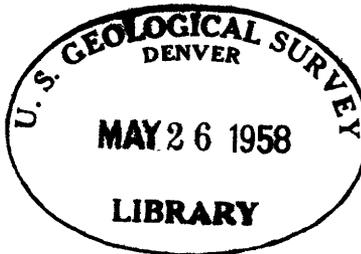# UNITED STATES GEOLOGICAL SURVEY.

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THE COLORIMETRIC DETERMINATION OF TOTAL IRON WITH O-PHENANTHROLINE

A Spectrophotometric Study

By
Frank Cuttitta

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May 1952

GEOLOGY AND MINERALOGY

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THE COLORIMETRIC DETERMINATION OF TOTAL IRON WITH

O-PHENANTHROLINE: A SPECTROPHOTOMETRIC STUDY *

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ABSTRACT

A study of the critical factors in the colorimetric determination of total iron in silicate and phosphate rocks, and in other nonmetallic materials is presented. It was desired to ascertain the wavelength of maximum absorbancy, the optimum concentration range for iron, the effect of different substances on the ferrous-o-phenanthroline system, and reproducibility of results. The sample is decomposed with $HF \cdot HNO_3 \cdot HClO_4$ in platinum, and the iron is determined colorimetrically with o-phenanthroline. No separations are made. Accurate results are obtained on a variety of materials.

INTRODUCTION

In order to check analytical methods for reliability, accuracy, and applicability prior to large-scale use in the laboratory, the o-phenanthroline colorimetric method for the determination of total iron was tested. The purpose of this report is to present a critical study of various factors that may affect the formation of the colored complex, including a study of the effect of varying concentrations of ions that may be encountered in the routine analysis of rocks and other nonmetallic materials. This work was done on behalf of the U. S. Atomic Energy Commission.

An iron-sensitive phenanthroline, 2-methyl-(1, 10)-phenanthroline was discovered by Gerdeissen (1889). However, he did not mention the ferrous iron complex; this was first reported by Blau (1888, 1889, and 1898) who synthesized o-phenanthroline. Following this original observation in 1898, little seems to have been done for three decades to use the fact analytically. Application of the ferrous iron o-phenanthroline complex as a redox indicator did not come until 1931, when it was introduced by Walden, Hammett, and Chapman (1931). Use of o-phenanthroline as a reagent for ferrous iron was reported by Saywell and Cunningham in 1937 and by Hummel and Willard in 1938. In 1938 an exhaustive study of the reaction was made by Fortune and Mellon. A summary of the work done with o-phenanthroline up to 1944 was made by Smith and Richter. A review of the known methods up to 1951 for the colorimetric determination of iron has been published by West (1951).

The active functional group through which o-phenanthroline owes its capacity to form complex cations of the chelate ring type when reacted with ferrous iron and other ions is the cyclic $= N - \overset{"}{C} - \overset{"}{C} - N =$ group. The generally accepted formula is:

$$Fe(C_{12}H_{10}N_2)_3$$

The metal ions, other than ferrous iron, that form complex cations with o-phenanthroline are Cd^{++}, Cu^{++}, Zn^{++}, Co^{++}, Ni^{++}, Cr^{+++}, and Ru^{++}. Almost all of these complex cations are practically, if not entirely, colorless. With the ferrous complex the resulting compound is red; with the ruthenium complex, yellow.

The common ferrous complex phenanthrolines that are most insoluble are perchlorate, periodate, dichromate, ferrocyanide, picrate, thiocyanate,

and persulfate salts.

In order to become better acquainted with the method--its limi-
tations and peculiarities--the following factors were studied:

1. Optimum conditions for color development and useful range.

2. Effects of possible interfering ions.

3. Reproducibility of results.

The procedure used to study the above factors was as follows.
The required amount of the standard iron solution was measured out and
the following reagents were added in the order mentioned: 1.0 ml of
conc. HCl; 2.0 ml of a 10 percent aqueous solution of $NH_2OH \cdot HCl$, 2.0
ml of a 0.25 percent aqueous solution of (1, 10)-phenanthroline, and
10.0 ml of a 25 percent aqueous solution of sodium acetate. According
to Fortune and Mellon (1938) and Bandemer and Schaible (1944), it is
important that the above reagents be added in the order mentioned. Solu-
tions of possible interfering ions were added before the addition of
$NH_2OH \cdot HCl$. The solution was then diluted to 25 ml with water. After
allowing the solutions to stand for at least 30 minutes, the optical
density was measured with a Beckman DU spectrophotometer; the absorption
was at a maximum at 510 mμ (slit width = 0.04 mm). Distilled water was
used in the 1.00-cm corex reference cell.

PROCEDURE FOR THE DETERMINATION OF TOTAL IRON

Apparatus and solutions

The absorbancy measurements were made with a Beckman DU spectro-
photometer equipped with 1.00-cm corex cells. The reference cell con-
tained distilled water unless otherwise stated. If distilled water was

not used, the "blank" in the reference beam of light was filled with a solution containing the same amount of hydroxylamine·HCl and o-phenanthroline as was used with the iron in the other cell.

All pH measurements were made with a continuous-indicating line-operated pH meter.

The standard solutions of iron were prepared by dissolving electrolytic iron wire in dilute hydrochloric acid. The solutions were then diluted to volumes such that 1.00 ml contained 20 γ Fe_2O_3, 50 γ Fe_2O_3, and 100 γ Fe_2O_3, respectively.

Both 0.10 and 0.25 percent solutions of o-phenanthroline were prepared by dissolving the monohydrate in doubly distilled, iron-free water. The reagent dissolves readily in water heated to about 80 C. It is important that the (1, 10)-phenanthroline monohydrate be free from impurities. Contamination is evidenced by a pink coloration of the crystalline material and a lowering of the melting point (99 - 100 C).

