INTRODUCTION
This method is based upon the oxidation of ferrous ion by persulfate in an acid solution at room temperature. A known excess of ferrous ion is added to the sample and the residual ferrous ion is titrated with standardized sulfato cerate. A blank determination should be run daily because ferrous solutions are slowly oxidized by air during use.

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
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 five (5) replicates on each of the following solutions during methods development.

1. A “fresh” Persulfate bleach tank solution prepared with all components at their respective “working tank” aim concentrations.
2. A “seasoned” Persulfate bleach tank solution analyzed as received, at 28.74 g/L Na₂S₂O₈.
3. The same “seasoned” solution as in number 2, above, reanalyzed after making an analytically weighed, standard addition of 8.5920 g/L Na₂S₂O₈.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean g/L Na₂S₂O₈</th>
<th>N</th>
<th>1s, g/L Na₂S₂O₈</th>
<th>95 Percent Confidence Estimate g/L Na₂S₂O₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Fresh” (prepared at 33.27 g/L)</td>
<td>32.27</td>
<td>5</td>
<td>0.059</td>
<td>± 0.16</td>
</tr>
<tr>
<td>“Seasoned” as Received</td>
<td>28.74</td>
<td>5</td>
<td>0.065</td>
<td>± 0.18</td>
</tr>
<tr>
<td>“Seasoned” plus Standard Addition</td>
<td>37.20</td>
<td>5</td>
<td>0.065</td>
<td>± 0.18</td>
</tr>
</tbody>
</table>

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 bias of −1.00 g/L Na₂S₂O₈ was found to be statistically significant at the 95 percent confidence level, however it was judged not to be 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 98.46 percent was significantly different from 100 percent at the 95 percent confidence level, but it was judged not to be practically significant.
REPRODUCIBILITY

Customer Standard Deviation, 1\(s_c\) & 95 Percent Confidence Estimate (not including bias)

Reproducibility or customer standard deviation (1\(s_c\)) 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 Persulfate bleach tank samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:

1. A “fresh” Persulfate bleach tank solution prepared with all components at their respective “working tank” aim concentrations.
2. A “seasoned” Persulfate bleach tank solution analyzed as received, at 27.19 g/L Na\(_2\)S\(_2\)O\(_8\).
3. The same “seasoned” solution as in number 2, above, analyzed in the same manner, after making a standard addition of 8.5912 g/L Na\(_2\)S\(_2\)O\(_8\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean g/L Na(_2)S(_2)O(_8)</th>
<th>N</th>
<th>Reproducibility Standard Deviation, 1(s_c) g/L Na(_2)S(_2)O(_8)</th>
<th>95 Percent Confidence Estimate g/L Na(_2)S(_2)O(_8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Fresh” (prepared at 33.01 g/L)</td>
<td>32.57</td>
<td>16</td>
<td>0.216</td>
<td>± 0.46</td>
</tr>
<tr>
<td>“Seasoned” as Received</td>
<td>27.19</td>
<td>16</td>
<td>0.233</td>
<td>± 0.50</td>
</tr>
<tr>
<td>“Seasoned” plus Standard Addition</td>
<td>35.41</td>
<td>16</td>
<td>0.197</td>
<td>± 0.42</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 is not determined for seasoned samples, since the component concentration level was not determined independent of the test method.

A bias of –0.44 g/L Na\(_2\)S\(_2\)O\(_8\) was found to be statistically significant at the 95 percent confidence level, however it was judged not to be 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 95.68 percent was significantly different from 100% at the 95 percent confidence level, however it was judged not to be practically significant.
APPARATUS

- Conical Flask with stopper (250-mL)
- 2 Tip-up pipettes (50-mL, 15-mL)
- Pipet (5-mL, 10-mL)

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.

REAGENTS

All reagents should be ACS Reagent Grade unless otherwise specified.

- 7.0 N sulfuric acid
- 0.25 N ferrous ammonium sulfate, \( \text{Fe(NH}_4\text{)}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} \)
- 0.0500 N sulfato cerate (standardized to four decimal place)
- Ferroin indicator solution
- 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

Determination of Persulfate

1. Pipet (wipe the pipet before leveling) 5.00 mL of sample into a 250 mL conical flask containing a magnetic stir bar.
2. Add 50 mL of reagent water from a tip-up pipet.
3. Add 15 mL of 7.0 N sulfuric acid from a tip-up pipet.

**Caution**

Acid, avoid contact with skin and eyes. In case of contact, flush with water.

4. Pipet (wipe the pipet before leveling) 10.0 mL of 0.25 N ferrous ammonium sulfate into the flask. Using a squeeze bottle, wash down the sides of the flask with reagent water.
5. Swirl the solution to mix, stopper the flask and let it stand for 3 minutes.

**Note:** Longer standing times do not adversely affect the titration providing the solution is protected from air.

6. Add 4 drops of ferroin indicator and titrate with 0.0500 N sulfato cerate to the first light cyan color.
7. Record the end point as mL A.

Determination of Reagent Blank

**Note:** A reagent blank should be run at least once per day because the 0.25 N ferrous ammonium sulfate will slowly change with usage.

1. Add 50 mL of reagent water, with a tip up pipet, to a 250 mL conical flask containing a magnetic stir bar.
2. Repeat steps 3 through 6 of Section A.
3. Record the end point as mL B.
CALCULATIONS

**For Sodium Persulfate, g/L**

\[
\text{g/L Na}_2\text{S}_2\text{O}_8 = \frac{(\text{mLs B} - \text{mLs A}) \times (\text{N cerate}) \times (\text{eq wt Na}_2\text{S}_2\text{O}_8)}{\text{mL Sample}}
\]

Where:

- \( \text{mLs B} \): volume of sulfato cerate in milliliters required to reach the equivalence point without the addition of sample (Blank)
- \( \text{mLs A} \): volume of sulfato cerate in milliliters required to reach the equivalence point with the addition of sample
- \( \text{N cerate} \): normality of the sulfato cerate in milliequivalents per milliliter (meq/mL)
- \( \text{eq wt Na}_2\text{S}_2\text{O}_8 \): equivalent weight of sodium persulfate in milligrams per milliequivalent (119.05 mg/meq)
- \( \text{mL Sample} \): volume of sample pipetted in step 1 of part A of procedure

If mL 0.0497 N sulfato cerate = 32.85 mLs

\( \text{mLs Blank} = 49.90 \text{ mLs} \)

\[
\text{g/L Na}_2\text{S}_2\text{O}_8 = \frac{(49.90 - 32.85) \times (0.0497) \times (119.05)}{5.00}
\]

\( \text{g/L Na}_2\text{S}_2\text{O}_8 = 20.18 \)