

## The Coprecipitation and Spectrophotometric Determination of Vanadium as 8-Hydroxyquinolate.

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Vanadium ion was coprecipitated as 8-hydroxyquinolate with *o*-phenylphenol and was determined spectrophotometrically by dissolving the precipitate with chloroform and by measuring directly the absorbance of the chloroform solution. Vanadium 8-hydroxyquinolate in chloroform solution containing *o*-phenylphenol had an absorption maximum at 610 m $\mu$ . The effects of pH, the reagent concentration, the amount of coprecipitant and the other variables were investigated to make possible the coprecipitation and spectrophotometric determination of vanadium. Beer's law was obeyed between 1.0 and 6.0  $\mu$ g of vanadium per ml in chloroform solution. Common di- and tervalent cations hardly interfered except ferric ion which caused a considerable positive error.

### I. INTRODUCTION

The method of coprecipitating trace metal ions with organic coprecipitants has been developed for the chemical separation of radioisotopes and the chemical enrichment of trace elements in natural water and biological materials<sup>1-8)</sup>. The use of the organic coprecipitants presents several advantages over the usual inorganic carrier coprecipitation techniques: Coprecipitants can be easily eliminated from the precipitates by ashing of them; coprecipitation occurs relatively selective and filtration is easy<sup>4)</sup>. The authors had been interested in this subject and published the work concerning the influence of organic coprecipitants on the coprecipitation efficiency of the metal 8-hydroxyquinolates<sup>9)</sup>. At that time it was suggested that a metal ion could be determined directly by the spectrophotometry, if the precipitate containing the metal chelate was filtered and dissolved in an organic solvent. The method based on the above idea, like solvent extraction and spectrophotometric method, is to be characterized by easy chemical treatment, selectivity and high efficiency of enrichment. The method was already adopted in the determination of iron with 8-hydroxyquinoline<sup>10)</sup> and of uranium with dibenzoylmethane<sup>11)</sup>.

The present method consists of introducing an appropriate organic reagent into the trace element solution, coprecipitating the trace element therefrom by a suitable organic coprecipitant and dissolving the precipitate by an organic solvent. In the present paper, vanadium was determined as 8-hydroxyquinolate by the coprecipitation and spectrophotometric method.

### II. EXPERIMENTAL

#### Reagents.

The standard vanadium solution was prepared by dissolving 0.2296 g of am-

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monium metavanadate in 25 ml of hot 4 *N* sulfuric acid and then diluting it with water to 1 *l* to make the solution of 100  $\mu\text{g V/ml}$ . Reagent grade *o*-phenylphenol (OPP) was purified by distilling it under reduced pressure. Commercial 8-hydroxyquinoline of reagent grade was dissolved in dilute hydrochloric acid.

The other chemicals were chemically pure or reagent grade materials.

### Apparatus.

A Shimadzu recording spectrophotometer, SV 50, was used for the measurement of the absorption spectra. For the quantitative measurement, a Hitachi manual spectrometer, Model 139, was used. Absorption cells with a path length of 1.00 cm were used. pH measurements were performed with a Hitachi-Horiba Model M-3 pH meter.

### Procedure.

The procedure for the coprecipitation experiment was, unless otherwise stated, as follows: To an aliquot of the solution containing 20  $\mu\text{g}$  of vanadium per ml, 1 ml of 0.01 *M* 8-hydroxyquinoline was added. If needed, an aqueous buffer was also added. The pH of the solution was then adjusted to the desired value by adding 1 *M* hydrochloric acid or 1 *M* sodium hydroxide. The aqueous phase was finally diluted to 50 ml by adding water and transferred to a 100 ml Erlenmeyer flask. Three tenth gram of *o*-phenylphenol which was crushed out in a mortar was added to it. After the flask had been properly stoppered, it was shaken for 30 min and allowed to settle. The solid phase was carefully filtered with a glassfilter, dissolved with chloroform and diluted to 10 ml. After the solution was filtered through a filter paper, the absorbance was measured at 610  $\text{m}\mu$  against a blank solution.

