



Separation/preconcentration and determination of vanadium with dispersive liquid–liquid microextraction based on solidification of floating organic drop (DLLME-SFO) and electrothermal atomic absorption spectrometry

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ARTICLE INFO

Article history:

Received 20 January 2010

Received in revised form 12 April 2010

Accepted 13 April 2010

Available online 20 April 2010

Keywords:

Vanadium determination

Liquid–liquid microextraction

Preconcentration/separation

Electrothermal atomic absorption spectrometry

ABSTRACT

A novel dispersive liquid–liquid microextraction based on solidification of floating organic drop (DLLME-SFO) for separation/preconcentration of ultra trace amount of vanadium and its determination with the electrothermal atomic absorption spectrometry (ETAAS) was developed. The DLLME-SFO behavior of vanadium (V) using N-benzoyl-N-phenylhydroxylamine (BPHA) as complexing agent was systematically investigated. The factors influencing the complex formation and extraction by DLLME-SFO method were optimized. Under the optimized conditions: 100 μL , 200 μL and 25 mL of extraction solvent (1-undecanol), disperser solvent (acetone) and sample volume, respectively, an enrichment factor of 184, a detection limit (based on $3S_b/m$) of 7 ng L^{-1} and a relative standard deviation of 4.6% (at 500 ng L^{-1}) were obtained. The calibration graph using the preconcentration system for vanadium was linear from 20 to 1000 ng L^{-1} with a correlation coefficient of 0.9996. The method was successfully applied for the determination of vanadium in water and parsley.

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1. Introduction

Despite being highly toxic in humans, vanadium in extremely small amounts is a nutritional requirement for many types of organisms, possibly including higher animals. These organisms contain the protein vanabins [1], the role of which is unclear. The biological and physiological characteristics of vanadium are dependent on its oxidation state. The dominant oxidation state of vanadium in aquatic environment is V(V) and V(IV), and V(V) is more toxic due to the structural analogy between the vanadate (H_2VO_4^-) and the phosphate ions (H_2PO_4^-) [2]. The vanadate (VO_4^{3-}), formed by hydrolysis of V_2O_5 at high pH, appears to inhibit enzymes that process phosphate (PO_4^{3-}). However, the exact mode of action remains elusive [3]. Vanadium enters the environment from natural resources, combustion of fuel oils and from various industrial processes including dyeing, ceramics, ink, catalyst and steel manufacturing. Vanadium, like other heavy metal ions, is not biodegradable and may be built up in certain organisms to the levels which are toxic. Thus, due to its dual character of essentially and toxicity, its determination in environmental samples has received considerable interest.

The determination of extremely low concentration of elements usually requires a separation and preconcentration step. Vari-

ous methods including liquid–liquid extraction [4,5], solid phase extraction [6–9], cloud point extraction [10–12], hollow fiber liquid phase microextraction [13] and flow injection system [14,15] have been applied for the separation and preconcentration of vanadium prior to its determination by atomic spectrometry. However, in recent years the liquid phase microextraction techniques has received a growing amount of attention due to its simplicity, low consumption of organic solvent, low cost, ease of operation and possibility of obtaining high enrichment factor [16]. From the introduction of the first paper on liquid phase microextraction (LPME) in 1996 [17], hitherto, different approaches of LPME such as single drop microextraction (SDME) [18–20], hollow fiber liquid phase microextraction (HF-LPME) [21], temperature-controlled ionic liquid dispersive liquid phase microextraction (TILDLM) [22], dispersive liquid–liquid microextraction (DLLME) [23–27], and solidification of floating organic drop microextraction (SFODME) [28,29] have been developed. DLLME and SFODME are the new microextraction techniques introduced in 2006 [23] and 2007 [28], respectively. DLLME is based on a ternary solvent system in which a mixture of extracting and dispersive solvent is rapidly injected into an aqueous sample containing the analytes of interest, which caused formation of a cloudy solution. In this system the equilibrium is reached quickly, due to the large surface area between the extraction solvent and the aqueous sample. The advantages of this method are: simplicity, rapidity, low cost, low organic solvent volume, high recovery and enrichment factor. However, one of its drawbacks is the limitation in the choice of the extraction solvents

