A Rapid Colorimetric Determination of Vanadium in Carbon Materials

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Introduction

Among heavy metal impurities found in the "electrolyte" (a concentrated sodium chloride solution), the undesirable effect of vanadium upon the chlorine-caustic electrolysis is particularly marked even at a low concentration.[1] Hence, the establishment of a reliable and rapid method of vanadium determination is desirable to estimate the quality of anode carbon and its raw materials and to improve upon it. Indeed, there have been many method tested and others proposed by various investigators. Some, however, are unsatisfactory because insufficient attention was paid to the possible escape of vanadium in the ashing process[2], while others involve some tedious processes unsuitable for use in industrial laboratories.

By overcoming these difficulties, the authors devised a new method having the following characteristics.

(1) Addition of sodium carbonate to the sample accelerates the ashing and guards against the escape of vanadium during the process.

(2) The use of ferric hydroxide gives a simple method for separation of vanadium which replaces E.B. Sandell's tedious processes of leaching the sodium carbonate cake and extracting the vanadium oxinate in the original phospho-tungstate method[3].

Procedure

Pulverize a 0.5–1.0 g. sample so that it can pass through a 100 mesh sieve. Grind the sieved sample in an agate mortar with 2 g. of sodium carbonate for a few minutes and transfer it into a quartz dish so as to make a thin layer. Place it in an electric furnace at 650–750°C and reduce it to ash. After complete ashing, dissolve the ash in sulfuric acid and boil for about five minutes.

Add 5 mg. of ferric iron and 50 ml. of distilled water to the solution thus obtained. Neutralize the solution roughly with sodium hydroxide (3N) while stirring constantly. The neutralization is completed by using six drops or less of ammonia (3N) to B. C. P. or *p*-nitrophenol as indicator. Filter and dissolve the precipitate into 20 ml. of a hot phosphoric acid (1 : 3). Add one ml. of sodium tungstate reagent (0.5M) and keep the solution boiling for about five minutes. After cooling to room temperature, transfer the solution into a 25 ml. measuring flask and fill it with distilled water to the 25 ml. mark. Then the optical density is measured spectrophotometrically at the wavelength of 410 mμ to determine the vanadium, using the working curve described by one of the authors.[4]

When the vanadium content of the sample is below 30 μg., it is advisable to prepare a standard solution of a concentration approximate to that of the sample, and to compare the color of the sample with the standard, using ordinary Nessler tubes of 8 mm. caliber and 35 cm. height. In this way even 5 μg. of vanadium can be determined.

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[1] G. Angel and T. Lundén, *J. Electrochem. Soc.*, **99**, 435 (1952).

[2] I. Iwasaki and I. Ukimoto, *J. Chem. Soc. Japan*, **63**, 1678 (1942).

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

[4] M. Tanaka, This Bulletin, **27**, 10 (1954).

Discussion

1) **Ashing.**—As shown in Table I, the presence of sodium carbonate hinders the escape of vanadium in the ashing process, which is considerable when it is absent. At the same time the carbonate accelerates ashing. Thus, in the presence of the salt, the ashing process which would otherwise require a full hour, is completed within twenty minutes at 650–750°C.

TABLE I

ANALYSES OF SEVERAL SAMPLES

Sample	Sample taken g.	V added μg.	V found μg.	V found* μg.
Coke No. 1	0.50	0	8	8.5
〃	0.50	23	30	—
Coke No. 2	0.50	0	226	230
Coke No. 2†	0.50	0	158	—
Coke No. 2†	0.50	0	181	—
Coke No. 3	1.00	0	18	16
〃	0.50	46	57	—
Graphite No. 4	0.50	0	128	133
〃	0.50	46	176	—
〃	0.50	92	224	—
Grrphite No. 4†	0.50	0	100	—
Graphite No. 4†	0.50	0	119	—
Graphite No. 5	0.50	0	8	9
Cathode of "AD" cell	0.50	0	10	12
(containing Mn)	0.50	23	34	—
〃	0.50	46	57	—

* Determined after the ashed mixture was once put to fusion.

