SPECTROPHOTOMETRIC DETERMINATION OF IRON IN ORES
WITH DIMETHYLGLYOXIME

by
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Iron is most often determined by oxidation and reduction titrimetric methods. Electrode deposition has been used and the colorimetric determination by the use of the thiocyanate method is well known. Other colorimetric methods have been examined and developed for ores by Mehlig and others (6, pp. 76-79; 7, pp. 52-55; 8, pp. 8-11).

The present system employing dimethylglyoxime is another case of applying a colorimetric procedure to the quantitative determination of iron in ores. A second aim of parallel importance is to supplement work by Mehlig (5, pp. 4-7; 6, pp. 76-79) which supports the view that macro constituents may be determined quantitatively by colorimetric methods and the spectrophotometer.

Dimethylglyoxime is undoubtedly best known for the determination of nickel, but it has found use as a reagent for other group eight elements, palladium and platinum (18, pp. 71-73; 15, P. 401). Other elements as copper, bismuth, cobalt and iron have been noted
to react with this reagent (18, pp.71-73). It is the last case that is of interest here. With iron, a pink to red color is developed which is often mistaken for the nickel reaction.

This reaction of ferrous iron with dimethylglyoxime was first seriously considered around the turn of the last century (15, pp.401-404; 16, pp.376-377) when a visual color comparison procedure was developed. More recently it has been considerably refined and extended to other dioximes (11, pp.423-425; 10, pp.1017-1020).

So far as can be ascertained the system has been employed only for determination of trace or slightly larger amounts of iron in materials. It is intended here to show that it may also be used to determine iron present as a major constituent in ores.
THEORETICAL CONSIDERATIONS

In order to relate the colored solution to the concentration a measure of the color is necessary. Absorption of radiant energy as light is the basis of the measurement. One of the fundamental laws, Lambert's law, states that each layer of equal thickness of the absorbing medium will absorb an equal fraction of the radiant energy that traverses it. The decrease in intensity for traversing a length, \( l \), is then,

\[
\frac{-dI}{dl} = k'I \quad \text{where} \quad I \text{ is intensity and}
\]

\( k' \) is a constant of proportionality. If this is integrated using the limits \( I_0 \) at \( l \) equals 0, and \( I \) at \( l \) equals \( l \), the result is,

\[
\ln \frac{I_0}{I} = k'l \quad \text{or,} \quad I = I_0e^{-k'l}.
\]

A second law with which the first is combined is Beer's law. This law expresses that the absorptive capacity of the colored medium is directly proportional to the number of absorbing entities (concentration). Here the decrease in intensity with increased concentration may be formulated,

\[
I = I_0e^{-k''c} \quad \text{where} \quad k'' \text{ is again a constant of proportionality and} \quad c, \text{ the concentration.}
\]
Grouping into a new constant, $k$, the constants $k'$, $k''$, and the factor for changing from natural logs to log to the base ten, the two laws can be combined.

$$\log_{10}\frac{I_0}{I} = k_0 \text{ or, } I = I_0 \times 10^{-k_0}$$

The factor, $\log_{10}\frac{I_0}{I}$, is termed the extinction which is an expression that will be used later. The new $k$ is the specific extinction coefficient and indicates the absorption due to a single molecule which is constant if the law holds.

In order to put the measurement of absorption on a workable basis it is necessary to allow for losses of light due to scattering and reflection at the two interfaces of glass and air, for instrumental scattering and other error. This is eliminated by measuring the intensity of a ray of monochromatic light passed through the colored solution and also the intensity of the ray through a colorless "blank" of similar refractive index and contained in a well-matched cell. This practice will give the ratio $I/I_0$ which is termed the transmittancy. If the basic law is recalled it is seen that the absolute intensity is not needed, but only the ratio is significant. For single colored constituents there are two general procedures that may be followed to obtain concentration
of the desired constituent from spectrophotometric data. In either case it is necessary to examine the color system using known concentrations of the substance under investigation. In the one case if Beer's law is followed, i.e. if absorption increases proportionally with the increase in concentration, the value of $k$ may be calculated from the experimental values for the remaining terms of the basic law equation. This $k$ in turn then is used for calculation of the per cent composition of the substance in the sample. In the other case, where Beer's law fails, a calibration curve may be drawn from the experimental values on a series of solutions of known concentration. The concentration of the unknown sample is then read off from the curve. Examples in the literature may be cited (5, pp.47; 8, pp.8-11).

