THE APPLICATION OF SALICYLALDOXIME TO THE
SPECTROPHOTOMETRIC DETERMINATION
OF IRON IN ORES

by

DOROTHY ELIZABETH DURST

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APPROVED:

_____

Professor of Chemistry

       In Charge of Major

_____

Head of Department of Chemistry

_____

Chairman of School Graduate Committee

_____

Dean of Graduate School

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INTRODUCTION

In referring to the very general belief that color-
imetric determinations are limited to maximum concentra-
tions of a few parts per million of desired constituent,
Mellon (17) pointed out the need for further study of
various color systems to determine the upper limit for re-
liable work with modern instruments.

Certain colorimetric methods have been adapted to
spectrophotometric use and it has been found that the
range of concentrations that can be determined effectively
is surprisingly high. Mehlig determined copper in ores
(9) that ranged from 2 to 21 per cent and iron in ores (11)
that ranged from 36 to 58 per cent. Mehlig and others
(14, 15, 16) also reported successful determinations of
iron in ores ranging up to 58 per cent.

Salicylaldoxime is well known as a quantitative
precipitating agent for copper (3), zinc (18), nickel (19),
lead (7), and palladium (5). It is also used in the sepa-
ration and determination of copper-cadmium mixtures (7)
and copper-nickel alloys (2). These metals form insoluble
chelate compounds with the reagent. Ferric iron is known
to interfere in these gravimetric methods by forming a
soluble colored complex that is entrained by the precipi-
tate and cannot be washed out. Biefeld and Howe (1)

studied this phenomenon and reported the entrainment of the iron complex occurred over the entire hydrogen-ion concentration studied and was not due to absorption alone. The amount entrained decreases with an increase in hydrogen-ion concentration.

Ephraim (4) in determining copper by precipitation with salicylaldoxime utilized the iron complex to aid in determining when the excess reagent had been completely removed from the precipitate. He added ferric chloride to successive portions of washings from the precipitate until no color was produced and consequently no more reagent was present.

Howe and Mellon (6) investigated the possibility of reversing the process and using salicylaldoxime as a color-forming reagent for ferric iron. They made a critical study of the soluble complex to determine optimum conditions under which it could be used for the colorimetric determination of iron.

The purpose of the work herein described was to develop a spectrophotometric method for the determination of iron in ores by the application of salicylaldoxime and in addition to illustrate further that macro constituents can be determined satisfactorily by spectrophotometric methods.

THEORETICAL CONSIDERATIONS

Absorption spectrophotometry is based on the absorptive capacity of a solution for radiant energy at a wave length where the colored solution displays a maximum absorption of light. The intensity of absorption of the monochromatic light is utilized in making quantitative determinations of a desired constituent.

In order to provide a logical basis for measuring the absorption of light, it is necessary to allow for losses by reflection and scattering at the boundaries of the cell containing the solution and also for the small losses caused by scattering within the liquid itself. This correction is made by comparing the intensity I of a ray that has passed through the colored solution with the intensity I_0 of the same ray after passage through a colorless solution of similar refractive index contained in an identical cell. The ratio I/I_0 is termed the transmittancy of the solution. Only the ratio is significant. The actual value of the intensity is not required. The logarithm of the reciprocal of transmittancy is termed extinction.

For single colored constituents there are two general procedures that may be followed to convert spectrophotometric data into terms of concentration of desired constituent.

One may work from a calibration curve coordinating concentration and transmittancy determined for a series of solutions of known concentrations. After determining the transmittancy for an unknown solution, its concentration may be read from the calibration curve. This technique may be used in all cases, but is confined largely to those systems which do not conform to the Beer-Lambert law. Manganese by periodate (10) and nickel by ammonia (12) are examples where this technique has been applied.

