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Flow Injection-spectrophotometric Method for Determination of Vanadium (V) and its Applications

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Abstract: A flow injection analysis determination of Vanadium (V) In waters using molybdenum yellow method was proposed. In acid solution, Vanadium (V) substitutes molybdenum (VI) of phosphdomolybate and form a Kiggen type heteropoly acid that has an absorption maximum at 390 nm. The method bases on the positive relationship between the absorbance and the concentration of vanadium. Calibration graph for vanadium were linear in the range 0.02-1.0 μg mL^{-1}. The relative standard deviation was 0.48% for 15 determinations of 0.1 μg mL^{-1} vanadium.

Key words: FIA, vanadium, molybdenum yellow method, spectrophotometry

Introduction

Vanadium is widespread in the environment, but it occurs at very low levels in natural waters, soils and in the atmosphere. Research showed that vanadium at the ng mL^{-1} level is benefit for cell growth, but is toxic at the higher μg mL^{-1} level. Vanadium (V) and vanadium (IV) are the stable oxidation states of vanadium (Shaopu *et al*., 1985). Evidences discovered that Vanadium (V) is more toxic than vanadium (IV) (Fichet and Miramand, 1998). It is reported that vanadium has reproductive toxicity (Aragón *et al*., 2005) and embryo toxicity (Paternain *et al*., 1987). And also vanadate has a toxic effect on the myocardium (Pytkowski *et al*., 1996). Although vanadium (V) and vanadium (IV) are the stable, vanadium (IV) can easily be oxidized to Vanadium (V) by atmospheric oxygen at higher pH values (>2.0) (Okamura *et al*., 2001). Vanadium in human body has relation to some diseases; excessive intake of vanadium does have harm to the body. The Vanadium (V) in body can be deoxidized to vanadium (IV), the later can oxidize many biochemicals and produce free radicals which damage the DNA (Rojas *et al*., 1999). So it is important to monitor the concentration of vanadium (V) in natural waters and industrial wastewaters.

Vanadium in environmental samples has been determined by Neutron Activation Analysis (NAA) (Richter *et al*., 2000), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (Wuilloud *et al*., 2000), Atomic Absorption Spectrometry (AAS) (Malgorzata *et al*., 1996), catalytic method (Shao, 1997) and spectrophotometry (Ahmed *et al*., 1999). The first two methods are disadvantageous in terms of cost and instruments. AAS is often lacking in sensitivity and affected by matrix conditions of samples. Catalytic solvent extractive methods are highly sensitive but are generally lacking in simplicity.

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In this study, we proposed a FIA-spectrophotometric method for the determination of vanadium (V). Under acid condition, vanadate can substitute the molybdate of phosphdomolybate ($PMo_{12}O_{40}$ in abbr.) heteropoly acid and forms phosphdomolybdovanadoate ($PMo_{12-n}V^{V}_{n}O_{40}$ in abbr.) heteropoly acid, which is kinetically stable at low concentration of vanadium (V). The complex of $PMo_{12-n}V_{n}$ in aqueous solution is yellow and has maximum absorption at 350-400 nm wavelengths. The so-called molybdenum yellow method has been used for spectrophotometry determination of inorganic ion such as PO_4^{3-}, VO_3^{-}, for the absorption of the complex has positive relation with the concentration of PO_4^{3-} and/or VO_3^{-}. Though vanadyl also can substitute the molybdate of $PMo_{12}O_{40}$, the complex of $Pmo_{12-n}V^{IV}_{n}O_{40}$ has no absorption at 350-400 nm wavelengths, it has maximum absorption at 790-820 nm wavelengths and the method using $PMo_{12-n}V^{IV}_{n}O_{40}$ is called molybdenum blue method.

Materials and Methods

Instruments and Apparatus

ZJ-1a Metallic Element Auto-analysis Instrument (China Patent ZL 03 234986.6), invented and produced by Prof. Zhang Xinshen of the Modern analysis and Separation Research Lab, Sichuan University, Chengdu, China

- Peristaltic Pump, Huxi analysis instrument factory, Shanghai, China
- Spectrumlab S54, Lengguang technology Co., Shanghai, China
- Chromatograph N2000, Zhejiang University, Hangzhou, China
- Microprocessor pH Meter, Hanna, Italy

Reagents and Samples Preparation

All chemicals used were of analytical-reagent grade and de-ionized water was used throughout.

R1:2.200 g of Ammonium Molybdate (JDC Moly Science and Technology Co. LTD, China) dissolved and diluted to 1000 mL with de-ionized water.

R2: 2.5 mL of hydrochloric acid (Chengdu chemical engineering reagent factory, Chengdu, China) and 1.5 mL of phosphorous acid (Chengdu chemical engineering reagent factory, Chengdu, China) dissolved and diluted to 1 000 mL with de-ionized water.

