trated sulfuric acid and the whole heated for 30 minutes longer. The soil was taken up and thoroughly washed with hot distilled water, the filtrate evaporated to dryness, and heated until free from nitrates. The residue was treated with dilute, arsenic-free sulfuric acid to which was added 20 cc. of stannous chloride solution, 1 cc. of which contained one-tenth of a gram of stannous chloride. This solution was slowly introduced into a Marsh apparatus, the glass tube through which the hydrogen was conducted being heated by means of an electric combustion furnace. The deposit of arsenic was carefully weighed on fine analytical balances. By this method very small quantities of arsenic can be accurately determined, as is shown by the reported results.

THE APPLICATION OF DIPHENYLCARBAZIDE AS INDICATOR IN THE TITRATION OF IRON WITH DICHROMATE.

BY O. L. BARNEBEY AND S. R. WILSON.

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Brandt[1] published, in 1906, a method using diphenylcarbazide,[2] called by him "diphenylcarbohydrazide," as an "inside indicator" for the titration of iron. Shortly after the publication of the article one of us tried the method as outlined by Brandt and by following his directions minutely could not obtain concordant results. A detailed study, however, developed an interesting and valuable modification of this method and likewise an application for the analysis of ores.

In 1900, Cazeneuve[3] pointed out the fact that diphenylcarbazide could be used to detect extremely small quantities of chromic acid, giving the sensitiveness as 1 : 1,000,000. Brandt carries the work further and uses this substance as an indicator for the titration of iron. He states that large amounts of hydrochloric acid and also manganese sulfate solution containing phosphoric acid must be present to prevent too rapid destruction of the indicator. His conditions for titration are 0.2 to 0.7 g. of iron, 60 to 80 cc. dilute hydrochloric acid (sp. gr. 1.12), 100 cc. manganese sulfate solution (containing 6 kg. manganese sulfate, 33 liters dilute sulfuric acid (1 : 3), 3 liters phosphoric acid (sp. gr. 1.7), diluted to 60 liters), diluted to a total volume of $1^1/_2$ liters and 5 cc. of a 0.1% solution of indicator added. Smaller amounts than 0.2 gram of iron may be titrated by slightly modifying the conditions.

The color changes involved are very marked. The first drop of dichromate added gives a pink or red tinge which becomes deep red as the titration proceeds. This color gradually changes to lavender, which seems to be caused by the complementary nature of the red compound and triva-

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[1] *Z. anal. Chem.*, 45, 95.

[2] Beilstein, Vol. 4, 671.

[3] *Bull. soc. chim.*, 23, 592, 701, 769.

lent chromium. The lavender fades out and finally the addition of one drop of the dichromate gives a sharp change to the clear green color of chromic chloride.

Experimental.

The indicator was prepared by heating 20 grams of urea with 200 cc. of phenylhydrazine gradually raising the temperature from 150 to 170° for about four hours. The resulting product was dissolved in hot alcohol, recrystallized by cooling, filtered and washed with cold alcohol. The recrystallization was repeated three times. The crystallin product was nearly pure white, but had a tendency to gradually become pink when exposed to the air for some time. The melting point was 163.5°.[1] The color tests outlined by Skinner and Ruheman[2] were also tried with positive results. Solution was effected by dissolving the indicator in strong acetic acid and diluting to an appropriate volume. One gram per liter is convenient.

A manganese sulfate solution was prepared by using the following proportions: 200 grams of manganese sulfate, 1100 cc. of dilute sulfuric acid containing one part of acid (sp. gr. 1.84) and three of water, 100 cc. of phosphoric acid (sp. gr. 1.70) diluted to two liters.

Titrating 25 cc. portions of a 0.1 *N* solution of ferrous iron and varying amounts of indicator, manganese sulfate solution and acid with 0.1 *N* dichromate solution required from 25.60 to 28.00 cc. of the latter. Using constant amounts of the iron, manganese sulfate solution and acid, having the indicator only as variable, gave results of the same order. However, by using constant amounts of indicator, variable amounts of manganese sulfate solution, variable amounts of acid and constant amounts of ferrous iron in a series of determinations practically the same quantity of dichromate was required in each titration.