A fuller treatment of the theory and application of color systems is given by Mellon (9, pp.88-101).
Cenco-Sheard Spectrophotometer. The instrument used to obtain the ratio of I/I₀ was the Cenco-Sheard Spectrophotometer. The entrance and exit slits were used at set values and the intensity of the incident light was regulated over the range of wave lengths by means of an iris diaphragm between the light source and the entrance slit. However, the diaphragm would not accommodate the entire range. The exit slit was set at 20 μm for the ranges 400 to 440 and 680 to 700 μm, a 10 μm slit for the ranges 440 to 480 and 640 to 680 μm, and the 5 μm slit was used for the middle range of 480 to 640 μm. The iris was regulated with the "blank" in the light path so that the galvanometer read 100. The colored solution was then exchanged for the blank by means of a sliding carriage. Since transmittancy is the ratio of the intensity of light passing through the colored solution to the intensity of that passing through the blank, the reading of the colored solution as registered on the galvanometer scale is the per cent transmittancy directly.

The cells were 1-cm. in length with pyrex windows.
The same cells were used for all measurements, one used exclusively for the blank and the other only for the colored solution.

**Beckman pH Meter.** All pH measurements were made with a Beckman Model H-2 pH Meter.

**Dimethylglyoxime.** A saturated solution of the reagent in 95% ethyl alcohol was used. This was determined to be approximately a 2.39 per cent solution at 26 degrees centigrade. The solution exhibited no apparent breakdown with time.

**Standard Iron Solution.** A sample, weighing 0.2250 gram, of an iron ore containing 44.44 per cent iron as determined by the dichromate method (4, p.242) was treated with concentrated hydrochloric acid in a 250-milliliter beaker and warmed on a hot plate at low heat until solution was complete or only a small white siliceous residue remained.

The cooled solution was transferred to a 1000-ml. volumetric flask and made up to volume at a regulated temperature. Each milliliter of the resulting solution contained 0.1 mg. of iron. Also each milliliter taken and made up to 100 ml. gave a solution whose concentration was 1 p.p.m. of iron.

**Hydroxylamine Hydrochloride.** An aqueous solution containing 10 grams per 100 milliliters.
**Ammonium Chloride.** An aqueous solution containing 200 grams of the salt per liter.

**Ammonium Hydroxide.** A commercial 15 M solution.
THE COLOR REACTION

When ferrous iron is mixed with dimethylglyoxime and ammonium hydroxide added a pink- to deep red-colored solution develops. The greater the concentration of iron the deeper the red color.

If dimethylglyoxime is designated as $D_2H_2$ and a molecule of ammonia as $A$, then the complex could be written as $(D_2H)_2A_2Fe$. Although this is the usual composition sometimes three molecules of ammonia are found associated with the complex (15, pp. 401-402).

Order of Adding Reagents. A study of the effect of the order of addition of reagents on the color reaction revealed that the order is rather critical. The iron should be reduced in an acid solution to attain full color production in a short period of time. The dimethylglyoxime must be present with the reduced iron when the mixture is made basic and all the reagents cannot be mixed and the iron added at the last. Some other orders than the one used develop maximum color after standing for a time, but for color development in ten to fifteen minutes the present procedure should be followed.

Influence of pH. Since hydrogen ion is involved in the color reaction it might be expected that the pH value
would have an influence on the color of the solution and that is the case. The color increases as the pH value increases. Following the recommendation of Baker, (11, p. 423) the pH was controlled at a value of 9.4 to 9.5. This was accomplished by the use of an ammonium chloride-ammonium hydroxide buffer solution. Checks were made with the pH meter from time to time throughout the experimental work in order to verify the correct value.

