

Cloud Point and Solid Phase Extraction of Vanadium in Surface and Bottled Mineral Water Samples Using 8-Hydroxyquinoline as a Complexing Reagent

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Cloud point extraction (CPE) and solid phase extraction (SPE) methods were developed for the determination of $\mu\text{g l}^{-1}$ of vanadium ions in surface, tap and bottled mineral water samples, based on the rapid reaction of vanadium(V) with 8-hydroxyquinoline (8-quinolinol) at pH 3-5. Both the sensitive extraction methods were successfully employed for the preconcentration of V in real samples. For CPE, V complexed with 8-quinolinol and then was entrapped in non-ionic surfactant Triton X-114, while for SPE, V was adsorbed on XAD -2 impregnated with 8-quinolinol. The experimental conditions for SPE (pH, eluent, and contact time between the liquid sample and the resin) and CPE (pH of sample solution, concentration of 8-quinolinol and Triton X-114, equilibration temperature and time period for shaking) were investigated in detail. The validity of SPE/CPE of V was checked by certified reference material of water (SRM-1643e). The extracted surfactant-rich phase (200 μl) was mixed with 200 μl of HNO_3 in ethanol and this final volume was injected into electrothermal atomic absorption spectrometry with different modifiers. Under these conditions, the preconcentration of 25 ml sample solution allowed the raising of an enrichment factor of 100 and 10 folds for CPE and SPE, respectively. The concentration of V in surface water (river and lake), tap water and bottled mineral water samples was found to be in the range of 1.30-19.9, 1.05-5.25 and 0.67-1.21 $\mu\text{g l}^{-1}$, respectively.

Keywords: Vanadium, Surface and bottled mineral water samples, 8-Quinolinol, XAD-2, Triton X-114, Cloud point extraction

INTRODUCTION

Vanadium(V) is widely distributed at low concentrations in the earth's crust and is known to be essential for living organisms, possessing specific physiological functions but it can be toxic when present in higher concentrations [1]. Vanadium compounds are released into the atmosphere mainly by burning fossil fuels and also from various industrial processes [2-3]. Recently, its compounds came into focus in medical science due to the discovery of their insulin-like properties [4]. On the other hand, excess intake of V inhibits biosynthesis of blood cholesterol and enzyme activities, and some diseases are induced because V may accumulate in

blood [5-6]. Therefore, the level of V in drinking water must be strictly controlled. Unlike organic pollutants, V is not biodegradable and it may build up in certain eco-systems to the level which may be toxic to living organisms [7]. The biological and physiological characteristics of V depend upon its oxidation states. Generally, V exists in two oxidation states (tetravalent and pentavalent) in aquatic environment, and V^{5+} is more toxic than V^{4+} [8]. Okamura *et al.* [9] reported that the oxidation state of V changes in aqueous solutions. The V^{4+} is gradually oxidized and could not exist in neutral and basic natural waters. Consequently, the predominant V species is V^{5+} in oxic environments.

Since one of the routes of V incorporation into the human body is water, its determination in this type of sample is very important in biochemical, geochemical and environmental

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studies [3,5,10]. Concentrations of V in drinking-water may range from about 0.2 to > 100 $\mu\text{g l}^{-1}$, typical values appear in between 1-6 $\mu\text{g l}^{-1}$ [11]. Vanadium is present in water at trace levels. Therefore, the quantification of V is required for evaluating the potential risk and benefits [12]. There are a variety of analytical techniques such as, atomic absorption spectrometry [13], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [14] and inductively coupled plasma-mass spectrometry (ICP-MS) [15] that are used for the determination of V in environmental samples because they have high sensitivity, selectivity and sample throughput. However, the cost of instrumentation may be prohibitive to many laboratories.

Electrothermal atomization atomic absorption spectrometry has been used to determine V in different media, but presents some problems owing to the formation of vanadium carbide during the ashing and atomization steps, which decreases the sensitivity. These problems are minimized by pre-heating the graphite tube before sample injection [16,17]. Although ETAAS is the most frequently used technique in the determination of traces of V, the low level of V concentration in water is not compatible with the detection limit of this technique. In order to achieve accurate, reliable and sensitive results, pre-concentrations and separations are needed [18,19].

The widely used techniques for the separation and preconcentration of V include solid phase extraction (SPE) [20,21] using different adsorbents, activated carbon adsorption [22], amberlite XAD resin [23], co-precipitation [24] and cloud point extraction (CPE) [25,26]. However, the conventional solvent extraction and co-precipitation are laborious and carry a risk of contamination. While the chromatographic techniques often suffer from such disadvantages as incomplete derivatization, being time consuming and complicated operating procedures, the SPE and CPE are impressive alternatives to the conventional solvent extraction because they enjoy high extraction efficiencies and pre-concentration factors, and use inexpensive, non-toxic reagents [27].