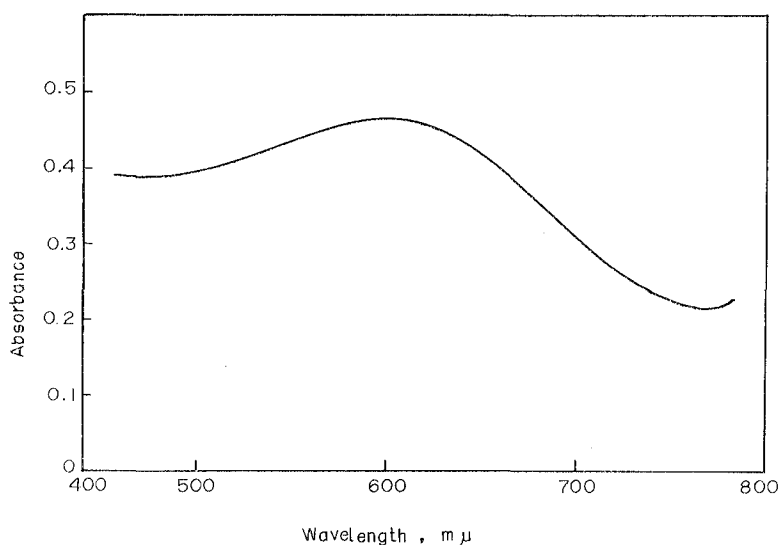


Fig. 1. Absorption spectrum of vanadium 8-hydroxyquinolate.  
V: 40  $\mu\text{g}$ , 8-hydroxyquinoline:  $2 \times 10^{-4}$  *M* in aqueous phase,  
OPP: 0.3 g, aqueous phase: 50 ml,  $\text{CHCl}_3$ : 10 ml, pH: 4.00,  
wave length: 610  $\text{m}\mu$

### III. RESULTS AND DISCUSSION

#### Absorption Spectrum.

The absorption spectrum shown in Fig. 1 was obtained on the chloroform solution which carried 40  $\mu\text{g}$  of vanadium as 8-hydroxyquinolate. It should be noted that in the solvent extraction method, the absorption maximum of vanadium 8-hydroxyquinolate is at 550  $m\mu$  in chloroform solution<sup>(12)</sup>, while in the present method the maximum of vanadium chelate is at 610  $m\mu$ , that is, there is a red shift. In addition, the absorbance is about twice as large in the latter method as that in the former one. This red shift and the increase of the absorbance may be caused by the fact that the vanadium chelate reacts with *o*-phenylphenol used as a coprecipitant to form the adduct complex. The reagent blank shows scarcely any absorbance in visible range, because the reagent does not coprecipitate into the precipitate<sup>(10)</sup>. In this experiment, the absorbance was measured at 610  $m\mu$  against a blank treated in the same way as the samples except that no vanadium was added.

#### The Effect of pH and 8-Hydroxyquinoline Concentration.

To establish the optimum pH range of the aqueous phase for the coprecipitation of vanadium, the dependence of the absorbance of the organic phase on the pH values was studied. In Fig. 2, the absorbances of the organic phase measured at 610  $m\mu$  are plotted against the pH at the several concentration of 8-hydroxyquinoline.

