamide.
5. Observe the appearance of the beakers' contents and refer to Table 1, *Decision Sheet for Determining Silver Concentration Range (10 mL Sample) Procedure A.*

Reporting Results

1. The results from these three cylinders permit the conclusion that the silver content of the fix is:
   a. less than 2 g/L
   b. between 2 and 4 g/L
   c. between 4 and 6 g/L
   d. over 6 g/L*
2. One more individual trial will suffice to establish the silver content between two silver concentrations 1.0 g/L apart (See *PROCEDURE B*).

* If the silver content is more than 6 g/L, dilute the sample with an equal volume of water and rerun the determinations corresponding to cylinders 2, 4, and 6. Remember to multiply any final answer by 2.

Table 1 Decision Sheet for Determining Silver Concentration Range (10 mL Sample) Procedure A

Cylinder No.	0.00926 N Thioacetamide Added	If the Contents of the Beaker Turns Color,* Amount of Silver in Fix is More Than	If the Contents of the Beaker Remains Clear,† Amount of Silver in Fix is Less Than
1	10	1.0 g/L	
2	20	2.0 g/L	
3	30	3.0 g/L	
4	40	4.0 g/L	
5	50	5.0 g/L	
6	60	6.0 g/L	

* The color in the beaker is greater than a blank consisting of appropriate amounts of sample, potassium ferricyanide, 6 N NaOH-EDTA reagent and water (in place of 0.00926 N thioacetamide) which have been filtered, the filtrate being collected in about 5 mL of water.

† The color in the beaker is not greater than a blank prepared as above.

PROCEDURE B

Determination of Silver in Thiosulfate Fixing Baths

Note: Procedure A has established the approximate silver concentration. If it is desirable to determine the concentration more precisely, it is necessary to "zero-in" on the end point by measuring volumes with pipets and burets and by using smaller increments of 0.00926 N thioacetamide in the end point region. This procedure establishes the silver content between two concentrations 0.1 g/L apart, with three or fewer trials.

Treatment of Sample

1. Pipet into 4 100-ml glass-stoppered graduated cylinders 10.0 mL of fixing bath. Using the markings on the cylinders, add to one of the cylinders 10 mL of 0.1 potassium ferricyanide, and 10 mL of 6 N accelerator reagent. Swirl to mix. If the resulting color is:
   a. **reddish-brown**, proceed to Step 2.
   b. **black**, add 10 mL more of 0.1 N potassium ferricyanide. Swirl to mix. Proceed to Step 2 if the resulting color is reddish-brown. If not, start over again using a fresh sample and a 0.2 M potassium ferricyanide reagent. Prepare the remaining cylinders similarly.
2. Add from a buret the appropriate amount of 0.00926 N thioacetamide to each cylinder.

Note: The appropriate amounts of 0.00926 N thioacetamide are selected from Table 2, *Decision Sheet for Determining Silver Concentration (10.00 mL Sample) Procedure B*, and are based on the silver concentration found in Procedure A. For example, if the concentration was found to be more than 2 but less than 3 grams per liter, the region to explore is between 2 and 3. Increments shown are in 1.0 mL 0.00926 N thioacetamide (equivalent to 0.1 g Ag/1). To obtain greater efficiency, the end point may be approached by trying one at about 2.5 g/L and then one at 2.3 g/L or 2.7 g/L, depending on the result obtained with 2.5 g/L.

3. Stopper and shake all cylinders vigorously for 5 seconds.
4. Filter approximately 20 mL of the contents of each cylinder through a Whatman No. 3 (12.5 cm diameter) filter paper and collect the filtrates in beakers containing approximately 5 mL of 0.00926 N thioacetamide each.

Reporting Results

Observe the appearance of the contents of the beakers and refer to Table 2, *Decision Sheet for Determining Silver Concentration (10.00 mL Sample) Procedure B*, for decisions, and details of further trials, if necessary.

