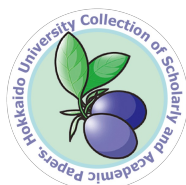




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Spectrophotometric Study of a Vanadium (V)-4-(2-pyridylazo)-resorcinol-CDTA System

Application for the Determination of Vanadium in Petroleum

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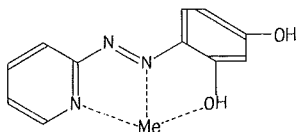
Abstract

A highly selective and sensitive spectrophotometric method for vanadium determination in petroleum, based on its color reaction with 4-(2-pyridylazo)-resorcinol and vanadium (V), is described. The colored complexes has its absorption maximum at $545\text{ m}\mu$ and its absorbance is constant at a pH range of 5.7 to 7.1 in 0.05 M phosphate buffer solution containing cyclohexandiaminetetra-acetic acid (CDTA). Beer's law is applicable up to $0.8\text{ }\mu\text{g V/ml}$ and the sensitivity of this method is $0.0014\text{ }\mu\text{g of V/cm}^2$. In the presence of CDTA this method is almost specific for vanadium (V), because other metal ions are screened out and do not interfere with the determination.

1. Introduction

Many methods for the spectrophotometric determination of vanadium in petroleum have been proposed¹⁻⁸⁾. The phosphotungstate²⁾ and hydrogenperoxide³⁾ methods have been used extensively. However, a more selective and sensitive method is in demand.

A metallochromic indicator 4-(2-pyridylazo)-resorcinol (PAR)⁷⁾



has also been proposed as a highly sensitive reagent for the colorimetric determination of a number of metals including uranium⁸⁾, lead⁸⁾, cobalt^{8),9)}, nickel¹⁰⁾, gallium^{11),12)}, niobium^{13),14)}, iron (III)¹⁵⁾, iron (II)¹⁶⁾, manganese¹⁷⁾, scandium^{18),19)}, and indium^{20),21)}. It is evident that 4-(2-pyridylazo)-resorcinol (PAR) shows only a slight selectivity, except for the reaction with iron (II) in city water samples, which is almost specific in the presence of ethylenediaminetetra-acetic acid (EDTA)¹⁶⁾. For other metals PAR can be used only in special cases, e.g., after separation of interfering metals by solvent extraction, ion exchange chromatography etc.

Recently, Shijo *et al.*²²⁾ and Kawahata *et al.*²³⁾ reported on the color reaction of PAR with vanadium (V) in citrate buffer solution (pH=6.8) and phosphate buffer

solution (pH=6.0 and 6.5), respectively. In their methods some metal ions can be masked with phosphate and citrate, however many heavy metal ions strongly interfere with the color reaction, especially, copper, nickel, iron (III), cobalt, zinc, chromium, mercury, tantalum and silver. Shijo *et al.*²²⁾ recommended this method for determination of vanadium after separation by ion exchange, however the method is complicate and time consuming.

The present authors showed that cyclohexandiaminetetra-acetic acid (CDTA) has only a very small effect on the color reaction of vanadium (V) with PAR and completely suppresses the color reaction of interfering metals such as mentioned above in moderate amounts²⁴⁾. Based on these results, a very simple method for a highly selective and sensitive determination of vanadium (V) in the presence of CDTA was proposed. Details of this method are described in the present paper.

2. Experimental

2.1 Reagents

0.1% PAR solution: Prepared by dissolving 0.1 g of PAR reagent (Dojindo Co. Ltd., Kumamoto, Japan) in 1 ml of 1 N sodium hydroxide solution and diluting to 100 ml with distilled water.

0.01 N CDTA solution: Prepared by dissolving 3.46 g of CDTA in 30 ml of 1 N sodium hydroxide solution and diluting it to 1 liter.

Buffer solution, pH=6.5: Prepared by mixing 0.5 M sodium monohydrogen phosphate and 0.5 M sodium dihydrogen phosphate solution.

