Ultraviolet Spectrophotometric Determination of Vanadium in Silicate Rocks

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The spectrophotometric determination of a metal using various mineral acids has the advantage of not requiring a special reagent such as organic reagents, besides having the merits of simplicity of operation and of giving comparative accuracy.

Several works have recently reported on the spectrophotometric determination of various metals, such as iron(III), lead and bismuth, in which sulfuric[1], perchloric[2,3], and hydrochloric acid[4-6] were used as reagents respectively. These methods are based on the absorbance measurement at maximum wavelength of the absorption band, which is considered to be due to the complexes formed between metallic ions and anions such as sulfate, hydroxy and chloride ions.

Regarding vanadium, there are a few articles on the spectrophotometric investigation of vanadium species in acidic media[7-9], but nothing on the spectrophotometric determination of vanadium with mineral acid.

Desesa and Rogers[4] have suggested, on the other hand, the possibility of the ultraviolet spectrophotometric determination of vanadium(V) with hydrochloric acid in their investigation of interference in the spectrophotometric determination of iron with hydrochloric acid.

The present paper is concerned with the investigation of the absorption spectra of vanadium(V) in a hydrochloric acid medium and with the application of their results to the spectrophotometric determination of vanadium(V) in silicate rock.

Experimental

Apparatus.—All absorbance measurements were carried out with a Shimadzu photoelectric spectrophotometer QB-50, with 1 cm. silica cells.

Reagents.—A standard vanadium solution was prepared by dissolving 0.4595 g. of analytical reagent grade ammonium metavanadate in 500 ml. of distilled water. One milliliter of this solution contained 200 μg. of vanadium. The solutions for the absorption spectra measurements were prepared by drying up the aliquots of the stock solution on the water bath and then dissolving the residues in hydrochloric acid solutions of various concentrations. All the other reagents used were of analytical reagent grade.

General Procedure.—Transfer about 2 g. of the rock samples to a platinum crucible and mix with 10 g. of anhydrous sodium carbonate. Fuse the mixture and allow it to cool to room temperature. Transfer the crucible and contents to a 300 ml. beaker and add a few milliliters of distilled water. Heat to boiling in order to loosen the residue in the crucible, and crush any large particles with a flattened stirring rod. Remove the crucible, and wash it sufficiently with water. Add 3 ml. of methyl alcohol to reduce the manganate, warm in the boiling water for 10 min., and filter through filter paper (Toyo-roshi 5B) into a 100 ml. beaker while the solution is hot. Wash the residue 2~3 times with 10 ml. of hot water, and add the washing to the filtrate. After cooling the filtrate, transfer it to a 100 ml. volumetric flask and dilute to the volume with distilled water. Add 25 ml. of this solution to an ion-exchange column containing Dowex-50 Na-form and collect the effluent in a 50 ml. flask. Rinse the column with several portions of water. After neutralizing the effluent, adjust the pH to 4.5~5.2 with acetate buffer and add 0.2 ml. of a 2.5% oxine solution with 2 N acetic acid and 2 ml. chloroform[10]. Shake for 1 min. to extract the vanadium oxinate, transfer the organic phase into a platinum crucible, then repeat the extraction three times and evaporate up to dryness. Add 0.2 g. of anhydrous sodium carbonate to the crucible containing the residue, and fuse it again to convert the vanadium into sodium vanadate. Dissolve the melt in a few milliliters of water. Transfer this solution into a 25 ml. volumetric flask, add 5 ml. of 5 N hydrochloric acid, and dilute to the volume with water. Measure the ultraviolet absorbance at 222 mμ. and obtain the concentration of vanadium from a calibration curve.

Results and Discussion

Absorption Spectra.—A series of complete absorption spectra for vanadium(V) in hydrochloric acid solutions of various concentrations

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[1] R. Bastian et al., *Anal. Chem.*, **25**, 284 (1957).

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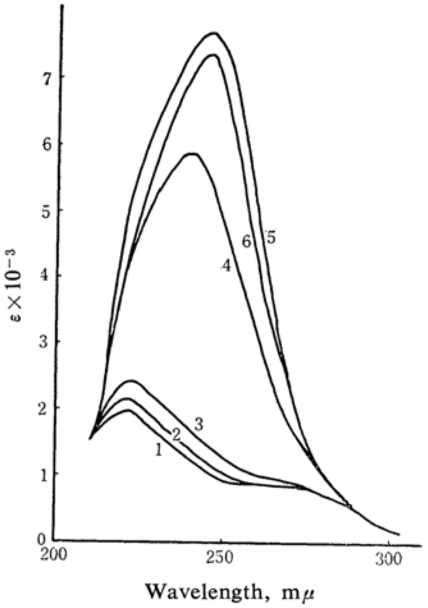

Fig. 1. Absorption spectra of vanadium in HCl.