† Ashed without sodium carbonate.

The process of ashing, here mentioned, is sufficient to bring the vanadium in the sample completely into a soluble form. As shown in the same table, the vanadium values do not increase after the ashed sample is once put to fusion. Consequently, fusion is dispensable in the present procedure.

Also it must be added that the wet method of combustion using sodium iodate[5] can successfully replace the ashing. The sieved sample (0.5 g.) is put into 10 ml. of concentrated sulfuric acid contained in a 100 ml. beaker. While the beaker is kept slightly heated, 8—9 g. of sodium iodate powder is added. A violent reaction occurs with a considerable sublimation of iodine, giving a yellowish color to the solution. Diluted with 30 ml. of distilled water, the solution is kept boiling until the iodine is completely expelled. Then the solution is ready for the procedure described above from the point of addition of ferric salt.

The iodate method may be recommended because of its rapidity, but it must be noted that it requires iodate which is expensive and considerable skill for the manipulation.

2) **Ferric Hydroxide as Vanadium Collector**[6].—In the present method, vanadium is collected and separated by ferric hydroxied from the ions of ammonium and potassium which may interfere with the final colorimetry. The following experiment shows that the vanadium collection is complete when it is conducted under the conditions prescribed in the procedure. A series of sulfuric acid solutions was prepared containing various amounts of vanadium, tetra- and quinquevalent in addition to 5 mg. iron. These solutions were processed according to the directions given in the procedure. Table II shows that the result is quite satisfactory. Also it is noticeable that during the process the tetravalent vanadium is completely oxidized into quinque-valent.

TABLE II

COLLECTION OF VANADIUM BY FERRIC HYDROXIDE

No. of experiment	V taken μg.	Valency	V found μg.	Recovery %
1	50	IV	50	100
2	125	IV	123	97
3	250	IV	248	99
4	200	V	201	100
5	300	V	295	98

3) **Interference by Large Amounts of Iron and/or Manganese and its Avoidance.**—When more than one mg. of manganese is present in the sulfuric acid solution, it is partly coprecipitated with ferric hydroxide and oxidized by the air into the tri-valent state, forming pink colored manganic phosphate by later treatment with phosphoric acid. Further, the color is intensified by the addition of sodium tungstate, causing remarkable error in the colorimetry. Also more than 10 mg. of iron cause a considerable error. E.B. Sandell avoided such interferences by sodium carbonate fusion and leaching of the cake obtained. In our procedure, the interfering manganese and iron can be separated as given in the following example: a series of 60 ml. of sulfuric acid solution (0.5N) was prepared in which various amounts of vanadium are contained in addition to 5 mg. each of iron and manganese. After the addition of one ml. of 30% hydrogen peroxide, the

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[5] T. Kiba, S. Ohashi, T. Takagi and Y. Hirota, *Japan Analyst* 2, No. 5, 446 (1953).

[6] K. Sugawara, M. Tanaka and H. Naito, This Bulletin, 26, 417 (1953).

solutions were neutralized with sodium hydroxide solution (3N) and 3—5 ml. of the same reagent were added in excess. After being stirred well, they were left standing at 70°C for about ten minutes until the decomposition of the hydrogen peroxide was complete. The precipitate was filtered off through a glass filter and the filtrate was processed according to the direction in the procedure. Table III proves that the separation was successful.

TABLE III
SEPARATION OF VANADIUM FROM MANGANESE AND IRON

No. of experiment	V taken μg.	V found μg.	Recovery %
1	0	0	—
2	11.5	12	104
3	23	23	100
4	115	118	103
5	230	237	103

4) **Other Interfering Elements.**—Ti, Zr, Bi, Sb, and Sn are considered possible as other interfering elements. Their contents in anode samples, however, are negligible so that a discussion on them can be dispensed with.

5) Table I shows some results of the application of the proposed method to coke and graphite samples and particularly a cathode sample of air depolarized cell. The latter was remarkably contamined with manganese. Consequently their analyses were carried out under the special directions given in the preceding article.

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