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EXPERIMENT STATION]

DIPHENYLAMINE AS INDICATOR IN THE DETERMINATION OF IRON IN SILICATES

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Since Knop¹ proposed the use of diphenylamine as internal indicator for titration of ferrous iron with dichromate, a number of investigators² have reported their experience with this indicator. Reports in general have been favorable, but it has been noted that the color change is not always sharp, and there is a blank attributed to the volume of oxidizing solution consumed by the indicator itself. The optimum conditions for use of this indicator have not been well defined. Knop stated that the presence of phosphoric acid is advantageous, destroying the yellow color due to ferric salts and so making the end-point more easily seen, but mentions no other advantage from its addition. In the titration of vanadic acid by ferrous sulfate and diphenylamine, Willard and Young² specified that the solution should be buffered by addition of sodium acetate sufficient for free hydrochloric and sulfuric acids, and phosphoric acid also added. The intense color of the indicator is developed by the vanadic acid to be determined, and discharged upon complete reduction with ferrous sulfate. They report a considerable blank correction. Sarver² states that diphenylamine sometimes gives erratic results in ferrous iron titrations with dichromate, but recommends it for the determination of ferrous oxide dissolved from a mineral by sulfuric or hydrochloric and hydrofluoric acids. The addition of excess boric acid and standard dichromate to minimize oxidation of the iron by air, and deliberate back titration with standard ferrous sulfate, are advised. He further states that it is best to keep the volume of solution small and to take the disappearance of the intense blue as the end-point, disregarding any blue tint which persists; fluoboric acid had no noticeable bad effect, but on the contrary seemed advantageous, brightening the color. Diphenylamine has been reported to be a very satisfactory indicator in titration of hydroquinone by ceric sulfate, in presence of either sulfuric or hydrochloric acid and absence of iron.³

Recently, the author had occasion to determine ferrous oxide in a mineral, and chose Sarver's procedure for the purpose. The decomposition of the sample having been effected in a 50-ml. platinum crucible, sufficiently

¹ Knop, *THIS JOURNAL*, **46**, 263 (1924).

² Sarver, *ibid.*, **49**, 1472 (1927); Schollenberger, *Soil Science*, **24**, 65 (1927); Willard and Young, *THIS JOURNAL*, **50**, 1334 (1928); *Ind. Eng. Chem.*, **20**, 769 (1928); Furman and Wallace, *THIS JOURNAL*, **52**, 1443 (1930); *ibid.*, **52**, 2347 (1930); Kolthoff and Sarver, *ibid.*, **52**, 4179 (1930).

³ Furman, *ibid.*, **50**, 1675 (1928).

large to permit titration in the crucible, the additions of boric acid and excess dichromate were omitted, as it was considered that there would be little chance for oxidation in the brief time required for titration. The solution was titrated directly by dichromate in the presence of sulfuric and free hydrofluoric acid. The brilliance and sharpness of appearance of the intense blue end-point color were surprising, entirely at variance with previous experience and Sarver's description of the behavior of the indicator. This suggested that free hydrofluoric acid may have a desirable effect upon the development of the indicator color⁴ and some experiments with solutions were undertaken in order to investigate the matter. The conditions chosen for these titrations were such as might prevail in a determination of ferrous oxide in a mineral by a procedure similar to Sarver's, namely, titration in small volume in presence of considerable concentrations of sulfuric or hydrochloric acid. It was also desired to determine whether total iron in the titrated solution could be determined by a titanous chloride-thiocyanate titration after the oxidation of the ferrous iron in the first titration with dichromate and diphenylamine. The behavior of diphenylamine on back titration with the reducing agent was of interest, so that the determination fitted in the plan for the work. The reduction titration following the oxidation titration would also serve as a check upon the latter and reveal error due to oxidation by air.

Twentieth normal solutions of ferrous ammonium sulfate and potassium dichromate were prepared by dissolving the proper weights of the pure salts in water, previously boiled and cooled, and diluting to volume. The iron solution was stabilized by addition of 1% sulfuric acid to the water. Titanous chloride of approximately the same strength was prepared by diluting the commercial 20% solution (iron-free) with 10% by volume hydrochloric acid, storing and dispensing from a small bore buret with atmosphere of hydrogen over the solution. The diphenylamine solution contained 0.5 g. in 50 ml. of concd. sulfuric acid, and two drops were used for each titration in 20–25 ml. initial volume. All reagents were of c. p. analyzed grade, and the same volumetric apparatus was used throughout with precautions to ensure constant delivery usual in careful work. The strengths of the dichromate and iron solutions were checked by permanganate titrations with sodium oxalate as standard, by direct titration of an aliquot of iron solution with dichromate and ferricyanide as external indicator and by electrometric titrations. All these indicated that the solutions were of equal normality, within 0.2%. In titrations with diphenylamine a tint which did not change in two minutes' standing was considered permanent.

