## Utilisation of solid phase extraction procedures for preconcentration and determination of vanadium and chromium in various types of water samples by atomic absorption spectrometry

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# Utilisation of solid phase extraction procedures for preconcentration and determination of vanadium and chromium in various types of water samples by atomic absorption spectrometry

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In the present work, sensitive and simple methods for determination of vanadium (V) by electrothermal atomic absorption spectrometry (ETAAS) and for determination of chromium (VI) by flame atomic absorption spectrometry (FAAS) after selective preconcentration by solid phase extraction (SPE) on a Chromabond® $NH_2$ column have been developed. The first procedure for the preconcentration of vanadium (V) is based on the adsorption of vanadium (V) as chelate with Alizarin Red S on the sorbent at pH 5.5. The second procedure was utilised for preconcentration of chromium (VI) and also for speciation of chromium (III) and chromium (VI) using the same column at pH 5.5 without chelating agent. The influence of various experimental variables affecting the recovery of SPE procedure, i.e. pH of the sample solution, concentration of chelating agent as well as volume and concentration of elution solution, were investigated. Under the optimised experimental conditions, the detection limits (calculated as three times the standard deviation (SD) of the blank signal, divided by the slope of the calibration graph) for vanadium (V) and chromium (VI) were 0.11 and $11.7 \, \mu g \, L^{-1}$, respectively. The developed methods were applied successfully to the determination of vanadium (V) and chromium (VI) in different water samples.

**Keywords:** vanadium; chromium; solid phase extraction; preconcentration; water samples; ETAAS; FAAS

## 1. Introduction

Vanadium is widely distributed and often present in low abundance in the earth's crust. It is anthropogenically released in large quantities into the environment, mainly the by burning of fossil fuels, especially oil, and various industrial processes. Natural source, in order of importance, are continental dusts, volcanoes, sea salt spray, forest fires and biogenic processes [1]. It is drained by rain from the soil into the groundwater from which it may be directly adsorbed by plants, and, consequently, it can be part of food chain. Vanadium can exist in many oxidation states in the range between 1 and 5 as well as the oxyanions and/or oxycations, but only V (IV) and V (V) are the possible oxidation forms in aqueous media. Both species have different nutritional and toxic properties [2]. All compounds of the vanadium are practically non-toxic at low concentration ($10 \, \mu mol \, L^{-1}$),

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but they can be toxic when present at higher concentration ($1 \, mmol \, L^{-1}$). Vanadium compounds have been proven to be associated with various implications in the pathogenesis of some human diseases and also in maintaining normal body functions [3]. Vanadium and its compounds are generally known to have insulin-mimetic activity, both *in vitro* and *in vivo* and may become useful in the future treatment of diabetes [4]. Vanadium toxic effects are so due to the fact of its property of inhibiting many enzymatic systems. Vanadate and vanadyl ions make chemical complexes exhibiting the property of inhibiting or increasing the activity of the enzymes participating in the DNA and RNA synthesis. This type of compounds may be considered mutagenic and genotoxic, with cytotoxic and aneuploidogenous effects [5].

Chromium is largely used in various industries, such as electroplating, tanning, paint and pigment production and metallurgy, which could possibly contaminate the environment. In environmental waters, chromium exists predominantly in two chemical forms: Cr (III) and Cr (VI). The toxicity of a chromium compound is closely dependent on its oxidation state. Chromium (III) is considered to be an essential element controlling glucose, lipid and protein metabolism in mammals, while chromium (VI) is definitely highly toxic for biological systems, having mutagenic and potential carcinogenic properties [6].

For the determination of very low concentrations of vanadium and chromium, sample pre-treatment, including analytes preconcentration, is frequently required even in the case of their determinations with sensitive detection techniques, such as atomic absorption spectrometry with flame (FAAS) and electrothermal (ETAAS) atomisers. Solid phase extraction (SPE) is now an attractive method for the preconcentration and/or separation of trace metal ions. Use of various types of sorbents in SPE has been gaining popularity because of high concentration ability and simply operation of SPE procedure.