1: $0.1\sim2$ N HCl
2: 4 N HCl
3: 6 N HCl
4: 8 N HCl
5: 10 N HCl
6: 11.4 N HCl

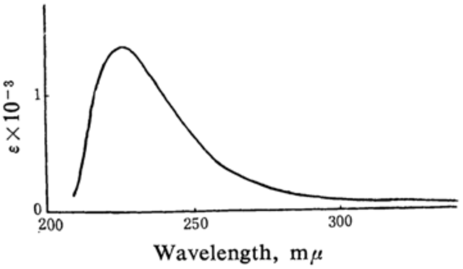

Fig. 2. Absorption spectrum of vanadyl(IV) ion (VO^{2+}) in 11.4 N HCl.

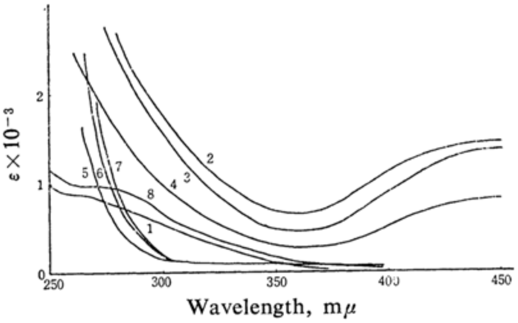

Fig. 3. Absorption spectra of vanadium. $H^+=10$ N.

1: 0.0 N Cl^-
2: 0.5 N Cl^-
3: 1.0 N Cl^-
4: 2.0 N Cl^-
5: 4.0 N Cl^-
6: 6.0 N Cl^-
7: 8.0 N Cl^-
8: 2.0 N H^+ 8.0 N Cl^-

is shown in Fig. 1. In a $0.1\sim2$ N hydrochloric acid solution, the absorption spectra hardly changed with the acid concentration, but in an acid solution more concentrated than in 4 N, the absorption band shifted to a longer wave length with the increasing acid concentration. The position of the maximum was 222 mμ for a $0.1\sim2$ N, but 246 mμ for an 11.4 N hydrochloric acid solution. In a $0.1\sim2$ N hydrochloric acid solution, vanadium(V) exists in the form of pervanadyl ion, VO_2^+ [7,9]. Moreover, the bathochromic and hyperchromic effects with hydrochloric acid, mentioned above, are presumably due to the formation of the higher complex species. The decrease of absorbance in an 11.4 N hydrochloric acid solution compared with that in a 10 N acid solution is attributed to the reduction of a part of vanadium(V) to vanadium(IV) by hydrochloric acid, because concentrated hydrochloric acid has a reducing power and reduces vanadium(V) slowly to vanadyl(IV) ion, VO^{2+}, which is the sole species of vanadium(IV) in a hydrochloric acid medium[11], and the molar extinction coefficient of vanadium(IV) is smaller than that of vanadium(V) in the near ultraviolet region (Fig. 2). Moreover, it is well known that when vanadium(V) is dissolved in an 11.4 N hydrochloric acid solution, the solution becomes intense brown. The absorption spectra for a series of solutions having a constant 10 N hydronium ion concentration but varying chloride concentrations, obtained by mixing hydrochloric acid and perchloric acid in various ratios are shown in Fig. 3. This red brown species, which has its absorption maximum at 450 mμ, was formed in a high hydronium ion concentration such as in 10 N, but it was not formed in a low concentration even if a solution of 8 N chloride concentration was used (Fig. 3). At a high hydronium ion concentration, with the increasing chloride concentration this species became unstable and was converted into vanadyl(IV) ion. From the facts that this species was formed at a high hydronium ion concentration, reduced to vanadyl ion easily, adsorbed by anion exchange resin[12], and extracted to tributyl phosphate, and that the species extracted to tributyl phosphate from the solution of low acid concentration was considered to be $VOCl_3$[13], this red brown complex seemed to be $VOCl_4^-$. The relation between the absorbance of the vanadium and the hydrochloric acid concentration of the solution

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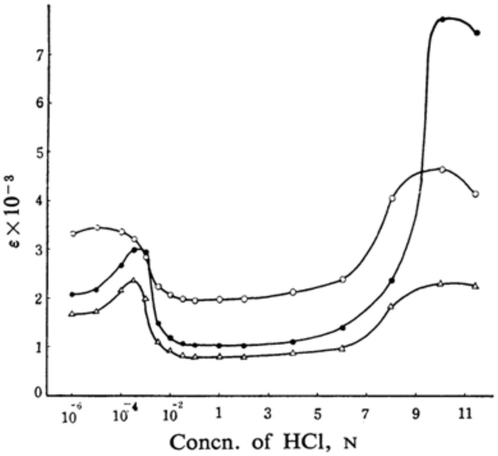

Fig. 4. Relation between the absorbance and the hydrochloric acid concentation.
-○- at 220 mμ -●- at 245 mμ
-△- at 270 mμ

at a specific wavelength is shown in Fig. 4; it is clear from this figure that in the range of hydrochloric acid concentrations from 0.1 to 2 N the effect of the acid concentration on the absorbance was very small and that the absorbance values are nearly equal.

Determination of Vanadium.—On the basis of the above results, a 1 N hydrochloric acid concentration and 222 mμ were chosen as the working conditions for the determination of vanadium making use of the absorption of pervanadyl ion.

