Study on Solid Phase Extraction and Spectrophotometric Determination of Vanadium with 2-(2-Quinolylazo)-5-Diethylaminophenol

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A sensitive, selective and rapid method has been developed for the determination μg/L level of vanadium ion based on the rapid reaction of vanadium(V) with 2-(2-quinolylazo)-5-diethylaminophenol (QADEAP) and the solid phase extraction of the colored chelate with C_{18} cartridge. The QADEAP reacts with V(V) in the presence of citric acid-sodium hydroxide buffer solution (pH = 3.5) and cetyl trimethylammonium bromide (CTMAB) medium to form a violet chelate of a molar ratio 1 : 2 (V(V) to QADEAP). This chelate was enriched by solid phase extraction with C_{18} cartridge and the enrichment factor of 50 was obtained by elution of the chelates from the cartridge with ethanol. The molar absorptivity of the chelate is 1.28×10^5 L mol^{-1} cm^{-1} at 590 nm in the measured solution. Beer's law is obeyed in the range of 0.01-0.6 μg/mL. The detection limit is 0.04 μg/L in the original samples. This method was applied to the determination of vanadium(V) in water and biological samples with good results.

Key Words : 2-(2-Quinolylazo)-5-diethylaminophenol, Vanadium, Spectrophotometry, Solid phase extraction

Introduction

Vanadium is an important element, not only for industry, but for biological systems as well.[1,2] Therefore, a wide variety of spectrophotometric methods for the determination of vanadium have been reported.[3-11] Each chromogenic system has its advantages and disadvantages with respect to sensitivity, selectivity and rapidity. In previous work, some 2-quinolylazo reagents were reported for the determination of metal ions.[12-16] This type of reagent has higher sensitivity than pyridylazo reagents because of its larger conjugated system. However, the utilization of 2-quinolylazo reagents for the determination of vanadium has not been reported yet. In this paper, we firstly studied the color reaction of QADEAP with vanadium(V) and the solid phase extraction of the colored chelate with C_{18} cartridge. Based on this, a highly sensitive, selective and rapid method for the determination of vanadium in water and biological samples was developed.

Experimental Section

Apparatus. A UV-160A spectrophotometer (Shimidzu, Japanese) equipped with a 1 cm microcell (0.5 mL) was used for all absorbance measurements. The pH values were determined with a Beckman Φ-200 pH meter. The extraction was performed on a Waters Solid Phase Extraction (SPE) Device (It is able to prepare twenty samples simultaneously), and Waters Sep-Pak C_{18} cartridge (1 cc/30 mg, 30 μm) (Waters corporation, USA) was used in this Experiment.

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Chemicals. All of the solutions were prepared with ultrapure water obtained by a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). High purity ethanol (Fisher Corporation, USA) was used. QADEAP was synthesized by our laboratory as following procedure: 2-aminoquinoline (6.9 g; 0.048 mol) was dissolved in 500 mL anhydrous ethanol. To which, sodamide (2.0 g; 0.051 mol) was added and the mixture was refluxed in boiling water bath for 5 h, followed by the addition of isoamyl nitrite (7.4 mL). The solution was refluxed for 30 min with boiling water bath, then the solution was cooled and placed over night under 0 ℃. The diazo salt was obtained by filtering this solution with an isolation yield of 92%. The diazo salt was dissolved in 200 mL anhydrous ethanol, followed by the addition of *m*-diethylaminophenol (6.6 g; 0.042 mol). The carbon dioxide was ventilated into the solution with stirring until the pH reaches to about 8.0. The solution stood for two days, then diluted the solution with 400 mL water and extracted with chloroform. The chloroform was evaporated and the residue was re-crystallized with 30% ethanol. The QADEAP was obtained with a yield of 28%. The structure of QADEAP was verified by elemental analysis, IR, ^{1}H NMR, and MS. Elemental analysis: $C_{19}H_{20}N_4O$ found (calculated) C 71.06 (71.23), N 17.13 (17.49), H 6.47 (6.29). IR (KBr) (cm^{-1}): 3610 ($\nu_{\text{-O-H}}$); 1050 ($\nu_{\text{-C-O-}}$); 1615, 1570, 1510, 1420 ($\nu_{\text{-C=C-, -N=N-}}$); 1375, 1326 ($\nu_{\text{C-N}}$); 2920, 2873 ($\nu_{\text{C-H}}$); 1465, 1380 ($\delta_{\text{C-H}}$); 3070, 3016 ($\sigma_{\text{Ar-H}}$); 1175, 1120, 865, 775, 730 ($\delta_{\text{Ar-H}}$). ^{1}H NMR (solvent: d_6-acetone) (δ ppm): 1.25 (t 6H, C-CH_3); 2.75 (q 4H, N-CH_2-); 2.25 (s 1H, -OH); 6.86-7.85 (m 9H, Ar-H). MS: 320 (M^+).