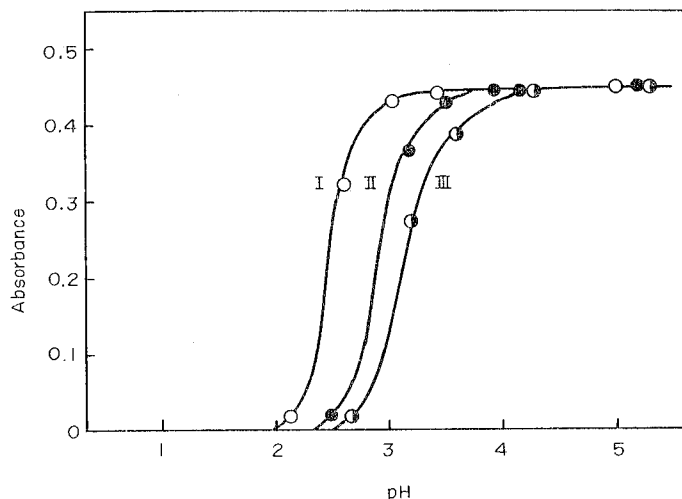


Fig. 2. Effect of pH and the reagent concentration.

8-Hydroxyquinoline: I:  $1.0 \times 10^{-3} M$ ,

II:  $2.0 \times 10^{-4} M$ ,

III:  $1.0 \times 10^{-4} M$ .

Others are same to in Fig. 1.

These coprecipitation curves of the vanadium chelate are similar to those of solvent extraction, though it is difficult for the present system to reach the state of true thermodynamic equilibrium. A nearly constant absorbance was obtained above pH 3.5 when the concentration of the ligand was  $2 \times 10^{-4} M$ . The pH value and the ligand concentration were kept at 4.00 and  $2 \times 10^{-4} M$ , respectively, throughout the experiments.

**The Effect of the Amount of *o*-Phenylphenol.**

Figure 3 shows the results of the study of the effect of *o*-phenylphenol on the absorbance of the organic phase. Little influence of the coprecipitant was observed on the absorbance above 0.3 g of *o*-phenylphenol.

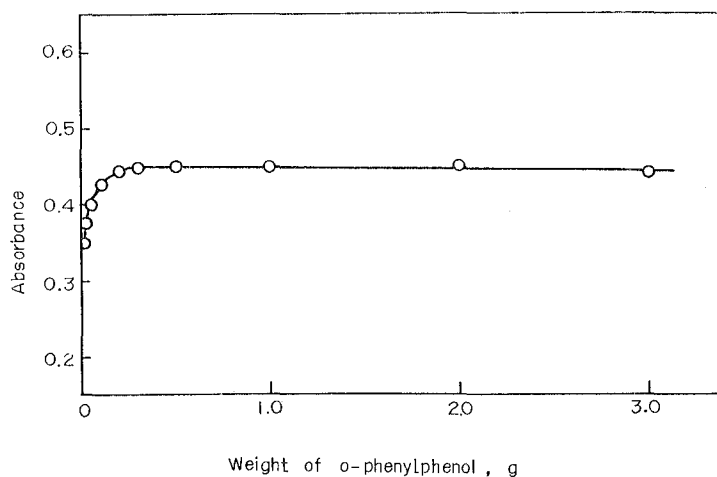


Fig. 3. Effect of *o*-phenylphenol.  
V: 40  $\mu$ g, wavelength: 610  $m\mu$ .

**Shaking Time.**

In order to investigate the effect of the shaking time, the absorbance of the organic phase was measured at 610  $m\mu$  at appropriate intervals of time. Figure 4 shows that a nearly constant absorbance is observed for the shaking time of more than 10 min.

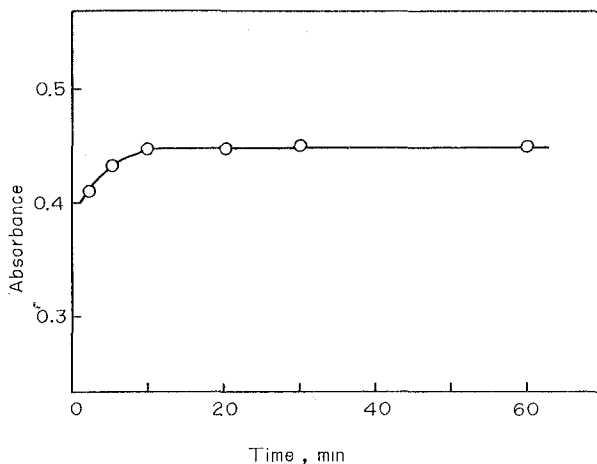


Fig. 4. Effect of shaking time.  
V: 40  $\mu$ g, wavelength: 610  $m\mu$ .

