A Rapid Spectrophotometric Method for Determination of a Minute Amount of Vanadium in Natural Waters

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(Received April 15, 1957)

In a previous paper[1] the writers reported with M. Tanaka a method for determining a minute quantity of vanadium in natural waters, consisting of the following three steps: 1) co-precipitation of vanadium with ferric hydroxide, 2) separation of the vanadium from the co-precipitant and from the accompanying elements, and 3) the final colorimetry of vanadium oxinate in pentanol.

The new method which we will detail below is an improvement on this previous method. The essential improvement is in simplifying the processes for vanadium separation from co-precipitant. The simplification is based upon the findings that so long as the solution is sufficiently cool below room temperature, tartrate can keep iron from hydroxide formation even in a strongly alkaline medium and that when the solution is warmed in this condition, iron and aluminium can easily be precipitated leaving vanadium completely in solution.

Experimental

Reagents.—*Mixed solution of sodium hydroxide and tartaric acid.*—Dissolve 30 g. of tartaric acid and 200 g. of sodium hydroxide in distilled water and dilute to 1000 ml.

Ferric chloride solution.—Dissolve 24.2 g. of ferric chloride crystal (the special grade for analytical purposes) in distilled water. Add 5 ml. of 6 N hydrochloric acid and dilute to 500 ml.

Sodium acetate buffer solution.—Dissolve 136 g. of sodium acetate in about 200 ml. of distilled water. Heat the solution on a water bath, then filter through a filterpaper. To the filtrate add 3 ml. of glacial acetic acid and dilute to 250 ml.

Oxine solution.—To 100 ml. of distilled water, dissolve 2 g. of oxine (special grade for analytical purposes) and 5 g. of malonic acid crystal.

Procedure.—Take a sample of 5—20 liters depending upon the probable content of vanadium. Acidify with hydrochloric acid. Then add a solution of ferric chloride, ferric nitrate or iron alum so that the solution contains 10 mg. iron per liter. While warming in a water bath, the solution is neutralized with 4 N aqueous ammonia to bromcresolpurple and the precipitate is collected by an automatic filter.

Gently burn to ashes the filterpaper with its contents in a platinum dish. To the ash add 5 ml. of 6 N hydrochloric acid. Then heat the dish with a cover on a steam bath. Loss of hydrochloric acid causes no essential trouble. The final volume of the hydrochloric acid must not exceed 5 ml. After complete dissolution, transfer the contents to a 100 ml. beaker. Wash the dish with 50 ml. of distilled water. With constant stirring, add 15 ml. of the tartrate-sodium hydroxide solution. The solution turns dark brown without precipitation.

Heat the solution on a steam bath until ferric hydroxide completely precipitates and the supernatant solution is left clear and colorless. The process usually takes 30 minutes and sometimes longer. After it has cooled to room temperature, dilute the solution exactly 100 ml. and put to centrifugation for 10 minutes at 3000 r.p.m.

Transfer 80 ml. of the supernatant solution to a 100 ml. beaker, neuturalize to *p*-nitrophenol with 4 N sulfuric acid. Then add 3 ml. of the same solution in excess. Heat in a water bath. To the hot solution add 2 ml. of the oxine solution, neutralize with 4 N ammonia and then add 4 ml. of the same reagent in excess, whereby a trace of iron which escaped from the previous precipitation process is fixed in the form of oxinate, partly precipitated and partly in solution. When the precipitate is appreciably great, it can be separated by centrifugation. Otherwise go directly on to the next process.

The next process is the extraction of the formed oxinate by an organic solvent. Transfer the solution into a separatory funnel and add about 20 ml. of benzene. Shake vigorously for one minute. Two benzene extractions are sufficient for complete removal of the iron oxinate.

Neutralize the remaining solution with 4 N sulfuric acid and add 3.0 ml. of the same acid in excess. Adjust the pH to nearly 4 by the addition of 4 ml. of a sodium acetate solution. Then add 1.0 ml. of an oxine solution and extract the formed vanadium oxinate by pentanol. The extraction is repeated until the final extract bears no perceptible coloration. Transfer the united extracts into a 10 ml. measuring flask and make up with pentanol to the mark. Then the optical density of the solution is determined by using a spectrophotometer at wave length of 475 mμ.

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[1] K. Sugawara, M. Tanaka, and H. Naitô, This Bulletin **26**, 417 (1953).

Discussion

Whether the vanadium co-precipitation with ferric hydroxide is complete or not depends upon the pH of the milieu. As shown in Table I[2], it is complete only within the pH range up to 9.6. Therefore, in the first step of the precedure the precipitation was arranged so that it occurs at that pH whereby a trace of vanadium can be completely collected in the coagulum.

TABLE I
VANADIUM CO-PRECIPITATION BY IRON AT VARIOUS pH VALUES

pH of the solution	Fe added mg.	V added μg.	V found in the ppt. μg.
7.9	2	33.0	33.2
8.8	2	33.0	32.2
9.6	2	33.0	33.2
10.8	2	33.0	<1
12.3	2	33.0	<1

The situation is quite contrary for the second step of the procedure where vanadium must remain in solution to its trace when hydroxides are precipitated. The requirement is that:

1) In the alkalinization process, iron and aluminium must be kept in solution until the pH of the solution becomes sufficiently high for these elements to precipitate free from a trace of vanadium.

2) Finding a process which causes a homogeneous precipitation at this pH of the iron and aluminium, which have been kept in solution up to the pH.

The addition of tartrate satisfies this requirement. At the stated pH, iron and aluminium can be masked by this substance at low temperatures and easily demasked with precipitation when warmed. Recovery of vanadium was the final question which was solved by the following experiment:

To a series of solutions containing various amounts of vanadium, 100 ml. of iron and 500 ml. of a tartaric acid solution were added. Each solution was made alkaline by the addition of 15 ml. of 5 N sodium hydroxide solution which had previously been cooled below room temperature. Then the solution was warmed in a boiling water bath whereby iron hydroxide was precipitated. The supernatant solution thus obtained was processed as given in the procedure. As shown in Table II, the recovery of vanadium is perfect.

TABLE II
RECOVERY OF VANADIUM FROM IRON PRECIPITATE

Fe added mg.	V added μg.	V found μg.	%
100	20	19.5	98
100	20	19.6	98
100	20	20.4	102
100	20	20.8	104
100	20	19.6	98
100	20	19.7	99
100	20	19.9	100
100	8	8.1	101
100	8	8.5	106

As to the amount of iron added, when it is less than 5 mg., separation is complete without the addition of tartrate, and when it exceeds 20 mg., hydrogen peroxide treatment is not sufficient for a complete separation, which can be first realized by the addition of tartrate.

Interferences by other elements. Some other elements remaining in the solution from which ferric hydroxide had been separated, interfere with the final colorimetry of vanadium by forming oxinates. By the addition of malonic acid, aluminium can be prevented from forming oxinate in a neutral or a slightly acidic solution. No harmful effect is caused by the presence of 50 mg. of aluminium, 10 mg. of manganese or zinc, and 1 mg. of cadmium, bismuth, copper, silver, mercury, tin, selenium, tungsten, molybdenum or titanium.

The present study was accomplished by using a Coleman Model 14 Universal Spectrophotometer supplied by the Elizabeth Thompson Science Fund. The writers express their appreciation to the Trustees of that Fund.

The senior writer is sorry to report the tragic death on October 11, 1956, of his co-worker, H. Naitô, when during his surveying work on Lake Kizaki-ko, rough water suddenly capsized the boat and was drowned.

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2) M. Tanaka, unpublished.