The Beer-Lambert law states that the intensity of a ray of monochromatic light upon entering an absorbing medium decreases exponentially in accordance with the concentration of solute, the thickness of the column of the liquid, and the nature of the substance. This may be expressed as

$$I = I_0 \times 10^{-elc}$$

where e is the molecular extinction coefficient, which is a measure of the absorption due to a single molecule and a constant for any given wave length; l is the thickness of the absorbing medium expressed in centimeters; c is the concentration of the colored solute expressed in moles per liter; and I_0 and I refer to the transmissions of the solvent and solution, respectively.

If the color system does obey the Beer-Lambert law, it is possible to use this equation for calculation of the concentration of the desired constituent, after the

molecular extinction coefficient for the system has been determined by use of solutions of known concentrations. Copper by ammonia (9) and by triethanolamine (13) and iron by salicylic acid (11), thioglycolic acid (15), and 2, 2'-dipyridyl (16) have been determined in this manner.

Ideally, the Beer-Lambert law should apply in all cases where no alteration of the solute molecules has occurred. If the solute molecules dissociate, ionize, or associate, the law does not necessarily hold. Due to discrepancies in instrument construction, however, a system that obeys Beer's law with one instrument may not with another. For that reason, it is necessary to determine the molecular extinction coefficient for a given system on the instrument to be used rather than to rely upon a published value.

EXPERIMENTAL

APPARATUS AND SOLUTIONS

Cenco-Sheard Spectrophotelometer. All spectrophotometric measurements were made with a Cenco-Sheard spectrophotelometer. It was found to be convenient to regulate the intensity of the incident light by means of the iris diaphragm opening so that when the "blank" solution was in position, the galvanometer pointer registered 100. Since transmittancy has been defined as the ratio of the intensity of light transmitted by the colored solution to the intensity of light transmitted by the "blank" solution, this adjustment made the galvanometer reading for the colored solution represent per cent transmittancy directly. This procedure was used in making all transmittancy measurements. The identical cells used were 1-cm. in length. The same cells were used throughout, one reserved only for the "blank" solution, the other only for the colored solutions.

Beckman pH meter. All pH measurements were made with a Beckman pH meter.

Salicylaldoxime. A solution of the reagent was made by dissolving 0.1 gram of solid salicylaldoxime, Eastman 2956, in 5 ml. of ethanol and diluting to 100 ml. with water. Since the solution became brown upon standing for a period of time, it was prepared on the day it was to be

used.

Standard Iron Solution. A portion, weighing 0.2250 gram, of an ore containing 44.44 per cent iron as determined by the dichromate titration method (8) was dissolved in 25 ml. of 12 N hydrochloric acid. Two milliliters of hydrogen peroxide were added to oxidize all the iron to the ferric condition. The solution was diluted with water to about 50 ml. to prevent volatilization of ferric chloride and boiled to remove the excess peroxide. The cooled solution was transferred to a 1000-ml. volumetric flask and made up to volume. Each milliliter contained 0.1 mg. of iron.

Ammonium Acetate. A solution was made by dissolving 250 grams of the solid in water and diluting to 1000 milliliters.

Hydrogen Peroxide. A commercial 3 per cent solution was used.

THE COLOR REACTION

The soluble colored complex that is formed when ferric iron reacts with salicylaldoxime has been assumed to have the following formula:

$$\text{structure: benzene ring with } C=N-OH \text{ and } O \rightarrow \overset{Fe}{\underset{3}{}}$$
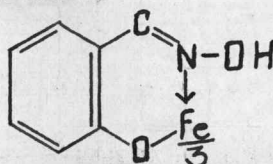
The hue of the solution is greatly dependent upon the hydrogen-ion concentration, changing from purple at a pH of 3 to yellow at a pH of 10 with a variation of hues at intermediate values.

The study of the color system included the determination of (a) a suitable pH value at which to make transmittancy measurements, (b) the wave length of light where the system displayed a maximum absorption, (c) factors affecting the color reaction and its development, and (d) the molecular extinction coefficient for the system.