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as it must be a high-density water immiscible solvent. In SFODME method a droplet of an immiscible solvent with a melting point of 10–30 °C is floated in the surface of an aqueous sample containing the analytes. The mixture is agitated to maximize contact area between the two solutions. The sample vial is then placed in an ice bath to solidify the droplet which is easily removed and allowed to melt for determination of analyte. This method had been used for the extraction of organic compounds [28] and metal ions [29–31] from water samples. In 2008, Leong and Huang [32] reported a novel variation of SFODME called DLLME-SFO; this method is based on the principle of DLLME and SODME, i.e. instead of maintaining one droplet of the extraction solvent in the sample, a dispersion of fine droplet is produced by injection of a mixed solution of the extraction and dispersive solvent into the sample. This produces a vast contact area between the extraction solvent and the sample which resulted in faster mass transfer and shorter extraction time. Like SFODME, the DLLME-SFO has the advantages of speed, simplicity, high efficiency, low cost, simple extraction apparatus and consumption of very small amount of low-toxic organic solvent. In addition, the extraction time of DLLME-SFO is even shorter than SFODME. This version of SFODME had been used for the extraction and determination of halogenated organic compounds and polycyclic aromatic hydrocarbons from the aqueous sample [33,34], and recently there is a report on its application on the extraction of inorganic compounds [35]. In this study, the possibility of extraction of metal ions with DLLME-SFO followed by its determination via ETAAS as a micro amount sample consumption technique was considered; and a novel method for the extraction and determination of vanadium (V) with N-benzoyl-N-phenylhydroxylamine (BPHA) as complexing agent was developed.

2. Experimental

2.1. Reagents and chemicals

All reagents used were of the highest purity available and at least of analytical reagent grade. A stock solution (100 mg L⁻¹) of V (V) was prepared by dissolving an accurate mass of 0.0230 g of NH₄VO₃ into a 100 mL flask and diluting to the mark with distilled water. Standard solutions were prepared daily from the stock solution by serial dilution with water. Deionized water was used throughout the sample preparation and all solutions were stored in pre-cleaned polypropylene (Nalgene, Lima, OH, USA) containers. 1-Undecanol, 1-dodecanol, 1,10-dicolorodecan, and n-hexadecane were obtained from Merck (Darmstadt, Germany). 1-Undecanol was used as extracting solvent. Acetonitrile, methanol, acetone and ethanol as dispersive solvents were purchased from Merck (Darmstadt, Germany). Sodium chloride (Merck, Darmstadt, Germany) was of the highest purity available.

2.2. Instrumentation

Varian Zeeman spectra atomic absorption spectrometer, Model 220 Z was used in this study. Recording of the absorbance signal profile was done using a PC. A Varian spectra-AA hollow cathode lamp for vanadium was used as the light source. The furnace tube was a standard platform tube with a pyrolytic graphite coating. The analytical wavelength (381.5 nm), spectral bandwidth (0.2 nm), and lamp current (20 mA) were used as recommended by the manufacturers. The furnace program was optimized and is given in Table 1. Peak height measurement was used for all quantifications. The pH measurements were carried out with a Metrohm pH meter (model 691, Switzerland) using a combined glass calomel electrode. The centrifuge (Hitachi, Universal 320, Tuttlingen, Germany) was used for centrifuging.

Table 1

Temperature program of ETAAS for the determination of vanadium.

Steps	Temperature (°C)	Time (s)	Argon flow rate (L min ⁻¹)
1	95	5	3
2	120	40	3
3	270	10	3
4	1000	6	3
5	1000	2	0
6	2700	3	0
7	2700	2	3

2.3. Sample preparation

The samples were filtered through a 0.45 μm Millipore filter; the pH was adjusted to ~3 using 0.1 mol L⁻¹ nitric acid and treated according to the given procedure.

0.25 g of parsley was first carbonized, and burned on a furnace at 650 °C for 3–4 h. The residue was cooled at room temperature, and was heated with 1.5 mL concentrated nitric acid and then filtered into 100 mL volumetric flask [36]. 25 mL of which was treated according to the given procedure.