Following the original work of Saywell and Cunningham (1937), hydroxylamine hydrochloride was used as the reducing agent in all work on interfering ions and in concentration tests. The 10 percent solution of hydroxylamine hydrochloride, used as the reducing agent for the iron, was prepared by dissolving the C. P. reagent in doubly distilled water.

Solutions used in the determination of interfering cations were prepared from the chloride or nitrate salts of the metals; the anion solutions were prepared from the sodium salts.

Sodium acetate was used to adjust the acidity to a pH of 3.5. Bandemer and Schaible (1944) have shown that it is important to add the sodium acetate solution to the acid solution of the sample after the

o-phenanthroline and the hydroxylamine have been added. A 25 percent solution of the reagent was prepared by dissolving C. P. sodium acetate hydrate in doubly distilled water.

Recommended general procedure

1. Weigh a 0.1000-g sample and transfer to a 70-ml round bottom platinum dish.

2. Ignite gently over a Meker burner to destroy organic matter.

3. Cool.

4. Add 5 ml HF, 10 ml (1:1)HNO_3, and 3 ml $HClO_4$ (measure $HClO_4$ accurately).

5. Bring to fumes of $HClO_4$ on hot plate and continue fuming for 2 to 3 minutes. Cool.

6. Wash down sides of platinum dish with not more than 5 ml of 1:1 HNO_3.

7. Place on hot plate again and heat until fumes of $HClO_4$ are evolved. Continue fuming for 2 to 3 minutes. Then cool.

8. Repeat steps 6 and 7.

9. After the last fuming, cool and add 25 to 40 ml water.

10. Heat the solution gently to boiling to dissolve all the soluble salts. Cool.

11. Filter through a no. 40 Whatman filter paper directly into a 250-ml volumetric flask. Wash residue thoroughly with hot water.

12. Dilute to volume (250 ml) with water after cooling to room temperature. Reject residue.

13. Transfer a 5-ml aliquot of the solution to a 25-ml volumetric flask.

14. Add to the 25-ml flask the following reagents in the order given. (The order of addition is important.) Shake flask after the addition of each reagent to effect complete mixing.

> 1 ml conc. HCl
>
> 2 ml 10 percent aqueous solution of hyroxylamine HCl.
>
> 2 ml 0.25 percent aqueous solution of o-phenanthroline.
>
> 10 ml 25 percent aqueous solution of sodium acetate.

15. Dilute to a volume of 25 ml and allow the solution to stand for 30 minutes to permit complete color development.

16. Read the optical density with a Beckman spectrophotometer at a wavelength of 510 mμ using distilled water in the blank cell. Use a 1-cm corex cell and silt width of 0.04 mm.

17. Obtain an optical density-concentration curve by plotting spectrophotometer density readings for the color developed with known quantities of Fe_2O_3.

18. The amount of Fe_2O_3 in the sample is read from this curve and the percent Fe_2O_3 in the sample is calculated.

Note: When large quantities of iron are present (more than 250 γ Fe_2O_3), the sample should be further diluted and more reagent added. Dilution should be sufficient to bring the iron concentration within limits of the calibration curve.

OPTIMUM CONDITIONS FOR COLOR DEVELOPMENT AND USEFUL RANGE

Iron concentration

The absorption spectra for various concentrations of Fe_2O_3 were determined and conformity to Beer's Law was found at 510 mμ for con-

centrations from 0 to 10 ppm Fe_2O_3 (0 to 250 γ Fe_2O_3). A good absorbancy maximum occurs at 510 mμ (distilled water in the reference cell) as shown in figure 1. Optical density measurements taken at 510 mμ over the range from 0.10 to 10 ppm (figure 2) were plotted against Fe concentration, and the straight line indicates very close conformity to Beer's Law. The maximum concentration which could be used with a 1.00-cm cell was found to be 10.0 ppm (250 γ) of iron. A concentration of 0.10 ppm gave a minimum transmittancy of 94 percent at this thickness.

Reference cell

The significance of the proper selection of the reference solution was studied. The absorption spectra were obtained using a solution containing the reagents as the reference solution. Figure 1 shows the absorption spectra obtained using distilled water as the reference solution. Using a "reagent blank" as the reference solution, no marked difference in the shape of the initial portion of the resulting curves was noted, measurements beyond 480 mμ coinciding with those of figure 1. Therefore, it seems unnecessary to utilize a reagent blank solution in the reference cell, so that the true absorption spectrum of the ferrous-o-phenanthroline complex can be obtained.