Selection of Suitable pH Value. The effect of pH value on the hue of the colored complex was studied by using solutions of the same iron content, but varying hydrogen-ion concentrations. The change of hue with change in pH value and the subsequent effect on the transmittancy is shown in Fig. 1. The color system was produced by measuring 5 ml. of standard iron solution from a microburette into a 100-ml. volumetric flask. Ten milliliters of salicylaldoxime reagent were added and the solution thoroughly

FIG. 1.
EFFECT—HYDROGEN ION CONCENTRATION
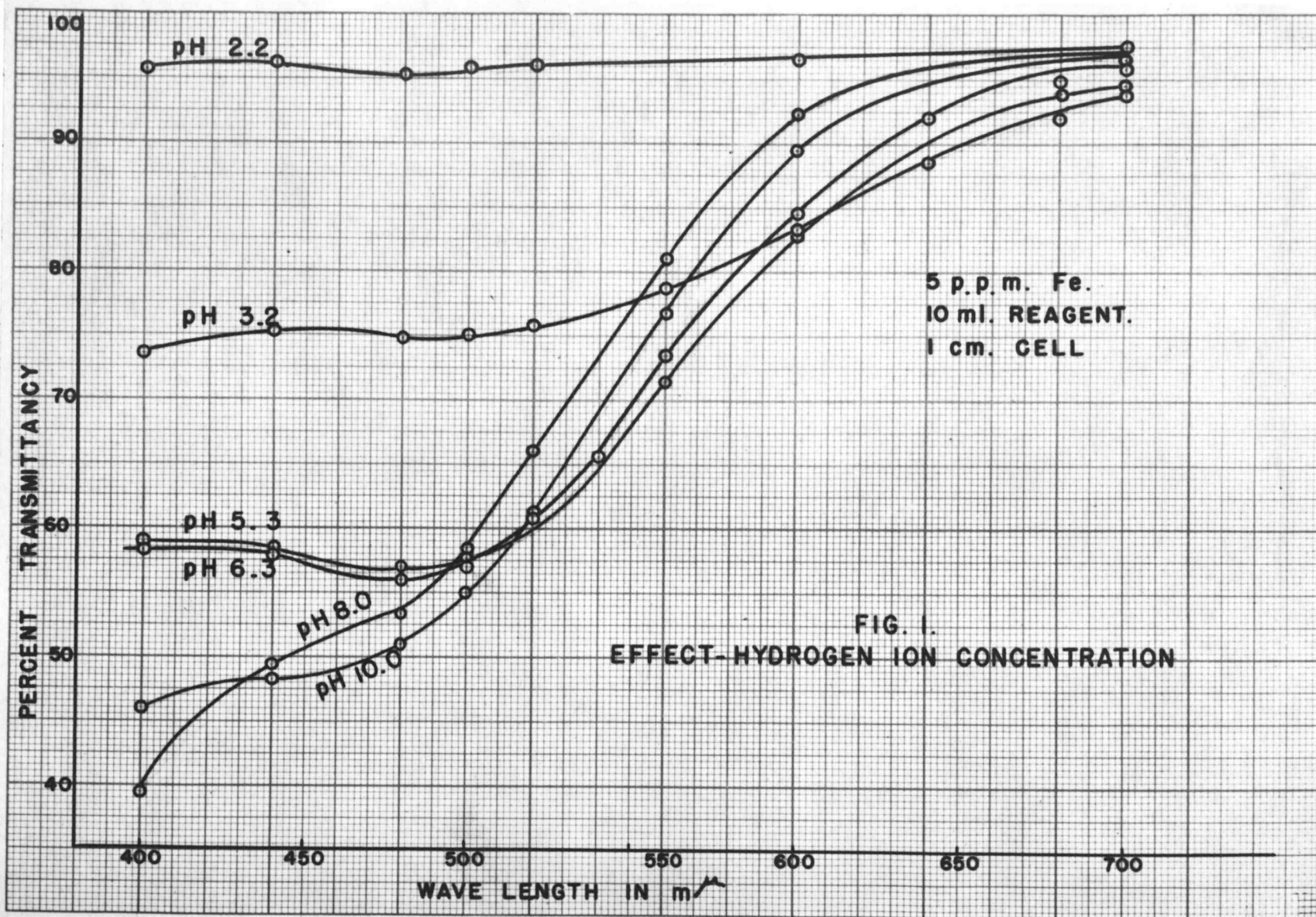
shaken. The pH value was adjusted by the addition of hydrochloric acid and ammonium hydroxide until an appropriate value was obtained. The solution was then made up to volume. A "blank" solution was prepared that contained the same concentration of all the reagents present in the colored solution except the iron. The final pH value of the solution was measured on a Beckman pH meter. Transmittancy for the solution was measured over a range of wave lengths varying from 380 to 700 m/^{u} by setting the wave length scale to the desired reading and adjusting the incident light by means of the entrance slit, exit slit, and the iris diaphragm so that the galvanometer reading for the colored solution represented per cent transmittancy.