**Stability.**

The absorbances of a sample solution, prepared under the optimum condition,

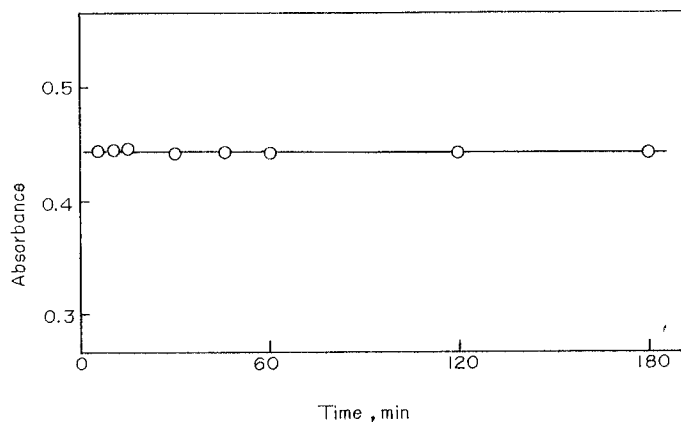


Fig. 5. Effect of standing time.  
V: 40  $\mu$ g, wavelength: 610  $m\mu$ .

were measured as a function of storage time after the preparation of the solution. There was no change of absorbance until 3 hours, as shown in Fig. 5.

#### Calibration.

To ascertain the adherence of the system to Beer's law, a calibration curve was prepared by coprecipitating different amounts of vanadium with 0.3 g of *o*-phenylphenol as 8-hydroxyquinolate. The absorbances of each solution were measured at 610  $m\mu$  against a blank which had been treated in a similar manner. The data showed a linear relationship between concentration and absorbance over the 10 to 60  $\mu$ g range of vanadium, as shown in Fig. 6. This calibration curve was in good agreement with the curve which was made by extracting vanadium with 8-hydroxy-

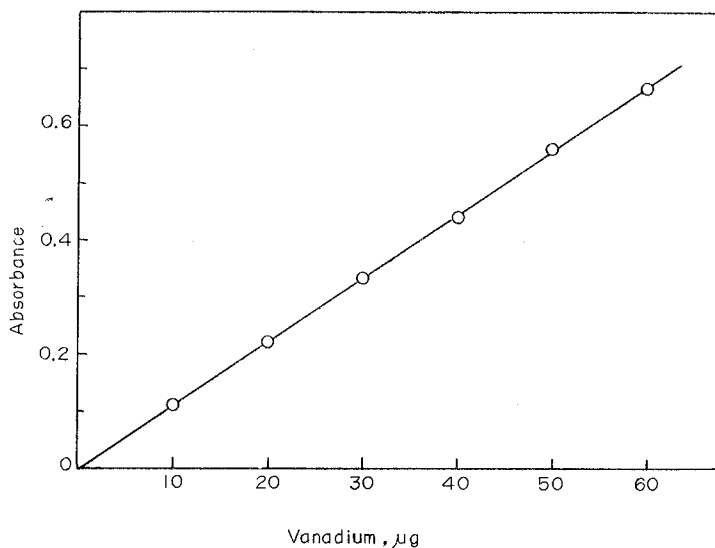


Fig. 6. Calibration curve of vanadium.  
wavelength: 610  $m\mu$ .

quinoline into 10 ml of chloroform with 0.3 g of the coprecipitant from 50 ml of the aqueous solution. This shows that the recovery of vanadium is almost quantitative.