⁴ After this paper had been submitted to the editors, the author's attention was called to the fact that Szabellédy, *Z. anal. Chem.*, **81**, 97 (1930), had previously observed that in the presence of fluorides the diphenylamine end-point is sharper and more satisfactory.

The results of the first series of titrations with diphenylamine as internal indicator are presented in Table I. Titrations 1-6 show that in the presence of hydrochloric or sulfuric acid alone diphenylamine is not a good indicator for titrating a ferrous solution with dichromate. The first blue tint (indicated by a sudden darkening of the yellow-green in the hydrochloric acid solutions) precedes complete oxidation of the iron. Taking the appearance of a permanent brilliant blue as the end-point, the indications are apparently quite good in hydrochloric acid, but still low in sulfuric acid solution. Increasing quantities of the latter make the results worse. Upon back titration with titanous chloride, the color fades in reverse order. The thiocyanate end-point in this titration is very sharp, but the results are evidently affected by the volume of dichromate required, hence depend upon the characteristics of diphenylamine in the first titration.

The addition of one-tenth the final volume of 85% phosphoric acid results in sharpening the diphenylamine end-point in a remarkable manner, reducing the volume of dichromate required to take the color from the first permanent blue tint to the brilliant blue end-point color to only about 0.02 ml. The disappearance of the color on back titration is not quite so sharp, but still very satisfactory. The thiocyanate end-point in presence of phosphoric acid was poor, the color for some time prior to the end-point being a faint yellow instead of deep yellow with a pronounced red tinge up to the last drop, as is normal. In the dichromate titration the phosphoric acid entirely destroyed the yellow due to the ferric ion and so made the appearance of the diphenylamine blue very distinct. However, it is plain that this is not the sole explanation for its good effect, as in the absence of phosphoric acid good results were obtained in the intensely yellow hydrochloric acid solutions (Titrations 1-3), while in sulfuric acid solutions (Titrations 4-6) the yellow color was much less, but the titrations less accurate. In Titration 12 the addition of 3 ml. of phosphoric acid was sufficient to destroy the yellow color, yet the results were low and were improved by a further addition of phosphoric acid. Apparently twice as much of phosphoric as of sulfuric acid is necessary for accurate results. The addition of phosphoric acid results in a greater volume of dichromate being required to develop the diphenylamine color, and this excess of oxidant causes an increase in the volume of titanous solution required to reduce the iron again, so that this does not appear to be due to the presence of an oxidizable impurity. The extra amount of phosphoric acid used in this titration did not make the thiocyanate end-point noticeably worse than with the smaller volume.

In Titrations 13-18 twice the volume of hydrofluoric acid (48%) was substituted for the phosphoric acid. The effect in sharpening the diphenylamine end-point is even more marked; the intense end-point color is

permanent after the addition of only 0.01 ml. of dichromate beyond that necessary to produce a faint tinge of blue, but is discharged with equal sharpness on back titration. The thiocyanate end-point in solutions containing free hydrofluoric acid is greatly in error, however, as the color is never intensely red, quickly becomes yellow as the reduction proceeds and even this disappears before all iron is reduced. The addition of boric acid in excess ties up all hydrofluoric acid as fluoboric acid, restores the yellow color of ferric iron or the intense blue of diphenylamine if present and just faded in back titration, and permits a very satisfactory end-point with thiocyanate. With all proportions of hydrochloric acid tried, the diphenylamine end-point in presence of free hydrofluoric acid was equally sharp, but the total volume of dichromate required to develop the color increased with proportion of hydrochloric acid.

