Determination of Sulfite in KODAK Reversal First Developer, Process D-94/D-95
D94-0002/1

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).

<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 39.189 g/L sodium sulfite</td>
<td>5</td>
<td>0.038 g/L Na_2 SO_3</td>
</tr>
<tr>
<td>Seasoned (mean = 30.004 g/L Na_2 SO_3)</td>
<td>5</td>
<td>0.53 g/L Na_2 SO_3</td>
</tr>
<tr>
<td>Seasoned sample + addition (mean = 43.007 g/L Na_2 SO_3)</td>
<td>5</td>
<td>0.18 g/L Na_2 SO_3</td>
</tr>
</tbody>
</table>

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.

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

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_2 SO_3). A seasoned sample of KODAK Reversal First Developer, Process D-94 analyzed to be 38.165 g/L Na_2 SO_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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(N)</th>
<th>Customer Standard Deviation, 1s_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh prepared at 39.165 g/L Na_2 SO_3</td>
<td>31</td>
<td>0.98 g/L Na_2 SO_3</td>
</tr>
<tr>
<td>Seasoned (mean = 30.020 g/L Na_2 SO_3)</td>
<td>32</td>
<td>0.57 g/L Na_2 SO_3</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>95 Percent Confidence Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh prepared at 40.116 g/L Na_2 SO_3</td>
<td>± 1.99 g/L Na_2 SO_3</td>
</tr>
<tr>
<td>Seasoned (mean = 30.020 g/L Na_2 SO_3)</td>
<td>± 1.16 g/L Na_2 SO_3</td>
</tr>
</tbody>
</table>
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 KNO₃ outer filling solution)
- Platinum inlay electrode, BECKMAN #39273 or equivalent

REAGENTS
Use ACS Reagent Grade reagents unless otherwise specified.
- 0.1 N Potassium Iodate, KIO₃ (standardized to 4 decimal places)
- 0.6 M Potassium Iodide, KI
- 0.1 N Sodium Thiosulfate, Na₂S₂O₃ (standardized to 4 decimal places)
- 7 N Sulfuric Acid, H₂SO₄
- 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 TEF cron-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:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration Rate</td>
<td>15 min/100% volume</td>
</tr>
<tr>
<td>Auto Control</td>
<td>OFF</td>
</tr>
<tr>
<td>Selector Switch</td>
<td>mV/pH</td>
</tr>
<tr>
<td>Measuring Span</td>
<td>500 mV</td>
</tr>
<tr>
<td>Buret Size</td>
<td>50 mL</td>
</tr>
<tr>
<td>Paper Drive</td>
<td>400mm/100% volume</td>
</tr>
<tr>
<td>Cut-off</td>
<td>OFF</td>
</tr>
<tr>
<td>Counter Voltage</td>
<td>0 mV</td>
</tr>
<tr>
<td>Zero-Point Shift</td>
<td>left margin</td>
</tr>
</tbody>
</table>

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

\[
\text{Na}_2\text{SO}_3, \text{ g/L} = \frac{(\text{mL B} - \text{mL A}) \times (N \text{ Na}_2\text{SO}_3) \times (\text{eq. wt.}) \times (1000)}{\text{(mL sample)}} \times (1000)
\]

\[
= \frac{(\text{mL B} - \text{mL A}) \times (N \text{ Na}_2\text{SO}_3) \times (63.02) \times (1000)}{(3) \times (1000)}
\]

Where:

- \(\text{mL A}\) = mL of \(\text{Na}_2\text{SO}_3\) consumed by sample
- \(\text{mL B}\) = mL of \(\text{Na}_2\text{SO}_3\) consumed by blank
- \(N \text{ Na}_2\text{SO}_3\) = Normality of \(\text{Na}_2\text{SO}_3\) in milleq./mL used for titration
- \(\text{eq. wt. Na}_2\text{SO}_3\) = 63.02 mg/meq
- \(\text{mL sample}\) = 3.0 mL
- 1000 = factor to convert mg to g in the numerator and mL to L in the denominator

Example:

\[
\text{Na}_2\text{SO}_3, \text{ g/L} = \frac{(40.32 - 21.98) \times (0.0996 N \text{ Na}_2\text{SO}_3) \times (63.02) \times (1000)}{(3)(1000)}
\]

\[
= 38.4 \text{ g/L Na}_2\text{SO}_3
\]