*Absorptiometric Determination of Micro-amounts of Iron in Nuclear Grade Graphite and Urania-Graphite Fuel; Nitroso R Salt Method after Coprecipitation of Iron with Manganese Dioxide**

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It has been necessary, in the author's laboratory, to determine micro-amounts of iron in nuclear grade graphite and urania-graphite fuel for a nuclear reactor. Spectrographic methods have been used to estimate the iron impurity in graphite. Recently[1], the impurity in graphite of high purity was determined after concentration by a chemical method. Little literature on absorptiometric determination of the impurity in nuclear grade graphite and urania-graphite fuel is seen at present. The author has applied a method with nitroso R salt, sodium 1-nitroso-2-naphthol-3, 6-disulfonate[2,3], to these samples because the reagent has the highest sensitivity to iron at present giving very stable green color[4]. In this paper, the effect of diverse ions, preliminary separation and contamination with foreign iron are discussed.

Experimental

Apparatus and Materials. — A Hitachi spectrophotometer, model EPU-2, was used for all measurements of absorbancy, matched 1 cm. cells being used. A Beckman pH-meter, model H-2, was used for acidity measurements. An electric furnace used for the ashing of samples was equipped with a protector assembled with fused silica plates to keep the sample out of possible contamination with dust from the wall of the furnace.

All the chemicals were of JIS special grade including starting materials in the following preparation of chemicals unless otherwise stated. Nitroso R salt was recrystallized from 50% aqueous ethanol. Hydrochloric acid and aqueous ammonia were purified by distillation. Cobalt sulfate was prepared by the pyrolysis of chloropentaminecobalt(III) chloride followed by furming with sulfuric acid and recrystallization. The cobalt complex was prepared according to the description by M. Biltz and W. Biltz[5]. Manganese chloride was prepared from iron-free potassium permanganate by reduction with

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1) A. A. Demidov and L. B. Gorbunova, *Zavodskaya Lab.*, **25**, 956 (1959); *Chem. Abstr.*, **54**, 10634 (1960).

2) C. P. Sideris, *Ind. Eng. Chem., Anal. Ed.*, **14**, 756 (1942).

3) Y. Oka and M. Miyamoto, *Japan Analyst*, (*Bunseki Kagaku*), **1**, 23 (1952); *Bull. Res. Inst. Min. Dress. Met., Tohoku Univ.*, **9**, 25 (1953).

4) Y. Oka and M. Miyamoto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 864 (1954); *Sci. Rep. RITU.*, **A7**, 84 (1955); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 672 (1955); *Sci. Rep. RITU.*, **A7**, 482 (1955).

5) M. Biltz and W. Biltz, "Ubungsbeispiele aus der unorganischen Experimentalchemie", (1920), p. 166.

ethanol and dissolution of resulting manganese dioxide followed by recrystallization. For the removal of iron impurity, the permanganate was dissolved in water containing a small amount of aluminum sulfate followed by the precipitation of aluminum hydroxide with aqueous ammonia.

Standard Iron Solution. — A solution containing 2 mg. of iron per milliliter was made by dissolving ammonium ferric sulfate in 0.1 N hydrochloric acid. The iron concentration was checked titrimetrically with a standard permanganate solution after the reduction of iron by stannous chloride. The iron solution was appropriately diluted in time for use.

Nitroso R Salt Solution. — 0.500 g. of the reagent was dissolved in 100 ml. of water.

Buffer Solution. — A 4.00 M solution of recrystallized sodium acetate.

Hydroxylamine Sulfate Solution. — 5.00 g. of the salt was dissolved in 100 ml. of water.

Manganese Solution.—A 0.2 M solution of manganese chloride.

Ammonium Carbonate Solution.—A 0.1 M solution was made by dissolving the salt in 0.3 N aqueous ammonia followed by standing over night and filteration.

Acidified Hydroxylamine Solution.—Three parts of the hydroxylamine sulfate solution were mixed with 1 part of 6 N hydrochloric acid.