Some papers have studied SPE as a possible method for vanadium preconcentration and speciation in combination with ETAAS. Polymer chelating resins Amberlite IRA-904 [7], different anion exchange resins [8–11], functionalised cellulose sorbent with phosphonic acid groups (Cellex P) [12] and silica gel modified with 3-aminopropyl-triethoxysilane [13] have been applied for the preconcentration and/or speciation of vanadium species in different water types.

Various different packing materials were used for the speciation, preconcentration and determination of chromium species in water samples by FAAS, like: silica gel chemically modified with niobium (V) oxide [14]; polystyrene–divinylbenzene (PS–DVB) copolymer functionalised with NDSA (2-naphthol-3,6-disulphonic acid) [15]; alumina functionalised with 2-pyridenecarboxyladehyde thiosemicarbazone [16]; polymeric chelating resins Amberlite XAD-1180 [17], Amberlite CG-50 [18], Chromosorb® 108 [19]; anion exchange resin Lichrolut® SAX (trimethylaminopropyl chlorid) [20] and polytetraflouroethylene (PTFE) as beads [21]. The Chromabond® $NH_2$ column was applied to separation and preconcentration of chromium (VI) in powder milk [22] and UHT milk samples [23] prior to its quantification by ETAAS.

Sodium alizarin-3-sulphonate, commonly known as Alizarin Red S (abbreviated as ARS), is a member of the hydroxyanthraquinone class of dyes and is well known for its chromophoric properties. It is a very suitable substance for the formation of chelates with different metal ions. Banerji and Dey [24] studied the chelate formation between vanadium (V) and ARS, its composition and stability by spectrophotometric measurements. This chelate is red in colour and is stable in pH range of 3.0–6.5. The chelate composition corresponds to 1: 2 ratio (metal: chelating agent). The chelate stability constant, expressed as a $\log K$ value at $25°C$, is $8.64 \pm 0.26$ [24].

In this study, the simple procedures for the determination of vanadium (V) using ETAAS and chromium (VI) using FAAS, after preconcentration of V (V)–ARS chelate and Cr (VI) ions on Chromabond® $NH_2$ columns, which contain silica gel modified with aminopropyl group, was developed. The various experimental variables affecting recovery of SPE procedure, i.e. pH of the sample solution, concentration of chelating agent as well as volume and concentration of elution solution, were evaluated. Finally, the optimised methods were successfully applied to the analyses of vanadium (V) and chromium (VI) in different water samples.

## 2. Experimental

### 2.1 *Apparatus and instrumental parameters*

A Perkin–Elmer® model 5100PC (PerkinElmer, Norwalk, Connecticut, USA) graphite furnace atomic absorption spectrometer (THGA tubes with integrated L'vov platform) equipped with Zeeman-effect background correction system 5100ZL and AS 71 furnace autosampler were used for vanadium determination. Integrated absorbance values computed by the AAS instrument were used exclusively for signal evaluation. The operational instrumental parameters and optimum charring and atomisation temperatures for the determination of vanadium are given in Table 1.

The determination of chromium was made by Perkin–Elmer® model 1100B (Perkin–Elmer®, Norwalk, Connecticut, USA) FAAS equipped with deuterium lamp background correction, using air-acetylene flame and hollow cathode lamp. The measurement conditions for Cr were as follows: wavelength $= 357.8$ nm, band pass $= 0.7$ nm, lamp current $= 25$ mA, fuel (acetylene) flow rate $= 2.5$ L min$^{-1}$, oxidant (air) flow rate $= 5$ L min$^{-1}$.

The SPE was carried out using Chromabond® $NH_2$ polypropylene columns containing aminopropyl-modified silica (45 μm particle size, 60 Å pore size) with 3 mL volume and 500 mg of sorbent obtained from Macherey–Nagel (Macherey–Nagel, Düren, Germany).