In solutions containing sulfuric and hydrofluoric acids the diphenylamine end-point was fully as satisfactory in development, but did not disappear quite so sharply on back titration. After addition of boric acid, the thiocyanate end-point was equally good, and the results of both titrations indicate that the relative proportions of hydrofluoric and sulfuric acids are of no importance (Titrations 16-18). However, other experiments to test the effect of dilution, in one keeping the concentration of sulfuric acid constant, indicated that the total volume of sulfuric acid present should not exceed that of hydrofluoric acid. Otherwise, the degree of dilution apparently made little difference, although not without practical importance since the color change is slow at high dilutions (Titrations 30-31).

In the presence of fluoboric acid with either sulfuric or hydrochloric acid (Titrations 19-24), the diphenylamine end-point was invariably premature in appearance and lacked sharpness. The behavior was similar to that of a solution containing sulfuric acid alone, and the bad effect of excessive concentration of the latter was increased. The only differences noted were an increase in the intensity of the color at corresponding stages of the titration, as noted by Sarver, and slightly more rapid color changes. Unlike phosphoric and hydrofluoric acids, fluoboric acid does not reduce the yellow color due to ferric ions, and has no bad effect upon the thiocyanate end-point.

The titration curves shown in Fig. 1 were drawn from potentiometric data, using a saturated potassium chloride-calomel electrode at approximately 25°. The volume of solution at the beginning was 20-25 ml. as in the titrations in Table I, contained in a 100-ml. beaker with rod for stirring. The color of the indicator was observed in these titrations, and its appearance noted on the curves as follows: first faint tinge permanent for one minute, an open circle; pronounced color about half that of the brilliant end-point, a circle with central dot; the usual brilliant end-point tint, a cross; maximum color developed by excess dichromate, an inked-in circle.

TABLE I
 TITRATION OF IRON

In solution containing 10 ml. of N 0.050 $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ with concentrated acid specified and 2 drops of diphenylamine solution diluted to 20–25 ml. with water by N 0.050 $\text{K}_2\text{Cr}_2\text{O}_7$. The oxidized iron then titrated with N 0.044 TiCl_3 and 0.5 g. of KCNS

Titration	Concd. acid, etc., added, ml.	Standard $\text{K}_2\text{Cr}_2\text{O}_7$ required Permanent blue tint, ml.	Brilliant end-point, ml.	Standard TiCl_3 required To fade all blue, ml.	To fade thio-cyanate color, ml.
1	HCl 1.5	9.62	9.97	0.38	11.30
2	HCl 3.0	9.50	10.00	.50	11.34
3	HCl 6.0	9.75	10.02	.20	11.30
4	H_2SO_4 1.5	9.40	9.95	.60	11.30
5	H_2SO_4 3.0	9.60	9.85	.42	11.15
6	H_2SO_4 6.0	8.0	8.9	1.0	10.12
	H_3PO_4 3.0 with				
7	HCl 1.5	10.02	10.04	0.03	11.35
8	HCl 3.0	10.03	10.05	.03	11.37
9	HCl 6.0	10.03	10.06	.05	11.40
	H_3PO_4 3.0 with				
10	H_2SO_4 1.5	10.05	10.07	.03	11.44
11	H_2SO_4 3.0	10.04	10.05	.03	11.42
12	H_2SO_4 6.0	9.85	9.87
	Added H_3PO_4 5.0	10.01	10.03	.02	11.45
	HF 6.0 with				
13	HCl 1.5	9.96	9.97	.01	11.37 ^a
14	HCl 3.0	10.04	10.05	.01	11.30 ^a
15	HCl 6.0	10.11	10.12	.01	11.29 ^a
	HF 6.0 with				
16	H_2SO_4 1.5	10.05	10.06	.02	11.30 ^a
17	H_2SO_4 3.0	10.05	10.06	.01	11.28 ^a
18	H_2SO_4 6.0	10.05	10.06	.02	11.28 ^a
	HF 6, H_3BO_3 4 g.				
19	HCl 1.5	9.88	10.01	.30	11.26
20	HCl 3.0	9.48	9.93	.35	11.18
21	HCl 6.0	9.58	10.00	.40	11.23
	HF 6, H_3BO_3 4 g.				
22	H_2SO_4 1.5	9.85	9.98	.35	11.25
23	H_2SO_4 3.0	9.73	9.93	.32	11.20
24	H_2SO_4 6.0	6.1	7.3	.75	8.3
	HF 6, H_2SO_4 3				
25	20 ml. Fe soln.	20.01	20.02	.01	22.60 ^a
26	{ 10 ml. Fe soln. }	10.04	10.05	.01	11.28 ^a
27		{ pyrex beaker }	10.05	10.06	.02
28	{ Same, titrated }	10.03	10.04	.02	11.31 ^a
29		{ in platinum }	10.01	10.02	.01
	HF 6, H_2SO_4 6				
30	Diluted to 200 ml.	10.09	10.10	.01	11.30 ^a
	HF 6, H_2SO_4 20				