2.4. Procedure

The pH of the sample was adjusted to ~3 using 0.1 mol L⁻¹ nitric acid. 25 mL of the solution was transferred into ~27 mL vial and a mixture of 80 μL 1-undecanol containing BPHA as complexing agent (0.03 mol L⁻¹) (extraction solvent) and 200 μL acetone (dispersive solvent) was rapidly injected into the aqueous sample containing vanadium. In this stage, a cloudy solution containing many dispersed fine droplets of BPHA in 1-undecanol was formed; the vanadium ions reacted with BPHA and were extracted into 1-undecanol in a few seconds. Then, the mixture was centrifuged for 2 min at 1500 rpm; the organic solvent droplet was floated on the surface of the aqueous solution due to its low density. The vial was then transferred into an ice bath and the organic solvent was solidified after 10 min and the solidified solvent was transferred into a conical vial where it melted immediately. Next, 20 μL of the extract was manually injected into the graphite furnace atomic absorption spectrometer for the determination of vanadium.

3. Results and discussion

The initial experiments indicated that when 1-undecanol containing the ligand N-benzoyl-N-phenylhydroxylamine (BPHA) was dispersed into an aqueous solution of vanadium, the vanadium is quickly complexed and extracted into the fine droplets of the organic solvent. The organic droplets were then floated and solidified on the surface of the aqueous solution and the vanadium in the extract was determined by ETAAS as a micro amount sample analysis technique. In order to obtain a high enrichment factor, different parameters affecting the complex formation, extraction and analyte determination were optimized using the univariable approach.

3.1. Optimization of the furnace temperature program

The drying, pyrolysis and atomization temperature for the determination of the vanadium in the extracts were optimized and the optimum conditions are presented in Table 1. Under the optimum condition, the peak was sharp and the background was minimized. With regard to the boiling point of 1-undecanol (243 °C), it was proved that for evaporation of solvent, a drying temperature of 270 °C with the hold time of 10 s is necessary.

Table 2
Properties of extraction solvent for the DLLME-SFO method.

Extraction solvent	Density (g mL ⁻¹)	Boiling point (°C)	Melting point (°C)
1-Undecanol	0.83	243	13–15
1-Dodecanol	0.83	259	22–24
1-10-Dichlorodecane	0.99	140–142	14–16
Hexadecane	0.77	287	18

3.2. Effects of the extraction solvent and its volume

In order to obtain high recovery and enrichment factor, the selection of organic solvent and its volume have an important role in the DLLME-SFO system. The extracting solvent must have low volatility, low water solubility, high solubility in dispersive solvent, capable of formation of cloudy solution in water in the presence of dispersive solvent, a melting point near to room temperature (in the range of 10–30 °C), no interference with the analytical techniques used for the determination of analyte, and a density lower than water. Accordingly, several extracting solvents, including 1-undecanol, 2-dodecanol, 1,10-dichlorodecane and n-hexadecane were investigated (Table 2). The solubility of n-hexadecane in the common dispersive solvent was low, so the extraction was performed with other solvents. The signal obtained with 1-undecanol was sharper, so it was selected as the extracting solvent. When the extraction was done with 1,10-dichlorodecane and 1-dodecanol, the signals obtained were about 85% and 69% of the signals of 1-undecanol respectively.

The influence of the volume of the 1-undecanol as the extraction solvent on the extraction efficiency was studied. For this purpose, different volumes of 1-undecanol (80–300 µL) were subjected to the same DLLME-SFO (the volume of the acetone was fixed at 200 µL) Fig. 1a. It was observed that by increasing the volume of 1-undecanol in acetone, the extract volume was increased while the analyte signal was decreased accordingly. However, the amount of vanadium in the extracts was the same in all volumes tested. Thus, in order to obtain high the enrichment factor, 80 µL of extraction solvent was selected in the further experiments.

3.3. Effects of type and volume of the disperser solvent

The disperser solvent in DLLME-SFO must be miscible with both water and extraction solvents. Thus, for the sake of acquiring the most suitable disperser solvent four types of disperser solvents, acetonitrile, acetone, ethanol and methanol were investigated. The result of this study shows that the analyte signal with acetone and

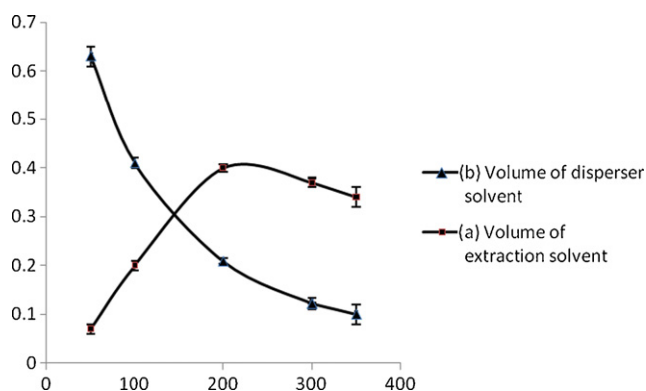


Fig. 1. Effect of solvents volume: (a) extraction solvent and (b) disperser solvent. Extraction conditions: concentration of vanadium, 0.5 µg L⁻¹; aqueous volume, 25 mL; (a) dispersive solvent 200 µL acetone, (b) organic volume, 80 µL of 1-undecanol containing BPHA (0.03 mol L⁻¹).