The pH value chosen for this work was 6.3 to 6.7. Within this range there is but slight variation of transmittancy and the value is easily obtained and maintained. An ammonium acetate solution was used to buffer the solution. The system has a bright orange-red hue at the chosen pH value.

Wave Length of Maximum Absorption. The point of maximum light absorption for the color system was determined by employing three solutions with concentrations of 1, 3, and 5 p.p.m. of iron.

To produce the color system, the amount of the standard iron solution required to give the desired concentration of iron was measured from a microburette into a
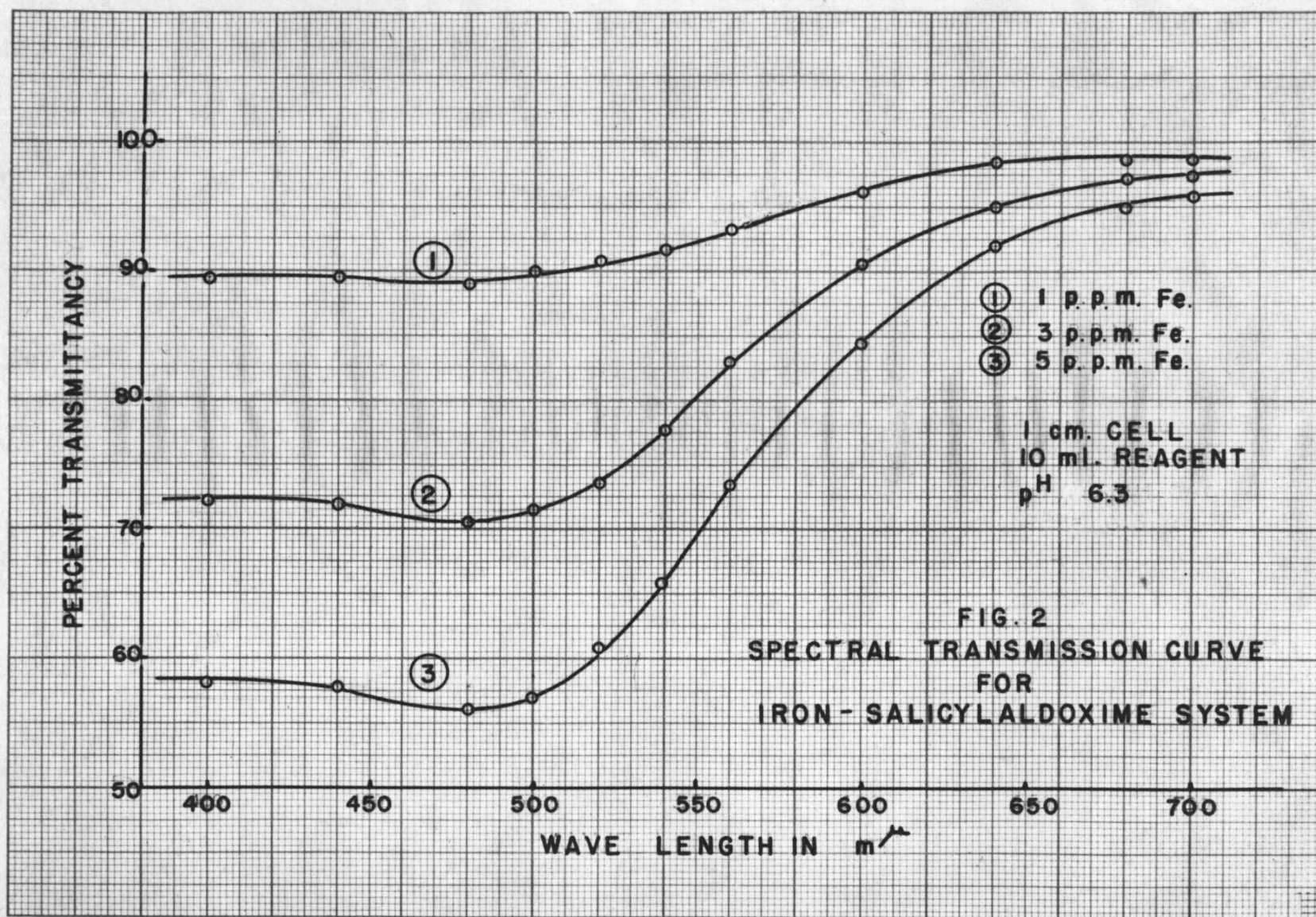
100-ml. volumetric flask. Ten milliliters of salicylal-
doxime reagent were added and the solution thoroughly sha-
ken. Ten milliliters of ammonium acetate solution were
added and the solution made up to volume. The color devel-
oped immediately. A "blank" solution was prepared by add-
ing 10 ml. of salicylaldoxime reagent and 10 ml. of ammon-
ium acetate solution to a 100-ml. volumetric flask and
making up to volume. Transmittancy measurements were made
by the same technique as was used in studying pH effect.
The spectral transmission curves are shown in Fig. 2.
Since maximum absorption occurred at 480 m/^{u}, this value
was used in making all further experimental measurements.
Factors Affecting the Color System. Studies were made to
determine the stability of the complex with respect to time.
The criterion set for stability was the ability to dupli-
cate transmittancy measurements after suitable time inter-
vals. Stability was found to be a function of the concen-
tration, the solutions changing in order of decreasing con-
centration. Solutions containing 1, 2, 3, 4, and 5 p.p.m.
of iron were used. The solution containing 5 p.p.m. was
stable for only 24 hours while that containing 1 p.p.m.
was stable at the end of a 48-hour period, but not after
72 hours. It was concluded that the time limit for making
measurements should be set at 24 hours in order to insure
reproducible results.

