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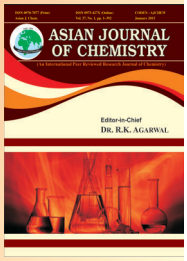

# Indirect Determination of Vanadium in Solution of Tannin Desulfurization with Hydride Generation Atomic Fluorescence Spectrometry

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A method of indirect determination of vanadium in the solution of tannin desulfurization was established with atomic fluorescence spectrometry. In an acidic medium, a heteropoly acid consisting of vanadium, arsenic and molybdenum was generated. The acid, after extracted into an organic solvent which was evaporated afterwards, was dissolved in a diluted hydrochloric acid and the arsenic in the heteropoly acid was determined in proportional to vanadium by hydride generation fluorescence spectrometry. This method demonstrated the merits of simple operation, high precision, fast and low cost performance. Detection limit was 0.2030 μg/mL, standard calibration linearity located in 2-20 μg/mL, relative deviation was 1.7 %, recoveries were 101.4-105.1 %.

**Keywords: Atomic fluorescence spectrometry, Extraction, Indirect determination, Arsenic vanadium molybdenum heteropoly acid.**

## INTRODUCTION

Vanadium is an indispensable material in modern industries[1], often added into iron and steel or used in industries as an alloy of titanium-aluminum-vanadium. Its compounds are also used in catalytical materials, cosmetics, fuels and battery, *etc*. Normally, its composition could be around 98 % in vanadium titano-magnetite; others could exist in phosphate rock ore, uranium sandstone, bauxite and tar sand crude oil with carbon. Extracting and using vanadium as a global business are developing quickly in terms of its wide applications[2,3]. Tannin desulfurization method is a technique used to remove the sulfur in coal chemical industries. Tannins, the main component in tannin extract and with the phenol or quinone structure of its polyols, determine the function of desulfurization. Vanadium as a catalyst is added into the solution containing sulfur, and the tetravalent vanadium coordinates the tannic acid to form a complex with blue colour and of great stability. The amount of vanadium plays a vital role on the degree of desulfurization.

A variety of samples are determined for their vanadium contents, including saline waters[4], petroleum and petroleum products[5,6], benfield sample[7], drinking water[8,9], soils and sediments[10], food samples[11], alloy steels and minerals[12], *etc*.

With the merit of its high sensitivity, spectrophotometry is widely used to determine trace amount of vanadium, its drawbacks of complicated operation, the slowness of colour development and cumbersome procedure are inevitable nevertheless. In addition, atomic absorption spectrophotometry[13-15], inductively coupled plasma spectrometry[16,17] and inductively coupled plasma mass spectrometry[18,19] are frequently used in the vanadium determination. However, the atomic fluorescence spectrometry developed for the determination of vanadium has not been reported.

A heteropoly acid[20] of arsenic-vanadium-molybdenum, extractable into organic solvent, produced in an acidic medium. The heteropoly acid remained after the solvent was evaporated; then dissolved in hydrochloric acid. The arsenic inside the acid was reduced and became its hydride, which was further introduced into an atomic fluorescence spectrometer to be determined in terms of vanadium. This method made it possible to determine vanadium by hydride generation fluorescence spectrometry, which further expands the cope of atomic fluorescence determination. The heteropoly acid extraction benefits vanadium to separate and enrich in the sample. The evaporation of organic solvent after the extraction takes place avoids damaging the tubing connected the peristaltic pump from the organic solvent. This method, due to its fitting the requirement of trace element determination for the instrumentation, has the merits of high sensitivity, low detection limit and good tolerance.

## EXPERIMENTAL

AFS-2202E double channel atomic fluorescence spectrometer (Beijing Kechuang Haiguang Inc, China) equipped with As hollow cathode lamp (Ferrous Metal Research Institute, China) was used to measure the intensity of target element. RE-52AA rotational evaporator (Shanghai Yarong Bio-Chem Manufacture, China) was utilized to conduct solvent evaporation. SHZ-DIII cyclic hydro type vacuum pump (Henan Yuhua Inc Ltd, China) was connected to the evaporator to obtain low pressure vacuum. HK52000 supersonic cleaner (Shanghai Hanke Scientific Instruments Inc Ltd) was operated to clean glass wares. AL104 analytical balance (Shanghai Miedler Toledo Instrument Co., Ltd) was used to obtain accurate weights. Instrument operation parameters are given in Table-1.

