Potentiometric Determination of Bromide in Reversal First Developer
D94-0001/1

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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
<th>Repeatability Standard Deviation, 1s_r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh tank prepared at 6.989 g/L NaBr</td>
<td>5</td>
<td>0.16 g/L NaBr</td>
</tr>
<tr>
<td>Seasoned sample (mean = 4.370 g/L NaBr)</td>
<td>5</td>
<td>0.056 g/L NaBr</td>
</tr>
<tr>
<td>Seasoned sample + addition (mean = 6.542 g/L NaBr)</td>
<td>5</td>
<td>0.032 g/L NaBr</td>
</tr>
</tbody>
</table>

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.

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.

\[
\text{Recovery} = \frac{(\bar{X}_{\text{seas + addition}} - \bar{X}_{\text{season}}) \times 100}{\text{known addition}}
\]

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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
<th>Customer Standard Deviation, 1s_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh tank prepared at 7.002 g/L NaBr</td>
<td>32</td>
<td>0.079 g/L NaBr</td>
</tr>
<tr>
<td>Seasoned sample (mean = 4.419 g/L NaBr)</td>
<td>32</td>
<td>0.073 g/L NaBr</td>
</tr>
</tbody>
</table>
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.

### 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, AgNO₃, 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, H₂SO₄

### PROCEDURE

1. Pipet 5.0 mL of sample into a 250-mL beaker containing 100 mL of reagent water and a TEFLOWN 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 AgNO₃. 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](image-url)
CALCULATIONS

mL AgNO₃ that would be consumed by the thiocyanate, as measured by Method D94-0003/1:

\[
NaSCN, \text{ g/L} = \frac{(\text{mL AgNO}_3)(\text{N AgNO}_3)(\text{eq. wt. NaSCN})(1000)}{\text{(mL sample)(1000)}}
\]

where:

- \text{N AgNO}_3 = \text{Normality of AgNO}_3 \text{ in meq./mL}
- \text{eq. wt.} = 81.08 \text{ mg/meq}
- \text{mL sample} = 5.0 \text{ mL}
- 1000 = \text{factor to convert mg to g in the numerator and mL to L in the denominator}

Solve the equation for mL AgNO₃

\[
5.97 \text{ g/L NaSCN} = \frac{(\text{mL AgNO}_3)(0.0491 \text{ N AgNO}_3)(81.08)(1000)}{(5.0)(1000)}
\]

\[
\text{mL AgNO}_3 = 7.50
\]

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:

- \text{mL AgNO}_3 \text{ titrated} = \text{Total mL AgNO}_3 \text{ consumed by both Br- and SCN-}
- \text{mL AgNO}_3 \text{ from thiocyanate} = \text{Calculated mL of AgNO}_3 \text{ from analyzed amount of sodium thiocyanate}
- \text{N AgNO}_3 = \text{Normality of AgNO}_3 \text{ in meq./mL}
- \text{eq. wt.} = 102.91 \text{ mg/meq}
- \text{mL sample} = 5.0
- 1000 = \text{factor to convert mg to g in the numerator and mL to L in the denominator}

Example:

\[
\text{NaBr, g/L} = \frac{[(14.2 \text{ mL AgNO}_3) - (7.50 \text{ mL AgNO}_3)](0.0491 \text{ N AgNO}_3)(102.91)(1000)}{(5.0)(1000)}
\]

\[
\text{NaBr, g/L} = 6.8 \text{ g/L}
\]