INTRODUCTION

Ferrocyanide is determined by an oxidation titration with standardized sulfato cerate in an acid solution. The reaction is:

\[ \text{Ce}^{4+} + \text{Fe(CN)}_6^{4-} \rightarrow \text{Ce}^{3+} + \text{Fe(CN)}_6^{3-} \]

The endpoint of the titration is detected potentiometrically. The electrodes used for the titration are a platinum indicator electrode and a double junction reference electrode. Results are reported in terms of potassium ferrocyanide trihydrate, \(K_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}\).

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS’s are available from your chemical supplier.

### PRECISION AND BIAS

**Repeatability Standard Deviation, 1s\(_r\) 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” ferricyanide bleach 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 4.9452 \(g/L\) \(K_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}\).
3. A “seasoned” ferricyanide bleach analyzed potentiometrically as received, at 3.5057 \(g/L\) \(K_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}\).
4. The same “seasoned” solution as in number 3, above, reanalyzed after making an analytically weighed, standard addition of 1.0280 \(g/L\) \(K_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}\).

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Mean (g/L) (K_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O})</th>
<th>(N)</th>
<th>Repeatability Standard Deviation, 1s(_r) (g/L) (K_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O})</th>
<th>95 Percent Confidence Estimate (g/L) (K_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O})</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Fresh”</td>
<td>0.073</td>
<td>3</td>
<td>0.0037</td>
<td>(\pm 0.016)</td>
</tr>
<tr>
<td>“Fresh&quot; plus Standard Addition</td>
<td>5.000</td>
<td>3</td>
<td>0.0024</td>
<td>(\pm 0.010)</td>
</tr>
<tr>
<td>“Seasoned&quot;, As Received</td>
<td>3.506</td>
<td>3</td>
<td>0.0002</td>
<td>(\pm 0.001)</td>
</tr>
<tr>
<td>“Seasoned&quot; plus Standard Addition</td>
<td>4.526</td>
<td>3</td>
<td>0.0023</td>
<td>(\pm 0.010)</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 99.27 percent was significantly different from 100 percent, but 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 99.27 percent was significantly different from 100 percent, but was judged not to be practically significant.

REPRODUCIBILITY
Customer Standard Deviation, 1s_c & 95 Percent Confidence Estimate (not including bias)
The 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 ferricyanide bleach samples, on two different days. Duplicate analyses were performed on each sample, on each of the two days. These samples were:
1. A fresh tank solution prepared at 40.000 g/L K_3Fe(CN)_6
2. The same “fresh” ferricyanide bleach sample as in number 1, above, analyzed in the same manner, after making a standard addition of 3.5540 g/L K_4Fe(CN)_6·3H_2O.
3. A seasoned ferricyanide bleach sample analyzed, as received, at 3.5540 g/L K_4Fe(CN)_6·3H_2O.
4. The same seasoned solution, as in number 3, above, analyzed in the same manner, after making a standard addition of 1.0917 g/L K_4Fe(CN)_6·3H_2O.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Mean (g/L K_4Fe(CN)_6·3H_2O)</th>
<th>N</th>
<th>Reproducibility Standard Deviation, 1s_c (g/L K_4Fe(CN)_6·3H_2O)</th>
<th>95 Percent Confidence Estimate (g/L K_4Fe(CN)_6·3H_2O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Fresh”</td>
<td>0.096</td>
<td>15</td>
<td>0.0065</td>
<td>± 0.014</td>
</tr>
<tr>
<td>“Fresh” plus Standard Addition</td>
<td>3.627</td>
<td>16</td>
<td>0.0210</td>
<td>± 0.045</td>
</tr>
<tr>
<td>“Seasoned”, As Received</td>
<td>3.506</td>
<td>16</td>
<td>0.0063</td>
<td>± 0.013</td>
</tr>
<tr>
<td>“Seasoned” plus Standard Addition</td>
<td>4.598</td>
<td>16</td>
<td>0.0146</td>
<td>± 0.031</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 99.33 percent was significantly different from 100 percent, but was judged not to be practically different.

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. The recovery of 100.01 percent was not statistically significantly different from 100 percent.

