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, 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.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Mean (g/L Ag)</th>
<th>N</th>
<th>Repeatability Standard Deviation, 1s, (g/L Ag)</th>
<th>95 Percent Confidence Estimate (g/L Ag)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Fresh”</td>
<td>0.0080</td>
<td>3</td>
<td>0.00346</td>
<td>± 0.0149</td>
</tr>
<tr>
<td>“Fresh” plus Standard Addition</td>
<td>1.1006</td>
<td>3</td>
<td>0.00294</td>
<td>± 0.0127</td>
</tr>
<tr>
<td>“Seasoned”, As Received</td>
<td>0.1547</td>
<td>3</td>
<td>0.00167</td>
<td>± 0.0072</td>
</tr>
<tr>
<td>“Seasoned” plus Standard Addition</td>
<td>0.2088</td>
<td>3</td>
<td>0.00184</td>
<td>± 0.0079</td>
</tr>
</tbody>
</table>

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.

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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean (g/L Ag)</th>
<th>N</th>
<th>$1s_c$ (g/L Ag)</th>
<th>95 Percent Confidence Estimate (g/L Ag)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Fresh”</td>
<td>0.0338</td>
<td>16</td>
<td>0.03073</td>
<td>± 0.0628</td>
</tr>
<tr>
<td>“Fresh” plus Standard Addition</td>
<td>0.5863</td>
<td>16</td>
<td>0.00833</td>
<td>± 0.0170</td>
</tr>
<tr>
<td>“Seasoned”, As Received</td>
<td>3.6301</td>
<td>16</td>
<td>0.01504</td>
<td>± 0.0307</td>
</tr>
<tr>
<td>“Seasoned” plus Standard Addition</td>
<td>4.5015</td>
<td>16</td>
<td>0.02787</td>
<td>± 0.0569</td>
</tr>
</tbody>
</table>

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.

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, Na₂S₂O₃
- 70.1 N Sodium Hydroxide/Ethylenedinitrilotetraacetic Acid (EDTA) reagent, 1 N NaOH/EDTA
- 4 g/L Gelatin
- 0.06 N Sodium Sulfide, Na₂S (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.

<table>
<thead>
<tr>
<th>Silver Concentration g/L</th>
<th>Sample, mL</th>
<th>1.0 M Sodium Thiosulfate, mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 1</td>
<td>300</td>
<td>0</td>
</tr>
<tr>
<td>1 to 3</td>
<td>100.0</td>
<td>200</td>
</tr>
<tr>
<td>More than 3</td>
<td>50.0</td>
<td>250</td>
</tr>
</tbody>
</table>

   * 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:

<table>
<thead>
<tr>
<th>Titration mode</th>
<th>mV/pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal chart span</td>
<td>750 mV</td>
</tr>
<tr>
<td>Autocontrol</td>
<td>OFF</td>
</tr>
<tr>
<td>Maximum titration speed</td>
<td>15 min/100% volume</td>
</tr>
<tr>
<td>Vertical chart span</td>
<td>400 mm/100% volume</td>
</tr>
<tr>
<td>Automatic titration stop (% U%)</td>
<td>OFF</td>
</tr>
<tr>
<td>Indicator electrode</td>
<td>Silver Billet BECKMAN, Model 39261 or equivalent</td>
</tr>
<tr>
<td>Reference electrode</td>
<td>Double-junction ORION, Model 900200 or equivalent</td>
</tr>
</tbody>
</table>

   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:

\[
g/l \text{ Ag} = \frac{(mL \text{ Na}_2\text{S}) (N \text{ Na}_2\text{S}) (\text{eq wt Ag}) (1000)}{(mL \text{ sample}) (1000)}
\]

Where:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL Na₂S</td>
<td>volume of sodium sulfide in milliliters required to reach the equivalence point</td>
</tr>
<tr>
<td>N Na₂S</td>
<td>normality of the sodium sulfide in milliequivalents per milliliter (meq/mL)</td>
</tr>
<tr>
<td>eq. wt. Ag</td>
<td>equivalent weight of silver in milligrams per milliequivalents [107.88 for Ag]</td>
</tr>
<tr>
<td>1000</td>
<td>factor to convert milligrams to grams of Ag</td>
</tr>
<tr>
<td>mL sample</td>
<td>milliliters of sample pipetted in step 1 of part A of procedure</td>
</tr>
<tr>
<td>1000</td>
<td>factor to convert mLs of sample to Liters</td>
</tr>
</tbody>
</table>

For samples containing less than 1 g/L silver:

\[
g/l \text{ Ag} = \frac{(mL \text{ Na}_2\text{S}) (N \text{ Na}_2\text{S}) (107.88) (1000)}{(300) (1000)}
\]

For samples containing 1 to 3 g/L silver:

\[
g/l \text{ Ag} = \frac{(mL \text{ Na}_2\text{S}) (N \text{ Na}_2\text{S}) (107.88) (1000)}{(100.00) (1000)}
\]

For samples containing more than 3 g/L silver:

\[
g/l \text{ Ag} = \frac{(mL \text{ Na}_2\text{S}) (N \text{ Na}_2\text{S}) (107.88) (1000)}{(50.00) (1000)}
\]