TABLE-1
PARAMETERS OF INSTRUMENTAL OPERATION

| Parameters | Values (As) |
|---|---|
| Negative voltage (V) | 300 |
| Lamp current (mA) | 60 |
| Height of atomizer (mm) | 8 |
| Carrier flow rate (mL/min) | 400 |
| Shield flow rate (mL/min) | 900 |
| Read time (s) | 10 |
| Delay time (s) | 3 |
| Measurement pattern | Std |
| Data acquisition pattern | Peak area |

**Stock solution of vanadium:** Ammonium metavanadate (2.2964 g) was accurately weighed in a 200 mL beaker, and dissolved with 5 % hydrochloric acid, after that, transferred into a 1000 mL volumetric flask and diluted to mark with water and mixed thoroughly. The concentration of the solution was 1 mg/mL vanadium, and the work solution was obtained by appropriate dilution.

Molybdenum and arsenic work solutions were prepared from their acquired standard solutions both of 1 mg/mL (National Iron and Steel Research Institute, China). $KBH_4$ solution (14g/L): NaOH of 0.5 g was weighed and dissolved in 100 mL water, and $KBH_4$ of 1.4 g was added in, freshly prepared when used. The mixed solution of thiourea and ascorbic acid of 5 %: thiourea (5 g) was weighed in a beaker with appropriate amount of water and dissolved supersonically; ascorbic acid (5 g) was added in and dissolved thoroughly; the solution was transferred into a 100 mL volumetric flask and diluted to mark with water, freshly prepared when used. *n*-Butyl alcohol, methyl isobutyl ketone, ethyl acetate, isoamyl alcohol, *n*-hexane and *n*-heptane were all of analytical reagent grade. Water was deionized.

**Sample preparation:** Tannin desulfurization solution of 5 mL was transferred in a beaker and an appropriate amount of aqua regia was added. The sample was placed on a hot plate to heat until brown fume to occur, and then removed from the plate and cooled to room temperature. Afterwards, the sample solution was transferred into a 1 L volumetric flask, diluted to mark with water and mixed completely, ready for use.

**Analytical method:** Arsenic and molybdenum working solutions, 1 mL each was pippeted into a 60 mL separatory funnel, respectively, 2 mL $H_2SO_4$ (3 mol/mL) were added, then mixed by an appropriate amount of vanadium standard solution or sample solution, made a total volume of 20 mL by adding water. After the funnel was settled for a while, 10 mL of *n*-butyl alcohol was used to extract. The solvent was removed in a rotational evaporator after the extraction finished. When the solvent was evaporated, the residue was dissolved and the flask was rinsed with 5 mL HCl of 3 mol/L into a 10 mL calorimetric tube. In the tube, 1 mL HCl of 50 %, 2.5 mL of thiourea and ascorbic acid of 5 % each were added, individually. Finally, the tube was made to constant volume of 10 mL with water and ready to determine.

## RESULTS AND DISCUSSION

**Effect of acids on the formation of heteropoly acid and its extraction:** The influence of acid variation on the heteropoly acid formation and extraction related to the anion of the acid was investigated for HCl, $HNO_3$ and $H_2SO_4$. It was found that arsenic-molybdenum-vanadium heteropoly acid was unable to be produced in the medium either HCl or $HNO_3$. However, in $H_2SO_4$, vanadium demonstrated a good linear relationship with arsenic fluorescence intensity. The acidity also played an important role in the formation of the heteropoly acid. When other components remained constant, in the variation of $H_2SO_4$ between 0.1 and 0.6 mol/L, the fluorescence intensity approached the maximum when acidity was 0.3 mol/L (Fig. 1).