A pH meter Radelkis model OP 211/1 (Radelkis, Budapest, Hungary) was employed for measuring pH values. PRO–PS Labconco system (Labconco, Kansas City, Kansas, USA) was used for producing of deionised water. All glassware and polypropylene

Table 1. Instrumental parameters and temperature program for the determination of vanadium by ETAAS.

| Wavelength | | | | 318.4 nm |
| --- | --- | --- | --- | --- |
| Lamp current | | | | 40 mA |
| Band pass | | | | 0.7 nm |
| Sample volume | | | | 20 μL |

| Step | Temperature (°C) | Ramp time (s) | Hold time (s) | Air flow rate (mL min$^{-1}$) |
| --- | --- | --- | --- | --- |
| Drying | 110 | 10 | 20 | 250 |
| Drying | 130 | 10 | 30 | 250 |
| Pyrolysis | 1500 | 10 | 20 | 250 |
| Atomisation | 2500 | 0 | 5 | 0 |
| Cleaning | 2600 | 1 | 2 | 250 |

materials were previously soaked in freshly prepared 10% (V/V) nitric acid for 24 h and rinsed thoroughly with deionised water before use.

## 2.2 *Reagents, standard solutions and samples*

All chemicals used were of analytical grade purity, and all solutions were prepared with deionised water (PRO–PS Labconco) freshly before use. Commercial atomic absorption standard solutions, containing $1000 \, mg \, L^{-1}$ of vanadium (IV) ($VOSO_4$ in $0.5 \, mol \, L^{-1}$ $H_2SO_4$) (Merck, Darmstadt, Germany) and $1000 \, mg \, L^{-1}$ of vanadium (V) ($NH_4VO_3$ in $1 \, mol \, L^{-1}$ $HNO_3$) (Bernd Kraft, Duisburg, Germany), were used. A standard solution containing $1000 \, mg \, L^{-1}$ of Cr (III) ($Cr(NO_3)_3$ in $0.5 \, mol \, L^{-1}$ $HNO_3$) (Merck) was used. Stock solution of chromium (VI) was prepared by dissolving of appropriate amount of $K_2CrO_4$ in deionised water. The calibration solutions were prepared by a serial dilution of stock solutions ($1000 \, mg \, L^{-1}$) in 0.2% (V/V) nitric acid (p.a., Merck) for vanadium and in 1% (V/V) nitric acid (p.a., Merck) for chromium.

Alizarin Red S (3, 4-dihydroxy-9,10-dioxo-2-anthracenesulphonic acid sodium salt) (p.a., Merck) was used as chelating agent for preconcentration of vanadium. Buffer solutions were prepared from acetic acid (p.a., Merck) and/or sodium acetate pentahydrate (p.a., Merck).

A model sample of synthetic river water was prepared by dissolving appropriate amounts of calcium chloride dihydrate, sodium chloride, magnesium sulphate heptahydrate, potassium chloride and ammonium hydrogen phosphate (p.a., Lachema, Brno, Czech Republic) [25]. A model sample of synthetic seawater was prepared by dissolving appropriate amounts of sodium chloride, boric acid, potassium bromide, potassium chloride, sodium sulphate, sodium hydrogen carbonate, sodium fluoride, strontium chloride hexahydrate, magnesium chloride hexahydrate (p.a., Lachema) and calcium chloride (p.a., Fluka AG, Buchs, S.G., Switzerland) [25]. Tap water was used as a real water sample.