Method. — The absorptiometric determination of iron was made as follows unless otherwise stated: a test solution was taken in a 25 ml. volumetric flask and neutralized with dilute aqueous ammonia either against a drop of a methyl orange indicator solution or till just before the precipitation of iron. Two milliliters of 0.1 N hydrochloric acid and 1.0 ml. of the hydroxylamine sulfate solution were added and the liquid was swirled well followed by dilution to about 20 ml. Two milliliters each of the reagent solution and the buffer solution were added in the order with stirring. The liquid was diluted to the mark. The flask was immersed in boiling water for about 10 min. followed by cooling to room temperature with running water. The intensity of the resulting color was measured at 715 and 650 mμ., the wavelength widths being 1.0 mμ.

The coprecipitation of iron with manganese dioxide was made as follows unless otherwise stated: to a test solution, 10 ml. of the manganese solution was added and the solution was diluted to about 100 ml. Ten milliliters of the ammonium carbonate solution was added. Five milliliters of about 3% hydrogen peroxide was added with stirring and the solution was heated on a boiling water bath for 30 to 40 min. The resulting precipitate was centrifuged at 3,000 r. p. m. for 10 min. followed by washing with about 15 ml. of water. It was dissolved in 5 ml. of the acidified hydroxylamine solution. The resulting solution was transferred into a quartz dish and evaporated on a water bath till dryness. The residue was taken with 2.0 ml. of hot 0.1 N hydrochloric acid and transferred into a 25 ml. volumetric flask for the determination of iron.

Results and Discussion

In the following discussions, a deviation within 2% was allowed.

Adjustment of Acidity and Effect of Diverse Ions.—An optimum pH-range for the full color development was reported by the present author[3] to be 5.3 to 6.5. The acidity of a test solution, which contains 0.5 to 4.0 ml. of 0.1 N hydrochloric acid can be satisfactorily adjusted within the optimum range by the addition of 2.0 ml. of the buffer solution.

Griffing and Mellon[6] reported the effect of many diverse ions. The present results obtained with several ions are shown in Table I. According to the previous workers, vanadium-(V) interferes strongly because of its color formation. The present result, however does not indicate any interference with the color intensity of iron complex by the presence of at least 10 p. p. m. of the ion. Manganese(II) gives an absorption band around 440 mμ. The strong effect of an increased amount of the reagent or the metal ion on the intensity of the band suggests that the manganese(II) complex formed is unstable. The instability of the complex permits the presence of a large amount of the metal ion without interference in the color development of iron. An intense red color of cobalt(III) complex, which has disappeared by the heating for completion of the color reaction of iron, gradually appears again when the solution is left to stand. Fortunately, the red complex does not give absorption at 715 mμ. Because of the high stability of the red complex, however, the use of increased amounts of the reagent is required for the full color development of iron. Uranium(VI) does not give any absorption in long wavelength region. The presence of a very large amount of the ion is thus permitted. This is parallel with Nageswara Rao and

TABLE I. EFFECT OF DIVERSE IONS ON THE DETERMINATION

Each test solution contains 2.00 p. p. m. of iron at the final concentration.

Diverse ions* added, p. p. m.		Errors, % 715 mμ	Errors, % 600 mμ	Amounts of the reagent soln. used, ml./25 ml.
Sodium	4,600	−0	1	2.00
Vanadium(V)	10	1	0	2.00
Manganese(II)	835	2	12	2.00
Cobalt(II)	10	2	45	4.00
Nickel	10	2	9	2.00
Uranium(VI)	4,760	1	5	2.00

* Added as sodium chloride, ammonium metavanadate, manganese chloride, nickel nitrate and uranyl nitrate, respectively.

6) M. Griffing and M. G. Mellon, *Anal. Chem.*, **19**, 1014 (1947).

Raghava Rao's results[7] on the reaction of uranyl ion with the reagent.

Removal of Diverse Ions by Coprecipitation of Iron with Manganese Dioxide. — Dean and Lady[8] selectively decomposed colored complexes of diverse ions with hydrazine under a carefully controlled condition without affecting the color intensity of the iron complex. Very recently, Ishii[9] extracted iron with tributyl phosphate for absorptiometric determination of iron impurity in uranium metal with 1, 10-phenanthroline. The present author coprecipitated iron with manganese from an ammoniacal carbonate solution leaving the diverse ions as well as uranium in the solution. The manganese was precipitated as dioxide by the oxidation of manganese(II) ion. The method is simple and appropriate for the extraction of iron out of sample solutions which contain "concentrated" uranium. Coprecipitation of iron with aluminum hydroxide was found unsuitable for the present purpose because of the resistance of the precipitate to dissolution in a dilute acid and of possible precipitation of aluminum hydroxide at the stage of the color development of the iron.