Acid concentration

In order to study the effect of acid concentration on the intensity of the color produced in solutions of rock samples, a series of solutions containing 0.1, 0.2, 0.5, 1, 2, 4, 6, 8, and 10 ppm Fe_2O_3 were prepared. The solutions also contained 80 ppm P_2O_5 and 2500 ppm ClO_4^-. These
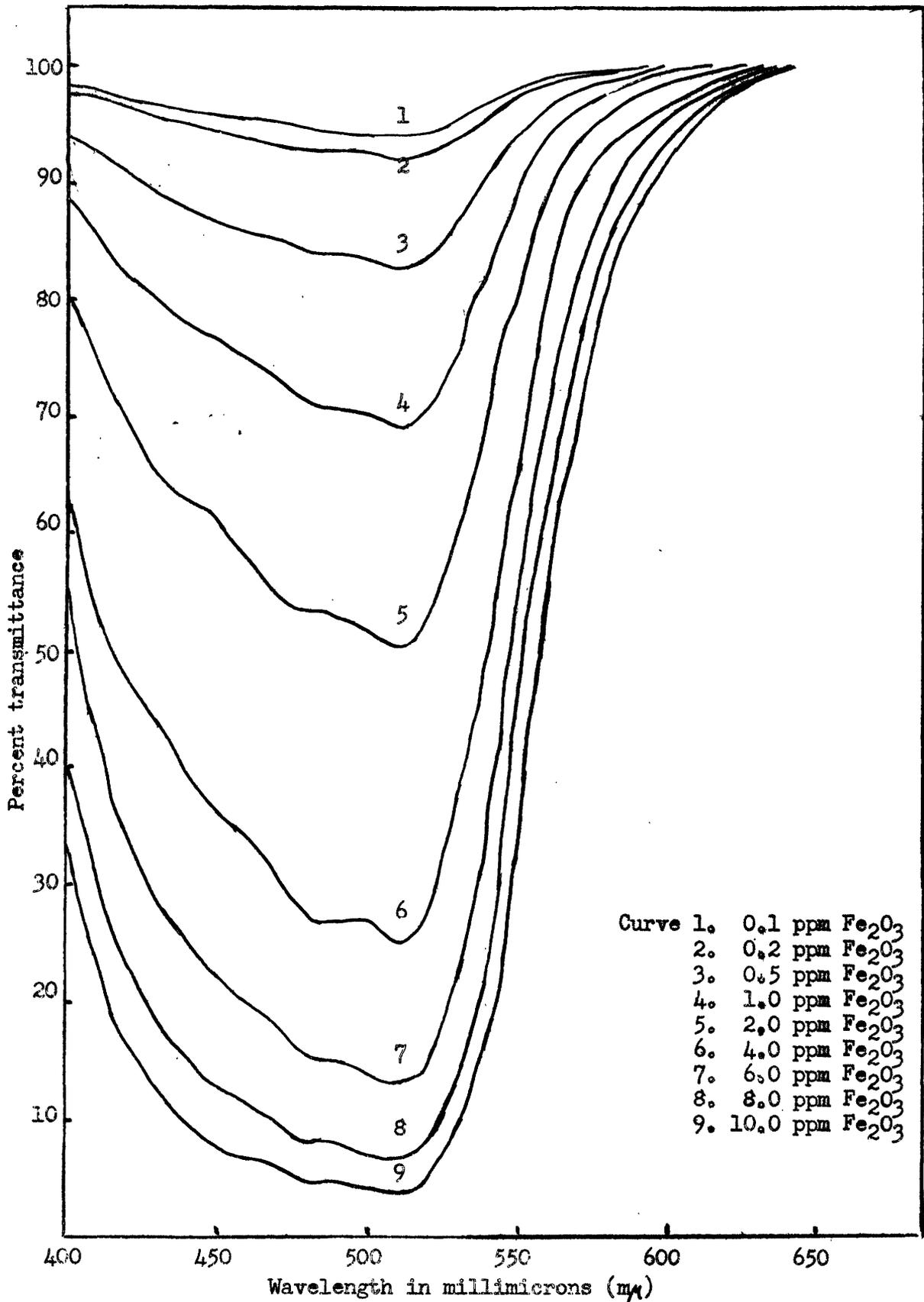
Figure 1.—Absorption spectra of ferrous-o-phenanthroline system
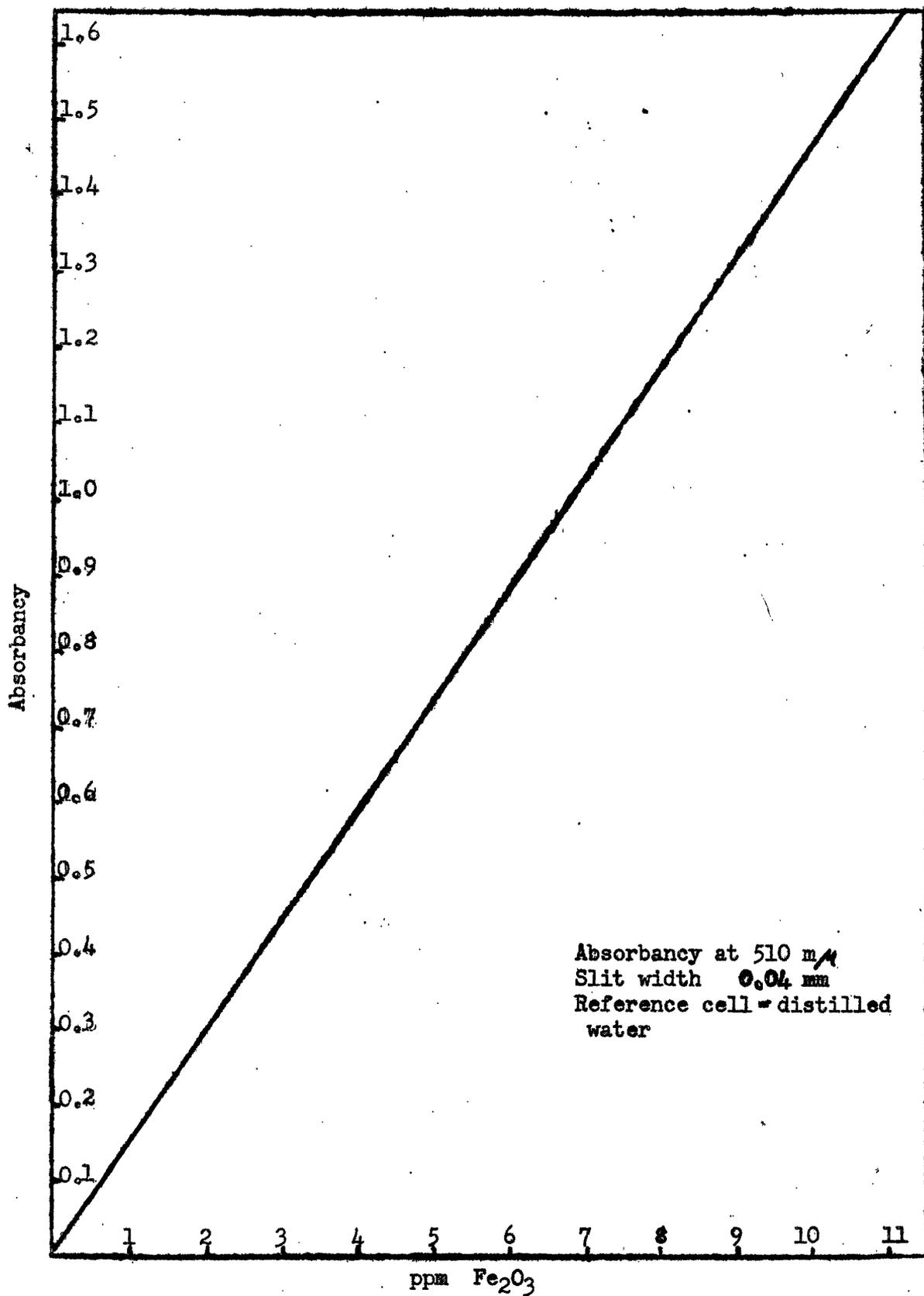(Reference, distilled water)