The 8-hydroxyquinoline (8-quinolinol/oxine) and its derivatives have been widely used as complexing agents, able to chelate a wide number of metal ions and generally used for the recovery and determination of metal ions by solvent

extraction [28]. However, research on V complexes with 8-quinolinol ligands or its derivatives has primarily concentrated on V^{5+} , because the V^{5+} makes stable complex with 8-quinolinol [29].

In the present work, advanced rapid extraction methods, cloud point extraction and solid phase extraction, using the same complexing reagent 8-quinolinol, were developed for the determination of $\mu\text{g l}^{-1}$ level of V ions in natural surface water, local municipal water supply and bottled mineral water samples. The enrichment of V ions by SPE comprises adsorption on XAD-2, modified with 8-quinolinol, while the preconcentration of V by CPE is based on the formation of a neutral hydrophobic complex with 8-quinolinol, which is subsequently trapped in the micellar phase of a nonionic surfactant (Triton X-114) at a temperature higher than cloud point. Several experimental variables affecting the CPE and SPE sensitivity and selectivity were investigated in detail. The precision, accuracy and interferences of the methods were also investigated. The analyte in surfactant rich phase and desorbed solution was determined by ETAAS with different modifiers including BaF_2 , $\text{Mg}(\text{NO}_3)_2$, $\text{Pd}(\text{NO}_3)_2$ and mixtures of $\text{Pd}(\text{NO}_3)_2$ and BaF_2 .

EXPERIMENTAL

Reagents and Apparatus

Ultrapure water obtained from ELGA lab water system (Bucks, UK) was used throughout the work. The non-ionic surfactant, Triton X-114, was obtained from Sigma (St. Louis, MO, USA) and was used without further purification. The chemicals used were of analytical grade, and all solutions were prepared with ultrapure water. A 2% solution of 8-hydroxyquinoline (Merck) was prepared by dissolving it in 10 ml ethanol (Merck) and diluting to 100 ml with 0.01 M acetic acid and kept in the refrigerator (4 °C) for one week. A solution of BaF_2 was used as the chemical modifier by dissolving 1 g of the salt (99.99% purity, Aldrich, Milwaukee WI, USA) in 100 ml of ultrapure water. The palladium nitrate solution of 1000 mg l^{-1} was prepared by dissolving 106.6 mg $\text{Pd}(\text{NO}_3)_2$ (Merck) in 50 ml of 0.1% (v/v) HNO_3 . A 1.0 M solution of $\text{Mg}(\text{NO}_3)_2$ (Merck) was prepared by dissolving 14.8 g $\text{Mg}(\text{NO}_3)_2$ in 100 ml of deionised water. The 0.01 M acetate buffer was used to control the pH of the solutions. The

pH of the samples was adjusted to the desired pH (3-8) by the addition of 0.1 M of each HCl or NaOH. To make sure of accuracy of the methodology, certified reference materials of water SRM 1643e (National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA) was used. All other chemicals were of analytical reagent grade and were used without further purification.

Apparatus

Instruments included a double beam Perkin Elmer atomic absorption spectrometer model 700 (Norwalk, CT, USA) equipped with a graphite furnace HGA-400, a pyrocoated graphite tube with integrated platform, an autosampler AS-800 and a deuterium lamp as the background correction system. Vanadium was measured at 318.5 nm with a V hollow cathode lamp and a slit width of 0.7 nm. Pyrocoated graphite tubes with an integrated L'vov platform and peak area integration were used. The graphite furnace program for V determination was temperature (°C)/ramp time (s)/hold time (s) for drying 100-150/1/10, ashing 1600/15/20 and atomization 2600/0/4, respectively, with Argon flow rate of 200 ml min⁻¹.