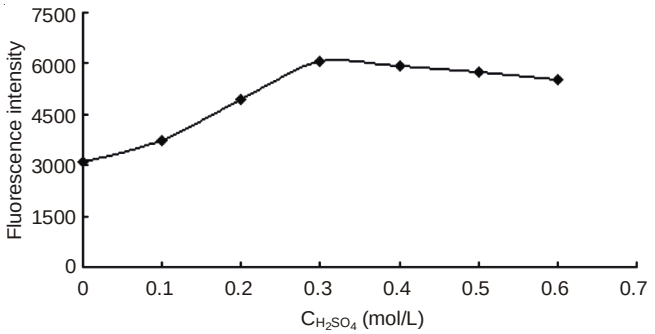


Fig. 1. Effect of acidity on the formation and extractability of arsenic-molybdenum-vanadium heteropoly acid

**Effect of solvent variation on the extractability of heteropoly acid:** When all the components in the aqueous phase were kept constant, the conventional solvents *n*-hexane, methyl-isobutyl ketone, *n*-heptane, dimethy carbonate, isoamyl alcohol, ethyl acetate and *n*-butyl alcohol were examined for the extractability of the arsenic-molybdenum-vanadium heteropoly acid. As shown in Fig. 2, *n*-butyl alcohol generated the best result among all candidates.

**Evaporation temperature of solvent:** Because the organic solvent containing the heteropoly acid eroded the tubing which introduced the sample into the instrumentation, thus, it must be removed. A rotational evaporator was employed to do the job. If the temperature was so low that the time for the evaporation would be long, however, if it was too high, the heteropoly acid would suffer loss. The temperature was investigated in the range of 65-90 °C (Fig. 3). It was evident that 75 °C was the appropriate temperature.

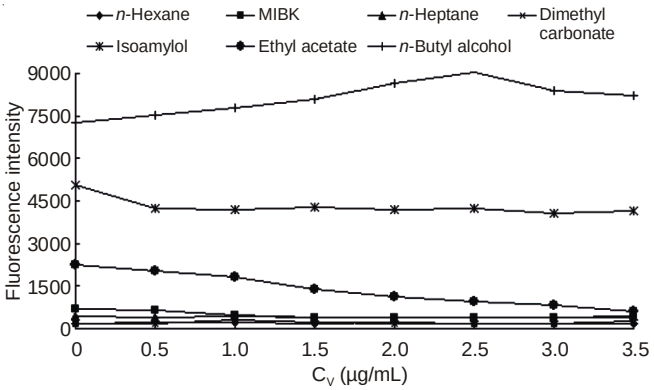


Fig. 2. Effect of solvent variation on the formation and extractability of arsenic-molybdenum-vanadium heteropoly acid

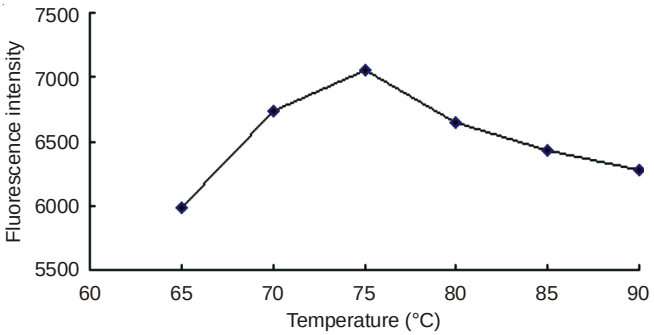


Fig. 3. Effect of temperature on the evaporation of solvent

**Effect of arsenic amount on the formation of heteropoly acid:** When the concentrations of vanadium and molybdenum were both of 2 μg/mL, the amount of arsenic was varied for finding the optimum concentration in the formation of heteropoly acid. It was observed in Fig. 4, the heteropoly acid reached equilibrium when the arsenic concentration was 6 μg/mL.