Series I of the table is a series of "blanks" obtained with an indicator solution (about 0.17% indicator) without the presence of ferrous iron and Series II in the presence of a constant quantity of iron in the ferrous state. Series I was obtained as follows: To about 300 to 400 cc. of water 10 cc. of strong hydrochloric acid, 10 cc. of manganese sulfate solution, and a measured amount of indicator solution are added followed by 3 cc. of 10% ferric chloride solution and the indicator titrated slowly with tenth normal dichromate, agitating very vigorously after the addition of each drop. The disappearance of the red and appearance of a pale green tint marks the end point. From three to five minutes must be taken for the titration to avoid over running the end. Series II varies from Series I only in the use of constant quantities of 0.1 *N* ferrous iron and the use of 0.1667 *N* dichromate solution.

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[1] Beilstein, *Loc. cit.*

[2] *J. Chem. Soc. (London)*, **53**, 551.

SERIES I.

HCl. Cc.	Indicator. Cc.	Manganese solution. Cc.	$FeCl_3$. Cc.	0.1 N $K_2Cr_2O_7$. Cc.
10	0.5	10	3	0.14
10	0.5	10	3	0.18
10	1.0	10	3	0.30
10	1.0	10	3	0.32
10	2.0	10	3	0.60
10	2.0	10	3	0.60
10	3.0	10	3	0.92
10	3.0	10	3	0.96
10	4.0	10	3	1.22
10	4.0	10	3	1.20
10	5.0	10	3	1.42
10	5.0	10	3	1.42
10	10.0	10	3	2.76
10	10.0	10	3	2.74
10	15.0	10	3	4.18
10	15.0	10	3	4.26

SERIES II.

10 cc. of ferrous iron solution are equivalent to 6 cc. of dichromate solution.

0.1 N ferrous iron solution. Cc.	HCl. Cc.	Manganese solution. Cc.	Indicator. Cc.	$FeCl_3$. Cc.	0.1667 N $K_2Cr_2O_7$. Cc.
10	10	10	2	3	6.36
10	10	10	2	3	6.36
10	10	10	5	3	6.90
10	10	10	5	3	6.86
10	10	10	10	3	7.62
10	10	10	10	3	7.66
10	10	10	15	3	8.46
10	10	10	15	3	8.48
None	10	10	5	3	0.86

A glance at these figures shows at once that the indicator itself is the cause for the variable results, the larger the amount of indicator used the more dichromate is necessary to complete the titration. A regular increase in quantity of dichromate is noticed in both series as the amount of indicator becomes larger. In Series II the value of 6 cc. of the oxidizing agent is closely approached in each titration if in each case the dichromate equivalent to the amount of indicator used is subtracted, thus, 5 cc. of the indicator required 0.86 cc. of dichromate with no ferrous iron present. Hence, if the value of this blank is subtracted from the value found with 10 cc. of ferrous iron and 5 cc. of indicator present, 6 cc. in one case and 6.04 cc. in the other is found to be the actual volume of oxidizing solution required. Brandt says nothing about this factor; in fact he even states that the quantity of indicator may be doubled and still have no appreciable effect on the titration. Although the titrations were made in a smaller volume than those of Brandt, yet using the dilution he recommends his results could not be confirmed. The work above suggested a direct ratio existing between oxidizing agent and indicator.

To test this ratio more rigidly an exactly 0.1% solution of the indicator was prepared and 10 cc. of this solution titrated with a solution of dichromate containing 0.00438 gram per cc., the latter being standardized against pure ferrous ammonium sulfate using ferricyanide as indicator on a spot plate. One and eight-tenths cc. of the dichromate or 0.0079 gram were required for the titration. Using the proportion:

Wt. of indicator : Wt. of dichromate : : Mol. wt. of indicator : Mol. wt. of dichromate.
0.01 : 0.0079 : : x : 294
$x = 370$