Sample Collection and Conditioning

The surface water samples (lake and river) were collected on alternate months in 2009 from different sampling sites of Jamshoro, Sindh (southern part of Pakistan), with the help of Global positioning system (GPS). The district under study is positioned between 25°19'-26°42' N and 67°12'-68°02' [30-32]. The sampling network was designed to cover a wide range of determinants of the whole district. From each sampling site, fresh surface water samples were collected from the main stream of the lake and river at five to six different sampling points with a depth of 20-30 cm. Surface water samples were collected using Van Dorn plastic bottles (1.5 l capacity) and kept in well-stoppered polyethylene plastic bottles which were soaked in 10% nitric acid for 24 h and rinsed with ultra pure water before use. As for the tap water samples, the municipal pipe water was allowed to run for 10 min and then approximately 1000 ml of water in beakers was collected (n = 25). All water samples were filtered through a 0.45 µm pore size membrane filter (Millipore Corporation, Bedford, MA, USA) immediately after sampling to remove suspended particulate matter. And finally, 20 bottles of four

different brands of mineral water which had been bottled on four different dates (5 bottles of each brand) were obtained from local markets of Sindh, Pakistan [33]. All water samples were acidified to pH 2 with concentrated HNO₃ and stored at 4 °C in bottles.

Solid-Phase Extraction

The XAD-2 (2.0 g) was added to 10 ml of 1% 8-quinolinol solution (prepared in 0.1 M ethanolic-acetic acid) and shaken (30 rpm) for one hour at room temperature. Afterwards, the resin was filtered out, washed with water, dried at room temperature and kept in desiccator on calcium sulphate. The dried resin filled in the column and was preconditioned with acetate buffer at pH 4-6. A 25 ml of standards (2-10 µg l⁻¹), and 50 ml of each real water samples were passed through the column at flow rate of 0.5-2 ml min⁻¹, controlled by a peristaltic pump. The adsorbed V was desorbed by different concentrations of HNO₃ which was then introduced with different modifiers into the electrothermal atomizer.

Cloud Point Extraction

For the preconcentration of V, aliquots of 25 ml of standard solutions in the concentration range 2.0-10 µg l⁻¹ of V and triplicate of each natural, tap and bottled mineral water samples (50 ml) were transferred into a centrifuge tube with glass stopper. 0.2-1.0 ml of 1% 8-quinolinol (0.55×10^{-3} - 2.76×10^{-3} M) and 0.1-0.5 ml of 1% Triton X-114 solution was added, then the pH was adjusted in the range of 2-8 using 0.1 M of NaOH/HCl with the help of pH-meter. The solution was heated in an ultrasonic water bath for 10-60 min at 40-80 °C and centrifuged at 3500 rpm ($1852 \times g$) for 2-10 min. When the solution was cooled in an ice bath for 5 min, the supernatant aqueous phase was discarded, and the remaining micellar phase was diluted with 0.2 ml of HNO₃ in ethanol (1:10 v/v). The volume of the surfactant-rich phase after the phase separation was measured using a graduated cylinder. The resulting solution was injected into the electrothermal atomizer with different modifiers separately.

RESULTS AND DISCUSSION

The 8-quinolinol reagent well known in analytical chemistry for being used in the complexation of most of the

metals in standard solvent-extraction methods [34,28]. To check the accuracy of the SPE and CPE, the results obtained from certified water samples were used for comparison purposes.

Optimization of SPE

Effect of pH on sorption. The retention of V was determined in the pH range of 2-8. A set of sub-samples of a real sample (volume 25 ml) was spiked with $10.0 \mu\text{g l}^{-1}$ of V. The effect of pH on the sorption efficiency of V on 8-quinolinol-modified XAD-2 from these solutions was studied. The pH profile for the sorption of V is shown in Fig. 1. It can be seen that the maximum adsorption of V is observed at the pH range of 4-5.5. At lower pH < 3.0 , V sorption on 8-quinolinol-immobilized XAD was very low. However, pH 4 was found to be sufficient for more than 80% sorption of V, whereas with pH 4.5 the sorption efficiency of V was found to be $> 95\%$. At pH > 5.5 the sorption efficiency was decreased.

Effects of flow rate. The sample flow-rate should be optimized to ensure quantitative retention along with the minimization of the time required for a single experiment. This parameter may have a direct effect on the breakthrough volume, and elevated flow-rates may reduce the breakthrough volume. The degree of V ion sorption on 8-quinolinol-immobilized-XAD packed column was studied at various flow rates of V ions solution controlled with a peristaltic pump. The flow rate for loading V ions was studied in the range of $0.5\text{-}2 \text{ ml min}^{-1}$. However, at a flow rate of 2 ml min^{-1} , a decrease in the sorption percentage was observed. For further work, a 1.0 ml min^{-1} flow rate was selected. The effect of the sample volume on the retention behavior of the V ions was examined. It was found that the recoveries were constant when up to 500 ml of the sample solution was used. At higher volumes, however, the recoveries for the analyte were decreased.