TABLE I (Concluded)

Titration	Concd. acid, etc., added, ml.	Standard $K_2Cr_2O_7$ required Permanent blue tint, ml.	Brilliant end-point, ml.	Standard $TiCl_3$ required To fade all blue, ml.	To fade thio-cyanate color, ml.
31	Diluted to 200 ml.	10.03	10.05
	Added HF 12	10.07	10.08	0.02	11.28 ^a

^a Four g. of powdered boric acid worked to a smooth paste with a little water added previous to titration with titanous chloride. Titration 31 had 10 g. of boric acid.

Curve I shows the effect of excessive concentration of sulfuric acid, about one-fourth the volume at the end of the titration. The e. m. f. readings are highest, and the maximum indicator color was developed prior to complete oxidation of iron.

Curve II shows the effect of fluoboric acid from 6 ml. of hydrofluoric acid, in the presence of 3 ml. of sulfuric acid in a final volume of approximately 30 ml. During the first part of its course this curve follows the first closely. The maximum color was developed just a little short of complete oxidation of iron.

Curve III indicates the effect of a moderate concentration of sulfuric acid, one-tenth the final volume. The development of color is premature, but the standard end-point color is reached at about the true end-point, as indicated by the titration curve.

Curve IV was intended to show the effect of the sulfate ion in a solution saturated with potassium sulfate upon the activity of sulfuric acid in one-tenth final volume. The common ion had a noticeable effect upon the e. m. f. without resulting in any important change in the position of the color or electrometric end-points.

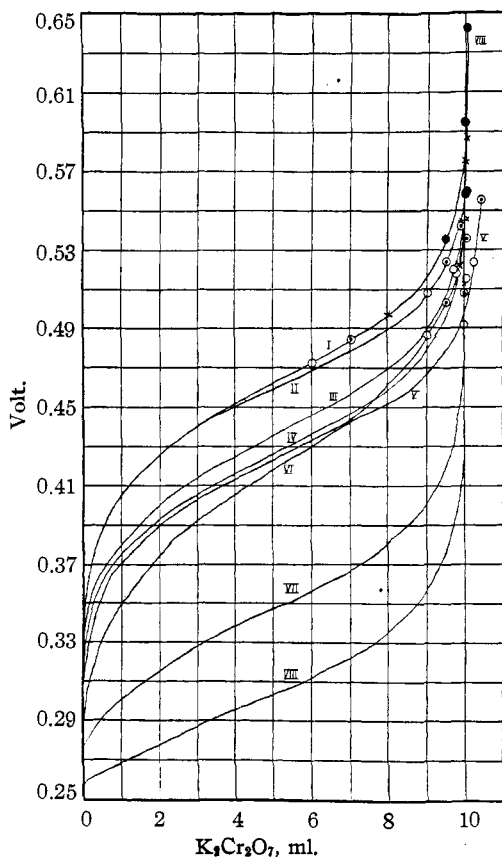


Fig. 1.—Electrometric titration of 10 ml. of 0.05 *N* ferrous ammonium sulfate with various additions by 0.05 *N* dichromate.

Curve V shows the effect of buffering with 5 g. of potassium acetate a solution containing 3 ml. of sulfuric acid in 30 ml. final volume. The effect upon both color and potentiometric end-points is bad, neither being developed by a considerable excess of dichromate. Willard and Young² recommended reduction of the effective acidity by addition of acetate and phosphoric acid only in the titration of an oxidizing agent by ferrous sulfate, and not in titration of ferrous salt by an oxidizing reagent.

Curve VI was determined in presence of one-fourth final volume of hydrochloric acid. The intense yellow interfered with observation of the diphenylamine end-point, but it could be seen that it was premature. The electrometric end-point was sharp and accurate.