Table 2 Decision Sheet for Determining Silver Concentration (10.00 mL Sample) Procedure B

Range g/L	0.00926 N Thioacetamide To Add	If the Contents of the Beaker Turns Color, Amount of Silver in Fix is More Than	If the Contents of the Beaker Remains Clear, Amount of Silver in Fix is Less Than
0	1.00	0.1 g/L	
	2.00	0.2 g/L	
	3.00	0.3 g/L	
	4.00	0.4 g/L	
	5.00	0.5 g/L	
	6.00	0.6 g/L	
	7.00	0.7 g/L	
	8.00	0.8 g/L	
	9.00	0.9 g/L	
1	10.00	1.0 g/L	
	11.00	1.1 g/L	
	12.00	1.2 g/L	
	13.00	1.3 g/L	
	14.00	1.4 g/L	
	15.00	1.5 g/L	
	16.00	1.6 g/L	
	17.00	1.7 g/L	
	18.00	1.8 g/L	
	19.00	1.9 g/L	
2	20.00	2.0 g/L	
	21.00	2.1 g/L	
	22.00	2.2 g/L	
	23.00	2.3 g/L	
	24.00	2.4 g/L	
	25.00	2.5 g/L	
	26.00	2.6 g/L	
	27.00	2.7 g/L	
	28.00	2.8 g/L	
	29.00	2.9 g/L	
3	30.00	3.0 g/L	
	31.00	3.1 g/L	
	32.00	3.2 g/L	
	33.00	3.3 g/L	
	34.00	3.4 g/L	
	35.00	3.5 g/L	
	36.00	3.6 g/L	
	37.00	3.7 g/L	
	38.00	3.8 g/L	
	39.00	3.9 g/L	
4	40.00	4.0 g/L	
	41.00	4.1 g/L	
	42.00	4.2 g/L	
	43.00	4.3 g/L	
	44.00	4.4 g/L	
	45.00	4.5 g/L	
	46.00	4.6 g/L	
	47.00	4.7 g/L	
	48.00	4.8 g/L	
	49.00	4.9 g/L	
5	50.00	5.0 g/L	
	51.00	5.1 g/L	
	52.00	5.2 g/L	
	53.00	5.3 g/L	
	54.00	5.4 g/L	
	55.00	5.5 g/L	
	56.00	5.6 g/L	
	57.00	5.7 g/L	
	58.00	5.8 g/L	
	59.00	5.9 g/L	
6	60.00	6.0 g/L	

PROCEDURE C

Determination of Silver in Thiosulfate Fixing Baths When Concentration of Silver is Less Than 0.5 Grams per Liter.

Note: When the concentration of silver is less than 0.5 g/L, it is possible to establish the silver content between two concentrations 0.05 g/L apart, using only graduated cylinders and the markings on the cylinders for all measurements.

Treatment of Sample

1. Obtain several 100-mL glass-stoppered graduated cylinders. Add to each 40 mL of fixing bath sample, 20 mL of 0.2 M potassium ferricyanide, and 20 mL of 6 N accelerator reagent. Stopper and shake to mix.
2. Add from a polyethylene squeeze bottle to one of the cylinders, 20 mL of 0.00926 N thioacetamide, and to a second cylinder, add 10 mL.

   Note: 20 mL of 0.00926 N thioacetamide is equivalent to 0.5 g/L of silver and 10 mL is equivalent to 0.25 g/L of silver.
3. Stopper and shake the cylinders vigorously for 5 seconds.
4. Filter approximately 20 mL of the contents of each cylinder through Whatman No. 3 (12.5 cm diameter) filter paper and collect the filtrates in beakers containing approximately 5 mL of 0.00926 N thioacetamide each.
5. Observe the appearance of the contents and refer to Table 3, *Decision Sheet for Procedure C (40 mL Sample)*, to make the next decision.

Reporting Results

1. These two trials determine that:
   a. The procedure is not applicable (silver content is greater than 0.5 g/L)
   b. The silver content is below 0.25 g/L
   c. The silver content is between 0.25 and 0.5 g/L
2. If the procedure is applicable, three or fewer trials will establish the silver content between two silver concentrations 0.05 grams per liter apart.