Effect of eluent. Different concentrations of HNO_3 (1-4 M) were applied for desorbing the retained V ions on 8-quinolinol immobilized-XAD. It was observed that the sorption of V on the 8-quinolinol-XAD-2 occurred at pH 4.5 and that 97-99% recovery of the V was achieved by the use of 2 M of nitric acid. It was observed that 3 ml of 2 M HNO_3 can strip the adsorbed V ions quantitatively, whereas 5 ml of the acid was used to recover the sorbed V. The nitric acid solution is suitable for desorbing different heavy metals adsorbed on

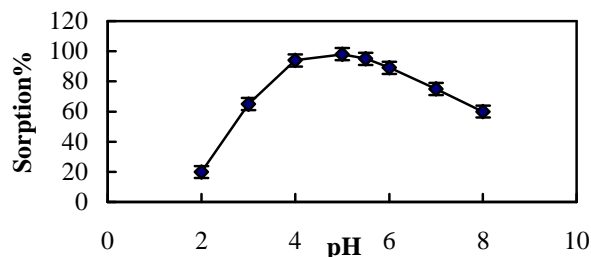


Fig. 1. Effect of pH on the sorption of vanadium ($10 \mu\text{g l}^{-1}$), resin dosage 2.0 g, flow rate $0.5\text{-}2 \text{ ml min}^{-1}$).

different solid phase [35].

Sorption capacity. The sorption capacity (maximum amount of a metal sorbed per gram of the matrix) for V ions was determined by the batch method. Triplicate solutions (25 ml) containing $100 \mu\text{g l}^{-1}$ of V, adjusted to pH 4.5 and diluted up to 50 ml, were placed in glass stoppered flasks (100 ml), then was added 8-quinolinol loaded XAD-2 (0.1 g), the flasks were stoppered and shaken for 30 min. The optimum sorption occurred after 20 min at room temperature $30.0 \pm 5.0 \text{ }^\circ\text{C}$. After filtering out the solid matrix, the filtrate was subjected to ETAAS to determine the capacity of the sorbent. The sorption capacity of V onto 8-quinolinol-XAD-2 resin was found to be in the range of $47.5\text{-}50.8 \mu\text{ mol g}^{-1}$. This capacity was also determined after one month, and during this period, no significant changes in the capacity were observed. The column properties remained constant up to 20 times. As a result, the sorbent needed to be conditioned for the subsequent sample enrichment. Hence, pumping 0.1 M HNO_3 solution, then deionised water, and finally buffer solution at pH 4-5 [36,37].

Optimization of CPE

The preconcentration of V is based on the formation of a neutral, hydrophobic complex with 8-quinolinol, which is subsequently trapped in the micellar phase of a non-ionic surfactant (Triton X-114). Employing the thermally induced phase extraction separation process known as CPE, the analyte is highly preconcentrated and free of interferences in a very small micellar phase. Several parameters play significant roles in the performance of the surfactant system that is used and its ability to aggregate, thus entrapping the analyte species. The pH, surfactant type and concentration, temperature, time and

complexing reagent concentration were all studied for the optimum analytical signals.

pH effects. To study the effect of pH, six sub-samples of surface water (50 ml) were replicated, bottled mineral water samples were spiked with $10 \mu\text{g l}^{-1}$ of V, the pH of each solution was adjusted to different pHs with HCl/NaOH, covering the pH range of (2-8), and then complexing reagents and surfactants at optimum levels were added. Figure 2 shows the effect of pH on the extraction recovery of V, which was calculated on the basis of the amounts of analyte in the surfactant rich solution after extraction at different pHs. As can be seen, the quantitative extraction ($> 95\%$) was obtained for V in the pH range of 4-5 at which the V-8-quinolinol complex was neutral (Fig. 3), but started to decrease at pH 5.5. At higher pH values, the complex possesses a negative charge, and it cannot be entrapped in the nonionic micelles, a behavior which is in accordance with the results of the previous studies [38]. Hence, pH 4.5 was chosen for CPE of V.

Effect of Triton X-114 concentration. The amount of Triton X-114 was not only affected by the extraction efficiency, but also by the volume of surfactant-rich phase. Due to lower cloud point temperature of Triton X-114, it avoids back extraction of analytes during the centrifugation. The variation in the analytical signal as a function of the concentration of Triton X-114 in the range 0.02-0.2% (v/v) was investigated. The result in Fig. 4 shows that the %recovery of V was decreased by increasing the Triton X-114 concentration up to 1% (v/v). At higher concentrations of