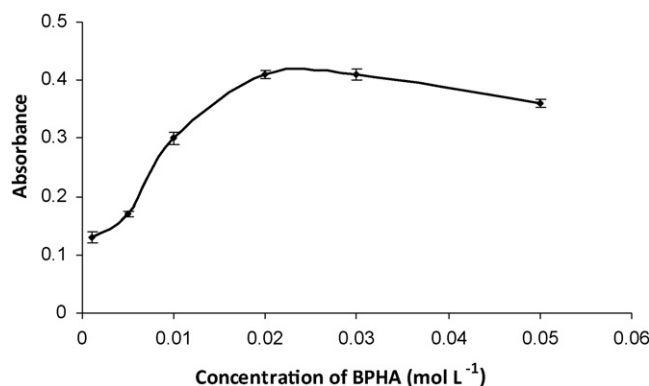


Fig. 2. Effect of BPHA on extraction of vanadium by DLLME-SFO. Extraction conditions: concentration of vanadium, 0.5 µg L⁻¹; aqueous volume, 25 mL; organic volume, 80 µL of 1-undecanol containing various concentration of BPHA; acetone volume 200 µL.

acetonitrile as the dispersive solvent was higher than that with ethanol and methanol. In this study acetone was selected as the most suitable dispersive solvent due to its low toxicity, low cost and high analyte signal.

The influence of the volume of acetone in the range of 50–350 µL on the extraction efficiency of vanadium was examined (the volume of 1-undecanol was fixed at 80 µL) (Fig. 1b). At the low volume of acetone the 1-undecanol was not completely dispersed and the extraction efficiency was low. The absorbance of analyte was maximized from 150 to 250 µL of acetone and then slightly decreased with further increase of the acetone volume. The slight decrease in absorbance in high volume of acetone is due to the increase of solubility of the vanadium complex in the aqueous solution containing high percentage of acetone. Thus 200 µL of acetone was used as the optimal volume of the dispersive solvent.

3.4. Effect of BPHA concentration

The efficiency of vanadium extraction was dependent on BPHA concentration as shown in Fig. 2. The recovery was increased by increasing the BPHA concentration up to 2×10^{-2} mol L⁻¹, quantitative extraction results within the BPHA concentration in the range of 2×10^{-2} to 3×10^{-2} mol L⁻¹. A further excess of BPHA would cause a slight decrease in extraction probably due to saturation of extracting solvent, which results in its extraction into aqueous phase [30]. Therefore a BPHA concentration of 3×10^{-2} mol L⁻¹ was chosen for further study.

3.5. Effect of sample pH

Sample pH has a significant effect on the formation of V-BPHA chelate and its subsequent extraction into organic phase. So the effect of sample pH on the extraction of vanadium (V) was studied by varying the pH within the range of 1–8. The pH was adjusted by using either nitric acid or ammonium hydroxide solution (0.1 mol L⁻¹) and keeping the other variable constant. Fig. 3 shows the influence of the sample pH on the analytical signal intensity. As it is demonstrated, the recovery of V (V)-BPHA chelate is nearly constant and maximum in the pH range of 2.5–3.5. The decrease in the extraction of vanadium at pH higher than 3.5 may be due to the conversion of V(V) into HVO_4^- and the HVO_4^{2-} forms.