Vanadium (V) solution: A stock solution (V: 1.0 g/l) was prepared by dissolving 0.234 g of NH_4VO_3 in 50 ml of 1:10 sulfuric acid solution and diluting it to 100 ml. A working standard solution was prepared by diluting 1 ml of this stock solution to 100 ml with distilled water. One milliliter of this solution contains 10 μg of vanadium.

All reagents were of analytical-grade purity.

2.2 Apparatus

Hitachi 124 type grating spectrophotometer with 1 cm quartz cells was used for recording the absorption spectra and for absorbance measurement. All pH measurements were made with a Toadenpa HM-5A pH meter with a glass electrode.

2.3 Procedure

Transfer 5~20 ml of slightly acidic sample solution containing 2~40 μg of vanadium (V) to a 50 ml graduated flask and add 4 ml of 0.01 M CDTA solution and 5 ml of phosphate buffer solution (pH=6.5) and mix well. Then, add 2 ml of 0.1% PAR solution and dilute to 50 ml with distilled water. After 5 minutes, measure the absorbance of the solution on a spectrophotometer at 545 m μ against a reagent blank containing the same concentration of PAR.

3. Results and discussion

3.1 Absorption spectra

In a slightly acidic to neutral medium vanadium forms a water soluble red complex with PAR (Fig. 1). The maximum absorption takes place at 545 m μ . The

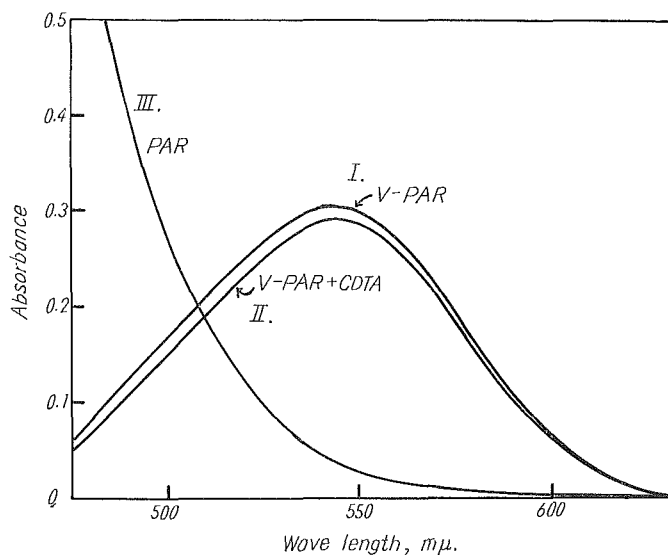


Fig. 1. Absorption spectra of the vanadium (V)-PAR complex and reagent blank (20 μg of V^{5+} ; 2 ml of 0.1% PAR solution).

I. Vanadium-PAR complex in the absence of CDTA, II. Vanadium-PAR complex in the presence of 40 μmol of CDTA, and III. Reagent blank in the presence of 40 μmol of CDTA in 50 ml.

molecular extinction coefficient was calculated from the curve I in Fig. 1 ($\epsilon_{545} = 3.8 \times 10^4$), classifying this coloration as one of the most sensitive reactions for vanadium (V). In the presence of CDTA, the absorbance of the solution is slightly decreased, but the shape of the absorption spectrum shows no changes. This result suggests that the forms of the PAR-vanadium (V) complexes are the same in both solutions with or without CDTA.

3.2 Composition and stability of the complex

Continuous variation plots, measuring the absorbance at 545 $\text{m}\mu$ (Fig. 2), shows the existence of the complex with a molar ratio of 1:1, V:PAR.

From the data shown in Fig. 2, curve I, conditional stability constant of vanadium-PAR complex, $K_{\text{V-PAR}}^{\text{con}}$ is evaluated as 5×10^5 .

$$K_{\text{V-PAR}}^{\text{con}} = \frac{[\text{VO}_2\text{PAR}]}{[\text{V}]_i [\text{PAR}]_i} \quad (1)$$

where $[\text{V}]_i$ = Total concentration of vanadium not bound to PAR
 $= [\text{VO}_2^+] + \sum [\text{V-phosphate complex}] = [\text{V}]_{\text{total}} + [\text{VO}_2\text{PAR}]$
 $[\text{PAR}]_i$ = Total concentration of PAR not bound to vanadium
 $= [\text{PAR}]_{\text{total}} - [\text{VO}_2\text{PAR}]$