Curve VII indicates the effect of one-tenth final volume each of sulfuric and 85% phosphoric acids. Phosphoric acid has a very pronounced effect in lowering the oxidation potential, and the standard end-point color is developed at the flex-point of the titration curve. All of the color changes are in the steep portion of the curve, explaining the sharpness of the indicator under these conditions.

Curve VIII shows that one-fifth volume hydrofluoric acid and one-tenth volume sulfuric acid has the optimum effect upon the sharpness of the color end-point with diphenylamine. The first portion of the curve is quite flat, indicating that hydrofluoric acid largely overcomes the oxidation-reduction buffer effect in iron solutions. The asymptotic portion of the curve begins with a sharp bend and is nearly vertical, so that a very small addition of dichromate results in a great increase in potential. The first appearance of color is apparently near the true flex-point of the curve, and other changes are well separated on the e. m. f. scale but produced by very small increments of oxidizing agent, explaining the apparent sensitivity of the indicator in this titration.

With the exception of Curve V, PH buffered by acetate, Curve VIII, determined in presence of free hydrofluoric acid, shows the greatest requirement of dichromate to develop color, *i. e.*, the highest blank. The explanation for this is that the depression in oxidation potential produced by the fluoride ion requires an appreciable addition of dichromate to raise it to the point at which the color appears. As shown very recently by Kolthoff and Sarver,² the product of the partial oxidation of diphenylamine is a true oxidation-reduction indicator, developing color at a definite oxidation potential. The experiments herein reported indicate that the development of color is affected by other factors also, *e. g.*, concentration of sulfuric acid. Under the conditions of a practical titration, the color change is perfectly reversible, as shown by such changes and e. m. f. readings on back titration with titanous chloride corresponding with those in the first titration. While Kolthoff and Sarver have shown that there is a certain consumption of oxidizing agent required for development of color,

it is evident that a part of the apparent blank noticed in titrations is simply the volume of dichromate necessary to raise the oxidation potential of the solution to the point at which the color appears.

The influence of phosphoric and hydrofluoric acids upon the diphenylamine end-point in iron titrations is due to inactivation of the ferric ion in compounds less ionized than the sulfate, chloride or fluoborate, and the same explanation also applies to the effect upon the thiocyanate end-point. Inactivation of the ferric ion is desirable in the oxidation titration, as it diminishes the buffer effect upon oxidation potential normal to mixtures containing both ferrous and ferric ions. It is undesirable in the reduction titration because ferric fluoride is evidently less dissociated than the thiocyanate, so that the colored compound is not formed.

The practical conclusion to be drawn from the foregoing is that the presence of hydrofluoric acid is advantageous in a titration of ferrous iron with diphenylamine as indicator. Addition of boric acid to inactivate the hydrofluoric acid employed in decomposition of a silicate for ferrous iron determination should be omitted. The reasons for this addition, first recommended by Barnebey,⁵ are not of importance if a proper procedure is followed. In the first place, the danger of oxidation by air of ferrous iron in the presence of free hydrofluoric acid has been overemphasized. As Hillebrand and Lundell⁶ state, if the solution is cooled before air comes in contact with it and the titration is completed without delay, there is no appreciable error from oxidation by exposure to air. Practically all chance of this can be avoided by titrating in the crucible in which the decomposition was effected. That this is practical is shown by the results obtained in Titrations 28 and 29 in Table I. In the second place, manganese, which is oxidized to the trivalent state by permanganate in the presence of free hydrofluoric acid, does not in the least interfere in a dichromate-diphenylamine titration. This was shown by titrating a solution containing 0.5 g. of manganous sulfate, 3 ml. of sulfuric and 6 ml. of hydrofluoric acids and 10 ml. of iron solution. A large excess of permanganate added to a similar mixture produced no permanganate color, but on addition of diphenylamine the intense color of the latter was developed instantly and required very nearly the theoretical volume of titanous chloride to discharge. Diphenylamine also gave correct indications in a similar direct titration with permanganate.

A further conclusion is that titration by standard titanous chloride solution with thiocyanate as indicator is a practical method for determination of total iron in the case of silicates completely decomposed by hydrofluoric and sulfuric acid treatment. It is only necessary to add excess boric

⁵ Barnebey, *THIS JOURNAL*, 37, 1481 (1915).