## 2.3 *General preconcentration procedures*

The proposed preconcentration procedures were tested with different model solutions before its application to the water samples. To different volumes of the sample solutions (up to 100 mL) containing vanadium (V), an appropriate amount of ARS was added to keep the concentration of ARS in the solution constant ($0.5 \, mg \, L^{-1}$). Then the pH of the sample solution was adjusted to 5.5 using acetate buffer and sample was applied through the previously conditioned SPE column. Column conditioning was achieved with 6 mL of $1 \, mol \, L^{-1}$ nitric acid followed by two column volumes (6 mL) of deionised water. Selective retention of vanadium (V)–ARS chelate in the column was quantitatively achieved by passing the sample through the column at a constant flow rate $3 \, mL \, min^{-1}$. After overflow of the sample the column was washed with 6 mL of deionised water, dried under vacuum and the retained vanadium (V) was eluted with 5 mL of $2 \, mol \, L^{-1}$ nitric acid (p.a., Merck). The same procedure was applied for the preconcentration of Cr (VI), but without addition of chelating agent (ARS). The retained chromium (VI) ions were eluted with 11 mL of $3 \, mol \, L^{-1}$ nitric acid (p.a., Merck).

The vanadium concentration in the eluate was determined by ETAAS under the optimised conditions (Table 1) and the concentration of chromium was determined by FAAS.

## 3. Results and discussion

### 3.1 *Preconcentration of vanadium (V) in water samples by SPE*

3.1.1 *Optimisation of the SPE procedure*

The various experimental parameters influencing recovery of SPE procedure, such as pH of the sample solution, concentration of chelating agent as well as concentration and volume of elution solution, were studied. For the optimisation of column preconcentration procedure, 50 mL of spiked standard solutions containing 60 μg L$^{-1}$ of vanadium (V) or vanadium (IV), ARS as chelating agent, nitric acid as elution solution and flow rate of 3 mL min$^{-1}$ were used.

The pH value of sample is important requirement for speciation analysis of vanadium. It was found [8,26] that solution of vanadium (V) prepared in deionised water was stable in the pH range of 2–9. By contrast, solution of vanadium (IV) was stable only at pH 2. Vanadium (IV) was gradually oxidised at pH 5.6 and fully transformed into vanadium (V) within several minutes, at pH = 9 the oxidation of vanadium (IV) was finished within 3 min. The oxidation rates of vanadium (IV) added to natural lake water (pH = 7.7) and seawater (pH = 7.9) were slower; the half-lives of about 15 and 7 min, respectively, were observed [26]. These results indicated that vanadium could not exist as vanadium (IV) in neutral and/or basic natural waters [8,26]. The retention of vanadium (V) and vanadium (IV) in the presence of 0.5 mg L$^{-1}$ ARS on the column as a function of pH was studied. However, chelate can be formed only between pentavalent vanadium and ARS. For this purpose, the pH of the sample solutions was adjusted in a range of 2–6.5 with acetic acid and/or sodium acetate solutions while keeping the other parameters constant and the general preconcentration procedure was applied. The results are shown in Figure 1. The optimum pH value of the sample solution for quantitative retention of vanadium (V)–ARS chelate was 5.5. As it can be seen in Figure 1, vanadium (IV) was subsequently oxidised from the pH = 2.0 and at pH = 5.5 it was completely transformed into vanadium (V). This fact is indicating that the proposed preconcentration procedure is not suitable for speciation of vanadium (IV) and vanadium (V).

The pH of sample solutions and also the concentration of chelating agent affect significantly the chelate formation and its adsorption on the sorbent surface. The effects
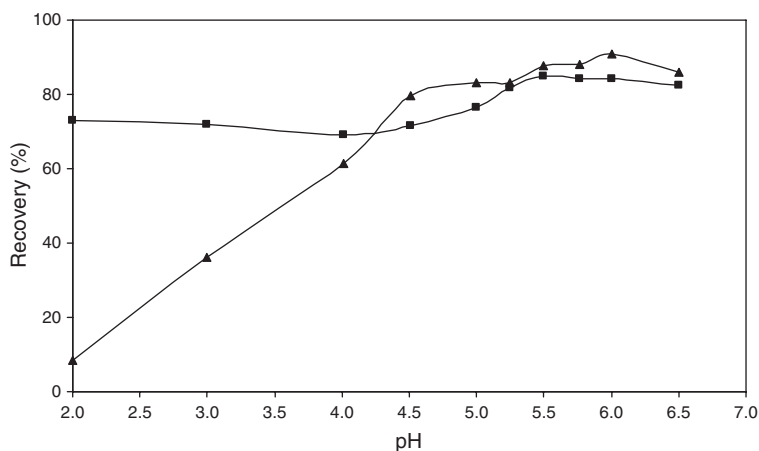