The stability constant of the complex, $K_{\text{V-PAR}}$ can be expressed as the function of acid dissociation constant of PAR, $K_{\text{PAR}}^{\text{H}} (= 10^{-12.5})^{25}$, and the over all stability constants of vanadium (V)-phosphate complexes, β_n ,

$$K_{\text{V-PAR}} = K_{\text{V-PAR}}^{\text{con}} \left\{ 1 + \beta_n [\text{H}_x\text{PO}_4^{(3-x)}]^n \right\} \left\{ 1 + \frac{[\text{H}^+]}{K_{\text{PAR}}^{\text{H}}} \right\} \quad (2)$$

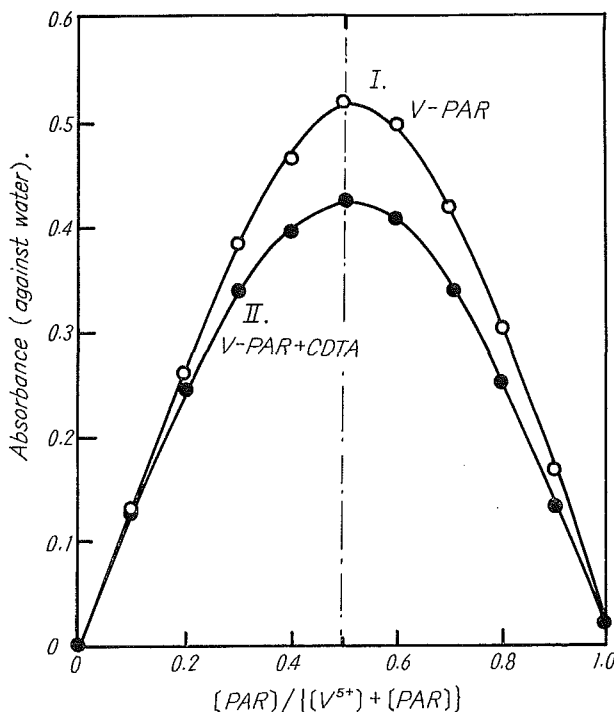


Fig. 2. Continuous variation plots for vanadium (V)-PAR complex at pH 6.5 in 0.05 M phosphate buffer solution. Total concentration of vanadium and PAR is 3.93×10^{-5} M.

I. In the presence of $40 \mu\text{mol}$ of CDTA in 50 ml
and II. In the absence of CDTA.

The exact value of K_{V-PAR} can not be obtained because of the lack of available data concerning the forms and the stability of phosphate complexes. However, considering that the last term of equation (2) is the order of 10^6 at pH=6.5 and assuming that the stability of the phosphate complexes is not so large, the value of K_{V-PAR} seems to be somewhat larger than the order of 10^{12-13} . This result suggests that the stability of the vanadium (V)-PAR complex is a similar order to that of the cobalt (II)-, nickel-, and zinc-PAR complexes²⁵.

3.3 Influence of pH on the absorbance

Results for the dependence of the absorbance on pH are shown in Fig. 3. The optimum pH-range for the formation of PAR-vanadium (V) complex in the presence of CDTA is 5.7 to 7.1.

3.4 Influence of CDTA and PAR concentration on the stability of the complex

The coloration develops slowly, reaching a maximum within 5 minutes after an addition of PAR at room temperature and remains stable for at least 30 minutes. The absorbance is slightly smaller than the value found in the absence of CDTA. However, its reproducibility is excellent under identical conditions. The decrease in absorbance corresponds to the concentration of CDTA almost linearly as shown in Fig. 4.