Figure 2.—Sensitivity and conformity of ferrous
phenanthroline system to Beer's Law

quantities of P_2O_5 and ClO_4^- represent the maximum amounts that would be in a solution prepared according to the recommended procedure. Density curves for solutions wherein the pH varied from 2.0 to 5.0 were exactly superimposed upon one another. These results indicated that the (1, 10) -phenanthroline-ferrous system was independent of pH in the region from 2 to 5. A pH of 3.5 was selected for the final procedure. Figure 3 is a graph of the density of the ferrous-phenanthroline solutions as a function of pH at two iron concentrations.

Effect of phenanthroline and hydroxylamine concentration

As the procedure is designed to determine no more than about 8 ppm (200 γ) of Fe_2O_3, solutions containing 0.8, 2.0, and 8.0 ppm of the Fe_2O_3 added as $(NH_4)_2SO_4 \cdot FeSO_4$ were prepared and the amount of phenanthroline was varied. The pH of the solution was 3.5. Figure 4 is a curve showing the optical density as a function of the phenanthroline concentration.

Using the maximum amount of phenanthroline solution needed (2 ml of 0.25 percent solution), the same three concentrations of iron were then tested for the effect of hyroxylamine concentration. Figure 5 plots the density of the ferrous-phenanthroline complex against the hydroxylamine concentration. For the final procedure it was decided to use 2 ml of a 0.25 percent phenanthroline solution and 2 ml of a 10 percent hydroxyla- mine hydrochloride solution.