Coprecipitation of Iron.—Figure 1 shows the completeness of the coprecipitation of iron with 1.2 mg. of manganese. Increases in the blank absorption at 715 and 600 mμ. may be attributed to iron impurity in the reagents used. Figure 2 shows the amounts of manganese required for complete precipitation of iron. It also indicates that 2 ml. of bromine water may be used as an oxidizing agent instead of hydrogen peroxide when the solution is boiled for 10 to 15 min. Hydrogen peroxide, however, is superior to bromine water because the former gives a well coagulated precipitate by warming on a water bath. Three milliliters of 3% hydrogen peroxide is sufficient for complete precipitation of manganese(II) ion. Precipitation of manganese by the reduction of permanganate[10] with formate, sulfite or ethanol[11] was found unsuitable for the present purpose because of difficulty in the collection of a very fine precipitate formed.

Filteration of the precipitate by a filter paper is unsuitable because of possible contamination with foreign iron from the filter. The amounts of iron impurity found in the Toyo, No. 5B (7 cm.) were 0.6 to 2.6 μg. per each filter. The precipitate is dissolved in the acidified hydroxylamine solution with ease. The minimum amount of the solvent required to dissolve the precipitate is 1.25 ml. A hot hydrogen peroxide solution containing hydrochloric or sulfuric acid, as the solvent, is inferior to the former.

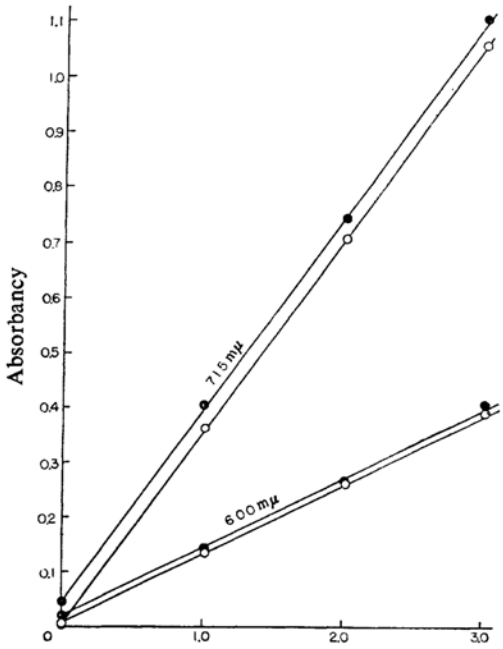

Fig. 1. Amounts of iron and color intensity. The final volume was 25 ml. ○, coprecipitation was not made; ●, coprecipitation with 1.2 mg. of manganese was made.

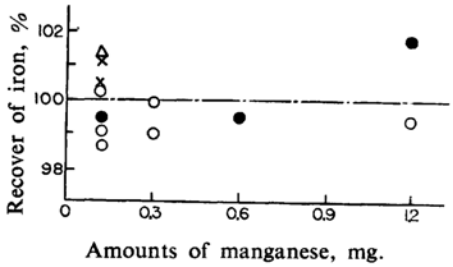

Fig. 2. Amounts manganese and recovery of iron by the coprecipitation.

Amounts of iron taken are: ●, 50 μg. (oxidation with bromine water); △, 25 μg.; ○, 50 μg. and ×, 75 μg.

Separation of Iron from Diverse Ions. — Results shown in Table II indicate that the separation by this method is effective to eliminate the diverse ions. One fourth milligram of platinum associated with uranium is satisfactorily removed from iron (cf. No. 5 in Table

7) M. Nageswara Rao and Bh. S. V. Raghava Rao, *Z. Anal. Chem.*, **142**, 161 (1954).
8) J. A. Dean and J. H. Lady, *Anal. Chem.*, **23**, 1096 (1951).
9) D. Ishii, *Japan Analyst* (*Bunseki Kagaku*), **9**, 693 (1960).
10) H. N. Stokes and J. R. Cain, *J. Am. Chem. Soc.*, **29**, 409 (1907).
11) E. B. Sandell, "Colorimetric Determination of Traces of Metals", Interscience Publishers, New York (1950), p. 374.