After obtaining a correct absorption value it was found that control of the pH value between 9.2 and 9.8 was sufficient. The extremes of these values gave a change in transmittancy of the order of 0.1 unit which is within the range of acceptable error.

Other Influencing Factors. The effect of diverse ions on the system has been studied and reported (11, pp. 423-425; 10, p. 1019). Some twenty-nine ions are covered in these articles along with their maximum ratio to iron by weight that can be tolerated.

The color fades with time and the stability was determined by making transmittancy measurements at convenient time intervals. It was found that the more concentrated iron solution was the least stable and in regular order the stability increased with the least concentrated solution containing 0.5 p.p.m. iron being the most stable.
The stability is also influenced by the reducing agent. The fading of the color is due to the reoxidation of the ferrous to ferric iron in ammoniacal solution by dissolved and atmospheric oxygen (12, p. 1113). Sodium dithionate has been used as a reducing agent and is said to have a stabilizing effect on the colored complex (1, p. 71; 10, p. 1018).

Hydroxylamine hydrochloride has been used successfully by various workers (10, pp. 1017-1020; 11, pp. 423-425). All color solutions in this work were made up with recently boiled and cooled, distilled water and were not exposed to the air any more than necessary. For the best results the transmittancy readings should be made within 24 hours of the time the colored solution is made up to volume.

Wave Length of Maximum Absorption. The wave length of maximum light absorption was determined by taking the absorption measurement of five solutions with concentrations of 0.5, 1.0, 2.0, 3.0 and 4.0 p.p.m. of iron.

The standard iron solutions were made up by measuring suitable aliquots from the standard iron solution into a 100-ml. volumetric flask, carrying out the color reaction and diluting up to volume at thirty degrees centigrade with boiled and cooled, distilled water, exactly as described in the procedure for the determination of iron (p. 17).
FIG. 1
SPECTRAL TRANSMISSION CURVE
FOR
IRON-DIMETHYLGLYOXIME SYSTEM

PERCENT TRANSMITTANCE

0 10 20 30 40 50 60 70 80 90 100

WAVE LENGTH IN MU

400 450 500 550 600 650 700

0.5 p.p.m., 1 p.p.m., 2 p.p.m., 3 p.p.m., 4 p.p.m.
The spectral transmission curves were obtained as shown in Fig. 1. The wave length of 525 μ was the point of maximum absorption for all concentrations and was the point used for the determination of the ores.

**Molecular Extinction Coefficient.** This value also comes from the transmittancy at 525 μ of the five solutions containing 0.5, 1.0, 2.0, 3.0 and 4.0 p.p.m. of iron. The entrance slit width was fixed at 1.5 mm. and the exit slit width at 5 μ.

It was previously determined that if Beer’s law is obeyed the specific extinction coefficient as determined for a given wave length is a constant. The molecular extinction coefficient is merely the specific coefficient multiplied by the molecular weight of the constituent to be determined. It too should be a constant.

When the extinction values were calculated and plotted against the respective concentrations a straight line resulted. See Fig. 2. This indicated that Beer’s law was obeyed and the calculated value of the molecular extinction coefficient, e, was constant. The calculation is made from the Beer-Lambert equation as follows.
\[ \log_{10} \frac{I_0}{I} = k \text{ cml solving for } k, \]

\[ k = \frac{\log_{10} \frac{I_0}{I}}{e \times 1} \quad \text{and,} \]

\[ e = Mk \quad \text{where } M \text{ is 55.85 or the} \]

atomic weight of iron and the other symbols have their previously stated significance. The average value of \( e \) was calculated to be 9498. See table I.
### TABLE I