I: de-ionized water, adjusted the pH to 2.0 with hydrochloric acid (1+1).

Vanadium (V) stock solution (0.10 mg mL^{-1}): 0.2296 g of Ammonium Metavanadate (Tianjin BoDi chemical engineering Co.LTD, Tianjin, China) dissolved in hot water, 1-2 mL of hydrochloric acid (1+1) was added and then diluted to 100 mL. More dilute standard solutions were prepared from this stock solution as when required and adjusted the pH 2.0 with hydrochloric acid (1+1).

Samples: Well water samples (from a leather factory located in Chengdu suburb), river water samples (from FuNan River, the mother river of Chengdu) and pool water sample (from HeHua pool in our university) were collected and filtered into polyethylene bottles. Before determination, the samples were adjusted the pH 2.0 with hydrochloric acid (1+1).

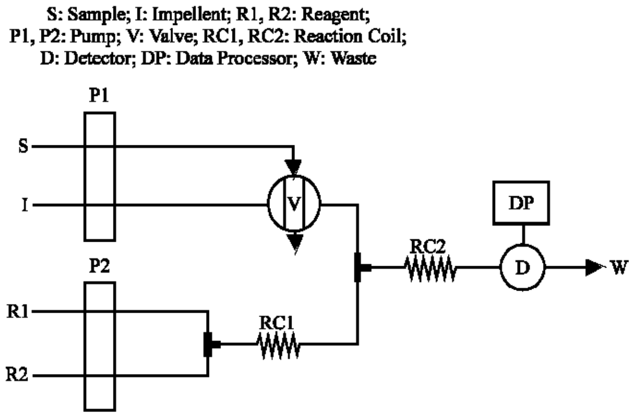

Fig. 1: Schematic of the flow injection system

Flow Injection Procedure

The manifold of the flow injection system used is shown as Fig.1. A 4-line system was used to determine the Vanadium (V). R1 and R2 were impelled to the three-way cock and mixed in RC1 to form color-developing reagent; the sample was injected into a six-way valve containing a volume control loop. When the instrument was turned to "analyze", the sample was impelled by the impellent to the three-way cock and mixed with the color-developing reagent in RC2. The colored complex was then formed and carried into the flow cell of the detector. The absorbance of the complex was measured at 390 nm. The data obtained with the chromatograph N2000 were automatically processed using SEPU1.0 software programmed by us. The tubes (0.5 mm i.d.) used were of PTFE material and the pump tubes were of silicon rubber material. The light path length of the glass flow cell was 15 mm. The flow-rate of P1 was 2.0 mL min^{-1} and P2 was 1.0 mL min^{-1}, respectively.

Results and Discussion

Reagent Concentration

The influence of reagent concentration was studied. The stability of the color developing reagent and the colored complex were investigated also.

The stability of the color-developing reagent and the colored complex was measured by their absorbance with Spectrumlab S54. The absorbance of the color-developing reagent formed from R1 and R2 was constant 0.5 min. after they were mixed. The mixture remained the constant absorbance for more than 24 h and precipitate occurred after three days. The absorbance of the colored complex formed from color-developing reagent and samples was stable after it was formed. Thus this system could be applied in flow injection analysis.

The concentrations of the reagents were selected as shown in 1.2. The color-developing reagent formed from this ratio of R1 and R2 was colorless. If the concentration was high, the stability of the color-developing reagent was not so good, high background noise was its phenomena. On the contrary, the sensitivity was not good enough.

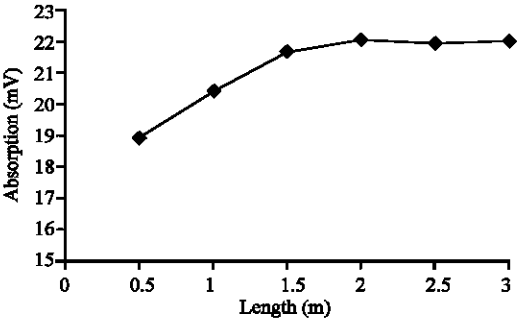

Fig. 2: Study of the effect of the length of RC1

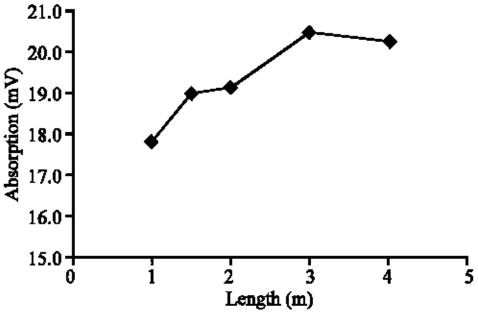

Fig. 3: Study of the effect of the length of RC2

Effect of Reaction Coil Lengths

Because the color-developing reagent and the colored complex were stability after 0.5 min. when they were formed, the lengths of RC1 and RC2 need not be very long. If the lengths were shorter, there would be not enough time to mix each other and the absorbance would not be stable. In order to have enough time for the reagents to mix thoroughly, 2.0 m of RC1 and 3.0 m of RC2, respectively, were chosen as the optimum (Fig. 2 and 3).