Table 3 Decision Sheet for Procedure C (40 mL Sample)

mL of 0.00926 N Thioacetamide Added	If the Contents of the Beaker Turns Color, Amount of Silver in Fix is More Than	If the Contents of the Beaker Remains Clear, Amount of Silver in Fix is Less Than
2	0.05 g/L	
4	0.10 g/L	
6	0.15 g/L	
8	0.20 g/L	
10	0.25 g/L	
12	0.30 g/L	
14	0.35 g/L	
16	0.40 g/L	
18	0.45 g/L	
20	0.50 g/L	

PROCEDURE D

Determination of Exhaustion of Kodak Chemical Recovery Cartridge

Note: When the concentration of silver in the effluent from the Recovery Cartridge exceeds 0.25 grams per litre, it can be assumed that the capacity of the cartridge has been exceeded. By selecting the 10 mL of 0.00926 thioacetamide (equivalent to 0.25 g/L of silver) and making only the one trial, a decision on exhaustion can be reached.

Treatment of Sample

1. Place in a 100-mL glass-stoppered graduated cylinder 40 mL of fixing bath sample, 20 mL of 0.2 M potassium ferricyanide, and 20 mL of 6 N accelerator reagent. Stopper and shake to mix.
2. Add 10 mL of 0.00926 N thioacetamide, stopper, and shake for 5 seconds.
3. Filter approximately 20 mL of the mixture through a Whatman No. 3 filter paper into a beaker containing approximately 5 mL of 0.00926 N thioacetamide.

Reporting Results

1. **Colored**, the recovery cartridge is exhausted.
2. **Clear**, the recovery cartridge is still serviceable.

The Determination of Specific Gravity for Photoprocessing Solutions Using Hydrometers

ULM-0002/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	All	All	All	All

INTRODUCTION

Specific gravity is the ratio of the mass of a body to the mass of an equal volume of some other substance taken as the standard or unit, the measurements being made at the same temperature or, as is sometimes the case, at a stated reference temperature.* Or stated more simply for liquids, specific gravity is the ratio of a mass of a body to the mass of an equal volume of water at a specified temperature.† The standard or unit for the measurement of the specific gravity of liquids is commonly gas-free, pure (e.g., distilled) water. Specific gravity can be used as a measure of the total amount of dissolved material in a solution.

"Specific gravity may be determined at any temperature and referred to water at the same temperature or at any desired temperature."* The temperature of measurement should be controlled and specified in all specific gravity measurements because the specific gravity of a solution is affected by temperature. Specific gravity should be stated as follows:

Specific gravity, x/y °C

Where

x = temperature of the material being measured

y = temperature of the water

e.g., 1.050, 25.0/15.56°C

In historical analytical methods related to photographic processing solutions,‡ an increase of 3°C causes a decrease of 0.001 (0.00033/°C) in the specific gravity of most photographic processing solutions. Standards of specific gravity for photographic processing solutions are set by analyzing standard mixes at 25°C. The superseded version of this method‡ specified the determination of specific gravity at 27°C. The temperature change to 25°C was made to be consistent with the method currently recommended for the measurement of pH in photographic processing solutions.§ A calculation described in Appendix A, *Estimation of Specific Gravity Conversion From One Temperature to Another*, estimates the effect of the temperature change from 27°C to 25°C on specific gravity.

PRECISION AND BIAS

Precision

All specific gravity readings for photographic processing solutions are made at 25 ± 0.25°C. Historically,‡ the variability of measurement has been expected to fall within ±± 0.002, 95 percent of the time. ASTM Standard D891-95¶ states that the precision of specific gravity by hydrometer should be determined for each chemical. For photoprocessing control, this is not practical. ASTM gives the following examples, however:

Repeatability (one analyst/one day):	$1s_r$ (single det'n.)	=	0.00020 (24 DF)
	95% Conf. Est.	=	± 0.0005
With-in Laboratory/ Between Days:	1s (single analyst)	=	0.0016 (12 DF)
	95% Conf. Est.	=	± 0.005

Bias

The bias¶ of this test method has not been determined due to the unavailability of suitable reference materials. However, bias is dependent upon the calibration of the hydrometer and the degree of control of the temperature of the hydrometer bath.