A 1.0×10^{-4} mol/L of QADEAP solution was prepared by dissolving QADEAP with 95% ethanol. A stock standard solution of vanadium (1.0 mg/mL) was obtained from

Chinese Standard Center, and a work solution of 0.2 μg/mL was prepared by diluting this solution. Citric acid-sodium hydroxide buffer solution (0.5 mol/L, pH = 3.5 (containing 0.1 mol/L Na_2EDTA and 0.5 mol/L NH_4F)) was prepared by dissolving 86 g of citric acid ($C_6H_8O_7$), 32.7 g of ethylenediamine tetraacetic acid disodium salt ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$) and 20.5 g NH_4F in 600 mL of water, then the solution was neutralized to pH 3.5 with 20% sodium hydroxide, and diluted to the volume of 1000 mL. Cetyl trimethylammonium bromide (CTMAB) solution (1.0%(w/v)) was prepared by dissolving CTMAB with 20% ethonal. All chemical used were of analytical grade unless otherwise stated.

Standard procedure. To a standard or sample solution containing no more than 1.2 μg of V(V) in a 100 mL of calibrated flask, 5 mL of citric acid-sodium hydroxide buffer solution (containing 0.1 mol/L Na_2EDTA and 0.5 mol/L NH_4F), 5.0 mL of 1.0×10^{-4} mol/L QADEAP solution and 3.0 mL of 1.0% CTMAB solution were added. The mixture was diluted to volume of 100 mL and mixed well. After 10 min, the solution passed through the C_{18} cartridge at a flow rate of 20 mL/min. The colored chelate would be retained on the cartridge. After the enrichment had finished, the retained chelates was eluted from the cartridge with 2.0 mL of ethanol at a flow rate 5 mL/min in reverse direction, and the eluent was adjusted to the accurate volume of 2.0 mL in a 2.0 mL calibrated flask by adding microamount of ethanol with a 500 μL syringes. The absorbance of this solution was measured at 590 nm in a 1 cm cell against a reagent blank prepared in a similar way without vanadium.

Results and Discussion

Absorption spectra. The absorption spectra of QADEAP and its V(V) complex under the optimum conditions are shown in Figure 1. The absorption peaks of QADEAP and its complex at pH 3.5 are located at 468 nm and 590 nm.

Effect of acidity. Results showed that the optimal pH for the reaction of V(V) with QADEAP is 2.2-4.0. A citric acid-sodium hydroxide buffer solution of pH 3.5 was recommended to control pH. As the use of 3.5-7.0 mL of the buffer solution (pH 3.5) per 100 mL of final solution was found to give a maximum and constant absorbance. The use of 5.0 mL buffer solution was recommended. The buffer solution containing 0.08-0.15 mol/L of Na_2EDTA and 0.4-0.6 mol/L of NH_4F could markedly increase the selectivity of this system. (Without Na_2EDTA and NH_4F in the buffer solution, the tolerance limits of foreign ions were 0.01 mg for Cu(II), Fe(III), Zn(II); 0.005 mg for Sn(IV), Pd(II), Co(II), Ni(II). However, the tolerance limits of foreign ions reached 3 mg for Fe(III); 0.3 mg for Cu(II), Zn(II); 0.1 mg for Co(II), Ni(II), Sn(IV); 0.05 mg for Pd(II) when Na_2EDTA and NH_4F existed in the buffer solution). Therefore, 0.1 mol/L of Na_2EDTA and 0.5 mol/L of NH_4F in the buffer were recommended.