VALUES OF SPECIFIC AND MOLECULAR EXTINCTION COEFFICIENTS

<table>
<thead>
<tr>
<th>Conc. of Iron p.p.m.</th>
<th>Specific Extinction Coefficient</th>
<th>Mol. Extinction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>171.3</td>
<td>9567</td>
</tr>
<tr>
<td>1.0</td>
<td>170.1</td>
<td>9500</td>
</tr>
<tr>
<td>2.0</td>
<td>170.5</td>
<td>9522</td>
</tr>
<tr>
<td>3.0</td>
<td>169.5</td>
<td>9467</td>
</tr>
<tr>
<td>4.0</td>
<td>168.9</td>
<td>9433</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>170.1</strong></td>
<td><strong>9498</strong></td>
</tr>
</tbody>
</table>
FIG. 2
CONFORMITY TO BEER'S LAW

EXTINCTION x 10 AT 525 M\(\mu\)

CONCENTRATION OF Fe IN p.p.m.
DETERMINATION OF IRON IN ORES

About 0.4 gram of sample was accurately weighed and transferred to a 250-ml. beaker. The ore was then treated with 25 ml. of concentrated hydrochloric acid, covered with a watch glass, and left on a hot plate at low heat until solution was complete or only a light colored siliceous residue remained. The cooled solution was filtered into a 1000-ml. volumetric flask and the residue was washed with 300 to 400 ml. of approximately 0.01M hydrochloric acid solution. The filtrate was made up to volume with distilled water at 30 degrees centigrade, and thoroughly shaken.

With a microburette 1 ml. of the iron solution was carefully measured into a 100-ml. volumetric flask and diluted with boiled and cooled, distilled water. Then in order were added 2 ml. of the hydroxylamine hydrochloride solution, 22.50 ml. of the ammonium chloride solution, and 2 ml. of the dimethylglyoxime reagent. After shaking, 10 ml. of the 15M ammonium hydroxide were introduced, the mixture was made up to volume with distilled water at 30 degrees, and thoroughly shaken.
The transmittancy was measured at 525 μm and the percentage of iron was calculated by use of the molecular extinction coefficient. The following example illustrates the method of calculation.

Experimental Data: weight of ore sample, 0.400 gram; transmittancy of the colored solution at 525 μm, 55.4%; length of cell, 1.0 cm., e, 9498. Solving the Beer-Lambert equation for c gives,

$$c = \frac{\log_{10} \frac{I_o}{I}}{e \times 1} \text{ moles of iron per liter}$$

Since $$I_o/I = 1/T$$ where T is the percent transmittancy,

$$c = \frac{\log_{10} \frac{1}{T}}{e \times 1} \text{ at. wt. Fe grams Fe per liter}$$

Since the final solution contained in 100 ml. 0.001th of the original solution,

$$\% \text{Fe} = \frac{\log_{10} \frac{1}{T} \times \text{at. wt. Fe} \times 1000 \times 100}{e \times 1 \times \text{wt. of sample} \times 10}$$

$$= \frac{\log_{10} 0.554 \times 55.85 \times 100 \times 100}{9498 \times 1.0 \times 0.4000}$$

$$\% \text{Fe} = 37.70$$
### TABLE II

RESULTS OBTAINED WITH DIMETHYLGLYOXIME

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Iron by Dichromate Method</th>
<th>Iron by Dimethylglyoxime Method</th>
<th>Deviation</th>
<th>Percentage Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.62</td>
<td>37.59</td>
<td>-0.03</td>
<td>0.079</td>
</tr>
<tr>
<td>2</td>
<td>36.84</td>
<td>36.85</td>
<td>+0.01</td>
<td>0.027</td>
</tr>
<tr>
<td>3</td>
<td>54.04</td>
<td>54.02</td>
<td>-0.02</td>
<td>0.037</td>
</tr>
<tr>
<td>4</td>
<td>56.00</td>
<td>56.04</td>
<td>+0.04</td>
<td>0.071</td>
</tr>
<tr>
<td>5</td>
<td>57.62</td>
<td>57.66</td>
<td>+0.04</td>
<td>0.069</td>
</tr>
<tr>
<td>6</td>
<td>52.20</td>
<td>52.17</td>
<td>-0.03</td>
<td>0.058</td>
</tr>
<tr>
<td>7</td>
<td>52.63</td>
<td>52.79</td>
<td>-0.04</td>
<td>0.076</td>
</tr>
<tr>
<td>8</td>
<td>57.90</td>
<td>57.90</td>
<td>0.00</td>
<td>0.000</td>
</tr>
<tr>
<td>9</td>
<td>51.52</td>
<td>51.55</td>
<td>+0.03</td>
<td>0.059</td>
</tr>
<tr>
<td>10</td>
<td>49.59</td>
<td>49.54</td>
<td>-0.05</td>
<td>0.101</td>
</tr>
</tbody>
</table>
TABLE III