As the iron in solution in the final procedure is in the ferric form, it is necessary to use a reducing agent. According to Fortune and Mellon (1938) and Saywell and Cunningham (1937), the most satisfactory reagent for this purpose is hydroxylamine hydrochloride, so we used a 10 percent solution of $NH_2OH \cdot HCl$ as the reducing agent.
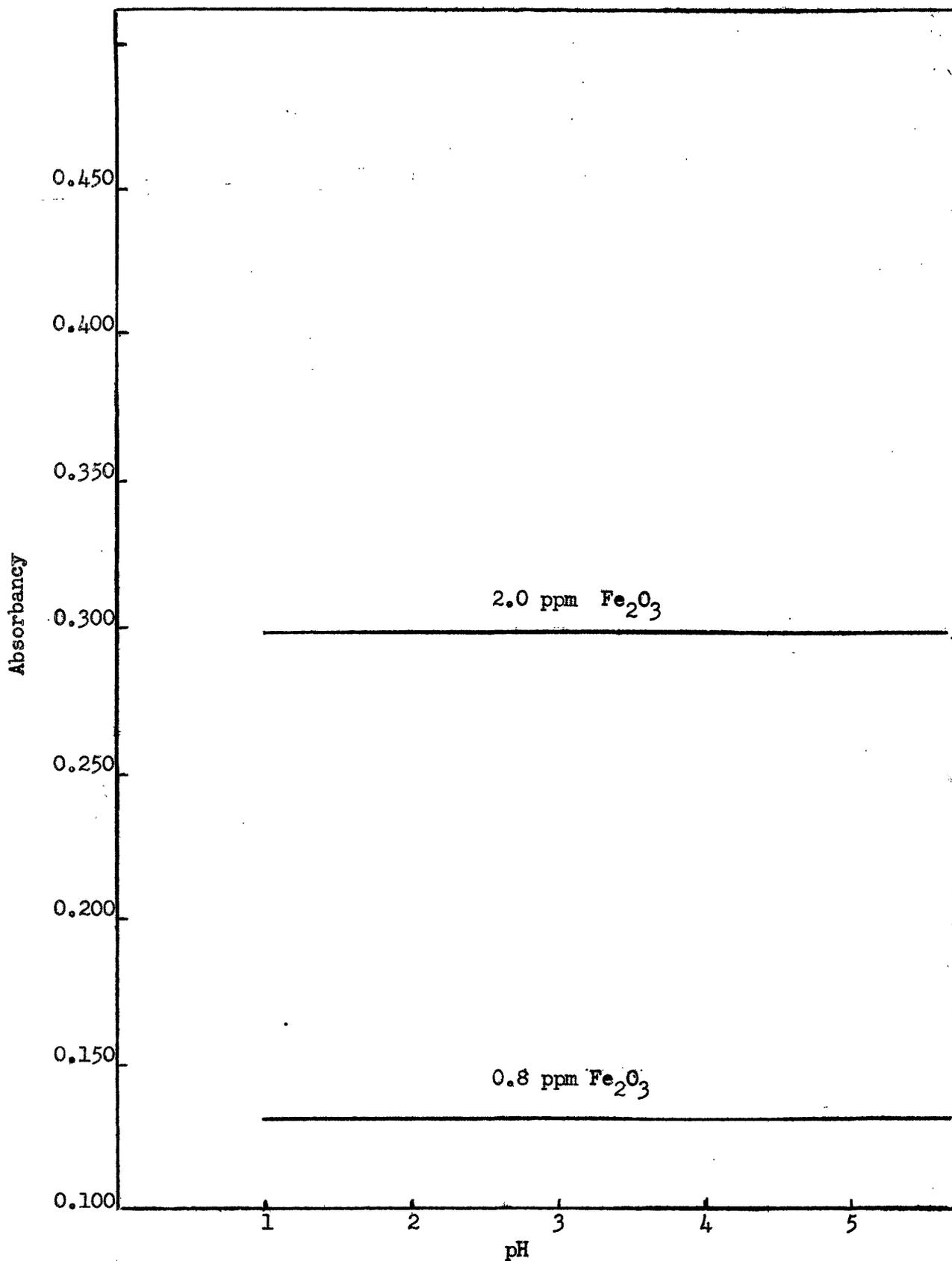
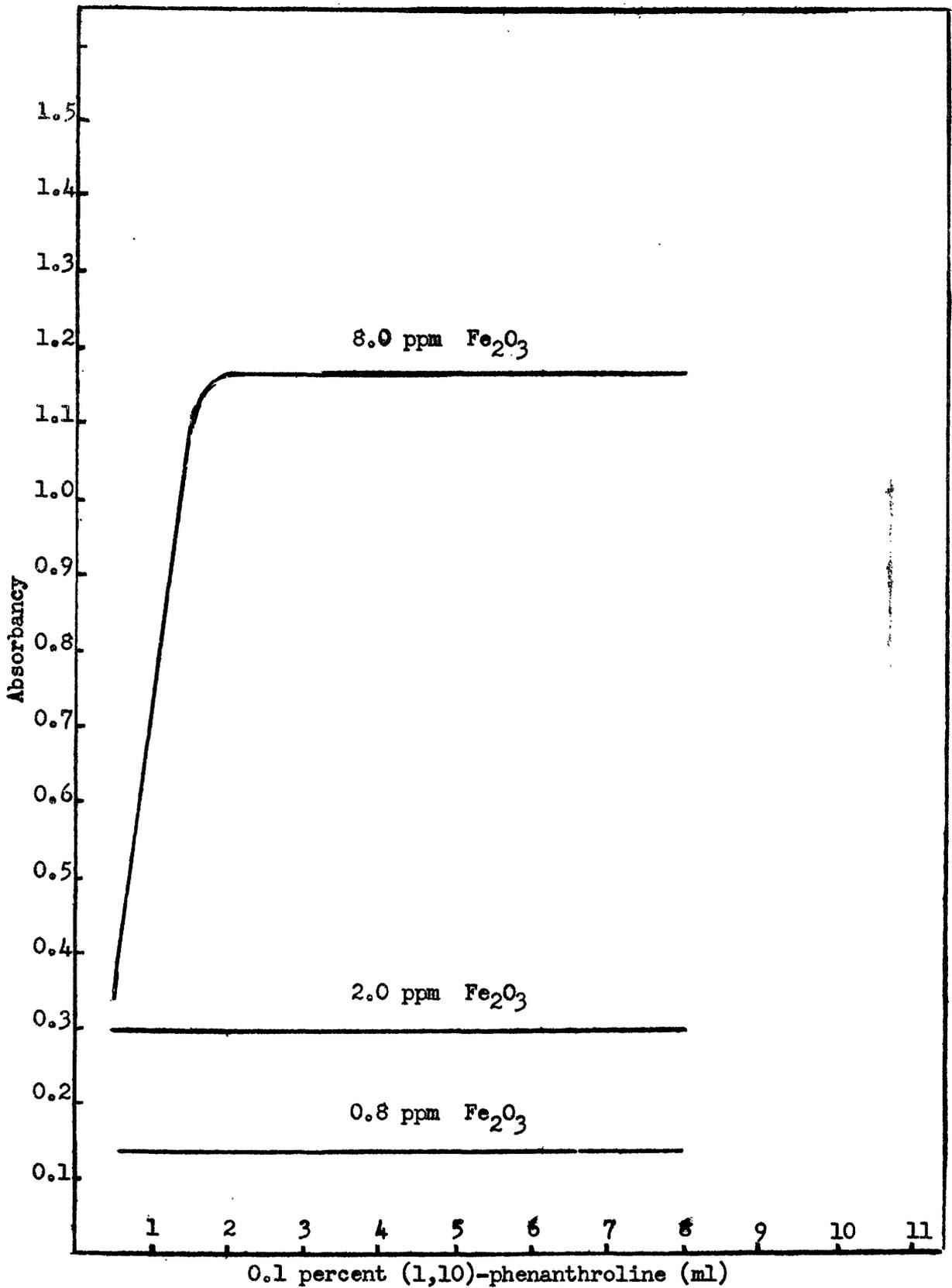Figure 3.—Effect of acid concentration on the ferrous-
o-phenanthroline system

