New Colorimetric Microdetermination of Vanadium in Natural Waters*

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I. General description

A new colorimetric method of the determination of vanadium was established which allows to separate and determine a few μg. of this element with a two figure accuracy from a bulk of water as large as 20 liters.

The procedure consists of three main steps: (1) Coprecipitation of the element with ferric hydroxide. (2) Separation of vanadium from the coprecipitant and other accompanied elements. (3) Final colorimetry of vanadium oxinate in amyl alcohol.

The concentration by coprecipitation saves much time, which is required in the ordinary evaporation method, and avoids at the same time loss of vanadium into a large bulk of residue, produced when the latter method is applied.

The intense coloration of vanadium oxinate in amyl alcohol makes the determination of a few μg. of the element possible(1), a quantity lying close to the limit in the current phosphotungstovanadate method(2).

II. Procedure

Step 1. Take a sample of 5 to 20 liters depending upon the probable content of vanadium. Acidify with hydrochloric acid, add ferric nitrate solution to give a solution containing 10 mg. of iron per liter and then 1 cc. of 1 M sodium hypochlorite solution per one liter. While warming on a water bath the solution is neutralized with 2 N ammonium hydroxide to bromthymol blue or bromcresol purple and then filtered.

Step 2. Ignite the paper and its contents in a platinum crucible. The ash is ground with 3 g. of anhydrous sodium carbonate in an agatemortar, transferred in a platinum crucible and fused for 40 to 60 minutes by a full burner. The cake obtained is transferred into a small beaker and the crucible is rinsed with hot water. Add 2 to 5 drops of hydrogen peroxide, then 30 to 40 cc. of water in order to digest the entire mass. When digestion is complete, the contents of the beaker are filtered through a small filter paper of fine texture which is previously washed with 20% hot solution of sodium carbonate. Wash the residue with hot 2% sodium carbonate solution.

Step 3. The joint filtrate is neutralized to p-nitrophenol by sulfuric acid in expelling the liberated carbon dioxide. Add 2.5 cc. of 4 N sulfuric acid in excess and set the solution aside to cool to room temperature. Add 1 cc. of 5% malonic acid solution and 0.5 cc. of 2% oxine solution. The whole is transferred into a separatory funnel and mixed with 4 cc. of 4 N sodium acetate for buffer with constant stirring. Add 3 cc. of chloroform, shake for one minute and the layers are left to separate. The chloroform layer is drawn off into a platinum crucible. Add 1 cc. of chloroform to the funnel to wash its stem. Then 2 cc. of chloroform and 0.2 cc. of oxine solution are added. Shake vigorously. After leaving it to stand still, the chloroform layer is drawn out into the platinum crucible. Two to three extractions are sufficient to remove all the oxinate when the last chloroform extract remains faintly yellowish due to oxine itself.

Step 4. Add 1 g. of sodium carbonate to the united chloroform extract, evaporate to dryness at a lower temperature on a water bath. The residue is heated by a burner in order to destroy the organic matter and finally fused by a full burner.

Step 5. The melt is digested with water, filtered and neutralized to p-nitrophenol. Adding 1 cc. of 4 N sulfuric acid, the solution is once heated to boil and left with immersing in cold water. The volume of the solution is made up to 70 to 100 cc. Add 0.5 cc. of the oxine solution and 6.0 cc. of 2 N ammonium hydroxide with constant stirring. In case any white precipitate is formed, the solution should be diluted till it dissolves. Transfer the solution into a separatory funnel, add 10 cc. of benzene and shake vigorously for one minute. Two benzene extractions remove ferric oxinate completely.

Step 6. The remaining aqueous layer is mixed with 4 cc. of sodium acetate solution and 4.5 cc. of 4 N sulfuric acid, whereby the pH is adjusted to about 4.

Add 0.2 cc. of the oxine solution and extract with amyl alcohol. The extraction is repeated till the final fraction bears no perceptible coloration. The united extract is transferred into a

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* The following two methods have been proposed for similar purposes; (1) M. Ishibashi, T. Shigematsu and Y. Nakagawa, *Bull. Inst. Chem. Research*, Kyoto Univ., Kyoto Japan. **24**, 68 (1951), (2) J. M. Bach and R. A. Treiles, *Bol. obras sanit. nacion Buenos Aires*, 5 127 (1941); *Chem. Abstracts*, **36**. 859 (1942); ibid., **35**, 545 (1941). In the former vanadium is coprecipitated with ferric cupferronate and determined by the current phosphotungstovanadate method, while in the latter the oxinate is extracted by isoamyl alcohol.