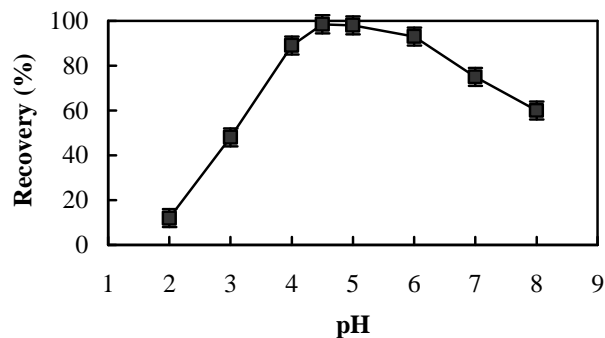


Fig. 2. Effect of pH on the %recovery: $10 \mu\text{g l}^{-1}$ V, 6.90×10^{-2} M quinoline, 0.1% (w/v) Triton X-114, Temp. 42°C , stirring time 15 min.

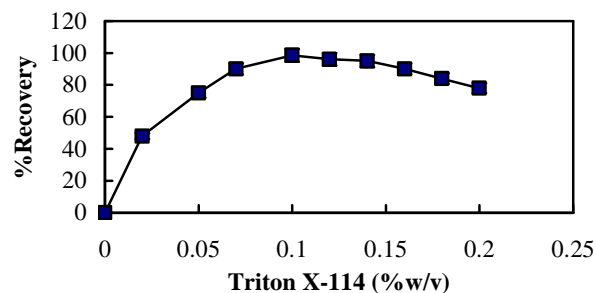


Fig. 4. Effect of Triton X-114 on the %recovery: $10 \mu\text{g l}^{-1}$ V, 6.90×10^{-2} M quinoline, pH 4.5, Temp. 42°C , stirring time 15 min.

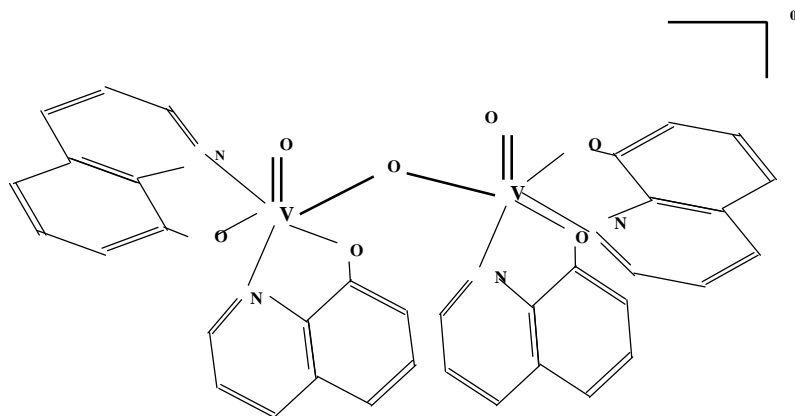


Fig. 3. Complex of vanadium(V) with 8-hydroxyquinoline.

Triton X-114, the signals decreased because of the increment in the overall analyte volumes and viscosity of the surfactant phase. In the present study, 0.1% (v/v) Triton X-114 was used for the optimum extraction of V.

Amount of 8-quinolinol. 0.2-1.0 ml of stock solution of 8-quinolinol (6.9×10^{-2} M) was added to the corresponding 0.552×10^{-3} - 2.76×10^{-3} M, to replicate the sub-samples of real water samples spiked with $10 \mu\text{g l}^{-1}$ of V solutions and Triton X-114 at the optimum pH and subjected to the extraction procedure. It was found that 0.5 ml of stock solution of 8-quinolinol was sufficient for the optimum amount of analyte extraction and that an excess of 8-quinolinol neither enhanced the extraction efficiency nor the adverse effects (Fig. 5).

The optimum amount of 8-quinolinol 0.5 ml corresponding to 1.38×10^{-3} M, was applied to 20, 50 and $100 \mu\text{g l}^{-1}$ of V solutions. The resulting surfactant rich phase was diluted 2, 5 and 10 times with acidic ethanolic solution, respectively, before being injected into the ETAAS. The signals obtained were all identical with those of the $10 \mu\text{g l}^{-1}$ of V solution, showing that 1.38×10^{-3} M of 8-quinolinol solution was sufficient for V concentrations up to at least $100 \mu\text{g l}^{-1}$.

