A SPECTROPHOTOMETRIC METHOD FOR THE
DETERMINATION OF IRON WITH THIOGLYCOLIC ACID

by

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INTRODUCTION

In recent years various spectrophotometric methods of analysis have been developed which make use either of a reference curve correlating transmittancy at a given wavelength with concentration or of the extinction coefficient of the color system at a given wavelength. Mehlig has determined manganese as permanganate (9) by the former procedure and copper with ammonia (10) and iron with salicylic acid (11) by the latter.

The reaction between thioglycolic acid and iron to give a reddish purple color has been known for many years, and the early investigators (1,4) attributed the color to a complex formed with ferric iron. However, Lyons (7) stated that the color was caused by a complex which was formed with ferrous, not ferric, iron. He concluded that any ferric iron is changed to the ferrous state by the thioglycolic acid, which acts as a reducing agent, and that the reddish purple color is due to the ferrous ion, while any blue color is produced by the ferric ion. Cannel and Richardson (3) found that ferric iron in the absence of oxygen gives a red color with this reagent.

Various investigators (2,5,14,16) have adapted the reaction to the colorimetric determination of iron in biological materials and foods. Swank and Mellon (15) have made a critical spectrophotometric study of the color
system with particular attention to the effect of diverse ions.

The purpose of the present work was to develop a method for the determination of iron in ores with thio-glycolic acid.

The writer found that the reddish purple color was caused by ferrous iron and that all iron must be in the ferrous condition if correct results are to be obtained. Since experiments showed that thioglycolic acid does not completely reduce the ferric iron, hydroxylamine hydrochloride, which was used by Saywell and Cunningham (13) in the colorimetric determination of iron with o-phenanthroline, was employed as the reducing agent.
THEORETICAL CONSIDERATIONS

All colorimetric quantitative analysis is based upon the fundamental Lambert-Beer equation,

\[ I = I_0 \times 10^{-ecl} \]

in which \( I_0 \) represents the intensity of the light entering the system at any given wavelength, \( I \) the intensity of the light transmitted by the system, \( l \) the length in centimeters of the solution through which the light passes, \( c \) the concentration in moles per liter of the substance absorbing the light, and \( e \) the molecular extinction coefficient, a constant which is a measure of the absorption due to a single molecule.

The most widely used colorimetric quantitative procedure involves the visual comparison of the color produced by a solution containing a definite concentration of an unknown substance with that of a solution produced by a color standard equivalent to, or containing a known concentration of, the desired constituent. In work of this type advantage is taken of the fact that, according to Beer's law, the transmission of light through the solution is an inverse function of both the length of the cell and the concentration of the colored substance. In the visual colorimeter the length of the column of the unknown solution is varied until the transmission through the standard and the unknown solution appears to be the same; the ratio
of the concentrations is then inversely proportional to the ratio of the lengths of the columns of solution, and concentration in the unknown solution may be determined by solving the simple proportions.

Although this method has its advantages, its limitations are twofold: the incident light is composed of a mixture of wave lengths and thus cannot be expected to obey Beer's law quantitatively, and the eye of the observer possesses very low sensitivity at the extreme ends of the spectrum and is not sufficiently able to distinguish between small variations in transmission.

The photoelectric colorimeter was developed in order to partially overcome these limitations. In this instrument reasonably monochromatic incident light is provided by means of a suitable light filter, and photoelectric measurement of transmission, using a photoelectric cell, photovoltaic cell, or thermocouple, eliminates errors due to lack of visual acuity on the part of the observer. The construction of a reference curve plotting percentage transmission as a function of the concentration permits the determination of the desired constituent in unknown solutions by a measurement of the transmittancy of the solutions.

In place of the light filter employed in the photoelectric colorimeter the spectrophotometer uses a diffraction
tion grating which enables it to provide practically pure monochromatic incident light. Photoelectric measurements made with the spectrophotometer make it possible to calculate concentrations from the fundamental Lambert-Beer equation, which may be conveniently stated as:

\[
\log \frac{I}{I_0} = -\varepsilon c \text{ or } \log \frac{I_0}{I} = \varepsilon c.
\]

The ratio \(\frac{I_0}{I}\) may be found by dividing 100 by the percentage transmittancy of the colored solution. If the length of the cell is known, the value of \(\varepsilon\), the molecular extinction coefficient, may be established at any given wave length. When this coefficient is known, the concentration of the colored constituent in the solution can be calculated by determining the transmittancy at the given wave length.
EXPERIMENTAL

APPARATUS AND SOLUTIONS

Cenco-Sheard Spectrophotometer. All absorption measurements were made with the Cenco-Sheard Spectrophotometer. In this instrument light from an external six-volt, eighteen-ampere ribbon filament lamp is reflected by a mirror to a Wallace concave replica grating, which can be rotated so as to permit the use of any desired wavelength. The light is, of course, diffracted in various directions in accordance with the grating theory, but a particular diffracted beam returns slightly above the incident beam and passes through the absorption cell to a photocell connected to a galvanometer which correlates transmission with deflection of the scale.