DUPLICATE RESULTS OBTAINED

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Run #1</th>
<th>Run #2</th>
<th>Difference</th>
<th>Percentage Deviation</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>37.70</td>
<td>37.47</td>
<td>0.23</td>
<td>0.61</td>
</tr>
<tr>
<td>2</td>
<td>36.88</td>
<td>36.81</td>
<td>0.07</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>53.97</td>
<td>54.07</td>
<td>0.10</td>
<td>0.02</td>
</tr>
<tr>
<td>4</td>
<td>56.11</td>
<td>55.96</td>
<td>0.15</td>
<td>0.27</td>
</tr>
<tr>
<td>5</td>
<td>57.66</td>
<td>57.66</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>6</td>
<td>52.22</td>
<td>52.11</td>
<td>0.11</td>
<td>0.21</td>
</tr>
<tr>
<td>7</td>
<td>52.34</td>
<td>52.73</td>
<td>0.11</td>
<td>0.21</td>
</tr>
<tr>
<td>8</td>
<td>57.83</td>
<td>57.96</td>
<td>0.13</td>
<td>0.22</td>
</tr>
<tr>
<td>9</td>
<td>51.63</td>
<td>51.48</td>
<td>0.15</td>
<td>0.29</td>
</tr>
<tr>
<td>10</td>
<td>49.54</td>
<td>49.54</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Average 0.11 0.19
RESULTS

The results obtained for ten ores are shown in Table II together with the values given by the dichromate titrimetric method. The greatest difference between the two methods was 0.05 per cent with an average difference of 0.03 per cent. The percentage error varied from -0.101 to +0.071 per cent with an average of -0.01 per cent. The difference between duplicate results is shown in Table III. Best results were obtained by taking the average of a large number of transmittancy measurements.
DISCUSSION

The results of the analysis of the ten ores would indicate that this spectrophotometric method can be used to measure iron as a macro constituent. This is shown by the close agreement with the values obtained by the recognized titrimetric method (4, p.242).

The method has been used for determination of iron in water (1, p.71) by a less exact method of visual comparison in Nessler tubes. The present method has the advantage of not requiring a series of standards for comparison.

The reaction has been used to determine ferrous in the presence of ferric iron by use of tartaric acid (17, p.15).

The method has the advantages of (1) few interferences, especially very few in the case of ores, (2) nearly immediate formation of color, (3) conformity to Beer's law in a workable range of concentration, (4) easily obtainable and inexpensive reagents and (5) independence of excess of the reagent.
SUMMARY

A spectrophotometric method for iron in ores has been developed, which depends upon the pink- to red-colored, soluble complex formed by ferrous iron with dimethylglyoxime in an ammoniacal solution.

The system was found to conform to Beer's law for the concentration range of 0.5 to 4 p.p.m. of iron. The peak of the absorption band, 525 μm, was used for the determination of the molecular extinction coefficient, which relates transmittancy and concentration of the iron.

The results demonstrated the accuracy of the method by favorable comparison with the results of the dichromate titrimetric method.

The method is easily operated and can be used for ores containing up to at least 58 per cent iron. It has several advantageous aspects with very few interfering diverse ions where iron ores are concerned.
BIBLIOGRAPHY