Figure 4.—Effect of phenanthroline concentration on the
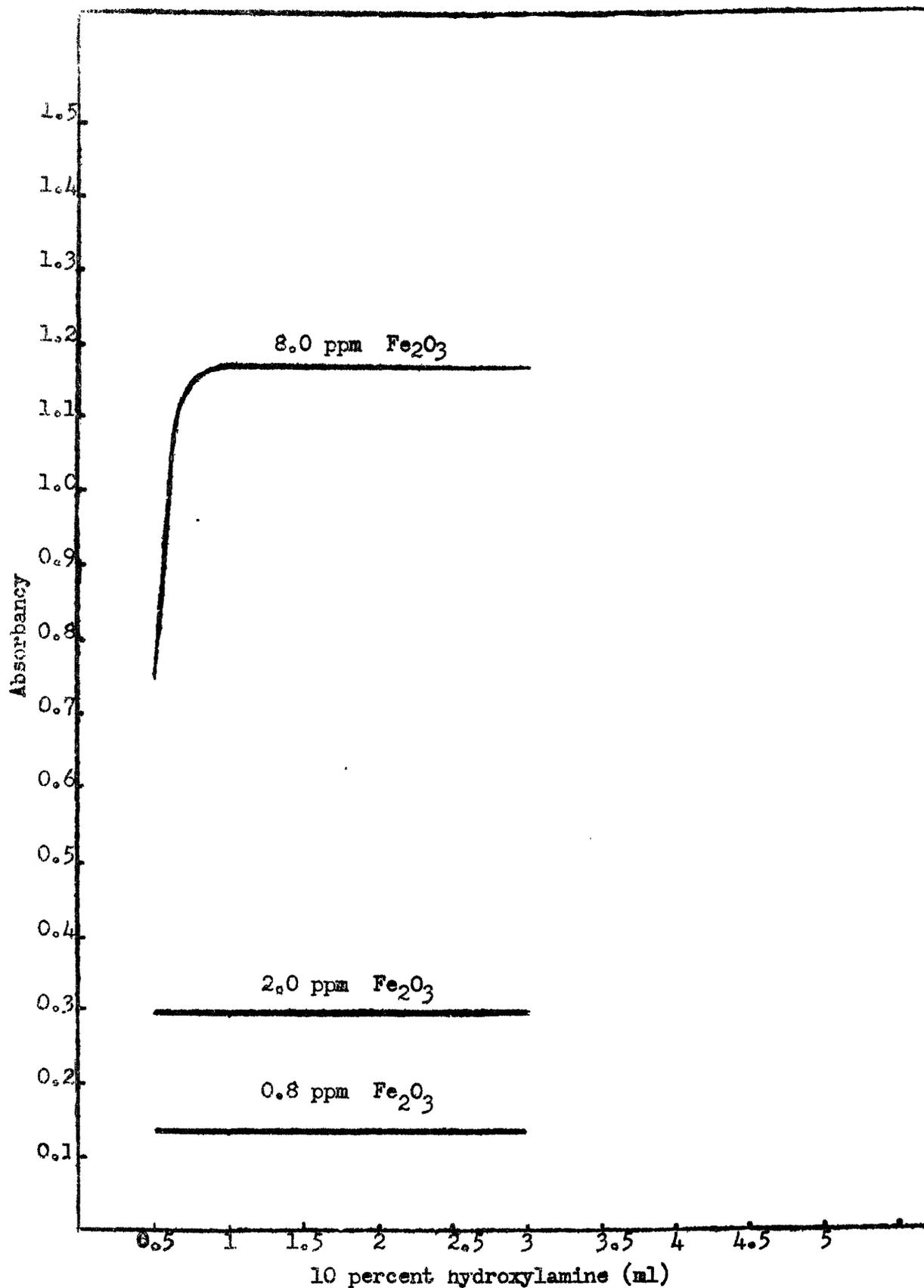ferrous-o-phenanthroline system

Figure 5.—Effect of hydroxylamine concentration on the
ferrous-o-phenanthroline system

EFFECT OF POSSIBLE INTERFERENCES

Perchlorate concentration

Bowen and Schairer (1932) found in a phase-equilibrium study of the ferrous oxide-silica system that platinum crucibles removed too much iron to be usable. They stated that platinum has a marked disadvantage for this purpose. Except under strongly oxidizing conditions, it reduces iron from its compounds and takes iron into solid solution. In all cases tested, some iron was removed from the charge by the platinum crucible. This phenomenon was circumvented in the present study by using fuming $HNO_3 \cdot HClO_4$.

According to some investigators (Fortune and Mellon, 1938; Smith and Richter, 1944; and Sandell, 1950) if perchlorate is present in more than small amounts, a precipitate of the slightly soluble o-phenanthroline perchlorate may be produced. Because in the final procedure the sample is decomposed with $HF \cdot HNO_3 \cdot HClO_4$ in platinum (no separations being made and the iron determined colorimetrically with o-phenanthroline), a study of the effect of various concentrations of $HClO_4$ was made using 0.8 and 2.0 ppm of Fe_2O_3 (added as $FeCl_3$).