However, the molecular weight of the indicator is 242, hence, the number of molecules reacting would be $370 \div 242 = 1.5$ for each molecule of dichromate, and the reaction would probably be

$$3C_{13}H_{14}N_4O + 2K_2Cr_2O_7 + 16HCl = 4CrCl_3 + 4KCl + 3C_{13}H_{10}N_4O + 14H_2O.$$

This equation is advanced for the lack of a better one at the present time. On the basis of three molecules of indicator being equivalent to two molecules of dichromate the following ratio holds: 3 mols. $C_{13}H_{14}N_4O$ (726) : 2 mols. $K_2Cr_2O_7$ (588) :: Wt. of indicator : Wt. of dichromate. Weighing out exactly 0.01 gram of indicator and using 0.02 *N* potassium dichromate solution required 8.24 cc., or 0.00807 gram of the latter. Theoretically calculating 0.01 gram of the indicator according to the above proportion gives 0.00809 gram of dichromate. In all likelihood side reactions may occur under some conditions of titration in which cases the agreement may not be so close to the theoretical.

This process was repeated, using permanganate instead of dichromate, and the theoretical ratio of five molecules of indicator to four of $KMnO_4$ verified by experiment. A standard solution of chlorine water was likewise used and the ratio of two molecules of Cl_2 to one of indicator found to exist.

Analysis of Iron Ores.

We find that this method of determining iron can be readily applied to the analysis of iron ores. A 0.5 gram (larger if the ore is of low grade) sample is weighed into a number two beaker. Pour over the sample 15 to 30 cc. of hydrochloric acid (sp. gr. 1.2), heat just below boiling, adding sufficient stannous chloride (200 grams of $SnCl_2.2H_2O$ and 150 cc. of hydrochloric acid (sp. gr. 1.20) per liter) to reduce most of the iron as it dissolves yet leaving a distinct yellow tinge in the solution when the solvent action has ceased.

If a dark residue remains, filter, wash free from hydrochloric acid and ignite the filter paper in a platinum crucible. Add a small quantity of sodium carbonate to ash, heat to quiet fusion. Cool, place crucible in a small beaker and dissolve the melt in a small portion of boiling water. Add solution and precipitate, if any, to the hydrochloric acid extraction.

Heat the solution to boiling, wash off the cover and the sides of the beaker with a small portion of water (the volume should not be over 30 to 40 cc.) and add stannous chloride drop by drop to the hot solution until one drop will give a colorless solution, then add one drop in excess. (If a larger excess of stannous chloride has been added, add potassium permanganate until a permanent yellow color appears then reduce as above.) Transfer to a liter beaker, dilute to about 500 or 600 cc., add 30 cc. of mercuric chloride (saturated solution), stir vigorously for a moment, then add 20 cc. of manganese sulfate solution followed by 10 cc. of concentrated hydrochloric acid and an exact volume (2 to 3 cc.) of the indicator. Titrate with standard dichromate. The first few drops added will cause an intense red color to appear. This color changes to a purple as the titration proceeds and as the end point is approached it gradually fades finally giving the sharp change to the chromic chloride. This gradual change minimizes the danger of overtitration and allows the titration to proceed rapidly. The buret reading is now taken. The dichromate value of the indicator is obtained by titrating the same volume of the indicator as was employed previously under the same conditions as those of an actual analysis except that 3 cc. of a 5% solution of ferric chloride are added preceding titration. The blank titration must be performed very slowly to avoid overtitration. Another method used to check the reducing value of the indicator solutions consisted in starting with a definit amount of ferrous iron in solution, adding the usual amounts of manganese sulfate, acid, and 2 cc. of indicator, then titrating. Utilizing the same amounts of ferrous iron, acid, manganese sulfate, and 4 cc. of indicator, again titrate. The difference between the two readings gives the reducing value of 2 cc. of the diphenylcarbazide. This scheme of titration of the blank allows a more rapid titration. Subtract the volume required for the blank from the original volume of dichromate and calculate the % of iron in the sample.

Series III contains the results obtained with four iron ore samples from the Lake Superior region. The "% iron" column in each case contains the % of iron obtained by the permanganate method.

