An Improved Method of the Colorimetric Determination of Chromium with Diphenylcarbazide

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Introduction

In 1900, Cazeneuve[1] discovered diphenylcarbazide which reacts with sexavalent chromium in acid solution giving an intensely red-violet oxidation product. Since then many successive workers[2] had employed this sensitive color reaction in determining a minute amount of chromium. Sandell[3] described a useful and accurate colorimetric method of estimating chromium in silicate rocks with this reagent, stating that a total sample of one gram is sufficient for the determination of as little as 0.001% of chromium.

In Japan, there have been some studies made on the chromium content in hot springs, coal ash, oceanic muds and volcanic rocks by applying this method. A remarkable conclusion through these series of studies is that the chromium content is so exceedingly small that the element is scarcely noticeable in several samples tested. It becomes of importance and interest, therefore, to study whether this

(1) P. Cazeneuve, *Bull. Soc. Chim.*, (3) **23**, 701 (1907); *Compt. Rend.*, **131**, 346 (1900).

(2) A. Moulin, *Chem. News*, **90**, 320 (1904); Mutger and Zon, *Ind. Eng. Chem.*, **4**, 493 (1921); B. S. Evans, *Analyst*, **46**, 285 (1921); N. M. Stover; *J. Am. Chem. Soc.*, **50**, 2363 (1928); B. Jones, *Analyst*, **55**, 318 (1930); F. Feigl, *Ang. Chem.*, **44**, 741 (1931).

(3) E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8**, 336 (1936).

scarcity is due to a characteristic of the sample tested or a defect in the method of determination used. During the author's geochemical investigation of chromium in Japanese brown coal, he gave a thorough study of this colorimetric method, because Sandell described the tendency of this method to give lower results in the chromium content, without giving any numerical data. The author found, too, that there was a tendency to lower results in this colorimetric method. Hence a number of experiments on this problem were conducted and it was found that this method can be improved to a certain extent by introducing oxidation with sodium peroxide, prior to color comparison.

The oxidation method for this purpose was tested using several oxidizing agents, and sodium peroxide in alkaline medium as well as potassium bromate in an acid medium were finally found most recommendable, though only the former will be described in this report.

In fact, the author was able to obtain remarkable results on the occurrence of chromium in Japanese brown coal and others, which evidently differ from those previously reported. These results will be given in another communication.[4] In this report, some sources of errors in Sandell's method are pointed out and an improved method will be described.

Experiment

In this color reaction chromium should be in the sexavalent state. But, in successive procedures recommended, there are some possibilities of reduction of the chromate formed in carbonate fusion to chromic ion. The possibilities are (a) the presence of alcohol added to reduce manganate before the melt is leached with water, (b) the presence of iron, especially in ferrous state, contrary to the general belief, in a water-leached solution as reported by the author[5] in his study of colorimetric determination of vanadium, (c) the inevitable contact of oxine and chloroform necessary to remove vanadium before the color comparison is made and (d) filtration through a filter paper to remove the droplets of chloroform. Naturally the purity of the reagents is taken into a sufficient consideration, but nevertheless it is difficult in actual practice to obtain entirely satisfactory reagents freed from impurities; hence it will cause other possibility of reduction.

The error due to the reason mentioned in (a) may be avoided by the careful addition of alcohol to reduce any manganate formed in the fusion. But to add alcohol just enough to reduce the manganate is a considerably difficult procedure, because even as little as a drop in excess will reduce the chromate.

Next quinquavalent vanadium interferes by reacting with the reagent in acid solution giving a strongly yellow-colored compound, and it is therefore necessary to remove it previously from the solution by the addition of oxine and the extraction with chloroform of the compound thus formed. But Sandell reported that sexavalent chromium is not reduced in this process. The author's opinion, however, is reverse to this statement.

On this ploblem, the study set by Hackel[6] may support the author's opinion that sexavalent chromium is easily reduced in an acid medium during the course of extraction. The author has experienced the reduction of this kind many times in the geochemical study of brown coal ash. Of course, unnecessary standing in contact with oxine after shaking to separate water layer from that of chloroform must be avoided. But it is difficult to separate the chloroform-water interface in a short time, as the trouble is caused by the prevention of coalescence of chloroform droplets after shaking.