Calibration Curve.—Using the standard solution, having the concentration of 200 p. p. m. of vanadium with 1 N hydrochloric acid, a series of 1 N hydrochloric acid solutions having various concentrations of vanadium from 0 to 25 p. p. m. was prepared; then the absorbance was measured at 222 mμ, using a 1N hydrochloric acid solution as reference. As shown in Fig. 5, Beer's law is obeyed up to 25 p. p. m. at 222 mμ.

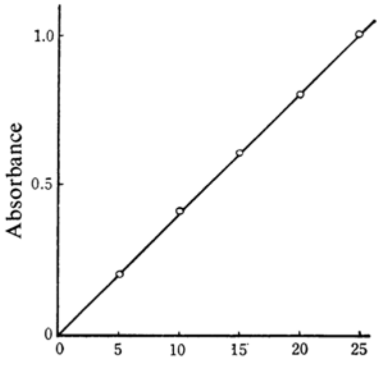

Fig. 5. Calibration curve at 222 mμ.
HCl : 1 N

Stability.—The stability of the system was then investigated for a week; it was found that the absorbance at 222 mμ did not change during this time, as is shown in Fig. 6.

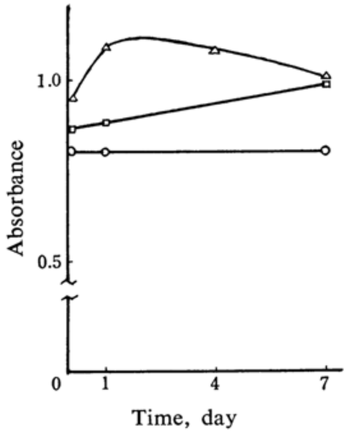

Fig. 6. Stability of absorbance at 222 mμ.
V(V) : 20 p. p. m.
-○- 0.1~2 N HCl -□- 4 N HCl
-△- 6 N HCl

Application of This Method to Silicate Rock Analysis.—After fusion and extraction with water as in the usual method, the sample solution was passed through a column of Dowex-50 Na-form. In the sample solution vanadium existed in the form of vanadate and was not adsorbed by cation exchange resin. However, in this treatment, silicate, phosphate, arsenate, chromate, molybdate and tungstate passed through together with vanadate. Therefore, the absorption spectra of all these elements were observed and are shown in Fig. 7. It is evident from this figure that chromium, molybdenum and tungsten seriously interfered with the determination of vanadium at 222 mμ. Of these three elements, chromium

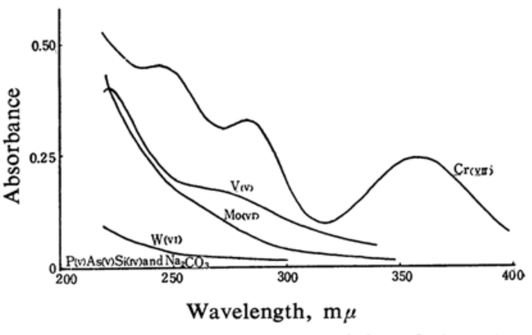

Fig. 7. Absorption spectra of interfering elements in 1N HCl solution.

V(V)	10 p. p. m.	P(V)	10 p. p. m.
Mo(VI)	10 p. p. m.	As(V)	10 p. p. m.
Cr(VII)	10 p. p. m.	Si(IV)	10 p. p. m.
W(VI)	10 p. p. m.	Na_2CO_3	2 g./50 ml.

TABLE I. DETERMINATION OF VANADIUM IN THE PRESENCE OF DIVERSE IONS

Vanadium taken, μg.	Diverse ion	Added as	Amt. added	Vanadium found μg.
200	—	—	—	205
200	—	—	—	198
200	Mo(VI)	$(NH_4)_2MoO_4$	50 μg.	240
200	W(VI)	Na_2WO_4	50 μg.	205
200	Cr(VII)	$KCrO_4$	50 μg.	195
200	Si(IV)	SiO_2	15 mg.	190
200	P(V)	K_2HPO_4	2 mg.	200
200	As(V)	Na_3AsO_4	2 mg.	202

could be separated from vanadium by oxine extraction, but the others could not be separated[14]. The results obtained by the general procedure are shown in Table I. Generally, however, these elements present in silicate rocks are very small quantities compared with vanadium, so the interference by these elements is negligible. The analyses of the Sekisonzan Lave of Asama and of the standard rock sample, diabase W-1, by this method gave the values of 0.024% and 0.043% respectively as V_2O_3; these values were consistent with the value of 0.021% obtained by the phosphotungstate method and with the average value of 0.038%[15].

Summary

1) The absorption spectra of vanadium(V) in the media of various concentrations of hydrochloric acid were studied.

2) A 1 N hydrochloric acid concentration was recommended as the working medium for the spectrophotometric determination of vanadium(V), because the change in the intensity of the absorbance with the change in the reagent concentration is slight.

3) Beer's law was obeyed up to 25 p. p. m. of the metal, measuring the absorbance at 222 mμ.

4) The analysis of the silicate rocks by this method was studied, and good results were obtained.

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