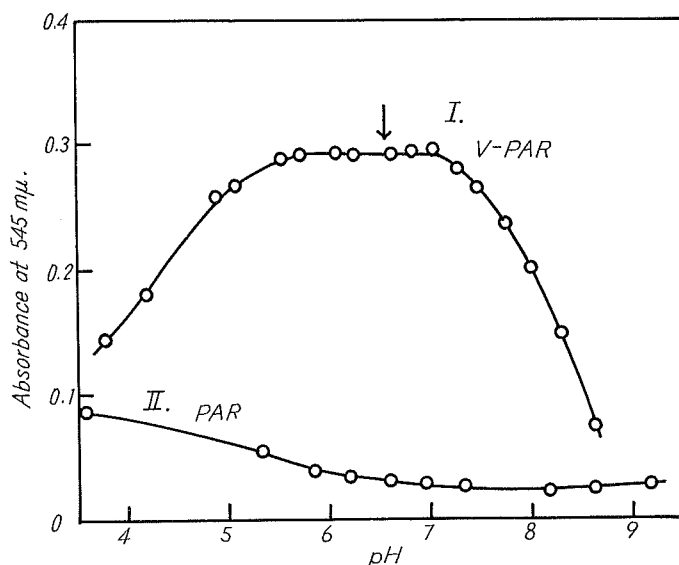


Fig. 3. Dependence of the absorbance of vanadium (V)-PAR complex and reagent blank on pH ($20 \mu\text{g}$ of V^{5+} ; 2 ml of 0.1% PAR solution; 4 ml of 0.01 M CDTA solution; at $545 \text{ m}\mu$.
I. Vanadium-PAR complex and II. Reagent blank.

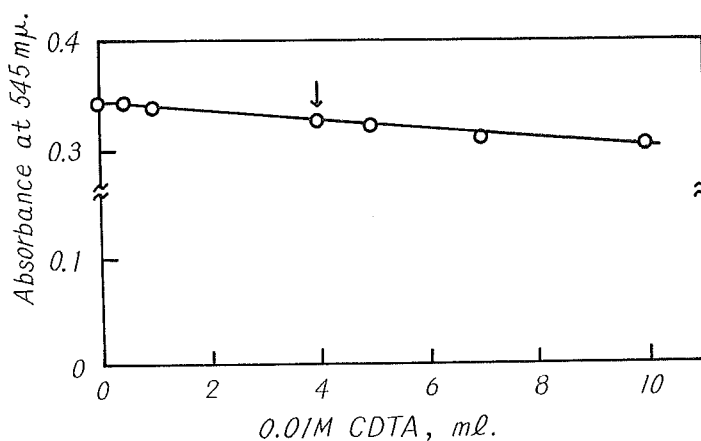


Fig. 4. Influence of CDTA on the absorbance of vanadium-PAR complex ($20 \mu\text{g}$ of V^{5+} ; 2 ml of 0.1% PAR solution; at $545 \text{ m}\mu$).

The absorbance of the color reaction also depends upon the concentration of PAR (Fig. 5), reaching a maximum value with 1.5 ml of 0.1% PAR solution (corresponds to about 15-fold excess in PAR) in the presence of $40 \mu\text{mol}$ of CDTA in the solution.

Conditional equilibrium constant K of the color reaction,



calculated from the data in Fig. 2, 4 and 5 by considering the existence of phosphate ion at pH 6.5, is found to be

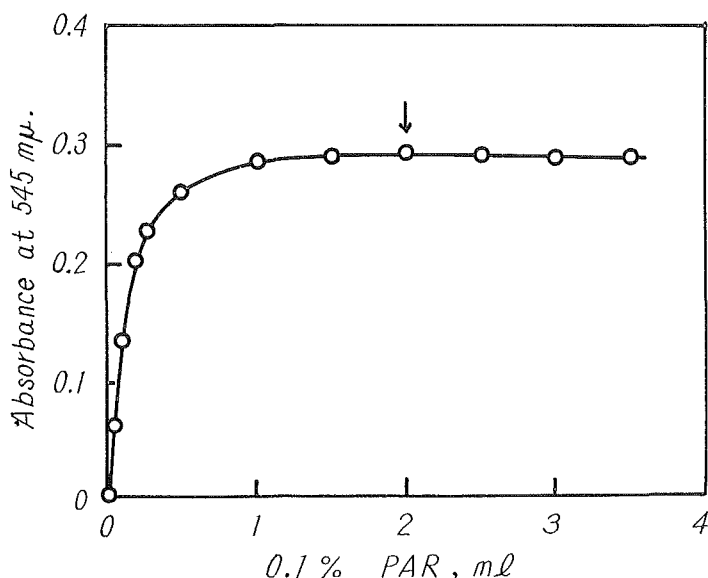


Fig. 5. Influence of the excess of PAR on the absorbance of vanadium (V)-PAR complex ($20 \mu\text{g}$ of V^{5+} ; 4 ml of 0.01 M CDTA solution; at $545 \text{ m}\mu$).