Several series of analyses, some with very small, others with larger amounts of iron, were made with results which check closely. With very small quantities of iron it is better to use a smaller quantity of indicator than with high iron content, adding some ferric chloride as in the blank determination. Titration of small amounts of iron should be made slowly with thorough agitation of the solution.

SERIES III.—IRON ORES.

Number.	% iron.	% found.	Deviation.
1	64.84	64.77	0.07
2	64.84	64.85	0.01
3	64.84	64.75	0.09
4	64.84	64.71	0.13
5	64.84	64.74	0.10
6	64.84	64.75	0.09
7	64.84	64.76	0.08
8	64.84	64.95	0.11
9	64.84	64.70	0.14
10	64.84	64.72	0.12
11	64.84	64.79	0.05
1	62.33	62.47	0.14
2	62.33	62.39	0.06
3	62.33	62.52	0.19
1	66.29	66.48	0.19
2	66.29	66.38	0.09
3	66.29	66.65	0.36[1]
4	66.29	66.29	0.00
5	66.29	66.34	0.05
1	28.15	28.19	0.04
2	28.15	28.24	0.09
3	28.15	28.20	0.05

A solution of the indicator has a tendency to decompose slowly when exposed to the air because of oxidation, hence solutions should be kept in well-stoppered bottles. Under ordinary laboratory conditions a solution should be prepared fresh every few days unless protected from the action of the air. We have kept indicator solutions several months in an atmosphere of carbon dioxide without appreciable decomposition. However, the only apparent difference is a lowering of the reducing power and a corresponding less intense coloration during titration, hence a larger amount of the partially oxidized indicator is necessary to give the same effect as a fresh or protected solution. Series IV contains the tabulated results of a number of blanks titrated with a constant amount of indi-

SERIES IV.

HCl. Cc.	Manganese solution. Cc.	Indicator. Cc.	$FeCl_3$. Cc.	0.1 N $K_2Cr_2O_7$. Cc.
20	10	5	0.16	1.10
20	10	5	0.50	1.02
20	10	5	1.00	1.00
20	10	5	5.00	0.96
20	10	5	10.00	1.04

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[1] The cause for this particularly high result was not known at the time of titration.

cator which had been exposed to the air in a bottle with the stopper removed. This is a portion of the same indicator solution employed several days previous in Series I and II.

Conclusions.

1. The end point is an excellent one.
2. The indicator is a reducing agent and is oxidized by the dichromate during the process of titration. A blank determination must be made to ascertain this reducing power.
3. With the above modification the method is applicable to the analysis of ores for their iron content.
4. Small amounts of iron can be determined within the accuracy of the other methods in common practice.
5. In all likelihood the principle involved can be utilized in a number of other analyses. This point is being investigated.

The oxygen ratio existing between the oxidizing agent and the indicator as obtained by different methods, the chemical reaction involved in causing the color change during titration, and the use of other compounds similar to diphenylcarbazide, especially those containing double bonds between the nitrogen atoms, are being likewise investigated.

We desire to express our appreciation to Dr. Benton Dales for his interest in the work throughout this investigation.

UNIVERSITY OF NEBRASKA, LINCOLN.

A PORTABLE PETTERSSON-PALMQVIST APPARATUS.

BY R. P. ANDERSON.

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The disagreeable and sometimes injurious effect of poor ventilation in crowded buildings is believed, at the present time, to be due to the accumulation of two products of respiration, carbon dioxide and water vapor.[1] Atmospheric air contains about 0.03% carbon dioxide and variable amounts of water vapor, while expired air normally contains about 4% of carbon dioxide and 6% of water vapor. An examination of the air in buildings to ascertain their fitness for human habitation includes determinations of carbon dioxide and moisture, but when the efficiency of a ventilating system is in question the determination of carbon dioxide is alone of value, since (1) the amount of water vapor normally present in the atmosphere is not constant, but varies within wide limits,[2] (2) water vapor is given off in varying quantities from the skin, and (3) the amount of water vapor in the air cannot increase indefinitely, but will

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[1] The presence of a poisonous organic product of respiration has been discredited by recent work in this field.

[2] The water content of the atmosphere at Ithaca varies from about 0.1 to 4.0% by volume, and even over a wider range on rare occasions.