Effect of time and temperature. The reaction takes about 40 min to be completed at room temperature, but the rate can easily be increased by heating. When it was subjected to heating in ultrasonic water bath in the range of 5-30 min, the formation of the complex was optimum at 15 min and longer heating times did not significantly affect the recoveries. Therefore, heating for 15 min in ultrasonic water bath was selected for the optimum recoveries of V. The effects of temperature on the analytical signal were studied in the range of 30-80 °C. Since, in the present study > 40 °C was used for the optimum extraction efficiency of V, so 45 °C was selected for the optimum extraction of V. The effect of centrifugation time upon extraction efficiency was studied in the range of 2-10 min. A centrifugation time of 6 min at 3500 rpm was selected as the optimum; because complete phase separation occurred at the end of this period and no appreciable improvements were observed for longer times.

Interference Studies for SPE and CPE

Certain experiments were performed to discover the degree to which the proposed method is susceptible to interference from elements known to interfere with the formation of V-8-

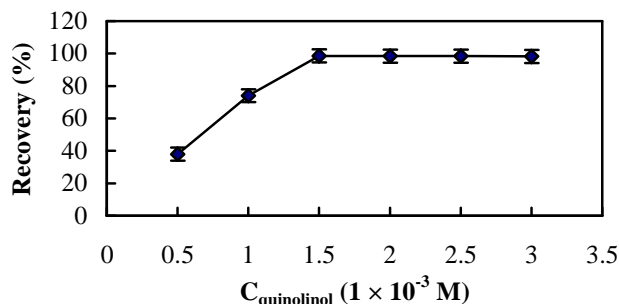


Fig. 5. Effect of oxine concentration on the %recovery: $10 \mu\text{g l}^{-1}$ V, 0.1% (w/v) Triton X-114, pH 4.5, Temp. 42 °C, stirring time 15 min.

quinolinol complex, or with the determination of V by ETAAS, including those forming refractory compounds at low temperatures. The interfering effects of several cations and anions (Al^{3+} , Ba^{2+} , Ca^{2+} , Fe^{3+} , Mg^{2+} , Mo^{4+} , CO_3^{2-} , F^- , SO_4^{2-} and Cl^-) on the SPE and CPE were assessed by means of spiking known amounts of the potential interferences in standard solution of V ($10 \mu\text{g l}^{-1}$). Interference was defined as being significant if a change of more than 10% in the measurements was observed. The determination of V was possible in the presence of an 800-fold excess of Ca, Mg and Ba, a 400-fold excess of Cd, Ni and Pb, a 300-fold excess of Al and a 200-fold excess of Mo and Fe. The amounts of these elements in water are less than what is necessary to cause interference. On the other hand amounts of anions usually present in water do not produce any interference. Commonly encountered matrix components such as alkali and alkaline earth elements generally do not form stable complexes and are not extracted in the proposed system. Since the 8-quinolinol is not selective for V because it reacts easily with a variety of metals, in the present study the CPE and SPE of V-8-quinolinol were relieved of the interference in question.

Calibration and Sensitivity

To obtain a calibration graph, standard V solutions containing 2 - $50 \mu\text{g l}^{-1}$ of V were made up to 50 ml with ultrapure water and subjected to CPE and SPE procedures separately. The calibration graphs were linear with correlation coefficients of 0.9995 and 0.998, respectively. The detection limit (LOD), calculated as the amount of V required to yield a

Table 1. Validation of Cloud Point Extraction (CPE) and Solid Phase Extraction (SPE) of Vanadium in Certified Sample of Water SRM 1643e Using Electro Thermal Atomic Absorption Spectrometry

Certified value of SRM 1643e (Water)	SPE $\bar{x} \mp ts / \sqrt{n}$	CPE $\bar{x} \mp ts / \sqrt{n}$	Paired t test ^a $t_{\text{Experimental}}$	
37.86 ± 0.59	36.9 ± 2.36 (97.5%)	37.3 ± 2.12 (98.5%)	0.458	
Validation of methods by standard addition method				
	Added ($\mu\text{g l}^{-1}$)	Experimental values		Paired t test ^a $t_{\text{Experimental}}$
		SPE	CPE	
Lake water (n = 6)	0	19.4 ± 1.12	19.9 ± 1.15	0.324
	2	20.8 ± 1.87 (97.2%)	21.5 ± 1.49 (98.2%)	0.368
	5	23.7 ± 2.1 (97.13%)	24.4 ± 1.80 (98%)	0.421
	10	28.5 ± 2.8 (96.93%)	29.43 ± 2.25 (98.4%)	0.415

^a $t_{\text{critical}} = 2.57$ at 95% confidence limit, (n = 6). Value in parenthesis () = %recovery.

net peak that was equal to three times the standard deviation of the back ground signal (3σ) was 50 ng l^{-1} . The accuracy of the method was checked by certified standard reference material, NIST SRM 1643e and standard additions method at three concentration levels, 2.0, 5.0 and $10 \mu\text{g l}^{-1}$ of V spiked with sub-samples of a surface water sample, before being subjected to CPE method (Table 1). The enrichment factors of SPE and CPE were 10 and 100, as the original volume used in the present experiments (50 ml) and the final volumes were 5 and 0.5 ml, respectively. The enrichment factor in CPE was ten times higher than that in SPE. The relative standard deviation (%RSD) for 10 replicates containing $10 \mu\text{g l}^{-1}$ of V for SPE and CPE were found to be in the range of 8.1-9.8% and 5.8-7.5%, respectively.