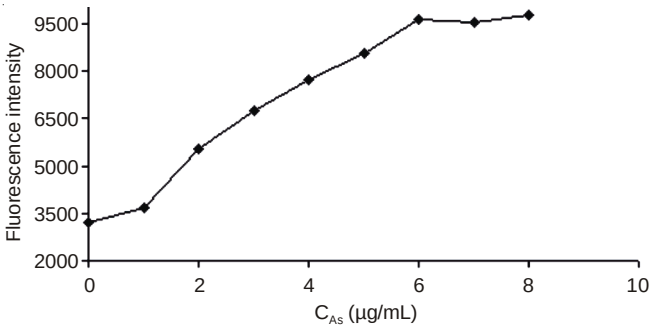


Fig. 4. Effect of dosage of arsenic in the aqueous phase

**Effect of molybdenum amount on the formation of heteropoly acid:** When vanadium and arsenic concentrations were 2 and 6 μg/mL, respectively, the molybdenum amount was enhanced gradually to find its optimum concentration in the formation of heteropoly acid. It was found that the molybdenum concentration of 2 μg/mL yielded the high amount of heteropoly acid.

**Effect of potassium borohydride amount on the generation of arsenic hydride:** Potassium borohydride worked as a reductant for the generation of arsenic hydride to separate and enrich the arsenic in the heteropoly acid. If its concentration was too high, potassium borohydride would not react the arsenic but the acid to generate a large amount of bobbles, deteriorating the determination of the sample. However, if its concentration was too low, potassium borohydride was unable to reduce the all of arsenic in the sample, which made the determination results low. When the concentration was examined in the range of 10-17 g/L, as shown in Fig. 5, the fluorescence intensity increased as the concentration increased. However, the enhancement became slower after 14 g/L.

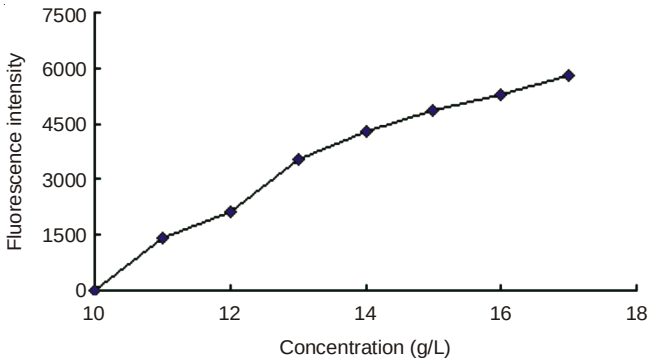


Fig. 5. Effect of concentration of $KBH_4$ on the fluorescence intensity

**Interferences:** The tolerances of the method were investigated for 1000 folds of $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Br^-$, $F^-$, $Cl^-$, $I^-$, $NO_3^-$, $SO_4^{2-}$, Cr(VI), Nb(V), Zr(IV), Ta(V) when vanadium concentration was 10 μg/mL. These ions did not create any interference when the deviation was kept within 5 %. However, Mn(VII) exhibited interference which could be inhibited by adding triethanolamine of 20 %.

**Dynamic standard calibration linearity and detection limit:** Under the optimum experimental condition, the method showed a linear relationship between the fluorescence intensity and vanadium concentration of 2-20 μg/mL with an equation of y = 103.71x – 4568.0 and regression coefficient of 0.9910. A low concentration of vanadium standard was determined 10 times, the relative standard deviation was calculated as 1.7 % and the detection limit of 0.2030 μg/mL was obtained based on 3 times of the standard deviation.

**Sample analysis:** With the optimum conditions of instrument and experiment, 6 samples of tannin desulfurization solution were determined by the proposed method and the recoveries were also performed. The results are listed in Table-2.