APPARATUS

Hydrometers

Hydrometers should meet the specifications in ASTM Standard E 100,** as follows:

Specific Gravity Range	ASTM Number
1.000 - 1.050	111H - 62
1.050 - 1.100	112H - 62
1.100 - 1.150	113H - 62
1.150 - 1.200	114H - 62
1.200 - 1.250	115H - 62
1.250 - 1.300	116H - 62

Note: The hydrometers recommended for determining specific gravity:

a. Are calibrated with reference to gas-free, distilled water at 60° F (15.56°C), although measurements are made at 25°C.

b. Have subdivisions at 0.0005.

c. Have intermediate lines at 0.001.

* Taylor, john K. in *Treatise on Analytical Chemistry*, 1st ec.; Kolthoff, I.M.; Elving, P.J.; Part 1, Theory and Practice, Interscience: New York, 1967; Volume 7, Chapter 81, p. 4563.

† *Handbook of Chemistry and Physics*, 3tth ed.; Hodgeman, Charles D., ed. In Chief; Chemical Rubber Publishing Co.; Cleveland, OH, 1995; p. 2831.

‡ *Determination of Specific Gravity of Processing Solutions*; ECP-2-701, TR Accession No. 206210L, 1974; Eastman Kodak Co., Rochester, NY.

§ Mevs, Judith M.; Jansen, Kathryn L. *pH Measurement of Photographic Processing Solutions*; KPCQ-A-PR-G-191-2, TR Accession No. 266951E, 1992; Eastman Kodak Co., Rochester, NY.

¶ *Standard Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals*; American Society for Testing and Materials: ASTM Designation D 891-95, Philadelphia, PA, August, 1995.

** *Specification for ASTM Hydometers*; American Society for Testing and Materials: ASTM Designation D 100-95, Philadelphia, PA, April, 1995.

d. Have main (numbered) lines at 0.005.

e. Are available from most suppliers of scientific products.

Hydrometer Cylinder

The hydometer cylinder should have a capacity such that:

a. Its inside diameter is 25.4 mm (1.0 in) ≥ the outside diameter of the hydrometer.

b. The lowest point of the hydrometer will be at least 25.4 mm (1.0 in) above the bottom of the cylinder.

Note: A 250 mL graduated cylinder is adequate for most measurements.

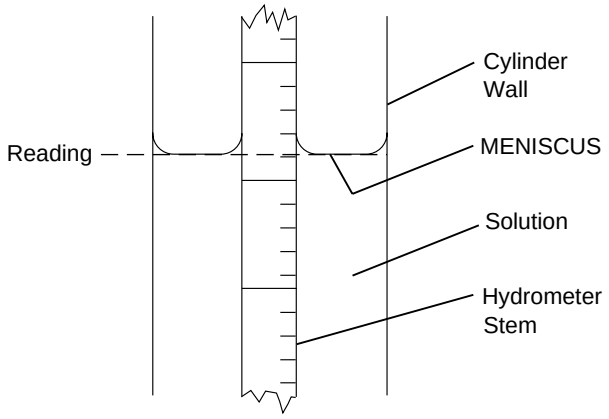
Water Bath (Constant Temperature)

The water bath should be of sufficient size to allow total immersion of the hydrometer cylinder, adjustable to 25°C, and able to control temperature ± 0.25°C (same requirements as the method for pH measurement[§]).

PROCEDURE

1. With the clean and dry hydrometer cylinder on a level support, fill the hydrometer cylinder with the sample and place in a vertical position in the water bath. Avoid the formation of bubbles in the cylinder.
2. Allow the sample to equilibrate in the water bath to a temperature of 25 ± 0.25°C.
3. Clean and dry the hydrometer thoroughly and carefully lower it into the sample to a level two smallest scale divisions below that at which it will float and then release the hydrometer.
4. Allow the sample temperature to re-equilibrate to 25 ± 0.25°C. Remove the cylinder from the water bath.
5. After the hydrometer has come to rest and has floated freely away from the walls of the cylinder, read the hydrometer at eye level. Take the reading at the level of the meniscus, where the sample surface seems to become a straight line cutting the hydrometer scale. See Figure 1, *Meniscus.*

Figure 1 Meniscus



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CALCULATION OF SPECIFIC GRAVITY

No calculations are required, as the hydrometers are direct reading and the final measurement requires no computation.