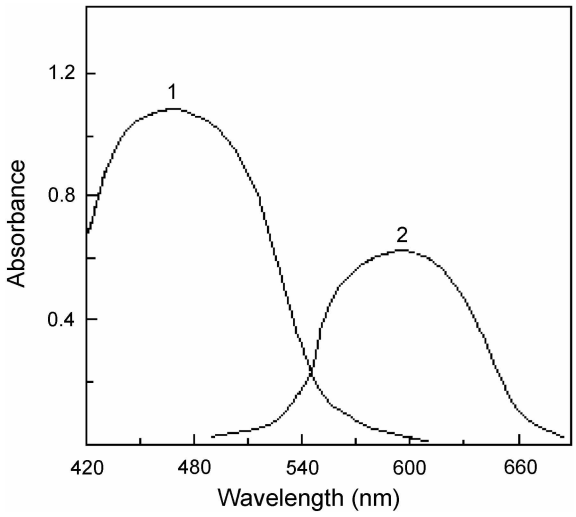

Figure 1. Absorption spectra of QADEAP and its V(V) complex: 1 QADEAP-CTMAB blank against water. 2 QADEAP-V(V)-CTMAB complex against reagent blank.

Effect of surfactants. The V(V)-QADEAP complex has a poor solubility in water solution. It is need to add a suitable amount of surfactants to enhance the solubility of the complex. Experiments showed that all the anionic surfactants, nonionic surfactants and cationic surfactants have good effect to enhance the solubility. In addition to enhance the solubility, in the nonionic surfactants and cationic surfactants medium, the sensitivity of the V(V)-QADEAP chelates was increased markedly too. The effect of the nonionic surfactants and cationic surfactants improving the sensitivity is shown in Table 1. The results show that CTMAB was the best additive and the use of 2.0-5.0 mL of CTMAB gives a constant and maximum. Accordingly, 3.0 mL CTMAB solution was recommended.

Effect of QADEAP concentration. For up to 1.2 μg of V(V), the use of about 5 mL of 1.0×10^{-4} mol/L of QADEAP solution has been found to be sufficient for a complete reaction. Accordingly, 5.0 mL of QADEAP solution was added in all further measurement.

Stability of the chromogenic system. After mixing the components, the absorbance reaches its maximum within 10 min at room temperature and remains stable for at least 16 h. When extracted into the ethanol medium, the chelate can keep stable at least 12 h.

Solid phase extraction. Both the enrichment and the elution were carried out on a Waters SPE device (It is able to prepare twenty samples simultaneously). The flow rate was set to 20 mL/min for enrichment and 5 mL/min for elution.

Table 1. The effect of surfactants on V(V)-QADEAP chromogenic system

Surfactant	Absence	CTMAB	CPB	TritonX-100	Emulsifier-OP	Tween-80	Tween-20
λ_{max} (nm)	584	590	590	586	586	586	586
ε ($\times 10^4$) L mol^{-1}.cm^{-1}	8.85	12.8	11.2	9.17	8.92	9.22	8.76

Some experiments were carried out in order to investigate the retention of QADEAP and its V(V) chelate on the cartridge. It was found that the QADEAP and its V(V) chelate could be retained on cartridge quantitatively when they pass the cartridge as aqueous solution. The capacity of the cartridge for QADEAP was 18 mg and for its V(V) chelate was 16 mg in a 100 mL of solution. In this experiments. the cartridge has adequate capacity to enrich the V(V)-QADEAP chelate and the excess QADEAP.

In order to choose a proper eluent for the retained QADEAP and its V(V) chelate. various of organic solvents were studied. It was found that the tetrahydrofuran. acetone. acetonitrile. ethanol and methanol could elute the QADEAP and its V(V) chelate from cartridge quantitatively. The ethanol has a low volatility. toxicity and price. so ethanol was selected as eluent. Experiment show that it was easier to elute the retained QADEAP and its V(V) chelate in reverse direction than in forward direction. so it is necessary to upturned cartridge during elution. 2.0 mL of ethanol was sufficient to elute the QADEAP and its V(V) chelate from cartridge at a flow rate of 5 mL/min. The volume of 2.0 mL eluent was used in this experience.