Table 1

Reduction Caused by Contact with Oxine

Chromium present, as Cr_2O_3, γ	Time in contact with oxine, hr.	Chromium found, γ	Error due to reduction, γ
121.7	1	113.3	− 8.4
	2	103.8	−17.9
	5	99.3	−22.4
	18	87.0	−34.7

Errors due to the reasons shown (b) and (d) will be discussed below.

Reduction by a Filter Paper.—Owing to a partial reduction of the chromate when a filter paper is used for the chromate solution, low results[7] may be obtained. This defect is produced in the case of acid medium and, even in alkaline solutions, it being more marked with a hot rather than a cold solution.

Therefore a sufficient care must be taken to avoid this defect which evidently becomes a

(4) Y. Murakami, this Bulletin, in press.
(5) Y. Murakami, this Bulletin, p. 153.
(6) O. Hackel, *Z. anal. Chem.*, **109**, 91 (1937).
(7) H. Jervis, *Chem. News*, **77**, 133 (1898); A. Allison, *ibid.*, **96**, 1 (1907); R. S. McBride and J. A. Scherrer, *J. Am. Chem. Soc.*, **39**, 928 (1917).

cause for a serious error, especially in a determination of a minute quantity of chromium.

Table 2

Reduction Due to a Filter Paper

With 10% sodium carbonate solution	Acidity of the solution before filtering					
	Expt. I			Expt. II		
	Alkaline	Neutral	Acidic	Alkaline	Neutral	Acidic
Not digested	80.7γ	79.6γ	71.6γ	19.5γ	18.2γ	15.0γ
Digested	81.6	—	81.6	20.3	—	20.0

It is necessary to remove the reducing matters in the filter paper in advance by digestion with a sodium hydroxide solution.[9] In order to obtain more accurate results the author recommends the washing of the filter paper previously with a 20% sodium carbonate solution as prescribed by Sandell and also the filtering of the solution containing chromate at room temperature.

Interference with Iron.—The coloration of chromium reacting with diphenylcarbazide is reliable only when it is present as sexavalent ion in acid medium. The author has already described that there are interferences with not only ferrous iron but also with, to a certain extent, ferric iron in the leached filtrate from the carbonate melt in the colorimetric determination of vanadium.[5] As this interference seems not to have been tested in the colorimetric determination of chromium by any others, a number of experiments have been carried out by the present author.

It has been found that an error occurs with ferrous iron more seriously than with ferric iron as shown in Table 3.

The presence of iron in the leached filtrate, contrary to general belief, results considerably from the peptization of hydrous ferric oxide by silica. It is reasonable to suppose that the reduction of chromate once formed during the carbonate fusion process may also occur owing to the presence of ferrous iron which is leached from the melt, when it is acidified.

Table 3

Interference Due to Ferric and Ferrous Iron

Present (Cr_2O_3), γ	Interfering ion, γ		Found (Cr_2O_3), γ	Difference, γ	Remarks
20.0	444	Fe^{+++}	12.3	− 7.7	$FeCl_3$
〃	888	〃	9.4	−10.6	〃
20.0	100	Fe^{+++}	17.4	− 2.6	Fe-alum
〃	200	〃	15.8	− 4.2	〃
〃	400	〃	12.7	− 7.3	〃
9.0	76.8	Fe^{++}	4.4	− 4.6	$FeSO_4$
〃	153.6	〃	3.5	− 5.5	〃
〃	230.4	〃	3.2	− 5.8	〃
18.0	76.8	Fe^{++}	7.0	−11.0	$FeSO_4$
〃	153.6	〃	4.7	−13.3	〃
〃	230.4	〃	4.6	−13.4	〃
27.0	76.8	Fe^{++}	12.2	−14.8	$FeSO_4$
〃	153.6	〃	7.3	−19.7	〃
〃	230.4	〃	6.3	−20.7	〃
39.3	0	Fe^{++}	39.3	0	$FeSO_4$
〃	3.8	〃	37.4	− 1.9	〃
〃	7.7	〃	34.2	− 5.1	〃
〃	19.2	〃	27.5	−11.8	〃
〃	38.4	〃	22.2	−17.1	〃
〃	57.8	〃	16.9	−22.4	〃