$$K = \frac{[\text{VO}_2\text{PAR}][\text{CDTA}]}{[\text{VO}_2\text{CDTA}][\text{PAR}]} = 10^{2.35 \pm 0.25} \quad (4)$$

where CDTA and PAR denote the total concentration of the species which is not bound to vanadium, respectively. Combining the value of K and $K_{\text{V-PAR}}^{\text{con}}$, conditional stability constant of vanadium (V)-CDTA complexes, $K_{\text{V-CDTA}}^{\text{con}}$, can be calculated.

$$K_{\text{V-CDTA}}^{\text{con}} = \frac{K_{\text{V-PAR}}^{\text{con}}}{K} = 10^{3.4} \quad (5)$$

Thus, in conditions, $[\text{CDTA}]/[\text{PAR}] = 4/1$, the absorbance may be almost independent of the nature of other metal ions present within certain limits of concentrations. This was confirmed by the results shown in Table I.

3.5 Calibration curve

The calibration curve for the determination of vanadium with PAR shows a good linearity for a concentration between 2 and $40 \mu\text{g}$ of vanadium/ 50 ml (Fig. 6). The sensitivity, Sandell Index, is $0.0014 \mu\text{g}$ of V/cm^2 at $545 \text{ m}\mu$. The sensitivity of this method is the largest among those of the other spectrophotometric methods of the greatest analytical importance, e.g., phosphotungstate method¹⁾ ($0.027 \mu\text{g}/\text{cm}^2$), hydrogen peroxide method²⁾ ($0.12 \mu\text{g}/\text{cm}^2$), 8-quinolinolate extraction method⁴⁾ ($0.0069 \mu\text{g}/\text{cm}^2$) and xlenol orange method⁶⁾ ($0.0026 \mu\text{g}/\text{cm}^2$).

3.6 Determination of vanadium (V) in the presence of other metal ions

The influence of foreign ions has been ascertained by the proposed procedure. Some results are given in Table I. These common ions in moderate amounts are screened by CDTA and do not interfere with the color reaction. Such screening behavior of CDTA is similar to that reported by Budevsky et. al.⁶⁾ in the xlenol

TABLE I. Determination of vanadium (V) in the presence of diverse metal ions

Foreign ion		Vanadium (V), μg		Differences μg
Form added	μg	Taken	Found	
None	—	10	10.0	0
	—	20	20.0	0
	—	30	29.7	- 0.3
	—	40	39.3	- 0.7
Ag (I) AgNO_3	100	20	20.8	0.8
	200	20	21.1	1.1
	500	20	Red ppt.	—
Al (III) $\text{KAl}(\text{SO}_3)_2$	500	20	20.2	0.3
	1000	20	White ppt.	—
Co (II) $\text{Co}(\text{NO}_3)_2$	500	20	20.2	0.2
Cr (III) $\text{Cr}(\text{NO}_3)_3$	500	20	19.9	- 0.1
Cu (II) $\text{Cu}(\text{NO}_3)_2$	100	20	20.2	0.2
	500	20	20.6	0.6
Fe (III) $\text{Fe}(\text{NO}_3)_3$	100	20	19.9	- 0.1
	500	20	19.9	- 0.1
Mg (II) MgCl_2	1000	20	20.8	0.8
Mn (II) MnCl_2	1100	20	20.2	0.2
Mo (VI) $(\text{NH}_4)_2\text{MoO}_4$	1000	20	20.0	0
Ni (II) NiSO_4	500	20	20.1	0.1
Pb (II) $\text{Pb}(\text{NO}_3)_2$	500	20	20.3	0.3
Hg (II) HgCl_2	100	20	20.7	0.7
	500	20	20.9	0.9
Sn (II) SnCl_2	500	20	20.6	0.6
	1000	20	19.4	- 0.6
Zn (II) ZnCl_2	100	20	20.0	0
	500	20	20.1	0.1
EDTA ⁴⁻ Na_2EDTA	40 μmol	20	0.8	- 19.2