Effect of Flow-rate of Solutions

Actually, there was a relationship between the flow rates of solution and the lengths of reaction coils. If the RCs were long, the flow rates should be fast in order to save time; if the RCs were short, the flow rates should be slow so there was enough time for the R1 and R2, color-developing reagent and samples to mix thoroughly. However, the flow rates of solutions affected the sensitivity. The faster rates had higher background noise that means bad sensitivity.

The flow rates varying the range from 0.5 mL min^{-1} to 3.0 mL min^{-1} were examined. In the range of 0.8 mL min^{-1} to 2.0 mL min^{-1}, the absorbance value was constant and the ratio of absorbance/noise was high. 2.0 of P1 and 1.0 mL min^{-1} of P2 were chosen as the optimum (Fig. 4).

Influence of Acidity

In acid solution, the $PMo_{12-n}V^{V}_{n}O_{40}$ heteropoly complex is stable and higher acidity has benefit for the formation of the complex. Investigation shown that the higher the acidity of the impellent, the higher absorbance of the colored complex. And because the color-developing reagent is of high acidity,

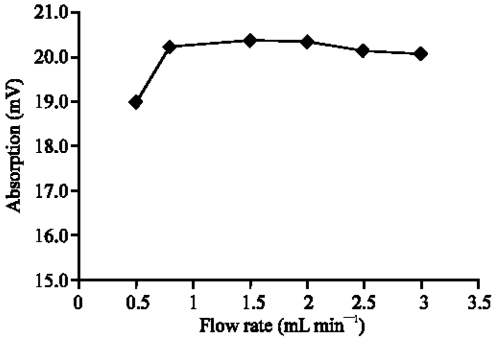

Fig. 4: Study of the effect of flow rate

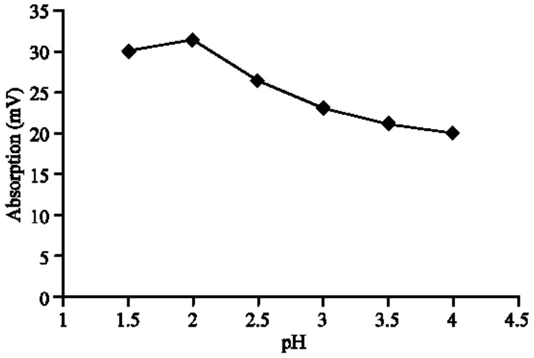

Fig. 5: Study of the effect of pH

the impellent was adjusted to pH 2.0 with hydrochloric acid (1+1). To match with the impellent, the standard solutions and samples were adjusted to pH 2.0 with hydrochloric acid (1+1) too (Fig. 5).

Samples Volume

In this system, the color-developing reagent was abundant; the absorbance of the colored complex had positive relation to the concentration of vanadium (V). In order to improve the sensitivity, a large volume was necessary. Of cause too large volume was unnecessary, for it would waste the reagents and time, also the shape of the peak was not good. A 350 μL volume control loop was selected (Fig. 6).

Effect of Temperature

High temperature gave high sensitivity. However, high temperature caused the air bubble in the flow route and this affected the determination badly. Adding a counterpressure coil or deair of the reagents before experiment had some improvement, but were not so great. The room temperature was selected.

Interference

In order to apply the proposed method to the determination of vanadium in environment and industrial waters, the interference of some possibly coexisting foreign inorganic ions was examined.

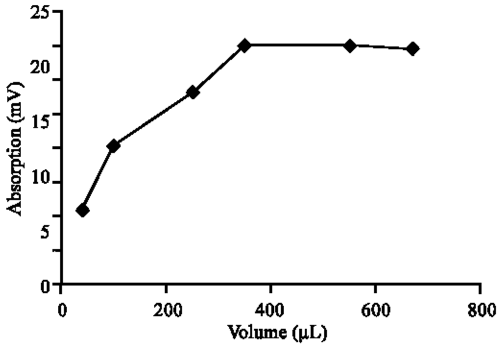

Fig. 6: Study of the effect of sample volume

A foreign ion was considered not to interfere if it caused a relative error less than ±5% during the determination of 0.05 µg mL^{-1} of vanadium (V). There was no interference from the following: 1000 fold amount of nitrate, sulfate, sulfite, chloride, bromide, iodide, carbonate, Na, K, NH_4^+, Zn, Al and Mn; 10 fold amount of Mg, Ca, Cr^{III}, Cr^{VI}, Ni, Co and Hg; and 5 fold amount of Cu and Fe^{III}. Those interference cations could be eliminated using a cation exchange resin column, Cu and Fe^{III} aslo could be eliminated by added fluoride.