Table 4

Rate of Reduction in the Presence of Fe

Time, min.	0	5	10	20	60
Found (as Cr_2O_3), γ	10.6	6.0	5.7	5.7	5.7
Difference, γ	− 7.4	−12.0	−12.3	−12.3	−12.3

Conditions: chromate present, 18.0γ as Cr_2O_3, ferrous iron added, 76.8γ as Fe.

Next a brief experiment on the interference of vanadium which form a strongly yellow-colored compound under the conditions recommended was carried out. It was shown that it is recommendable to remove vanadium by the addition of oxine as described, even if the amount of V_2O_3 does not exceed that of Cr_2O_3, as it darkens the hue of the solution. Usually it gives an erroneous increase to the results. Besides these ions, other ions such as cited in the following table were tested for the interferences which may be expected in the filtrate, but no serious interference was observed.

Necessity of the Oxidation.—Some sources of errors, especially those responsible for a negative error due to the reduction of chromate to chromic ion in colorimetric determination by diphenylcarbazide have been pointed out and examined, but some of the sources as described above may be easily avoided. However, the errors may be considerable in samples containing a relatively large amount of iron. Among a number of errors, this reduction due to ferrous iron and oxine is especially fatal to the determination, although many other complicated factors also play a part in leading to erroneous results.

The oxidation to chromate is therefore

(8) W. F. Hillebrand, *U. S. Geol. Survey Bull.*, **422**, 147 (1912); R. S. McBride and J. A. Scherrer, *loc. cit.*; R. W. Curtis and J. Finkelstein, *Ind. Eng. Chem. Anal. Ed.*, **5**, 318 (1933).

Table 5

Interference due to Vanadium and Other Ions

Chromate present (as Cr_2O_3), γ	Interfering ion, γ	Chromate found (as Cr_2O_3), γ	Difference, γ	Remarks
20.0	10 as V_2O_5	20.5	+ 0.5	Sodium metavanadate
〃	20 〃	20.3	+ 0.3	
〃	30 〃	20.8	+ 0.8	
〃	40 〃	20.3	+ 0.3	
〃	100 〃	21.1	+ 1.1	
〃	300 〃	—	—	Darkens the coloration
20.0	10 V_2O_5 + 0 Fe^{++}	20.5	+ 0.5	Sodium metavanadate and ferrous sulfate
〃	20 V_2O_5 + 76.8 Fe^{++}	7.6	−12.4	
20.0	20 V_2O_5 + 0 Fe^{++}	20.3	+ 0.3	Sodium metavanadate and ferrous sulfate
〃	20 V_2O_5 + 76.8 Fe^{++}	8.9	−11.1	
20.0	100 V_2O_5 + 70 Fe^{++}	21.1	+ 1.1	Sodium metavanadate and ferrous sulfate
〃	100 V_2O_5 + 76.8 Fe^{++}	9.4	−10.6	
20.0	1000 Cl^-	19.8	− 0.2	Sodium chloride
〃	1009 Al^{+++}	19.3	− 0.7	Aluminium sulfate
〃	990 Mg^{++}	19.6	− 0.4	Magnesium sulfate
〃	1070 PO_4^{---}	19.6	− 0.4	Sodium phosphate

required for accurate determination. Comparative studies on the oxidation method were performed and it was found that sodium peroxide in an alkaline medium (or potassium bromate in the presence of sulfuric acid) is most appropriate for this purpose.

Oxidation with Sodium Peroxide. — Sodium peroxide has been preferably used for the oxidation of chromium. Some workers have described that the complete decomposition of its excess is possible by boiling the alkaline solution for 10 to 20 minutes. However, others have described that the decomposition is difficult only by boiling if not impossible.