Thioglycolic Acid. Ten milliliters of thioglycolic acid were made alkaline with ammonium hydroxide, and the resulting solution was diluted with distilled water to 100 ml.

Hydroxylamine Hydrochloride. Ten grams of hydroxylamine hydrochloride were dissolved in 100 ml. of distilled water.

Standard Iron Solution. A standard solution was prepared by dissolving 0.7026 gram of 99.95 per cent pure ferrous ammonium sulfate hexahydrate in water, adding 25 ml. of 12N hydrochloric acid, and diluting to 1000 ml. with
distilled water. Each milliliter of this solution contained 0.1 mg. of iron.
THE COLOR REACTION

To produce the color system the amount of the standard solution of iron required to give the desired concentration of iron was accurately measured into a 100-ml. volumetric flask, and 1 ml. of hydroxylamine hydrochloride solution was added to reduce any iron which might have been oxidized by dissolved oxygen. The solution was diluted to approximately 25 ml. and was allowed to stand for one-half hour to insure complete reduction. Because the color will develop only in alkaline solution, 10 ml. of 3M ammonium hydroxide were added, followed by 2 ml. of thioglycolic acid, and the volume was accurately made up to 100 ml. The reagents must be added in the order named, as any change in this order will result in a change of hue of the system. The color developed immediately, but faded on standing. However, at any time during a period of two hours it was possible to restore the original color intensity by agitation with air. After two hours the original color intensity was probably restored upon agitation, but it faded too rapidly to permit a measurement to be taken. All transmission measurements were made with a Cenco-Sheard Spectrophotometer by setting the wave-length scale, adjusting the incident light by means of an iris diaphragm to provide the desired displacement of the pointer on the galvanometer scale, and reading the transmission of the standard solution and of
the blank solvent. The transmittancy was calculated by dividing the former by the latter. The entrance slit was set at a width of 1 mm, and the exit slit at a width of 5 m. A 1-cm. cell was used throughout. All measurements were made at 535 m, the peak of the absorption band found by Swank and Mellon (15).

That Beer's law is obeyed for solutions containing up to and including 4 parts per million is proved by the straight line which results when the logarithms of the observed transmittancies at 535 m for four solutions containing 1 to 4 parts per million of iron were plotted against the respective concentrations. However, above 4 parts per million this line begins to curve, as shown in Figure 1, and Beer's law no longer holds.
Figure 1 - Conformity To Beer's Law

Log Percent Transmittancy At 5535 µm

Milligrams Of Iron Per Liter
MOLECULAR EXTINCTION COEFFICIENT

The molecular extinction coefficient was calculated from standard iron solutions containing from 1 to 4 parts per million of iron; the wave-length scale was set at 535 m., the peak of the absorption band. Each reading of the galvanometer scale was checked to 0.1 per cent, and the cell used had a length of 1 cm. Transmittancies were determined by dividing the transmission of the solution by that of the solvent, and the extinction coefficient was then calculated from the Lambert-Beer equation, which states when solved for e:

\[ e = \frac{I_0 \log \frac{I}{I}}{Lc} \]

The average value obtained for e with the thioglycolic acid complex was 3736. See Table I.
<table>
<thead>
<tr>
<th>P.p.m. of Iron</th>
<th>Molecular Extinction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3742</td>
</tr>
<tr>
<td>2</td>
<td>3733</td>
</tr>
<tr>
<td>3</td>
<td>3735</td>
</tr>
<tr>
<td>4</td>
<td>3736</td>
</tr>
</tbody>
</table>

Average = 3736
DETERMINATION OF IRON IN ORES

The method was tested by application to the determination of iron in ores in which iron had already been determined by the usual dichromate method. Because Beer's law is obeyed only up to 4 parts of iron per million, a weight of ore was taken which provided a concentration within this range at the dilutions used.