Calibration curve and sensitivity. The calibration curve shown that Beer's law is obeyed in the concentration range of 0.01-0.6 μg V(V) per mL in the measured solution. The linear regression equation obtained was: A = 2.512 C (μg/mL) + 0.0206, (r = 0.9994). The molar absorptivity was calculated to be 1.28×10^5 L·mol^{-1}·cm^{-1} at 590 nm. The relative standard deviation at a concentration level of 0.04 μg of V(V) per mL (11 repeat determination) was 1.68%. The detection limit is 0.04 μg/L in original samples.

Composition of the complex. The composition of the complex was determined by continuous variation and molar ratio method. Both showed that the molar ratio of V(V) to QADEAP is 1 : 2.

Interference. The selectivity of the proposed method was investigated by the determination of 1.0 μg/100 mL V(V) in the presence of various ions within a relative error of ± 5%.

Table 2. Tolerance limits for the determination of 1.0 μg of V(V) with QADEAP (Relative error ± 5%)

Ion added	Tolerate (mg)
NO_3^-, K^+, borate, tartaric acid	80
Li^+, Al^{3+}, PO_4^{3-}, SO_4^{2-}, ClO_4^-, oxalic acid, CO_3^{2-}, ClO_4^-	20
Ca^{2+}, Mg^{2+}, SO_3^{2-}, Sr^{2-}, Ba^{2+}, IO_3^-, BrO_3^-, B(III), ClO_3^-, Fe^{3+}	3
Mn^{2+}, Ce(IV), W(WI), Mo(VI), Cr^{3-}, Fe^{2-}	1
Ti(IV), Bi(III), Cr(VI), Zr(IV), Zn^{2+}, Cu^{2-}	0.3
Tl (III), Cd^{2+}, La^{3+}, Sn(IV), Co^{2+}, Ni^{2+}, (Pt(IV)*, Ag^{+*})	0.1
Ru(III), Bi(III), Pb^{2+}, Hg^{2+}, Sb^{3+}, Pd^2, Os(VIII)	0.05
Se(IV), Te(IV), Au^{3+}, $S_2O_3^{2-}$, Zr(IV), Th(IV)	0.02
Ir(IV), Rh(III), Ru(III), U(IV)	0.01
Pt(IV), Ag^+	0.005

*masking with NH_4SCN.

The results are given in Table 2. Results show that Ag(I), Pt(IV) gives a serious interfere. These interferes can be eliminated by mask with NH_4SCN. This method is highly selective.

Application. The proposed method has been successfully applied to the determination of vanadium(V) in biological samples and water samples.

For biological samples. 0.20 g of sample was weighted accurately into the Teflon high-pressure microwave acid digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai. China). 2.5 mL of concentrated nitric acid and 2.5 mL of 30% hydrogen peroxide were added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven (Model WL 5001, 1000 W. Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for 6.0 min. The digest was evaporated to near dryness. The residue was dissolved with 1% of hydrochloric acid. and the vanadium(V) contents were analyzed according to general procedure. The results are shown in Table 3.

For water sample, the samples were filtrated by 0.45 μm

Table 3. Determination of vanadium in certified standard biological samples

Sample	Standard value (μg/g)[a]	This method (μg/g)	RSD, % (n = 5)[b]
Human hair (GBW07601)	As(0.28), B(1.3), Bi(0.34), Ca(2900), Cd(0.11), Ce(1.2), Co(0.71), Cr(0.37), Cu(10.2), Fe(54), Hg(0.36), Mg(360), Mn(6.3), V(1.73), Ni(0.83), Pb(8.8)	1.81	2.4
Tea Leaf (GBW08505)	As(0.191), Ba(15.7), Ca(2840), Cd(0.032), Co(0.2), Cr(0.8), Cu(16.2), Fe(373), Hg(0.004), Mg(2240), Mn(766), Ni(7.61), V(3.12), Pb(1.06), Se(0.041), Zn(38.7)	3.05	2.1

[a]Average of five times determination results. [b]RSD was obtained from the determination of the same samples for 5 times.