Matrix Modifiers

Vanadium is a refractory element as well as a carbide-forming one. Its atomization is carried out at very high temperatures in the graphite tube. The atomization efficiency could be obviously improved by increasing the atomization temperature, but at the same time, the deterioration of the

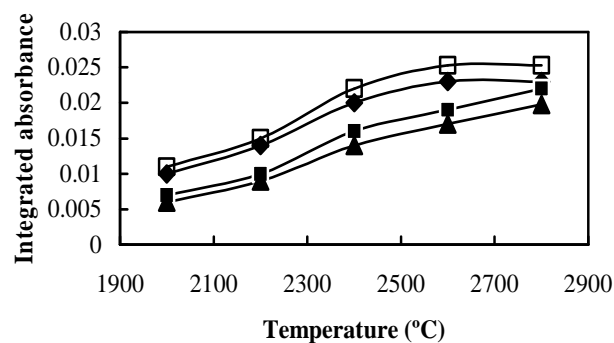


Fig. 6. Integrated absorbance values of standard solution after CPE with various chemical modifiers at various atomization temperature: (◆) BaF₂, (■) Pd(NO₃)₂, (▲) Mg(NO₃)₂, (□) mixture.

graphite tube occurs and its frequent change is required. For the improvement of V signal, different modifiers, Mg(NO₃)₂, Pd(NO₃)₂, BaF₂ and mixtures of Pd(NO₃)₂ and BaF₂ (1:1) were tested. Figure 6 shows that the use of BaF₂ as the chemical

modifier was more efficient than the other two modifiers. Probably, the positive effect on sensitivity is caused by the formation of volatile compounds between V and fluoride [39].

The maximum experimental atomization temperature to obtain optimum sensitivity for all of the modifiers studied was 2800 °C. While with BaF₂, the maximum intensity was obtained at 2600 °C, a plateau phase (increasing the temperature did not improve absorbance values) was attained at up to 2800 °C. The 3000 °C was the highest attainable temperature in the used furnace.

Integrated absorbance values enhanced 5-10%, when a mixture of Pd(NO₃)₂ and BaF₂ with standards and samples was injected into the furnace. Research indicated that the ashing step (1500-1600 °C) was not influenced significantly by the modifiers under study, but the signal intensity clearly increased in the atomic curve and the atomization temperature was selected at 2800 °C. Thus, for the subsequent work a mixture of two modifiers was used.

Applications

It is very important and vital to determine trace amounts of V in water samples. The proposed methods (CPE and SPE) were applied for the analysis of V in surface water (lake, river, tap water) and twenty different bottled mineral water samples. The standard additions were compared in both methods in order to find out the most suitable calibration strategy for the quantification of V in real and bottled mineral water samples. Each sample was checked out for three times.

Three point calibration curves for standard addition (0, 2, 5 and 10 µg l⁻¹) of V showed excellent linearity $R^2 = 0.998$ and 0.9995 for CPE and SPE, respectively, which provides adequate sensitivity and accuracy for both methods. The concentration of V in bottled mineral water samples was determined by both SPE and CPE, and was found to be in the range of 0.65-2.75 µg l⁻¹ (Table 2). Nowadays a wide variety of branded as well as non-branded bottled water is available in Pakistan. This wide selection reflects diverse consumer demand for safe and good quality of water falling within WHO recommendation.