⁶ Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 775.

acid to the solution just titrated for ferrous iron, as fluoboric acid is harmless, while hydrofluoric acid is very detrimental to either the thiocyanate or methylene blue end-points. The two titrations fit well together; both are at their best when the volume of solution is small and the sulfuric acid concentration is high, about one-tenth final volume being near the optimum. Both titrations show very sharp and distinct color changes at the end-point, so that it is practical to titrate in the platinum crucible in which the sample was decomposed. The observation that hydrofluoric acid lowers the oxidation potential of ferric solutions indicates that decomposition in platinum is probably safer than might be inferred from the known fact that ferric chloride is reduced to some extent by long contact with platinum.

Sarver² described a transparent cover of bakelite for a platinum crucible to be used in decomposing the sample of mineral for ferrous iron determination. He neglected, however, to publish a cut of his apparatus, nor was it described in much detail. The author had one made⁷ which has given good results in use. It is shown in Fig. 2.

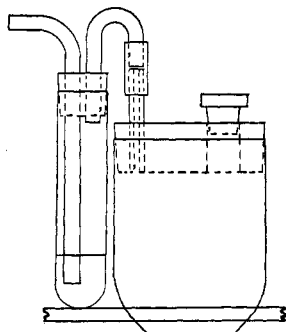


Fig. 2.—Platinum crucible with bakelite cover in place and trap attached.

The taper is polished, and makes an almost gas-tight joint with the edge of the crucible. It is provided with a tube of bakelite for leading in carbon dioxide from a Kipp generator, and a stoppered opening for adding reagents, stirring, etc. In use the procedure has been as follows: the ground sample is weighed and transferred to the 50-ml. crucible for which the cover was made. The latter is firmly placed, and the crucible set in a hole in asbestos board over a micro burner. By means of a short rubber tube a small bubble counter attached to the source of carbon dioxide is connected to the bakelite tube and the gas allowed to flow for a sufficient time, to expel air from the crucible. About 6 ml. of boiled and cooled water is added, followed by the careful addition of 6 ml. of 1:1 sulfuric acid. This mixture is heated to boiling, while the flow of gas continues. The stopper is removed and 6 ml. of hydrofluoric acid poured in from a small crucible in which it may be measured with sufficient accuracy. By moving the asbestos board the acid in the crucible may be stirred, so that undissolved particles are more easily visible. The gas pressure is kept on all the while and the crucible heated carefully, but the acid need not be boiled vigorously. As the stopper is in place during this time, no air can enter and but little carbon dioxide is used. When decomposition is complete, heating is discontinued and the crucible allowed to cool. When it can be handled without discomfort, it may be lifted from the asbestos board and set in a dish of water to cool more rapidly. When quite cold the stopper is removed and sufficient water added to dilute the solution to about 25 ml. Two drops of diphenylamine solution are added, and the dichromate added carefully, stirring with a platinum spatula. As soon as a drop of the dichromate produces a permanent blue color, the iron is entirely oxidized and the titration of ferrous iron finished. If total iron is to be determined, 4 g. of boric acid rubbed to a smooth paste with a little water, to avoid lumps, is added and stirred until dissolved. This is likely to intensify the blue color of diphenylamine, but it is of no

⁷ By the Apex Specialties Corp., 1184 Flushing Ave., Brooklyn, N. Y.

consequence as it will disappear later. Five ml. of 10% potassium thiocyanate solution is added, followed by standard titanous chloride until all red has disappeared, and any remaining yellow ceases to diminish with another fractional drop of the solution. If the crucible becomes too full during the course of titration, it is placed in a beaker and upset, the titration being continued without removing the crucible. Even if the solution contains free hydrofluoric acid, the amount of iron dissolved from a pyrex beaker in a short time will cause no appreciable error. After addition of boric acid, the glass is not attacked at all.

Bakelite is not an ideal material for the crucible cover, being somewhat attacked by the hot acid vapors, and evidently decomposed at the surface to some extent, as a pronounced phenolic odor was noted in the solution obtained the first time the cover was used, and poor results were obtained in this titration. After use a half dozen times the odor was no longer noticeable, the behavior on titration was normal and the blank determination indicated that only 0.02 ml. each of 0.05 *N* dichromate and titanous chloride were necessary for good end-points. By this time the surface of the cover had been attacked to such an extent that it was no longer transparent, so that the stopper had to be removed when it was desired to observe the progress of solution. Escape of gas during the time the stopper is removed is sufficient to prevent entrance of air, and there need be no error from oxidation.