APPENDIX A

Estimation of Specific Gravity Conversion From One Temperature to Another

If it is assumed that the change in specific gravity with temperature is approximately 0.001 per 3°C (0.00033/°) for all processing solutions (see the *INTRODUCTION*), the specific gravity can be converted from one temperature to another by:

$$\text{specific gravity @ } T_2/y = (T_1 - T_2)k + \text{specific gravity @ } T_1/y$$

Where

T_1 = original temperature, °C
T_2 = second temperature, °C
k = change in specific gravity per °C (0.00033)
y = a constant (temperature of the water standard)

Example:

T_1 = original temperature, 27.0°C
T_2 = second temperature, 25.0°C
k = change in specific gravity per °C (0.00033)

specific gravity @ T_2/y = (27.0 - 25.0)(0.00033) + 1.020
specific gravity @ T_2/y = 0.00066 + 1.020
specific gravity @ T_2/y = 1.021

Instructions for Performance Checks of Ultraviolet-Visible Spectrophotometers and Quartz Cells

ULM-0001/1

Process	ECN-2	ECP-2D	VNF-1/LC	RVNP
Formulas	All	All	All	All

INTRODUCTION

Performance checks for ultraviolet-visible spectrophotometers consist of a wavelength and photometric accuracy check. The visible and ultraviolet regions are checked for wavelength accuracy at 485.8 nm and 278.7 nm, respectively, with a holmium oxide solution (NIST Standard Reference Material 2034). A holmium oxide glass filter (Corning No. 3130) can be used to check wavelength accuracy at 453.2 nm and 279.4 nm, instead of the holmium oxide solution. The photometric accuracy is checked in the visible and ultraviolet region at 500 nm and 280 nm, respectively, with a metal-on-quartz filter (NIST Standard Reference Material 2031).

Absorption cells should only serve as a holder for the sample and not contribute to the measured absorbance. There are almost always differences between cells. Cells should always be placed in the cell holder the same way and the holder placed the same way in the instrument. Mechanical repeatability should not contribute significant error to the analytical procedure. The most common cause for significant differences between absorption cells is dirty windows. To test cleanliness, a quartz cell check is required for spectrophotometric methods that do not involve the measurement of a blank. The quartz cell is filled with reagent water and an absorbance reading against air is taken at 650 nm in the visible region and 240 nm in the ultraviolet region. The acceptable absorbance of ≤ 0.093 for each of these wavelengths are taken from ASTM E 275-931. They serve as useful control levels for analyses that use precalibrated equations in the calculations.

Record all data from the performance checks on trend or control charts.

APPARATUS

- 1 cm Quartz Cell
- Metal-on-Quartz Filter (NIST Standard Reference Materia 2031)
- Holmium Oxide Solution in Ampouled Cell (NIST Standard Reference Material 2034)
- Holmium Oxide Glass Filter (Corning No. 3130)

REAGENTS

- Water, Type I Reagent- This method uses reagent water equivalent to or purer than Type I grade, as defined in ASTM Standard D 1193.
- Acid-Alcohol Cleaning Solution- One part 3 N hydrochloric acid and one part 3A or isopropyl alcohol.

PROCEDURE

Preparation of Spectrophotometer

1. Follow the manufacturer's instructions for operating the instrument, including the warm-up times for the instrument and it's lamps.
2. Use the appropriate lamp, as indicated:

Wavelength Range	Lamp
200 - 380 nm	Hydrogen or Deuterium
380 - 780 nm	Tungsten

Caution

The hydrogen or deuterium lamp can produce a severe burn on skin or to unprotected eyes. Do not look directly at the lamp. If it is necessary to examine or adjust the lamp, use goggles that will absorb the dangerous ultraviolet radiation.

Spectrophotometer Checks

Wavelength Check in Visible and Ultraviolet Region

Perform this procedure at least once a month, or if the photometric accuracy check fails.