TABLE-2
VANADIUM CONTENTS DETERMINED IN TANNIN DESULFURIZATION SOLUTIONS (n = 6)

| No. | Found (μg/mL) | Added (μg/mL) | Determined (μg/mL) | Recovery (%) | RSD (%) |
|---|---|---|---|---|---|
| 1 | 1.966 | 2.000 | 3.972 | 103.1 | 2.1 |
| 2 | 2.264 | 2.000 | 4.316 | 105.1 | 5.2 |
| 3 | 2.120 | 2.000 | 4.151 | 103.1 | 2.7 |
| 4 | 2.007 | 2.000 | 4.035 | 101.4 | 4.5 |
| 5 | 2.559 | 2.000 | 4.608 | 102.5 | 2.9 |

## Conclusion

Based upon the principle of arsenic determination by atomic fluorescence spectrometry, the indirect determination of vanadium in tannin desulfurization solutions was established.

Spiked recoveries of 101.4-105.1 % were obtained when the method was submitted to determine the real world samples, generating satisfactory results. Benefited from solvent extraction, the method showed the enrichment and separation of the analyte, which enhanced the analytical accuracy and eliminated the interferences. A simple operation, low cost and feasible system was also achieved.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. R. Dobrowolski, A. Adamczyk and M. Otto, *Talanta*, **113**, 19 (2013).
2. M. Schreiber, M. Harrer, A. Whitehead, H. Bucsich, M. Dragschitz, E. Seifert and P. Tymciw, *J. Power Sources*, **206**, 483 (2012).
3. K.K. Sahu, A. Agrawal and D. Mishra, *J. Environ. Manage.*, **125**, 68 (2013).
4. J.J. Pinto, M. Garcia-Vargas and C. Moreno, *Talanta*, **103**, 161 (2013).
5. F.A.C. Amorim, B. Welz, A.C.S. Costa, F.G. Lepri, M.R. Vale and S.L.C. Ferreira, *Talanta*, **72**, 349 (2007).
6. R.E. Santelli, M.A. Bezerra, A.S. Freire, E.P. Oliveira and M.F.B. de Carvalho, *Fuel*, **87**, 1617 (2008).
7. M.S. Qureshi, A.R. Mohd Yusoff, A. Shah, A. Nafady and Sirajuddin, *Talanta*, **132**, 541 (2015).
8. R.G. Wuilloud, J.A. Salonia, R.A. Olsina and L.D. Martinez, *Spectrochim. Acta B*, **55**, 671 (2000).
9. A.L. Alvarado-Gámez, M.A. Alonso-Lomillo, O. Domínguez-Renedo and M.J. Arcos-Martínez, *J. Electroanal. Chem.*, **693**, 51 (2013).
10. R. Dobrowolski, A. Adamczyk and M. Otto, *Talanta*, **113**, 19 (2013).
11. T.G. Naeemullah, T.G. Kazi and M. Tuzen, *Food Chem.*, **172**, 161 (2015).
12. A. Varghese and L. George, *Spectrochim. Acta A*, **95**, 46 (2012).
13. F. Amorim, B. Welz, A. Costa, F. Lepri, M. Vale and S. Ferreira, *Talanta*, **72**, 349 (2007).
14. S.B. Mathew, G. Pataila, A.K. Pillai and V.K. Gupta, *Spectrochim. Acta A*, **81**, 774 (2011).
15. K. Suresh Kumar, S.H. Kang, K. Suvardhan and K. Kiran, *Environ. Toxicol. Pharmacol.*, **24**, 37 (2007).
16. I. Aydin, F. Aydin and C. Hamamci, *Microchem. J.*, **108**, 64 (2013).
17. G.M. Wuilloud, J.C.A. de Wuilloud, R.G. Wuilloud, M.F. Silva, R.A. Olsina and L.D. Martinez, *Talanta*, **58**, 619 (2002).
18. N. Kilibarda, S.E. Afton, J.M. Harrington, F. Yan and K.E. Levine, *J. Chromatogr. A*, **1304**, 121 (2013).
19. A. Dinca, T.P. Davis, K.J. Fisher, D.R. Smith and G.D. Willett, *Int. J. Mass Spectrom.*, **182-183**, 73 (1999).
20. W. Alharbi, E. Brown, E.F. Kozhevnikova and I.V. Kozhevnikov, *J. Catal.*, **319**, 174 (2014).