APPARATUS
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.
- Pipette, (50.0-mL)
- Tip-up pipette, (50-mL)
- Beaker, (600-mL, 400-mL)
- METROHM 536 Titrator or equivalent with a DOSIMAT and a 20-mL burette
- Platinum indicator electrode, BECKMAN, Model 39273 or equivalent
- Double junction reference electrode, ORION Model 900200 or equivalent
- Filling solutions:
  - ORION No. 900002 (inner chamber)
  - ORION No. 900003 (outer chamber)

REAGENTS
All reagents should be ACS Reagent Grade unless otherwise specified.
- 0.0500 N Sulfato Cerate
  (standardized to 4 decimal places)
- 7.0 N Sulfuric Acid
- 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
Treatment of Sample
1. Pipet (wipe the pipet before leveling) the sample of ferricyanide bleach into a beaker according to the following table:

<table>
<thead>
<tr>
<th>Expected Concentration of $K_4Fe(CN)_6\cdot3H_2O$ (g/L)</th>
<th>Beaker Size (mLs)</th>
<th>Sample (mLs)</th>
<th>Reagent Water (mLs)</th>
<th>7.0N $H_2SO_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below 5</td>
<td>600</td>
<td>200.00</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Between 5 and 10</td>
<td>600</td>
<td>100.00</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>Between 10 and 20</td>
<td>400</td>
<td>50.00</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>Between 20 and 40</td>
<td>400</td>
<td>25.00</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>Between 40 and 80</td>
<td>400</td>
<td>10.00</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>Between 80 and 200</td>
<td>400</td>
<td>5.00</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>Over 200</td>
<td>400</td>
<td>2.00</td>
<td>200</td>
<td>50</td>
</tr>
</tbody>
</table>

2. Add reagent water from a graduated cylinder according to the table in step 1.
3. Add 7.0 N sulfuric acid from a tip-up pipet according to the table in step 1. Mix thoroughly.

Potentiometric Titration of Sample
1. Titrate the solution with 0.0500 N sulfato cerate, using a METROHM Titrator or equivalent.
   a. Set the following parameters on the METROHM Titrator:
      | Titration mode | mV/pH     |
      | Horizontal chart span | 500 mV |
      | Autocontrol            | OFF     |
      | Maximum titration speed | 15 min/100% volume |
      | Vertical chart span    | 400 mm/100% volume |
      | Automatic titration stop (U%) | OFF |
      | Indicator electrode    | Platinum, BECKMAN, Model 39273 or equivalent |
      | Reference electrode    | Double-junction ORION, Model 900200 or equivalent |
   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 0.0500 N sulfato cerate through the inflection.
   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 $K_4Fe(CN)_6$:

$$\text{g/L } K_4Fe(CN)_6 \cdot 3H_2O = \frac{(\text{mL sulfato cerate}) \cdot (N \text{ sulfato cerate}) \cdot (\text{eq. wt. } K_4Fe(CN)_6 \cdot 3H_2O) \cdot (1000)}{(\text{mL sample}) \cdot (1000)}$$

where:

- mL sulfato cerate = volume of sulfato cerate in milliliters required to reach the equivalence point
- $N = \text{normality of sulfato cerate in milliequivalents per milliliter (meq/mL)}$
- eq. wt. = equivalent weight of ferrocyanide in milligrams per milliequivalents [422.41 for $K_4Fe(CN)_6 \cdot 3H_2O$]
- 1000 = factor to convert milligrams to grams of ferrocyanide
- mL sample = milliliters of sample pipetted in step 1 of the Treatment of Sample
- 1000 = factor to convert mLs of sample to liters

If mL 0.0500 $N$ sulfato cerate = 16.41 mLs:

$$\text{g/L } K_4Fe(CN)_6 \cdot 3H_2O = \frac{(16.41 \cdot 0.0500 \cdot 422.41 \cdot (1000))}{(50.0 \cdot (1000))}$$

$$\text{g/L } K_4Fe(CN)_6 \cdot 3H_2O = 6.93$$

Figure 1: S-shaped Curves