### The Effect of Diverse Ions.

In order to test the effect of diverse ions upon the vanadium determination, absorbance measurements were made for the solutions containing 40  $\mu\text{g}$  of vanadium and the various diverse ions. The pH value of the solution was adjusted to 4.00. The results are presented in Table I. Of the diverse ions tested, ferric ion interfered especially because it became a black solution. Bismuth and zirconium also interfered because of the formation of hydroxide.

Table 1. Effect of diverse ions.

| Ion     | Added, mg | V found*, $\mu\text{g}$ |
|---------|-----------|-------------------------|
| Al $3+$ | 0.2       | 41                      |
| Bi $3+$ | 0.1       | 40                      |
|         | 0.5       | 32                      |
| Co $2+$ | 0.5       | 38                      |
| Cr $3+$ | 1.0       | 39                      |
| Cu $2+$ | 0.1       | 41                      |
| Ca $2+$ | 1.0       | 40                      |
| Cd $2+$ | 0.1       | 39                      |
| Eu $3+$ | 1.0       | 40                      |
| Fe $3+$ | 0.01      | 45                      |
|         | 0.005     | 42                      |
| In $3+$ | 0.1       | 40                      |
| Mg $2+$ | 1.0       | 40                      |
| Mn $2+$ | 0.5       | 40                      |
| Mo $6+$ | 0.1       | 40                      |
| Ni $2+$ | 1.0       | 40                      |
| Pb $2+$ | 1.0       | 39                      |
| Sb $3+$ | 1.0       | 39                      |
| Sc $3+$ | 1.0       | 41                      |
| Sn $4+$ | 0.1       | 39                      |
| Sr $2+$ | 1.0       | 40                      |
| Ti $4+$ | 0.02      | 41                      |
| Zn $2+$ | 0.1       | 39                      |
| Zr $4+$ | 0.1       | 33                      |

\* 40  $\mu\text{g}$  of vanadium ion was taken.

### The Effect of the Volume of the Aqueous Solution.

The recovery of vanadium was examined by varying volumes of the sample solution and the amounts of *o*-phenylphenol. As Table II shows, a nearly quantitative recovery was obtained when the coprecipitant increased as the volume of the sample solution increased, though the recovery lowered a little in the 4 l sample solution.

Table 2. The effect of the volume of the solution and the amount of coprecipitant.

| Volume, l | Coprecipitant, g | Recovery, % |
|-----------|------------------|-------------|
| 1         | 1                | 100         |
| 2         | 2                | 98          |
| 3         | 3                | 98          |
| 4         | 3.5              | 94          |

## REFERENCES

- (1) H.V. Weiss and M.G. Lai, *Anal. Chem.*, **32**, 475 (1960).
- (2) H.V. Weiss, M.G. Lai and A. Gillespie, *Anal. Chim. Acta*, **25**, 550 (1961).
- (3) H.V. Weiss and M.G. Lai, *ibid.*, **28**, 242 (1963).
- (4) V.I. Kuznetsov, in "Radioisotopes in Scientific Research," Vol. II (ed. R.C. Extermann), Pergamon Press, London (1958), pp. 264-283.
- (5) S. Hirano, A. Mizuike and Y. Ujihira, *Bunseki Kagaku (Japan Analyst)*, **12**, 160 (1963).
- (6) Y. Ujihira, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 642 (1963).
- (7) Y. Ujihira, *Bunseki Kagaku (Japan Analyst)*, **14**, 399 (1965).
- (8) Y. Ujihira and E. Niki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 620 (1966).
- (9) M. Matsui, M. Munakata and T. Shigematsu, *This Bulletin*, **45**, 273 (1967).
- (10) T. Shigematsu, M. Matsui, M. Munakata and T. Sumida, *Bull. Chem. Soc. Japan*, **41**, 609 (1968).
- (11) T. Shigematsu, M. Tabushi, M. Matsui and M. Munakata, *ibid.*, **41**, 1610 (1968).
- (12) N.A. Talvitie, *Anal. Chem.*, **25**, 604 (1953).