TABLE II. ERRORS OF THE DETERMINATION AFTER THE PRELIMINARY SEPARATION

Each test solution contains 50.00 μg. of iron

No.	Divers ions added, mg.	Errors, %		Amounts of the reagent soln. used, ml./25 ml.
		715 mμ	600 mμ	
1	Cu(II), 0.25	−1	−1	2.00
		0	1	2.00
		−1	−1	2.00
2	Cr(VI), 0.25	−0	−2	2.00
		−0	−1	2.00
		2	1	2.00
3	Co(II), 5.0	−13	−5	4.00
4	Pt(VI), 2.0	12	19	2.00
		12	18	2.00
5	Pt(VI), 0.25; U(VI), 100	−0	−1	2.00
		−1	−1	2.00
		−1	−0	2.00
6	Cu(II), V(V), P (phosphate), Cr(VI), Co(II) and Ni; 0.25 of each. U(VI), 100	0	4	2.00
		0	21	2.00
		0	17	2.00
		−0	30	4.00
		−0	32	4.00
7	Cu(II), V(V), P(phosphate), Cr(VI), Co(II), Ni and Pt(IV); 0.25 of each. U(VI), 100	2	19	2.00
		3	31	2.00
		3	30	2.00

II) while the presence of the same amount of platinum associated with many diverse ions altogether tends to give a slight positive error (cf. No. 7). The removal of cobalt is not effective (cf. No. 3). Sixty five to seventy-one percent of the original cobalt was found in manganese dioxide precipitated from a solution containing 0.25 mg. of cobalt and 50 μg. of iron.

Determination of Iron Impurity in Nuclear Grade Graphite and Urania-Graphite Fuel. — Copper and Chromium, which may strongly interfere with the absorptiometry, are scarcely found in appreciable amounts in nuclear grade graphite. This enables us to apply the method to samples of the graphite without any preliminary separation. The method can be applied to samples of ordinary grade graphite in the same way because iron forms the greater part of the impurities in general. In this case, absorption at 600 mμ. may be used to check the degree of interference by diverse impurities comparing the intensity of the absorption with that obtained at 715 mμ. Preliminary separation is required in the case of urania-graphite fuel because of comparatively large amounts of impurities in the urania component.

Sampling.—Contamination with foreign iron should be avoided during the sampling of analytical specimens. The use of a drill tipped with a tungsten-cobalt alloy, G2[12], is suitable for the sampling from graphite blocks by drilling. In the author's experience, the weight loss of the drill was 1.2 mg. when 2 kg. of graphite was pulverized by the drilling while the loss of an alloyed steel drill was about 6 mg. (3 p. p. m. as to the graphite) under the same conditions. The average hardness of the graphite blocks used was 27.3 by Shore unit. Crashing with a press and pulverizing in an agate mortor may also be done.

Contamination with Foreign Iron from Platinum Crucibles. — It was said that[11] platinum wares contain iron impurity which may be dissolved out with hot acids, giving erroneous results in determinations of micro-amounts of iron. The present author evaporated 4 ml. each of 18 N sulfuric acid in platinum crucibles on a hot plate till dryness. The crucibles were cleaned by pyrosulfate fusion and immersion in 1 to 1 hydrochloric acid successively before use. Each residue was taken with 1 ml. of hot water followed by the determination of iron. Results are shown in Fig. 3. The amounts of iron extracted from the platinum crucibles do not depend on the fuming time. This was confirmed by a statistical treatment of the data. The average amount of the iron extracted is 1 μg. which is the same amount as that found in the sulfuric acid used. From the results, platinum crucibles cleaned carefully may be used for ashing of samples and fuming with sulfuric or perchloric acid. Porcelain crucibles, "SCP" Brand, may also be used. The above fuming test applied to the crucibles gave substantially

12) JIS, H 5501 (1953).