The results are shown in figures 6 and 7. It was found that varying amounts up to 2500 ppm of ClO_4^- have no effect upon the maximum absorbancy measured within 24 hours. Greater concentrations (up to 5000 ppm) showed no change in density if measured within 30 minutes. However, upon standing the greater concentrations of ClO_4^- were found to diminish the coloration and also decrease the absorbancy as measured at 510 mμ . As reproducible results were obtained using less than 2500 ppm ClO_4^-, the
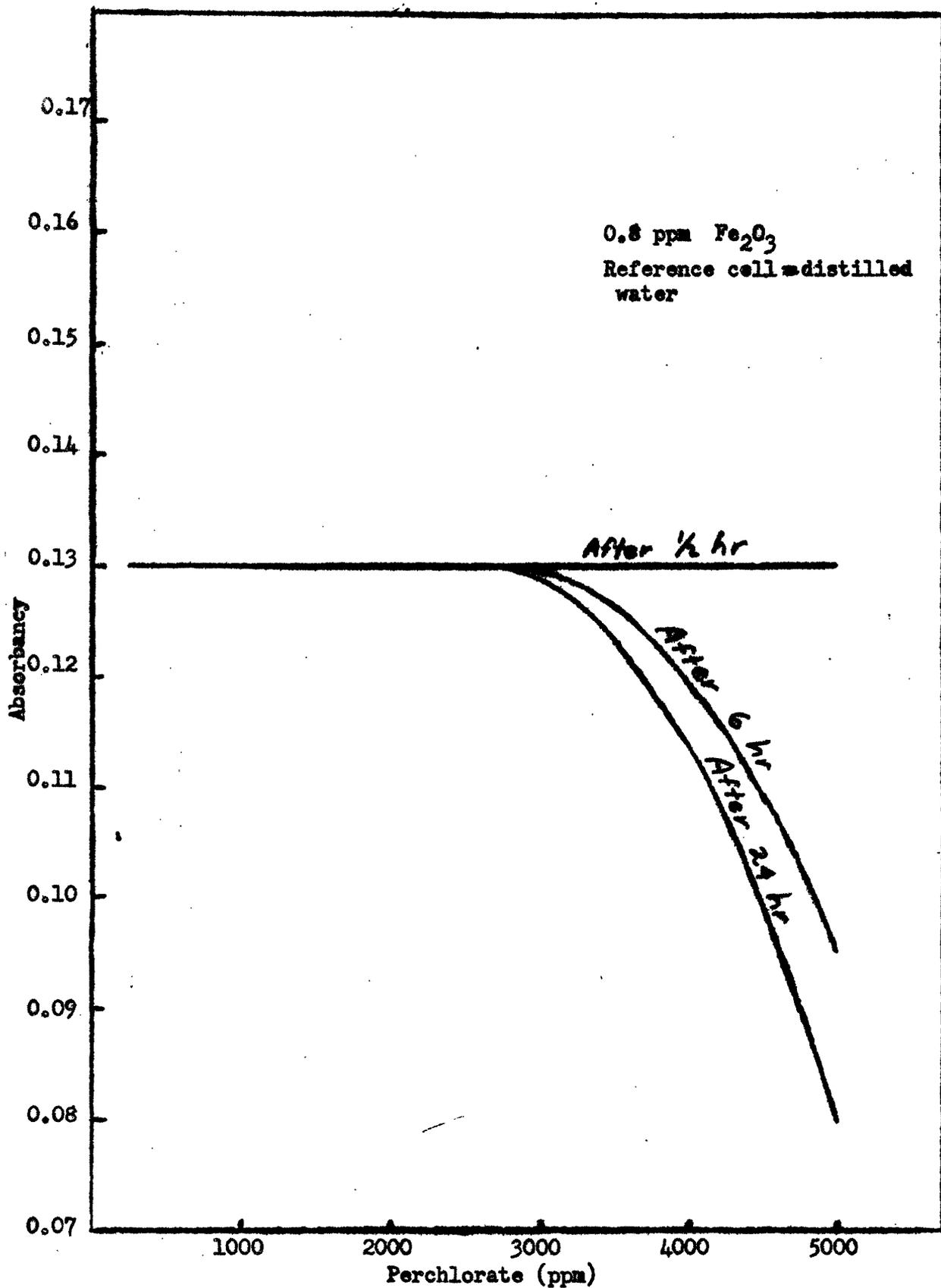
Figure 6.—Effect of perchlorate concentration on the
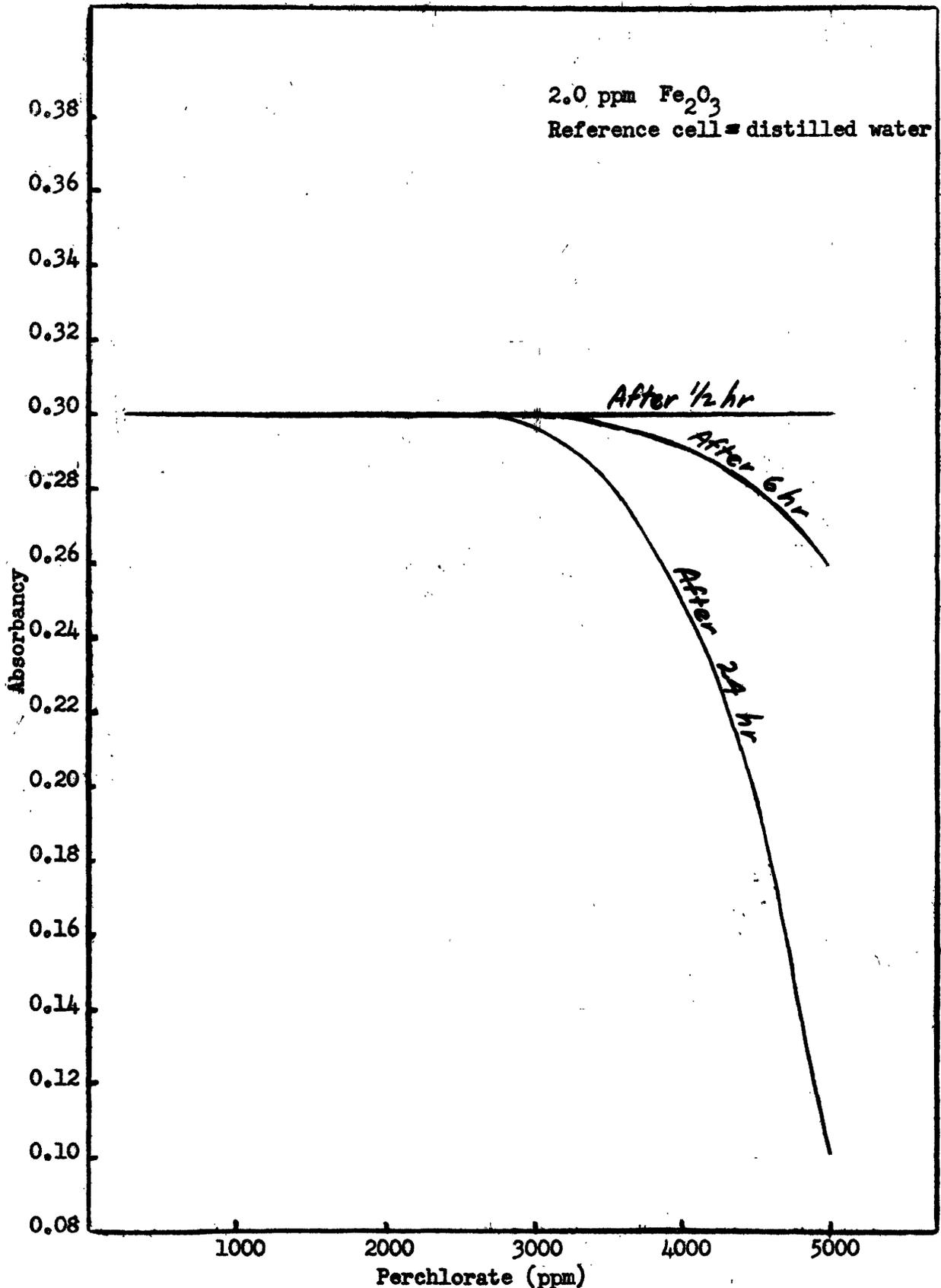ferrous-o-phenanthroline system

Figure 7.—Effect of perchlorate concentration on the
ferrous-o-phenanthroline system

use of 3 ml of 72 percent $HClO_4$ was chosen for the final procedure. Accord-
ing to the final procedure, this amount of $HClO_4$ will yield a final per-
chlorate ion concentration of less than 2500 ppm depending on the length
of fuming time.

