

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:

$$\text{KI, g/L} = \frac{(\text{mL AgNO}_3) (\text{N AgNO}_3) (\text{millieq. wt. KI})}{0.00833 \text{ L Sample}}$$

Where:

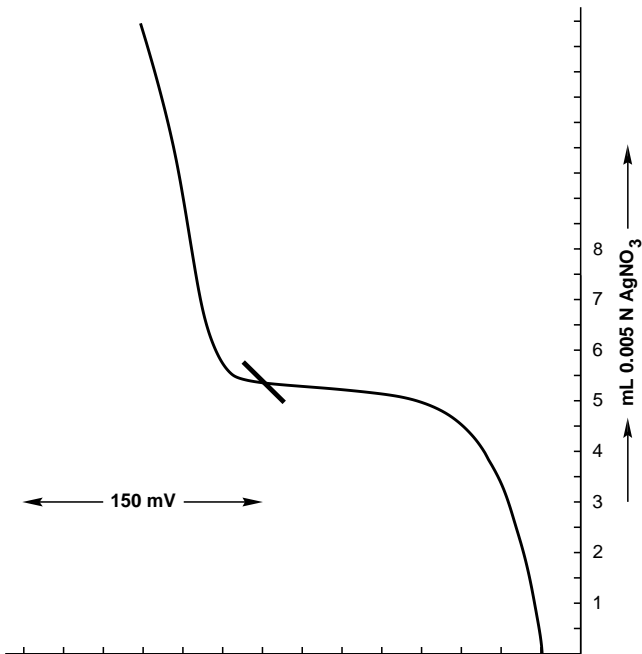
N AgNO₃ = Normality of N AgNO₃ in meq/mL

milliequivalent wt = 0.16601 g/meq KI

Example:

$$\begin{aligned} \text{KI, g/L} &= \frac{(5.77 \text{ mL AgNO}_3) (0.0050 \text{ N AgNO}_3) (0.16601)}{0.00833 \text{ L Sample}} \\ &= 0.57 \end{aligned}$$

Figure 1 Example Potassium Iodide Titration Curve of ECP-2 Fixer Bath



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