TABLE III. IRON IMPURITY IN GRAPHITE AND URANIA-GRAPHITE FUEL

	Iron found, p. p. m.					
	Without the preliminary septn.			With the preliminary septn.		
	715 mμ	600 mμ	Difference	715 mμ	600 mμ	Difference
Natural graphite	151×10	158×10	7×10	—	—	—
Nuclear grade graphite, A	40.4	40.5	0.1	—	—	—
B	24.4	26.2	1.8	—	—	—
C	5.4	7.0	1.6	5.3	5.4	0.1
Urania-graphite fuel, A	47.0	60.2	13.2	59.4	59.1	0.3
B	32.0	41.9	9.9	52.1	51.6	0.5

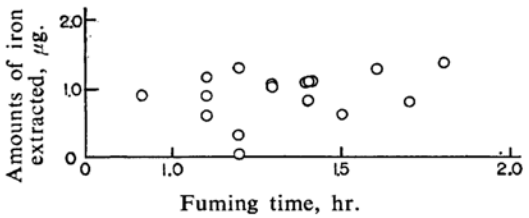

Fig. 3. Fuming time and amounts of iron extracted from platinum crucibles
Capacity of platinum curcibles, 30 ml.; 18 N sulfuric acid, 4.00 ml.; heated on a hot plate.

the same results as those obtained in the case of the platinum crucibles.

Recommended Procedure. — Five grams of a graphite sample is ashed in a platinum crucible at about 800°C. Washed oxygen gas may be introduced into the furnace, if necessary. The ash is treated with 2 ml. of 6 N hydrochloric acid on a water bath and evaporated to dryness. The ash dissolves during the evaporation. Colored insoluble matter, if any, should be completely dissolved with the aid of 1 ml. of hydrofluoric acid followed by fuming with 1 ml. of perchloric or sulfuric acid till dryness. The resulting residue is taken with 10 ml. of 0.1 N hydrochloric acid. The solution is diluted to 50.00 ml. Ten milliliter portions of the test solution are taken in a 25 ml. volumetric flask. One milliliter of the hydroxylamine sulfate solution is added and the determination is made as described in the section "Experimental", the color intensity being measured at 715 mμ. For the preparation of the working curve a set of standard iron solutions containing 0, 1, 2 and 3 p. p. m. at the final concentrations is used.

The amount of a sample to be taken may be reduced to less than 1 g. depending on the content of iron impurity in the sample when the whole of the test solution is used for the color development. The author, however, recommends the use of 5 g. of a sample, which contains a very small amount of iron impurity, to reduce errors due to contamination and segregation of the iron impurity. The lower limit of the determination may be expected to be 2 p. p. m.

In the case of samples of urania-graphite fuel, the coprecipitation of iron should be made as described in the section "Experimental." In this case, the fuming with perchloric acid is made prior to the coprecipitation to convert chromium impurity into chromate ion. Blank tests are required when either or both the fuming and the coprecipitation are carried out.

Iron impurities in several samples determined by the method are shown in Table III. Results obtained at 600 mμ. are also shown for comparison. In the case of samples of the urania-graphite fuel, low results were obtained when the removal of diverse ions was ommitted. They are thought to be due to the consumption of the reagent by large amounts of diverse ions present.

Summary

An absorptiometric determination of micro-amounts of iron with nitroso R salt was satisfactorily applied to the routine analysis of nuclear grade graphite. An ashed sample is brought into a solution and the color of iron is developed by the reagent with the aid of hydroxylamine sulfate. Adjustment of pH to the optimum range is easily made by the addition of a definite amount of an acetate buffer. The intensity of the color is measured at 715 mμ. The range of the determination covers 2 to 75 p. p. m. when 1 g. of a sample is taken, the final volume being 25 ml. In the case of a sample of urania-graphite fuel, the ash is fumed with perchloric acid and a preliminary separation is made by coprecipitation with manganese dioxide which is produced by the oxidation of manganese(II) ion with hydrogen peroxide in a hot ammoniacal carbonate solution. The recovery of

iron is quantitative and the removal of diverse ions is satisfactory. All of the uranium is also removed here. Contamination with foreign iron from a drill used for sampling and from the platinum or percelain crucibles used is negligible. The effect of diverse ions on the absorptiometry was also examined.

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