3.6. Effect of extraction time

An optimum extraction time is the minimum time necessary to achieve equilibrium between the aqueous and the organic phase so that the extraction of the analyte, the sensitivity, and the speed

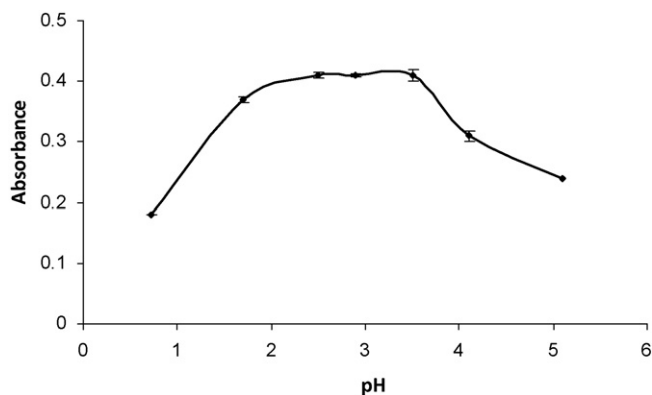


Fig. 3. Effect of pH on extraction of vanadium by DLLME-SFO. Extraction conditions: concentration of vanadium, $0.5 \mu\text{g L}^{-1}$; aqueous volume, 25 mL; organic volume, 80 μL of 1-undecanol containing BPHA (0.03 mol L^{-1}); acetone volume 200 μL .

of extraction is maximized. The extraction time is considered as the time interval between the injection moment of the acetone/1-undecanol mixture and the moment of the starting centrifugation process. The influence of the extraction time on the extraction efficiency was studied in the range of 5 s to 10 min under constant experimental conditions. The results indicate that the extraction time has no significant effect on the extraction efficiency. This is due to the fact that after formation of the cloudy solution, the surface area between the extraction solvent and aqueous phase is infinitely large. Thus, the extraction equilibrium is achieved very fast which shortened the time of extraction procedure. This is one of the considerable advantages of the DLLME-SFO method over the SFODME technique. The most time consuming step in the DLLME-SFO is centrifugation and solidification that takes about 10 min.

3.7. Salt effect

In order to investigate the influence of the ionic strength on the DLLME-SFO performance, several experiments were performed with different NaCl concentrations (0.0 – 1.0 mol L^{-1}) while keeping other experimental parameters constant. The results indicated that the salt added up to a concentration of 0.5 mol L^{-1} has no significant effect on the extraction efficiency. However, a further increase in salt concentration causes a decrease in signal absorbance which can be related to the decrease of 1-undecanol (extraction solvent) solubility in aqueous phase at high ionic strength. This observation suggests the possibility of applying this method for the separation of vanadium from saline solutions up to 0.5 mol L^{-1} .

3.8. Coexisting ions interference

The coexisting ions commonly found in environmental samples were added individually to the samples and its effects on the analytical signal intensity were investigated under the optimized conditions. The major components in seawater did not interfere with the preconcentration of vanadium by the proposed method. The tolerance limit was set as the amount of ion required to cause an error of $\pm 5\%$ in the determination of vanadium. The results of this investigation are summarized in Table 3, indicating that the vanadium recoveries were almost quantitative in the presence of the excessive amount of the possible interfering cations and anions.

3.9. Quantitative aspects

A calibration curve was constructed by preconcentrating 25 mL of the sample standard solution (20 – 1000 ng L^{-1}). Under the optimum experimental conditions, the equation of calibration graph

Table 3

Effect of diverse ions on the recovery of vanadium. (vanadium concentration: $0.3 \mu\text{g L}^{-1}$).

Coexisting ions	Molar ratio (ion/vanadium)	Recovery (%)
Al^{3+}	1000	101.3 ± 2
Cu^{2+}	250	105 ± 1
Zn^{2+}	1000	103 ± 2
Ni^{2+}	1000	104.7 ± 4
Cd^{2+}	500	103 ± 3
Co^{2+}	1000	99.7 ± 3
Cr^{2+}	1000	95.1 ± 1
Mg^{2+}	1000	104.2 ± 2
Ca^{2+}	1000	101.5 ± 4
Fe^{3+}	50	100.9 ± 5
NO_3^-	1000	97.5 ± 3
Cl^-	1000	98.0 ± 1
Na^+	1000	100.8 ± 3
K^+	1000	99.0 ± 2.5

was $A = 0.0004C + 0.0499$ (where A is the absorbance and C is the concentration of vanadium (ng L^{-1}) in the aqueous phase) with the correlation coefficient of 0.9996. The enrichment factor was calculated as the ratio of the slope of a calibration curve prepared from aqueous solutions submitted to the recommended extraction procedure, and that obtained without the preconcentration and found to be 184. The limits of detection (LOD) and quantification defined as the three and ten times of the ratio of the standard deviation of blank measurements to the slope of the calibration curve after preconcentration, were found to be 7 and 20 ng L^{-1} respectively. The relative standard deviation (R.S.D.) for 7 replicate measurements at 500 ng L^{-1} of $V(V)$ was $\pm 4.6\%$.