About 0.4000 gram of iron ore was accurately weighed and transferred to a 250-ml. beaker. Twenty-five milliliters of concentrated hydrochloric acid were added, the beaker was covered with a watch glass, and the mixture was warmed on a hot plate until solution had been effected or only a white, siliceous residue remained. The solution was transferred to a 1000-ml. volumetric flask, filtering if necessary and thoroughly washing any residue, diluted to the mark, and thoroughly shaken. An aliquot of 1 ml. was accurately measured with a micro-burette into a 100-ml. volumetric flask, and 1 ml. of hydroxylamine hydrochloride solution was added together with enough water to make the volume about 25 ml. The solution was allowed to stand one-half hour to insure complete reduction. Ten milliliters of 3M ammonium hydroxide and 2 ml. of thioglycolic acid reagent were then added, and the solution was diluted to the mark and thoroughly mixed. Transmission measurements of this solution in a 1-cm. cell were made at
535 mμ. The transmittancy was obtained by multiplying the transmission by 100 and dividing by the transmission of a blank solution. The percentage of iron was calculated by use of e, the molecular extinction coefficient.

Solved for c, the Lambert-Beer equation reads:

\[
\frac{I_o}{I} \log \left( \frac{55.84}{e} \right) \frac{I_o}{I} \log \left( \frac{55.84}{el} \right) = \text{grams Fe/liter}
\]

Since \( I = \frac{\text{Transmission of solution} \times 100}{\text{Transmission of solvent}} \), and \( I_o = 100 \),

\[
c = \frac{55.84}{el} \log \frac{\text{transmission of solvent}}{\text{transmission of solution}}
\]

Since the final solution contained 0.001 of the original sample in 100 ml. of solution:

\[
\% \text{Fe} = \frac{55.84 \times 100 \times 100}{e \times 1 \times \text{wt. of sample}} \log \frac{\text{transmission of solvent}}{\text{transmission of solution}}
\]

The calculation is thus relatively simple.
RESULTS

Results obtained for twenty-one iron ores are shown in Table II, which also includes for comparison the values given by the dichromate titrimetric method (8). Since the scale of the galvanometer can only be read to 0.1 scale division, corresponding to about 0.13 per cent iron in an ore containing 50 per cent iron, the average of several readings was taken for the transmission.

The results were within ±0.10 per cent of the values given by the dichromate method, and the average deviation was 0.04 per cent. Results may be duplicated on the same samples with a precision of about ±0.05 per cent. The percentage error ranged from -0.235 per cent to +0.262 per cent with an average of +0.030 per cent.
Table II

Results Obtained With Thioglycolic Acid

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Iron by Dichromate Method</th>
<th>Transmittancy of Solution at 535 m(\mu)</th>
<th>Iron Obtained from Transmittancy at 535 m(\mu)</th>
<th>Deviation</th>
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<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>28.22</td>
<td>84.0</td>
<td>28.27</td>
<td>+0.05</td>
</tr>
<tr>
<td>2</td>
<td>33.95</td>
<td>81.1</td>
<td>33.99</td>
<td>+0.04</td>
</tr>
<tr>
<td>3</td>
<td>38.25</td>
<td>79.0</td>
<td>38.20</td>
<td>-0.05</td>
</tr>
<tr>
<td>4</td>
<td>42.52</td>
<td>77.0</td>
<td>42.42</td>
<td>-0.10</td>
</tr>
<tr>
<td>5</td>
<td>37.62</td>
<td>79.3</td>
<td>37.64</td>
<td>+0.02</td>
</tr>
<tr>
<td>6</td>
<td>36.84</td>
<td>79.7</td>
<td>36.85</td>
<td>+0.01</td>
</tr>
<tr>
<td>7</td>
<td>36.12</td>
<td>80.0</td>
<td>36.21</td>
<td>+0.09</td>
</tr>
<tr>
<td>8</td>
<td>35.11</td>
<td>80.5</td>
<td>35.20</td>
<td>+0.09</td>
</tr>
<tr>
<td>9</td>
<td>34.45</td>
<td>80.9</td>
<td>34.40</td>
<td>-0.05</td>
</tr>
<tr>
<td>10</td>
<td>52.83</td>
<td>72.2</td>
<td>52.86</td>
<td>+0.03</td>
</tr>
<tr>
<td>11</td>
<td>57.90</td>
<td>70.0</td>
<td>57.88</td>
<td>-0.02</td>
</tr>
<tr>
<td>12</td>
<td>51.52</td>
<td>72.8</td>
<td>51.52</td>
<td>0.00</td>
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<td>49.59</td>
<td>73.7</td>
<td>49.52</td>
<td>-0.07</td>
</tr>
<tr>
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<td>52.20</td>
<td>72.5</td>
<td>52.19</td>
<td>-0.01</td>
</tr>
<tr>
<td>15</td>
<td>54.04</td>
<td>71.7</td>
<td>53.99</td>
<td>-0.05</td>
</tr>
<tr>
<td>16</td>
<td>56.00</td>
<td>70.8</td>
<td>56.04</td>
<td>+0.04</td>
</tr>
<tr>
<td>17</td>
<td>57.62</td>
<td>70.1</td>
<td>57.65</td>
<td>+0.03</td>
</tr>
<tr>
<td>18</td>
<td>34.30</td>
<td>80.9</td>
<td>34.39</td>
<td>+0.09</td>
</tr>
<tr>
<td>19</td>
<td>41.73</td>
<td>77.3</td>
<td>41.78</td>
<td>+0.05</td>
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<tr>
<td>20</td>
<td>44.44</td>
<td>76.0</td>
<td>44.44</td>
<td>0.00</td>
</tr>
<tr>
<td>21</td>
<td>46.48</td>
<td>75.1</td>
<td>46.47</td>
<td>-0.01</td>
</tr>
</tbody>
</table>
DISCUSSION