The effect of excess reagent was also observed.

FIG. 2
SPECTRAL TRANSMISSION CURVE
FOR
IRON - SALICYLALDOXIME SYSTEM

① 1 p.p.m. Fe.
② 3 p.p.m. Fe.
③ 5 p.p.m. Fe.

1 cm. CELL
10 ml. REAGENT
pH 6.3

Again, the criterion for interference was the ability to obtain duplicate transmittancy readings. Solutions containing the same concentration of iron, but varying amounts of reagents were used. It was found that as long as enough reagent was present to react with all the iron, no adverse effect was evident. This is in agreement with Howe and Mellon (6).

The amount of acid used in solution of the ore and the amount of ammonium acetate added were important because the pH had to be adjusted to a specified value. By using the designated amounts of each reagent the pH value was automatically obtained. Variation from these amounts produced a variation in pH value.

Howe and Mellon (6) made an extensive study of the effect of diverse ions on the color system. They found the interference to be of two types: (a) ions that interfere by producing a color, either of their own or by forming a complex with the reagent and (b) ions that form complexes with the iron and prevent formation of the salicylaldoxime complex.

Molybdate, cobaltous, and uranyl ions form colored soluble complexes with the reagent and must be absent. Ions such as chromic, chromate, permanganate, etc., must be absent because of their characteristic color.

Tartrate, citrate, oxalate, cyanide, carbonate, borate, and phosphate interfere seriously, probably

because of complexes formed with iron.