1) E. Sudo, *J. Chem. Soc. Japan*, **72**, 817 (1951).

2) E. B. Sandell, "Colorimetric Determination of Traces of Metals" Interscience Publishers Inc. New York, p. 607 (1950).

10 cc. measuring flask and diluted to the mark with amyl alcohol. Then the optical density of the solution is determined by the spectrophotometer at wavelength of 475 mμ.

III. Discussion

1) Ferric hydroxide as coprecipitant.—The recovery of vanadium in the coprecipitation with ferric hydroxide is practically 100% at the pH ranges of bromthymol blue and bromcresol purple. The following experiment showed this.

Various amounts of iron and vanadium were added to dilute hydrochloric acid solution, neutralized with ammonium hydroxide to different kinds of indicator whose Hp ranges differ. The vanadium content of the formed precipitate was determined (See Table 1).

Table 1

Optimum pH Range for the Coprecipitation of Vanadium with Ferric Hydroxide

Indicator	pH range	V added μg.	V found μg.	Error %
Methyl orange	3.1−4.5	27.9	26.0	−6.8
Bromcresol purple	5.2−6.8	27.9	28.0	+0.4
Bromthymol blue	6.0−7.6	27.9	28.1	+0.7
Phenolphthalein	8.0−9.8	27.9	26.7	−4.3
Ammonia in excess		27.9	26.4	−4.7

It is also notable that five dissolution-precipitations of the precipitate did not give any loss.

2) Amount of iron required for the complete precipitation of vanadium.—Seven mg. of iron per liter is sufficient to precipitate 0−27.9 μg. of vanadium and an amount up to 150 mg. gives no interference. Table 2 shows it.

Table 2

Coprecipitation of Vanadium with Ferric Hydroxide

Fe added mg.	V added μg.	V found μg.	Error %
150	0	< 1.0	
150	27.9	26.8	− 3.9
100	27.9	27.6	− 1.1
50	27.9	27.6	− 1.1
10	27.9	28.1	+ 0.7
10	27.9	28.3	+ 1.4
10	27.9	28.0	+ 0.4
7	27.9	27.9	0.0
7	27.9	28.1	+ 0.7
5	27.9	26.2	− 6.1
5	279	239	−14.3
2	27.9	17.8	−36.2
0	27.9	1.3	−95.4

3) Separation of iron from vanadium.—Oxine gives colored compounds with various kinds of elements other than vanadium, which can be extracted by organic solvents. Thus careful separations of these elements are required to precede a successful determination of vanadium.

Iron is the first to be considered, its separation being caused at two different stages in the writers' procedure; (1) leaching process of the melt of carbonate fusion and (2) oxinate extraction by benzene.

According to E. B. Sandell the recovery of vanadium at (1) is complete for silicate materials. The writers confirmed it on melts particularly rich in iron as shown in Table 3

Table 3

Separation of Vanadium from Iron in Step (1)

Fe added mg.	V added μg.	V found μg.	Error %
50	27.9	27.7	−0.7
50	27.9	27.6	−1.1
150	0	<1.0	

In order to check the point (2), the following experiment was done.

Different amounts of iron and vanadium were added to a series of 50 cc. waters, containing 3 g. of sodium carbonate, which were divided into four groups to be treated in different ways. Group 1. After being neutralized with sulfuric acid to phenolphthalein, oxine was added and the formed ferric oxinate was separated by shaking with benzene. Groups 2 and 3. After being neutralized with sulfuric acid, 1 cc. and 0.5 cc. of 2 N sodium carbonate solution were added respectively and then oxine. The formed oxinate was extracted by benzene. Group 4. 1 cc. of $4N$ sulfuric acid was added in excess after it was neutralized. Oxine was then added and the solution was made alkaline with 6 cc. of $2N$ ammonium hydroxide. The formed oxinate was extracted. The residual solutions from the four different treatments were regulated to *pH* 4 with a mixture of sulfuric acid and sodium acetate, then extracted by amyl alcohol. Vanadium was determined in the extract. Table 4 shows the result in which Group 4 gives the best result.