Unsatisfactory results were obtained when thioglycolic acid alone was the reducing agent; complete reduction was obtained by using hydroxylamine hydrochloride. Stannous chloride, the usual iron reductant, is impractical since bivalent tin, if present in a concentration above 20 mg. per 100 ml., bleaches the color of the system (15).

Various workers have found the color system to be stable for 30 minutes (15), and according to some observers the original color intensity, after slight fading has occurred, can be restored by agitation with air. Swank and Mellon (15) have reported that solutions stored in Erlenmeyer flasks and protected from light showed no evidence of fading after 12 hours and were stable for at least 6 hours when exposed to diffuse daylight. The writer found that the original color intensity faded after 2 hours and could not be restored, even by thorough agitation with air. The presence of the reducing agent, hydroxylamine hydrochloride, may account for the difference of color stability from that previously reported.

Swank and Mellon (15) in their study of the effect of diverse ions found that there is much less interference by anions than is true for those color systems which are based on reaction with ferric iron. This system is almost
completely free from interference by phosphate, pyrophosphate, fluoride, tartrate, citrate, and oxalate ions, all of which exhibit a strong tendency to form stable, colorless complexes with ferric iron. A number of cations were found to interfere, especially cobalt, nickel, copper, lead, and bivalent tin, but most of these are seldom found in appreciable amounts in iron ores.

The ammonium hydroxide concentration must not vary since, as Yoe and Crumpler (17) have pointed out, ammonia solutions show an appreciable absorption of light in the visible region. Mehlig (10) in his work on the colorimetric determination of copper with ammonia showed by means of curves that the hue gradually changes as the concentration varies. In the present work a 3M solution (15) was used throughout.

Since the method can be used to determine iron in very low concentrations and since few diverse ions interfere with the color, it can advantageously be adapted to the determination of iron in food and biological materials, as well as in analytical reagents. At the present time several large manufacturers are using the colorimetric method for routine analysis.

Important advantages of this method over many colorimetric methods for iron are: (a) the pH value need not be regulated closely, (b) the color system conforms to Beer's law at low concentrations, (c) the color is not
dependent upon the reagent concentration, and (d) the color forms immediately, thereby requiring much less time than some methods. The color, while not extremely stable, does not fade so rapidly that measurements are difficult.

The advantages of this method over the salicylic acid spectrophotometric method for iron (11) are its greater freedom from interference by diverse ions and its much wider pH range. The advantages over the nitro-O-phenanthroline spectrophotometric method for iron (12) are that much less time is required for the development of color and there is less interference by anions.

A disadvantage of this method is the fact that the color formation occurs only in alkaline solution. Thus, any metal hydroxides or hydrated oxides that are precipitated in alkaline solution must be removed by filtration before measurements can be made. Normally, iron ores are free from such metals.
SUMMARY

A spectrophotometric method has been developed for the determination of iron in ores which depends upon reducing the iron with hydroxylamine hydrochloride and measuring the light transmittancy at 535μ of the colored solution produced by thioglycolic acid in ammoniacal solution. The transmittancy is quantitatively related to the iron concentration, which may be calculated by the use of the molecular extinction coefficient of the system.

Results obtained by this method agree very closely with those obtained by the dichromate titrimetric method.

The method is easily carried out and requires much less time than the usual titrimetric methods.

The range of concentration over which the quantitative determination of iron may be made has been ascertained.

Very few diverse ions interfere with the color.
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