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

<table>
<thead>
<tr>
<th>Process</th>
<th>ECN-2</th>
<th>ECP-2D</th>
<th>VNF-1/LC</th>
<th>RVNP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formulas</td>
<td>SB-34</td>
<td>SB-34R</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

PRECISION AND BIAS
Repeatability Standard Deviation, 1s, 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)

<table>
<thead>
<tr>
<th>Samples (Process ECN-2 KUL Bleach)</th>
<th>Mean Level (g/L NaBr) (N)</th>
<th>Repeatability Standard Deviation, 1s (g/L NaBr)</th>
<th>95 Percent Confidence Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Fresh&quot; at &quot;Aim&quot; (44.066 g/L NaBr)</td>
<td>44.553 5 0.16</td>
<td>± 0.44</td>
<td></td>
</tr>
<tr>
<td>&quot;Seasoned&quot;, As Received</td>
<td>52.448 5 0.12</td>
<td>± 0.33</td>
<td></td>
</tr>
<tr>
<td>&quot;Seasoned&quot; with Standard Addition</td>
<td>68.087 5 0.24</td>
<td>± 0.67</td>
<td></td>
</tr>
</tbody>
</table>

### Samples (Process ECP-2D KUL Bleach)

<table>
<thead>
<tr>
<th>Samples (Process ECP-2D KUL Bleach)</th>
<th>Mean Level (g/L NaBr) (N)</th>
<th>Repeatability Standard Deviation, 1s (g/L NaBr)</th>
<th>95 Percent Confidence Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Fresh&quot; at &quot;Aim&quot; (77.764 g/L NaBr)</td>
<td>78.589 5 0.77</td>
<td>± 2.1</td>
<td></td>
</tr>
<tr>
<td>&quot;Seasoned&quot;, As Received</td>
<td>71.734 5 0.43</td>
<td>± 1.2</td>
<td></td>
</tr>
<tr>
<td>&quot;Seasoned&quot; with Standard Addition</td>
<td>92.895 5 0.56</td>
<td>± 1.6</td>
<td></td>
</tr>
</tbody>
</table>
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 & 95 Percent Confidence Estimate (not including bias)
The customer standard deviation (1s) 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

<table>
<thead>
<tr>
<th>Samples (Process ECN-2 KUL Bleach)</th>
<th>Mean Level (g/L NaBr)</th>
<th>Reproducibility Standard Deviation, 1s (g/L NaBr)</th>
<th>95 Percent Confidence Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Fresh&quot; at &quot;Aim&quot; (44.096 g/L NaBr)</td>
<td>44.133 16 0.34</td>
<td>± 0.72</td>
<td></td>
</tr>
<tr>
<td>&quot;Seasoned&quot;, as received</td>
<td>52.686 16 0.19</td>
<td>± 0.41</td>
<td></td>
</tr>
<tr>
<td>&quot;Seasoned&quot; with standard addition</td>
<td>67.357 16 0.29</td>
<td>± 0.62</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Samples (Process ECP-2D KUL Bleach)</th>
<th>Mean Level (g/L NaBr)</th>
<th>Reproducibility Standard Deviation, 1s (g/L NaBr)</th>
<th>95 Percent Confidence Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Fresh&quot; at &quot;Aim&quot; (44.096 g/L NaBr)</td>
<td>77.217 16 0.43</td>
<td>± 0.91</td>
<td></td>
</tr>
<tr>
<td>&quot;Seasoned&quot;, as received</td>
<td>78.226 16 0.24</td>
<td>± 0.51</td>
<td></td>
</tr>
<tr>
<td>&quot;Seasoned&quot; with standard addition</td>
<td>99.810 16 0.41</td>
<td>± 0.88</td>
<td></td>
</tr>
</tbody>
</table>
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) H₂SO₄
- Silver nitrate, (0.05 N) AgNO₃, 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:

<table>
<thead>
<tr>
<th>Setting</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal chart span</td>
<td>750 mV</td>
</tr>
<tr>
<td>Maximum titration speed</td>
<td>15 min/100% volume</td>
</tr>
<tr>
<td>Automatic titration stop (%U)</td>
<td>OFF</td>
</tr>
<tr>
<td>Vertical chart span</td>
<td>400 mm/100% volume</td>
</tr>
<tr>
<td>Automatic titration speed</td>
<td>OFF</td>
</tr>
<tr>
<td>Titrination mode</td>
<td>mV/pH</td>
</tr>
</tbody>
</table>

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

$$\text{NaBr, g/L} = \frac{(\text{mL AgNO}_3) \times (N \text{ AgNO}_3) \times (\text{eq. wt. NaBr}) \times (1000)}{\text{(mL sample)} \times (1000)}$$

where:

- $\text{mL AgNO}_3 = \text{mL AgNO}_3$ consumed
- $N \text{ AgNO}_3 = \text{Normality of AgNO}_3$ in meq./mL used for titration
- $\text{eq. wt. NaBr} = 102.91 \text{ mg/eq}$
- $\text{mL sample} = 1.0 \text{ mL (effective sample size)}$
- $1000 = \text{factor to convert meq to eq in the numerator and mL to L in the denominator}$

$$\text{NaBr, g/L} = \frac{(15.32 \text{ mL AgNO}_3) \times (0.0495 N \text{ AgNO}_3) \times (102.91) \times (1000)}{1.0 \text{ mL} \times (1000)}$$

Example:

$$\text{NaBr, g/L} = \frac{(15.32 \text{ mL AgNO}_3) \times (0.0495 N \text{ AgNO}_3) \times (102.91) \times (1000)}{1.0 \text{ mL} \times (1000)}$$

$$\text{NaBr, g/L} = 78.7 \text{ g/L}$$