Table 4

Separation of Vanadium from Iron in Step (2)

	Fe added µg.	V added µg.	V found µg.	Error %
Group 1	0	55.8	55.0	− 1.4
	0	0	<1.0	
	100	55.8	47.3	−13.7
Group 2	0	55.8	55.1	− 1.3
	100	0	<1.0	
	100	55.8	55.1	− 1.3
	100	55.8	61.3	+ 9.9
Group 3	100	55.8	54.0	− 2.9
	100	55.8	55.0	− 1.4
Group 4	100	55.8	56.0	+ 0.4
	100	55.8	55.9	+ 0.2
	100	55.8	55.8	0
	100	55.8	56.3	+ 0.9

4) **Interference by other elements.**—Aluminum, manganese and silicon are other elements which are usually encountered in tural waters and coprecipitated with iron, thus probably causing some interference.

Aluminum.—A greater part of aluminum moves into the filtrate, when the melt from carbonate fusion is leached and expected to be extracted by organic solvents, in forming oxinate at a *pH* range 4.5—9.8[3]. The oxinate formation, however, can be avoided by masking the element with malonic acid in a slightly acidic solution. The following experiment shows it.

A series of acid solutions containing various amounts of vanadium, 10 mg. of aluminum and 50 mg. of iron was treated with ammonium hydroxide. The precipitates obtained were processed following the steps 2—6 in the procedure to determine vanadium. The result is given in Table 5.

Manganese.—Manganese is reduced by hydrogen peroxide to form precipitate in step 2 of the procedure. In case the manganese content is large, there may form a large bulk of precipitate with a considerable retention of vanadium. However it was shown that an amount of manganese up to 50 mg. does not matter as shown in Table 5.

Table 5

Interferences by Aluminium and Manganese

		Fe added mg.	V added µg.	V found µg.	Error %
Al	10 mg.	50	0.0	<1.0	
	”	”	27.9	27.7	−0.7
	”	”	11.2	10.9	−2.7
	”	”	5.6	5.5	−1.8
Mn	5 mg.	10	27.9	27.9	0
	50	”	27.9	26.4	−5.4

Table 6

Examples of Application

Description	Sample taken	V added	V found
Ground water rich in silicate from a well in the campus of Nagoya University (126 mg. SiO_2/L)	10 L		13.7 µg.
	10 ”	11.2 µg.	24.6 ”
Surface water of Lake Yogo-ko, Shiga Pref. (Aug., 1951)	20 ”		8.9 ”
Surface water of Lake Kizaki-ko, Nagano Pref. (Dec., 1952)	20 ”		3.9 ”
A spring water from Higashiyama area, Nagoya City	20 ”		0.8 ”
Bottom deposits of Lake Yogo-ko	24.7 mg.		0.018%*
	24.7 ”		0.017 ”
	24.7 ”		0.018 ”

* by the current phosphotungstovanadate method.

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[3] E. Sudo, *J. Chem. Soc. Japan*, **72**, 718 (1951).

Silicon.—Silicon in the water is coprecipitated with iron and separates as jelly, when the melt from carbonate fusion is leached and neutralized, thus any vanadium is probably retained. However the retention does not occur so long as the silica content of the water does not exceed 126 mg. per liter: an analysis of a 10 liter sample of well water originally containing 1.26g. of SiO_2 and 13.7 μg. of vanadium, with an additional 11.2 μg. of the latter element, gave a satisfactory vanadium value, 24.6 μg. (See Table 6).

5) **Colorimetry.**—The following is notable concerning the colorimetry of vanadium oxinate in amyl alcohol.

a) The Lambert-Beer's law is strictly obeyed from 0.00 up to 10.0 μg. of vanadium per ml. In case the optical density at 475 mμ is measured, using "Coleman model 14 Universal spectrophotometer", the following relation holds good;

$$X=\frac{E-0.023}{0.0117}$$

where X—the amount of vanadium in μg. per 10 ml. of amyl alcohol
E—the optical density when an accessory "round cuvette", with effective cell thickness 13.06 mm., is used

b) The color developed undergoes no measurable change within 24 hours.

c) The recovery of vanadium by extraction depends largely on the quality of amyl alcohol. Hence a careful purification of amyl alcohol is needed and a preliminary test of its quality by extracting a known amount of vanadium is recommended.

6) **Appilcation to silicate materials.**—The present method, originally developed for water analysis, may be applied to common silicate materials. An example of its application to the bottom deposits of Lake Yogo-ko, Shiga Prefecture, is given in comparing with the value for the same sample by the current phosphotungstovanadate method at the bottom of Table 6, in which some data for terrestrial waters are collected.

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