Lead, zinc, mercury, beryllium, and aluminum will not interfere provided sufficient reagent is present for them to form soluble complexes.

Ions which hydrolyze to form hydrated oxides in neutral solution interfere unless removed by filtration.

Iodide, sulfite, and other reducing ions interfere because of their reducing action on the ferric iron. This type of interference is not serious, however, since it can be eliminated by preliminary oxidation.

It should be emphasized that none of the preceding interferences are encountered in a normal iron ore and therefore present no serious detractions from the merits of the method.

The order of addition of reagents was found to be an important factor in obtaining reproducible results. If the ammonium acetate solution were added before the salicylaldoxime, duplicate results were not obtained. The interference was attributed to a possible formation of ferric acetate.

Molecular Extinction Coefficient. In order to determine if the color system conformed to Beer's law, transmittancies for five solutions containing from 1 to 5 p.p.m. of iron were measured. The color was developed as was done in determining the point of maximum absorption. The wave length scale was set at 480 m/u, the entrance slit was set

at 0.7 mm. and the exit slit at 10 m/^{u}. These adjustments remained the same throughout. One-centimeter absorption cells were used. The incident light was so adjusted that the galvanometer reading of the colored solution represented per cent transmittancy. The galvanometer was read to the nearest 0.1 unit.

When the extinctions for the five standard solutions were plotted against their respective concentrations, a straight line resulted, as shown in Fig. 3. This indicates Beer's law is obeyed for these concentrations. It was then possible to calculate a molecular extinction coefficient for the system.

The calculation was made in the following manner: The Beer-Lambert equation solved for e gives,

$$e = \frac{\log I_0/I}{c \times l}$$

However, since $I/I_0 = T$

the equation may be written

$$e = \frac{\log 1/T}{c \times l}$$

The average value obtained for e with the salicylaldoxime-iron complex was 2828. See Table 1.