1. Check the ampouled cell containing the holmium oxide solution for surface contamination; wipe clean with an optical lens tissue.
2. Insert the ampouled cell into the sample holder of the spectrophotometer after zeroing the instrument from 200 nm – 780 nm (air vs. air).
3. Scan from 200 nm – 780 nm using the wavelength control (monochromator) in 0.5 nm increments.
4. Record the wavelengths at which the maximum absorbance is observed near 485.8 nm and 278.7 nm. The recorded wavelengths should be within ± 0.5 nm of these expected values. If they are not, then contact the instrument manufacturer.

Photometric Accuracy Check in Visible and Ultraviolet Region

Perform this procedure at least once a day.

1. Adjust the spectrophotometer to read an absorbance of 0 at 280 nm and 500 nm (air vs. air).
2. Check the metal on quartz filter for surface contamination; wipe clean with an optical lens tissue.
3. Place the filter in sample holder.
4. Read and record the absorbance value at 280 nm and 500 nm.
5. The absorbances at each of these wavelengths should be within trend or control chart limits established for the spectrophotometer. If they are not, then do a wavelength accuracy check as described in *Wavelength Check in Visible and Ultraviolet Region*.

Quartz Cell Check

Perform the quartz cell check whenever a spectrophotometric method is used that does not require the measurement of a blank.

1. Inspect the cell for cracks, chips, and discoloration. If any are found, use another cell.
2. Rinse the cell with reagent water several times.
3. Fill the cell with reagent water.
   a. Wipe all outside surfaces of the cell completely dry with optical lens tissue, making sure all traces of lint are removed.
   b. Do not touch either of the optical faces with bare fingers.
   c. Look through the cell toward a light. Make sure nothing is in the water or on the optical surfaces of the cell (this includes tiny air bubbles, streaks, water spots, lint, fingerprints and anything else that might create an imperfection in the optical path).
4. Set the wavelength of the spectrophotometer to 240 nm for the ultraviolet range, or 650 nm for the visible range.
   a. Make sure that the cell holder is positioned correctly in the sample compartment.
5. Adjust the spectrophotometer to read an absorbance of 0 at the set wavelength.
6. Insert the cell in the cell holder.
   a. The correct cell position is determined in the initial cell check. There is usually a difference in absorbance if the cell is placed in the holder in a reversed position.

      Rotating the cell 180° in its holder should not give an absorbance difference greater than 0.005.1
   b. The cell must fit firmly and squarely into the holder (no weak or misaligned springs or corrosion).
   c. The optical surfaces of the cell must be perfectly aligned (at right angles) with the light beam of the spectrophotometer.
7. Measure and record the absorbance reading.
8. The absorbance for each wavelength should be ≤ 0.093.
9. If the control limits exceed 0.093, do the following to clean the cell:
   a. Soak the cell in water or a mild sulfonic detergent.
   b. If residue persists, soak the cell in a mixture of: one volume of concentrate hydrochloric acid, three volumes of reagent water, and four volumes of methanol.

Caution

Prepare and use this mixture only in an adequate fume hood.

   c. Alkaline solutions, detergents containing optical bleaches, abrasive powders, fluorides, and materials that might etch optical windows should be avoided.
10. Rinse the cell thoroughly with reagent water.
11. If the reading is still high, check the purity of the reagent water or use another quartz cell.

Note:

- Do not store a cell in reagent water; let air dry.
- Do not use swabs or other mechanical devices to remove surface contamination; use acid/alcohol cleaning solution.

Sample Measurement

1. Perform the quartz cell check procedure, if the method does not require a blank. If it does involve the measurement of a blank, make sure that the cell is clean.
2. Follow steps 1 - 7 of the *Quartz Cell Check*, but substitute the sample for reagent water and use the wavelength indicated in the specific method (step 4 of the *Quartz Cell Check*).
3. Rinse the cell with reagent water.
4. Measure the absorbance of the blank, if the method requires one.
5. Using the appropriate calculation or table, determine the concentration of the component being measured.

REFERENCES

1. *Standard Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near-Infrared Spectrophotometers*; American Society for Testing and materials: ASTM designation E 275-93, Philadelphia, PA, February 1994.
2. *Standard Terminology Relating to molecular Spectroscopy*; American Society for Testing and materials: ASTM designation E 131-94, Philadelphia, PA, August 1994.

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