Different ions

An advantage of o-phenanthroline over some of the other iron reagents
is in the possibility of using it in slightly acidic solutions so that the
hydroxides and phosphates of many metals are not precipitated. However
it has been found (Fortune and Mellon, 1938; Smith and Richter, 1944;
Brabson et al., 1946; and Sandell, 1950) that phosphate ion may cause
difficulties under certain conditions if present in quantities greater than
20 ppm of P_2O_5(pH 2 to 9).

The phosphate ion and other major elements occurring in phosphate
and silicate rocks were tested for possible interferences. The effect
of these different ions was studied using 20 γ Fe_2O_3 and 50 γ Fe_2O_3.
Absorbancy readings were taken at 510 mμ (slit width = 0.04 mm) in order
to determine any changes in the maximum absorbancy. A negligible error
was obtained with 200 ppm Al, 200 ppm Ca, 10 ppm Ce^{3+}, 200 ppm F, 100 ppm
Mg, 80 ppm U^{4+}, 200 ppm U^{6+}, 80 ppm P_2O_5, and 500 ppm Mn. These amounts
far exceed the concentrations of the different ions that can be present
in the final procedure.

The ions that might interfere and the maximum amounts permissible
without interference, as determined by Fortune and Mellon (1938), are
given in table 1. Based on the 2 mg sample (in a 25-ml volume) used in
the final procedure, the maximum permissible concentrations (in percent)

of the elements that may be present in the original sample have been calculated and are listed in the third column of table 1. If present at all, the percent of these ions would be extremely low in the materials for which this procedure was tried and for which it is recommended. No interference is expected from this source. However, any change in hue or any precipitation should serve as a warning that the material needs further study.

REPRODUCIBILITY OF RESULTS

Table 2 gives the results of repeated determinations for Fe_2O_3 on 10 Bureau of Standards samples.

It can be seen from table 2 that the maximum absolute difference between four determinations on the same sample (No. 104) is 0.19 percent or about 2.7 percent of the total Fe_2O_3 content. These figures are from careful painstaking work. The accuracy is also $\pm$ 2.7 percent. This is seen from the results on the Bureau of Standards sample taking 7.07 percent as the "true" value. Accurate results were obtained with a wide variety of other samples, including various silicate and phosphate rocks, limestones, and fluorspar.

SUMMARY

A spectrophotometric study confirms that o-phenanthroline is an excellent reagent for the determination of total iron in silicates and phosphates.

1. It is a very sensitive method with a range of from 0.10 to 10.0 ppm Fe_2O_3 in a 1.00-cm light path.

Table 1.--Effect of different ions on the ferrous-o-phenanthroline system

Ion	Permissible amount (ppm) in 25 ml of final solution	Maximum permissible concentration in sample (percent)	Effect	Optimum pH
Antimony	30	37.5	Precipitates basic salts	3.0 - 5.5
Beryllium	50	62.5		
Bismuth	None		Precipitate	
Cadmium	50	62.5	Precipitate	
Chromium	20	25.0	Change in hue	
Cobalt	10	12.5	Yellow color	3 - 5
Copper	10	12.5		2.5 - 4.0
Dichromate	20	25.0	Change in hue	
Mercuric	1	1.25	Precipitate	
Mercurous	10	12.5		3 - 9
Molybdenum	10	12.5	Ppt when $pH < 4.5$	> 4.5
Nickel	2	2.5	Change in hue	
Silver	None		Precipitate	
Tungsten	5	6.25	Fading	
Zinc	10	12.5	Precipitate	

Table 2.--Analyses of National Bureau of Standards samples

No.	Material	Percent Fe$_2$O$_3$ by NBS	1st	Percent Fe$_2$O$_3$ found 2d	3d	4th
1a	Limestone 1/	1.63	1.68	1.60	1.57	1.62
56 a	Phosphate 1/	2.18	2.13	2.14	2.21	2.23
76	Burnt refractory 1/	2.38	2.36	2.30	2.28	2.42
77	Burnt refractory 1/	0.90	0.85	0.80	0.82	0.86
79	Fluorspar 2/	0.15	0.18	0.20	0.21	0.17
80	Glass 2/	0.065	0.071	0.064	0.061	0.059
88	Dolomite 2/	0.084	0.079	0.082	0.078	0.086
98	Plastic clay 1/	2.05	1.98	2.09	2.01	2.00
104	Magnesite 1/	7.07	6.92	7.02	6.88	7.01
120	Fla. phosphate 1/	0.89	0.93	0.85	0.82	0.83

Treat a 0.1000-g sample with HF, HNO$_3$, and 3 ml HClO$_4$, and bring to fumes of HClO$_4$.

1/ Dilute to 250 ml and use 5-ml aliquot; make final volume to 25 ml.

2/ Dilute to 100 ml and use 5-ml aliquot; make final volume to 25 ml.

2. Two milliliters of an aqueous 0.25 percent solution of o-phenanthroline are required to produce the maximum color with 8.0 ppm of iron.

3. The color reaction conforms to Beer's Law over the entire range of concentrations studied.

4. pH has no effect on the intensity of the color over the applicable range, 2.0 to 5.0.

There are very few ions (Cu, Ag, and Bi) that seriously interfere with the production of the quantitative color reaction. These are not normally found in shales and silicate and phosphate rocks in amounts that would interfere.

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