Sarver² has stated that the chief reason for the use of dichromate rather than permanganate for titration of ferrous iron dissolved from a sample of mineral is the decreased tendency to oxidation of organic matter by dichromate, so that the latter would be expected to furnish more accurate results in its presence. The author has made a few experiments to determine whether organic matter has an appreciable effect upon the dichromate-diphenylamine titration in presence of sulfuric and hydrofluoric acids. Ammonium oxalate equivalent to 14 ml. of 0.05 *N* solution was added to a mixture of 10 ml. of 0.05 *N* ferric sulfate, 6 ml. hydrofluoric and 3 ml. of sulfuric acids, total volume, 20 ml. This was boiled for fifteen minutes in a platinum crucible, simulating the conditions of an actual determination of ferrous oxide in a mineral. Upon titration, 0.02 ml. of dichromate produced a permanent diphenylamine end-point and the usual amount of titanous chloride solution was consumed in reducing the iron, indicating no reduction of ferric salt by the oxalate, and that the latter does not by itself consume dichromate during the titration. However, in similar experiments in which an aliquot of ferrous solution also was added, from 10 to 25% excess dichromate was required to produce the diphenylamine end-point, but in the back titration with titanous chloride only the amount corresponding to the total iron content was consumed. These results indicate that organic matter, at least oxalic acid, can cause high results for ferrous iron, but only in proportion to the amount of the latter present. Numerous examples of similar reactions are known, in which a substance is not normally oxidized by dichromate, but is oxidized to a certain extent when accompanied by an easily oxidized substance. This has been explained as being due to intermediate formation of Cr^{V} which has higher oxidizing potential than Cr^{VI} .³ The brightening of the diphenylamine color noted when a trace of ferrous salt is added to a slightly overrun titration with dichromate is possibly another instance, but the presence of ferrous iron is not essential to formation of color.

Summary

The properties of diphenylamine as indicator in dichromate titration of a solution containing ferrous iron, hydrofluoric and sulfuric or hydrochloric acids, as obtained in the determination of ferrous oxide in a silicate, have

³ Lang and Kurtz, *Z. anorg. allgem. Chem.*, **181**, 111 (1929).

been investigated. In presence of sufficient hydrofluoric acid in proportion to sulfuric or hydrochloric acid, diphenylamine is an excellent indicator for this titration. The presence of diphenylamine does not prevent an accurate determination of the total iron in the solution by a reduction titration with titanous chloride and thiocyanate indicator, following the oxidation titration, provided the hydrofluoric acid necessary in the first titration is inactivated by addition of excess boric acid prior to the second.

Potentiometric titration curves show that the pronounced effect of hydrofluoric (also phosphoric) acid in increasing the sharpness of the diphenylamine end-point in iron titrations is due to a lowering of the oxidation potential in a solution containing both ferrous and ferric ions, which is high enough under the usual conditions of the titration to cause the indicator color to develop prior to complete oxidation of the iron. The effect of these reagents upon the thiocyanate end-point in the reduction titration and upon the color of solutions containing ferric salts indicates that the underlying cause is the slight dissociation of ferric fluoride (or phosphate).

Based upon these observations, an improved procedure for the determination of ferrous and ferric oxides in silicates is described. Manganese does not interfere in the dichromate titration with diphenylamine in the presence of hydrofluoric acid, but it is shown that in the presence of organic matter results for ferrous oxide may be expected to be high in proportion to the amount of ferrous oxide actually present.

WOOSTER, OHIO

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THE REDUCTION POTENTIAL OF THE CERIC-CEROUS ELECTRODE

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Introduction

The only work upon the reduction potential of the ceric-cerous electrode recorded in the literature is the early research of Bauer and Glaessner,² which involved several factors that diminished its accuracy and reliability. Thus the measurements were made at room temperature, no statement being made about its constancy, and a saturated solution of potassium chloride was used to eliminate liquid potentials. In view of these imperfections and of the recent interest in the use of ceric sulfate solutions for analytical work,^{3,4} it seemed advisable to make a thorough study of the

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² Bauer and Glaessner, *Z. Elektrochem.*, 9, 534 (1903).

³ Willard and Young, *THIS JOURNAL*, 50, 1322 (1928), *et seq.*

⁴ Furman, *ibid.*, 50, 755 (1928), *et seq.*