Table 4. Determination of vanadium in water samples

Samples	Vanadium Found (ng/mL)		RSD% (N = 5)[b]	Average recovery %
	The Proposed Method [a]	ICP-MS Method		
Panlong River Water	32.1	35.4	2.1	97
Diangci Lake Water	43.2	44.5	2.3	102
Kunming Tap Water	26.5	23.8	2.4	98

[a]Average of five times determination results. [b]RSD was obtained from the determination of the same samples for 5 times.

filter, and the vanadium(V) contents were analyzed according to the general procedure. The results were shown in Table 4. together with the results of a recovery test by adding 0.2 μg of vanadium(V) in samples. A standard method using ICP-MS has also been used as reference method. The results are also shown in Table 4.

Conclusion

This method is highly selective and highly sensitive. QADEAP is one of the sensitive and selective spectrophotometric reagents for vanadium. The molar absorptivity of the chelate reaches 1.28×10^5 L·mol^{-1}·cm^{-1} in measured solution. Most foreign ions do not interfered with the determination when masked with Na_2EDTA and NH_4F. By solid phase extraction with C_{18} cartridge. the QADEAP-V(V) chelate in 100 mL solution can be concentrated to 2.0 mL. The detection limit is 0.04 μg/L in original samples. and μg/L level of vanadium in water can be determined with good results. The consuming of organic solvents in this method is much lower than those consumed in liquid-liquid extraction method. Because ethanol has a lower volatility and toxicity. this method is more safe than those method using other organic solvents. By using Waters SPE device. twenty samples can be prepared simultaneously. This method is rapid for simultaneously preparing large amount of sample.

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References

1. Henk. H. G.; Jaap. B.; Gerard. V. K. *Chemical Society Reviews* **2002**. *31*(6). 357-364.
2. Hogan. G. R. *Bulletin of Environmental Contamination and Toxicology* **2000**. *64*(4). 606-610.
3. Agnihotri, N.; Dass. R.; Mehta, J. R. *Chemical Analysis (Warsaw)* *44*(4). 418-425.
4. Costa. A. C. S.; Teixeira. L. S. G.; Jaeger. H. V.; Ferreira. S. L. C. *Mikrochimica Acta* **1998**. *130*. 41-45.
5. Yang. G. Y.; Yin. J. Y.; Liu. M.; Hu. Q. H. *Chinese Journal of Analytical Chemistry (Fenxi Huaxue)* **1999**. *27*(1). 10-13.
6. Starczewska. B. *Journal of Trace and Microprobe Techniques* **2002**. *20*(3). 377-384.
7. Melwanki. M. B.; Seetharamappa. J.; Masti. S. *Analytical Sciences* **2001**. *17*(8). 979-982.
8. Zhou. S. P.; Yang. G. Y.; Yin. J. Y.; Wu. C. H. *Chinese Journal of Analytical Chemistry (Fenxi Huaxue)* **2000**. *28*(7). 890-892.
9. Safavi. A.; Nezhad. M. R. *Analytica Chimica Acta* **2002**. *9*(1/2). 283-289.
10. Gavazov. K.; Simeonova. Z. H.; Alexandrov. A. *Talanta* **2000**. *52*(3). 539-544.
11. Miura. J.; Hoshion. H.; Yotsuyanagi. T. *Analytical Chimica Acta* **1990**. *233*. 121-127.
12. Ishizuki. T.; Tsuzuki. M.; Yuchi. A.; Ozawa. T.; Wada. H.; Nakagawa. G. *Analytica Chimica Acta* **1993**. *272*. 161-165.
13. Yang. G. Y.; Hu. Q. F.; Yang. J. H.; Huang. Z. J.; Yin. J. Y. *Analytical. Sciences* **2003**. *19*(2). 299-303.
14. Simgh. I.; Poonam, M. *Talanta* **1984**. *31*. 109-114.
15. Hu. Q. H.; Yang. G. Y.; Huang. Z. J.; Yin. J. Y. *Talanta* **2002**. *58*. 467-473.
16. Hu. Q. F.; Yang. G. Y.; Yang. J. H.; Yin. J. Y. *Journal of Environment Monitoring* **2002**. *4*(6). 956-959.