orange method. In the xylenol orange method, 0.4 μmol of MoO_4^{3-} ion interfere with the determination⁶⁾, but in our PAR method at least up to 10 μmol of MoO_4^{2-} ions do not interfere as shown in Table I.

For the determination of total vanadium in a sample containing vanadium of other valence states than V, the following procedure is recommended: oxidize the vanadium to the valence state V with potassium permanganate in a diluted sulfuric acid solution at 70~80°C and then reduce the excess permanganate ion with sodium nitrite. Then, the sulfuric acid in the solution is neutralized and vanadium (V) is determined by the recommended procedure. Manganese added in the above procedure does not interfere with the determination as shown in Table I.

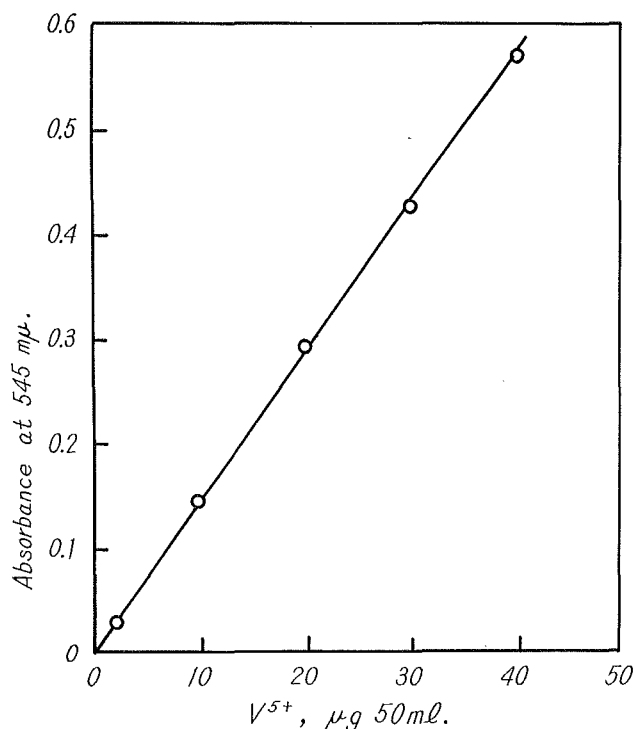


Fig. 6. Calibration curve.

3.7 Determination of vanadium in petroleum

Treat a petroleum sample, estimated to contain a minimum of 2.0 μg of vanadium, with the wet oxidation method proposed in our previous paper²⁶⁾, and obtain an inorganic salt solution. After oxidizing the vanadium to the valence state V by the procedure recommended above, vanadium is determined by the proposed procedure. Some results are given in Table II. The results obtained by our method are in good agreement with the standard method of ASTM (phosphotungstate method)²⁷⁾.

TABLE II. Determination of vanadium in petroleum*

No.	ASTM Method ²⁷⁾	PAR Method
1	26.0 ppm	26.2 ppm
2	26.4	26.0
3	26.6	25.9
4	27.0	26.2
5	26.6	26.3
6	26.4	26.1
average	26.5 ppm	26.1 ppm

* petroleum sample: Kuwait crude oil.

3.8 Precision

An estimate of the precision of this method is ascertained from the results of 10 samples, each containing 20.0 μg of vanadium. These samples give a mean absorbance of 0.290 at 545 $\text{m}\mu$. The standard deviation was 0.003 absorbance unit, or a relative standard deviation of 1%.

4. Conclusions

The proposed PAR method with CDTA as a masking agent, being highly selective and sensitive, can be successfully applied to the determination of trace amounts of vanadium in various samples such as in petroleum and in biological samples and in water.

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