3.10. Application

The reliability of the recommended procedure was examined through the determination of vanadium in Tap water, well water, river water and sea water (Caspian Sea). The accuracy of the method was verified by the analysis of the samples spiked with the known amount of vanadium, and comparing the results with the data obtained by means of the accepted method of extraction of vanadium by ammonium pyrolydinedithiocarbamate (APDC) and determination by graphite furnace atomic absorption spectrometry (ETAAS) [37]. As illustrated in Table 5, the recoveries of the added vanadium are good, and at the 95% confidence limit, there is no significant difference between the results of the developed and accepted methods. These results indicate that the matrices of the tap, well, river and sea water samples had little effect on the DLLME-SFO–ETAAS method for the determination of vanadium.

Furthermore, the procedure was applied to the determination of vanadium in parsley. The samples were prepared as described in Section 2.3 and 25 mL of it was treated according to the recommended procedure. In order to do the recovery test, known amounts of vanadium were also spiked into the samples. The results are also given in Table 4, showing favorable agreement between the added and measured amounts of vanadium. Thus, the method is capable of the measurement of vanadium in these matrices.

3.11. Comparison with other methods

Separation and determination of vanadium by the developed DLLME-SFO–ETAAS method was compared with the other preconcentration methods used for the determination of vanadium and the results are shown in Table 5. As it is shown, the enrichment factor of DLLME-SFO–ETAAS method is higher and, consequently, its detection limit is lower than that of the other reported methods.

Table 4
Determination of vanadium in real samples.

Sample	Added	Found	Recovery (%)	Standard method [37]
Tap water ($\mu\text{g L}^{-1}$)	0	0.44 ± 0.01	–	0.43 ± 0.02
	0.50	0.92 ± 0.02	96	0.97 ± 0.04
River water ($\mu\text{g L}^{-1}$)	0	0.21 ± 0.01	–	0.20 ± 0.01
	0.50	0.70 ± 0.03	98	0.71 ± 0.01
	0.70	0.90 ± 0.01	99	0.92 ± 0.03
Sea water ($\mu\text{g L}^{-1}$)	0	0.73 ± 0.01	–	0.73 ± 0.02
	0.20	0.92 ± 0.03	105	0.93 ± 0.03
	0.25	0.97 ± 0.02	96	0.97 ± 0.01
Ground water	0	0.44 ± 0.02	–	–
	0.3	0.75 ± 0.01	103	–
Parsley ($\mu\text{g g}^{-1}$)	0	0.30 ± 0.02	–	–
	0.20	0.50 ± 0.01	100	–

Table 5
Characteristic performance data obtained by using the proposed and others reported methods for vanadium determination.

Method	Calibration range ($\mu\text{g L}^{-1}$)	Enrichment factor	R.S.D. (%)	LOD ($\mu\text{g L}^{-1}$)	Sample volume (mL)	Refs.
HF-LPME-(ETV) ICP-OES	0.75–75	74	5.3	71 for V(V) 86 for V(IV)	3.5	[13]
CPE-GFAAS	4.3–130	10	4.3	0.7	5	[11]
SPE-Spectrophot.	10–450	100	1.34	3.2	10	[6]
TILDME-GFAAS	5	40	4.3	0.0049	2	[22]
CPE-AAS	10–120	79	3.6	0.6	10	[12]
DLLME-SFO-ETAAS	0.02–1	184	4.6	0.007	25	This work

4. Conclusion

It has been demonstrated that DLLME-SFO combined with ETAAS can be used as a powerful tool for the preconcentration and determination of metal ions from aqueous samples. It has also been shown that the vanadium-BPHA can be extracted into 1-undecanol. Furthermore, the proposed DLLME-SFO method, permits effective separation and preconcentration of vanadium and final determination by ETAAS in several categories of natural water and vegetable samples.

The main benefits of the system were the minimum use of toxic organic solvent consumption, rejection of matrix constituent, low cost, enhancement of sensitivity and the high enrichment factor. Future work will be directed at the extraction of other metals using various ligand and assessment of capability of method for multi-element enrichment from different matrices.

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