It must be remembered that in an acid solution sodium peroxide or the resultant hydrogen peroxide will cause reduction of chromate, so that it should be expelled out of the alkaline solution before proceeding with sulfuric acid for its complete acidification. As it may be supposed that even a trace of it will cause a serious error in the microdetermination, a number of experiments were carried out for it. To ensure a complete decomposition the addition of glasswool, active charcoal or manganese dioxide previously freed from contaminable matters, was tried, vigorous and continuous strirring being made during the addition. As a result of these experiments manganese dioxide was found most suitable for this purpose.

The effects of iron as well as vanadate ions were examined on the power to decompose hydrogen peroxide produced from sodium peroxide. However, no significant interference was observed.

The reproducibility and accuracy of this oxidizing procedure are not necessarily sufficient as shown in the following table, but it may serve to remove the difficulties mentioned.

Practically satisfactory results were obtained by the following procedure. Though a complete oxidation can be expected only when a sodium peroxide fusion is used instead of a usual carbonate fusion, the latter was preferably used as iron abundantly appears in the leached filtrate of a sodium peroxide fusion melt.

Procedure.— After vanadium is extracted (as referred to in a separate report)[5] as oxyquinolate by chloroform, it is made faintly alkaline with sodium hydroxide.

Add 0.05 to 0.01 g. of sodium peroxide to the alkaline solution and boil for approximately 10 minutes, stirring continuously. If necessary, continue the boiling after adding some water. After the bubbling due to the decomposition of sodium peroxide has ceased, add a few lumps of manganese dioxide, previously freed

(10) Ist application will be reported in near future.

from all contaminable matters, which may start the bubbling again.

Then cool the solution under tap water after the bubbling has almost ceased, filter off the manganese dioxide by using a filter paper digested with a 20% sodium carbonate solution, and add 1.5 ml. of 4 *N* sulfuric acid. At this stage the total volume of the solution should not exceed 20 ml. A mixture of 1 ml. of 0.25% solution of diphenylcarbazide in acetone (1 : 1), 1 ml. of 6 *N* sulfuric acid and 2 to 3 ml. of water is added. Then the solution is thoroughly mixed and made up to 25 ml. The red-violet color develops very rapidly and the comparison is made without unnecessary delay with Pulfurich photometer using S 55 filter (550 mμ.).

To show the improvements made with this procedure, as compared with the old method, the content of chromium in brown coal and rocks was determined. This sufficiently proved the necessity of introducing the oxidizing process in the procedure.

Table 6

Improved Results with Oxidation Method and its Reproducibility

Sample		Sample taken, g.	Found (as Cr_2O_3), r	Chromium content, %	Remarks
Brown coal ash	No. 1	1.0018	227	0.0227	
			380	0.0373	Oxidation method
	No. 2	1.1972	3.3	0.0003	
		1.0862	11.5	0.0011	〃
	No. 3	1.0054	22.5	0.0023	
		1.0018	38.0	0.0038	〃
	No. 4	0.7036	4.3	0.0006	
			21.2	0.0030	〃
Iron sand		1.0797	270	0.0251	
			306	0.0283	〃
Olivin basalt		1.0062	180	0.0175	
		1.0062	225	0.0221	〃
			224	0.0223	〃
			210	0.0208	〃
Nepheline bassalt		1.0035	126	0.0126	
			146	0.0145	〃
			144	0.0144	〃

Summary

The colorimetric method of determining chromium in silicate rocks with diphenylcarbazide has the defect resulting in a distinct tendency for producing slightly lower figures as recognized already. After a thorough study of the method the author pointed out the possible sources for the serious errors, especially for those which give negative results. Thus the oxidation method in an alkaline medium was proposed, which was compared with the widely used old method.

The accuracy and reproducibility of this method are not entirely satisfactory but so far it will serve as the most accurate method. The content of chromium in brown coal in Japan determined by this oxidation method with sodium peroxide will be reported in a later communication.

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