The concentrations of V in tap, river and lake water samples were found to be in the range of 1.05-5.25, 3.84-7.52, and 15.8-25.2 µg l⁻¹, respectively (Table 3). Vanadium

dissolves in natural waters as V⁴⁺ and V⁵⁺. The V⁴⁺ is gradually oxidized and could not exist in neutral and basic natural waters. Consequently, the predominant vanadium species is V⁵⁺ in oxic environments [12]. In oxic waters the dominant vanadium species is V⁵⁺, while in reducing environments, V⁴⁺ exists as vanadyl ion (VO²⁺), a most stable oxo cation, and its various hydrolysis products, V⁵⁺ is practically the only existing form of V at pH > 6.0 [40]. As the pH of all the water samples under study were > 7 (Table 3); therefore, V is found in the form of V⁵⁺. It is reported that in areas where V is abundant due to the local hydrogeology, discrimination of V⁴⁺ and V⁵⁺ in the water used for human consumption is important in terms of risk assessment due to the different toxicological properties of the two oxidation states. In such areas the V intake from water can be one order of magnitude higher than that from food, the latter being estimated as 10-20 µg day⁻¹ [41]. However, too much intake of V may be harmful to humans. There are cases of V poisoning the symptoms of which are nervous depression, coughing, vomiting, diarrhoea, anaemia and so on [42]. Consequently, it is of great importance and crucial for the environment science and life science to determine trace V in water samples. The results obtained from tap water samples were in good agreement with those reported by Sabbioni [43] and Bermejo-Barrera [17]. The reported mean values of V concentration in drinking waters vary between 5.00 and 6.63 µg l⁻¹ while our values for river, lake and tap water samples were found to be higher than those reported earlier [42]. It was observed that the concentration of V in tap, river and bottled mineral water was lower than 10 µg l⁻¹, while in lake water samples higher amount of V was found. This can be attributed to the reduction in precipitation, surface wastage runoff with rainwater into the lake.

All this provides evidence that anthropogenic and geological environment play a key role in the distribution of V in the lake whose water we examined. In terms of consumer safety, the concentration of V in tap and bottled mineral water was not high but precautionary measures are needed. No final conclusion can be drawn however, since neither WHO nor the European Union have set a maximum limit for V in drinking and/or mineral water, or a tolerable upper level for oral V intake for that matter.

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Table 2. Determination of V in Bottled Mineral Water Samples ($\mu\text{g l}^{-1}$)

Samples	CPE	SPE
BMW-1	0.65 ± 0.01	0.64 ± 0.03
BMW-2	0.67 ± 0.06	0.63 ± 0.07
BMW-3	0.75 ± 0.02	0.72 ± 0.03
BMW-4	0.80 ± 0.17	0.77 ± 0.14
BMW-5	0.85 ± 0.06	0.81 ± 0.05
BMW-6	0.91 ± 0.14	0.89 ± 0.15
BMW-7	0.94 ± 0.09	0.92 ± 0.08
BMW-8	1.0 ± 0.12	0.96 ± 0.15
BMW-9	1.02 ± 0.16	0.99 ± 0.19
BMW-10	1.05 ± 0.05	0.98 ± 0.08
BMW-11	1.10 ± 0.09	1.07 ± 0.10
BMW-12	1.20 ± 0.13	1.17 ± 0.14
BMW-13	1.21 ± 0.08	1.19 ± 0.09
BMW-14	1.22 ± 0.15	1.21 ± 0.14
BMW-15	1.25 ± 0.09	1.23 ± 0.10
BMW-16	1.27 ± 0.15	1.22 ± 0.17
BMW-17	1.40 ± 0.10	1.39 ± 0.12
BMW-18	1.64 ± 0.10	1.60 ± 0.11
BMW-19	2.2 ± 0.20	2.19 ± 0.22
BMW-20	2.75 ± 0.08	2.71 ± 0.09

Table 3. Ranges of pH and V Concentration in the Surface and Drinking Water Samples of District Jamshoro, Sindh, Pakistan

Parameter	Unit	WHO Values	Tap water n = 120 mean ± Std.	River water n = 30 mean ± Std.	Lake water n = 30 Range/mean ± Std.
pH	-	6.5-8.5	7.27	7.2	7.4
V	$\mu\text{g l}^{-1}$	100	3.21 ± 1.20	5.4 ± 1.26	19.9 ± 3.24

CONCLUSIONS

The SPE and CPE of V in different water samples using the same complexing reagent (8-quinolinol) and a surfactant

(Triton X-114) was investigated. The extraction percentage was influenced by pH, 8-quinolinol and Triton X-114 concentrations. The results of this work clearly show the utility and validity of both proposed methods. Although the

SPE and CPE afford powerful tools for the selective determination of V at trace levels, because they allow an additional 10-50-fold preconcentration of V, respectively. The cloud point extraction is more easy, safe, rapid, and inexpensive methodology for the enrichment of trace quantity of V in aqueous phase as compared to the solid phase extraction method. The combined matrix modifier improves the signal intensity. Therefore, the CPE method provides a rapid alternative to the SPE. The proposed methods can be applied to the determination of trace levels of V in various water samples. The lake water samples contain higher levels of V than river water samples.

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