Results

Under the selected experimental conditions, the linear relation between the absorption intensity and the concentration of vanadium was constructed over the range 0.02-1.0 µg mL^{-1} of standard Vanadium (V) solutions. The linear regression equation is $A = 14.021C-0.2518$, $R^2 = 0.9943$. The RSD = 0.48% (n = 15) obtained by injecting 0.10 µg mL^{-1} standard Vanadium (V) solution. The detect limit calculated from three times the average background noise was 0.005 µg mL^{-1} of vanadium (V).

This method was applied in determine the vanadium in waters successfully. Sample 1 and 2 were well waters, sample 3 and 4 were river waters and sample 5 was pool water. All the samples were measured at the day they were collected (Table 1).

Table 1: Determination of vanadium in waters (n = 5)

		Recovery		
Samples	Content µg mL^{-1}	Added µg mL^{-1}	Found µg mL^{-1}	R±SD µg mL^{-1}
1	0.068	0.1	0.159	94.6±0.3
		0.2	0.269	100.4±0.1
2	0.079	0.1	0.188	105.0±0.4
		0.2	0.27	96.8±0.1
3	0.033	0.1	0.126	94.7±0.4
		0.2	0.229	98.3±0.2
4	0.028	0.1	0.12	93.8±0.5
		0.2	0.223	97.8±0.3
5	0.02	0.1	0.124	103.3±0.4
		0.2	0.225	102.2±0.4

R = Recovery , SD = Standard Deviation

Conclusions

The content of vanadium in the well water is somewhat high, but in the normal ranges of 0.2-100 μg L^{-1}.

The proposed method is sensitive for the determination of vanadium and it is excellent in terms of simplicity and ease to operate. The method can be successfully applied to monitor the amount of vanadium in natural waters.

Acknowledgement

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References

Ahmed, M.J. and B. Saera, 1999. Spectrophotometric method for determination of vanadium and its application to industrial, environmental, biological and soil samples. Talanta, 48: 1085-1094.

Aragón, M.A., M.E. Ayala and T.I. Fortoul *et al*., 2005. Vanadium induced ultrastructural changes and apoptosis in male germ cells. Reprod. Toxicol., 20: 127-134.

Malgorzata, B., M. Krzysztof and K. Jerzy, 1996. Determination of aluminum, barium, molybdenum, scandium, berylium, titanium, vanadium, fluoride and boron in highly salinated waters. Water Sci. Technol., 33: 349-356.

Fichet, D. and P. Miramand, 1998. Vanadium toxicity to three marine invertebrates larvae: *Crassostrea gigas*, *Paracentrotus lividus* and *Artemia salina*. Chemosphere, 37: 1363-1368.

Shaopu, L., Z. Pengming and Z. Guoxuan *et al*., 1985. Theory and Application of Metal Chemistry Analysis. SiChuan Sci. Technol. Press, pp: 327.

Okamura K., M. Sugiyama and H. Obata *et al*., 2001. Automated determination of vanadium (IV) and (V) in natural waters based on chelating resin separation and catalytic detection with Bindschedler's green leuco base. Anal. Chim. Acta, 443: 143-151.

Paternain, J.L., J.L. Domingo and J.M. Llobet *et al*., 1987. Embryotoxic effect of sodium metavanadate administered to rays during organogenesis. Rev. Esp. Fisiol., 43: 223-228.

Bohdan, P. and J. Hamann, 1996. Effects of *in vivo* vanadate administration on calcium exchange and contractile force of rat ventricular myocardium. Toxicol. Lett., 3: 167-173.

Richter, D., R.A. Forrest and H. Freiesleben *et al*., 2000. Measurement and analysis of radioactivity induced in steels and a vanadium alloy by 14-MeV neutrons, J. Nuc. Materials, 283-287: 1434-1437.

Rojas E., L.A. Herrera and L.A. Poirier, 1999. Are metals dietary carcinogens? Mutation Res., 443: 157-181.

Shao, Q., 1997. Determination of vanadium in coal by catalytic spectrophotometry. Fuel and Energy Abstr., 38: 447.

Wuilloud, R.G., J.A. Salonia and J.A. Gásquez *et al*., 2000. On-line pre-concentration system for vanadium determination in drinking water using flow injection-inductively coupled plasma atomic emission spectrometry, Anal. Chim. Acta, 420: 73-79.