FIG. 3
CONFORMITY TO BEER'S LAW
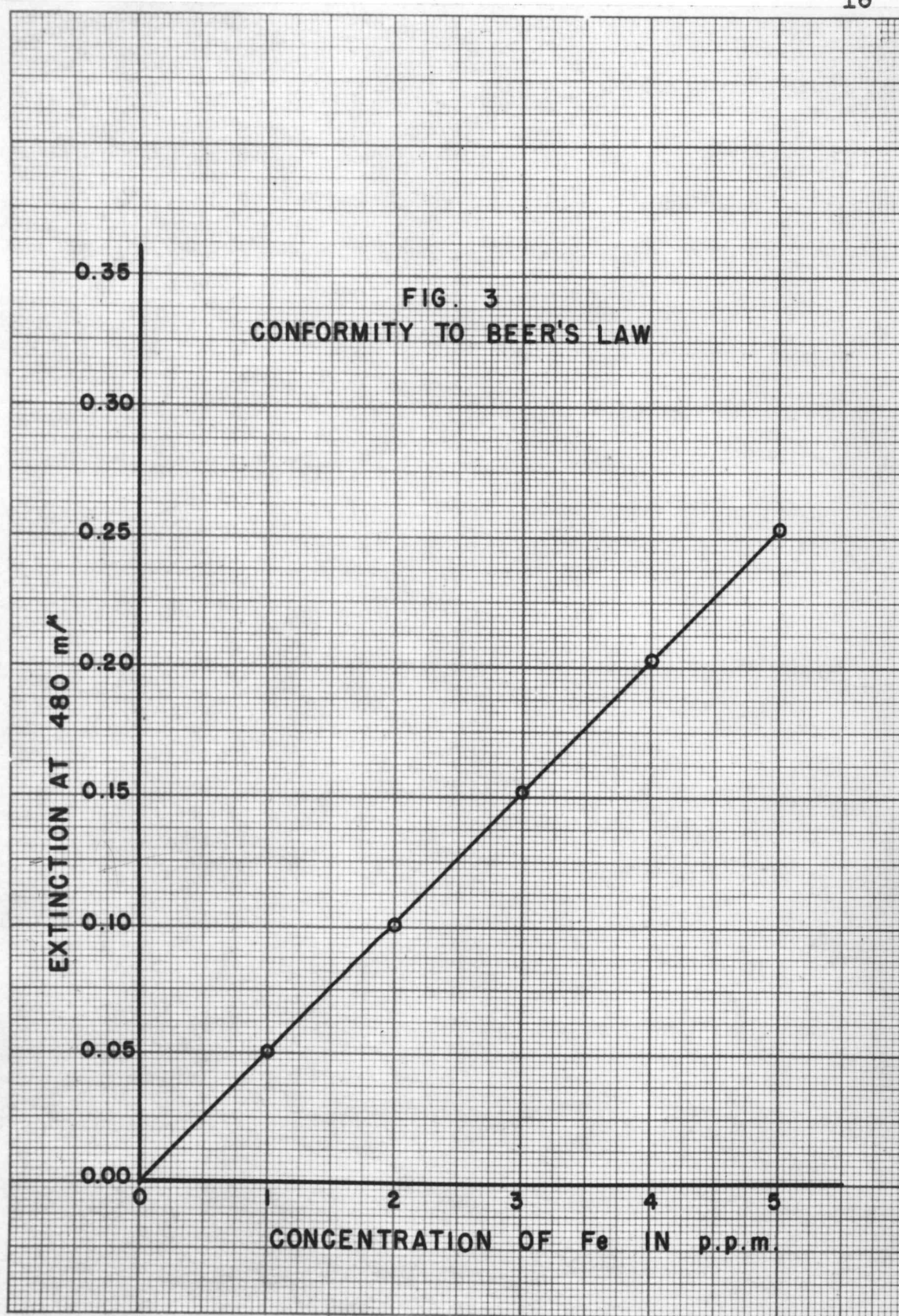
Table I

Determination of Molecular Extinction Coefficient

P.p.m. of Iron	Molecular Extinction Coefficient
1	2826
2	2829
3	2826
4	2830
5	2831
	Average = 2828

DETERMINATION OF IRON IN ORES

Approximately 0.4 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 warmed on a hot plate until solution was complete or only a white siliceous residue remained. Two milliliters of 3 per cent hydrogen peroxide were added to oxidize any ferrous iron to the ferric state. The solution was diluted with water to about 50 ml. to prevent volatilization of ferric chloride and boiled to remove the excess peroxide. The cooled solution was transferred to a 1000-ml. volumetric flask, diluted to the mark, thoroughly shaken, and allowed to stand until any residue had settled. An aliquot of 1 ml. taken from the top portion of the solution was carefully measured with a microburette into a 100-ml. volumetric flask and diluted with water to approximately 25 ml. Ten milliliters of 0.1 per cent salicylaldoxime reagent were added, and after mixing well, 10 ml. of ammonium acetate solution were added. The solution was then made up to volume and thoroughly shaken. A portion of the solution was reserved for measuring the hydrogen-ion concentration. A "blank" solution was prepared by adding 10 ml. of salicylaldoxime and 10 ml. of ammonium acetate to a 100-ml. volumetric flask and making up to volume. The

transmission was measured in exactly the same manner as was used in determining the molecular extinction coefficient. Using the value of e as determined, the percentage of iron in the ore was calculated.

The following example illustrates the method of calculation.

Experimental Data: weight of sample – 0.4020 gram; transmittancy of colored solution – 78.3% at 480 m/^{u}; cell length – 10 cm.; e – 2828.

The Beer-Lambert equation solved for c gives

$$c = \frac{\log 1/T}{e \times l} \text{ moles of iron per liter}$$

Therefore,

$$c = \frac{\log 1/T \times \text{mol. wt. Fe}}{e \times l} \text{ gram of Fe per liter.}$$

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

$$\% \text{ Fe} = \frac{\text{mol. wt. Fe} \times 100 \times 100 \times \log 1/T}{e \times l \times \text{wt. of sample}}$$

$$= \frac{55.84 \times 100 \times 100 \times \log 1/0.783}{2828 \times 1 \times 0.4020}$$

$$= 52.13\%$$

RESULTS

The method was tested by applying it to the determination of iron in ores in which iron had previously been determined by the dichromate titration method (8). The results obtained for 20 ores and a sample of iron wire are shown in Table II along with the value obtained by the dichromate method. In no case was the difference between the two methods greater than ± 0.14 per cent and the average difference was 0.05 per cent. The percentage error ranged from -0.141 to + 0.406 per cent with an average of + 0.020 per cent. Since the scale of the galvanometer can be read only to 0.1 scale unit, corresponding to about 0.25 per cent iron in an ore containing 50 per cent iron, the average of several readings was taken for the transmittancy. Although the precision is not high, the average value of the results of at least two or more determinations for a given sample checks closely with the dichromate method. Only those results which agreed to within at least 0.5 per cent of each other were used in calculating average values.

Table II

Results Obtained with Salicylaldoxime

Sample No.	Iron by Dichromate Method %	Iron by Salicylaldoxime Method %	Deviation %	Percentage Error %
1	28.22	28.24	+0.02	+0.071
2	33.95	34.02	+0.07	+0.206
3	38.25	38.28	+0.03	+0.078
4	42.52	42.46	-0.06	-0.141
5	37.62	37.65	+0.03	+0.082
6	36.84	36.79	-0.05	-0.135
7	36.12	36.09	-0.03	-0.083
8	35.11	35.19	+0.08	+0.228
9	34.45	34.59	+0.14	+0.406
10	51.52	51.54	+0.02	+0.039
11	49.59	49.55	-0.04	-0.081
12	54.04	54.04	+0.00	+0.000
13	56.00	56.12	+0.12	+0.214
14	52.20	52.13	-0.07	-0.134
15	57.62	57.60	-0.02	-0.035
16	52.83	52.90	+0.07	+0.133
17	57.90	57.84	-0.06	-0.103
18	34.30	34.17	-0.13	-0.379
19	41.73	41.72	-0.01	-0.024
20	46.48	46.46	-0.02	-0.043
21	99.70	99.68	-0.02	-0.021

DISCUSSION

The results of the analysis of twenty ores and a practically pure iron wire sample show that the spectrophotometric method is sensitive for large percentages of the desired constituent. They also show that the method is as accurate as the titration method. The result of the iron wire analysis is significant in showing that the method is applicable to the determination of macro constituents.

The spectrophotometric method for iron using salicylaldoxime has an advantage over the visual colorimetric method since it does not require a series of color standards and eliminates entirely matching color shades by eye.

Its advantage over the photoelectric colorimetric method consists in not requiring the use of a light filter or color screen. It may be observed from the absorption curve for the system that there is a sharp slope increase after the maximum point of absorption. Therefore, the light filter used should include wave length 480 m/^{u} but not above 520 m/^{u}. This greatly limits the extent of suitable filters.

Advantages of the spectrophotometric method in general include (a) immediate formation of a color which is stable for 24 hours, (b) the system conforms to Beer's law, (c) the color is independent of excess reagent,

(d) the method is rapid and involves few steps, and (e) the reagent is not only inexpensive, but very little is required.

SUMMARY

A spectrophotometric method has been developed for the determination of iron in ores which depends upon the formation of a soluble colored complex of iron with salicylaldoxime and measuring the light transmittancy at 480 m/^{u} of the colored solution. The transmittancy is quantitatively related to the iron concentration, which may be calculated by use of the molecular extinction coefficient for the system.

Results obtained by this method agree very closely with those obtained by the dichromate titrimetric method. The results further demonstrate that macro constituents can be satisfactorily determined by spectrophotometric methods.

The method is easily and rapidly carried out. It possesses several advantages over existing colorimetric methods for iron.

The diverse ions which interfere with the color system are not normally present in an iron ore.

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