Figure 1. Effect of pH on the selective SPE of V (V) (■) and V (IV) (▲) (60 μg L$^{-1}$ of each species) as chelates with ARS on Chromabond NH$_2$ columns.

of ARS concentration in the range $0.5$–$5 \, mg \, L^{-1}$ were studied to find the optimum concentration. The absorbance of the solution was recorded in the whole studied range of ARS concentrations. It was found that the concentration of ARS (in the studied concentration range) has no influence on the absorbance of solution after chelate was formed. Therefore, a constant concentration of ARS solution ($0.5 \, mg \, L^{-1}$) was used for further studies.

A solution of $HNO_3$ was chosen as eluent due to the fact that nitric acid is commonly used in AAS as the solvent. The elution studies were performed with different concentrations of nitric acid $0.5$, $1.0$, $1.5$, $2.0$, $2.5$ and $3.0 \, mol \, L^{-1}$ and the recoveries were 95.9, 95.9, 97.0, 97.6, 96.5 and 95.9%, respectively. The optimum concentration of eluent was found to be $2 \, mol \, L^{-1}$. To obtain a higher preconcentration factor, the volume of the eluent solution must be as low as possible. Various volumes of $2 \, mol \, L^{-1} \, HNO_3$, in the range of $1$–$10 \, mL$, were tested for desorption of retained vanadium (V)–ARS chelate from the sorbent. The recoveries were in the range of 90.8–98.2%. The best results were achieved with $5 \, mL$ of $2 \, mol \, L^{-1}$ nitric acid solution.

As a result of the optimisation study for the preconcentration of vanadium (V) by SPE, the pH of sample solution 5.5, concentration of ARS $0.5 \, mg \, L^{-1}$, elution volume $5 \, mL$ of nitric acid and concentration $2 \, mol \, L^{-1}$ of nitric acid were found to be optimum for this purpose.

### 3.1.2 *Application of the optimised SPE procedure to water samples*

The SPE method optimised in this work was finally examined for the determination of vanadium (V) by ETASS in different water samples (drinking water, synthetic river water and synthetic seawater). As it is shown from the results given in Table 2, the proposed SPE method could be applied successfully for the preconcentration of trace amounts of vanadium (V) in different spiked water samples. The recovery values of vanadium (V) for preconcentration factors of 4, 10 and 20 were in the range of 95.5–103%.

The repeatability was calculated using relative standard deviation (SD). The repeatability of measurements tested for four determinations ($5 \, \mu g \, L^{-1}$ vanadium (V)) by proposed preconcentration procedure was found to be 2.54, 2.18 and 2.32% in drinking, synthetic river water and synthetic seawater, respectively. The linear range

Table 2. Results for vanadium (V) preconcentration in spiked water samples.

| Sample | Preconcentration factor | Added V (V) ($\mu g \, L^{-1}$) | Determined V (V)[a] ($\mu g \, L^{-1}$) | Recovery (%) |
|---|---|---|---|---|
| Drinking water | 4 | 5.0 | $19.1 \pm 1.01$ | 95.5 |
| | 10 | | $50.8 \pm 1.87$ | 102 |
| | 20 | | $95.8 \pm 2.43$ | 95.8 |
| Synthetic river water | 4 | 5.0 | $20.4 \pm 1.21$ | 102 |
| | 10 | | $51.5 \pm 1.93$ | 103 |
| | 20 | | $102 \pm 2.22$ | 102 |
| Synthetic seawater | 4 | 5.0 | $19.8 \pm 1.22$ | 99.0 |
| | 10 | | $47.8 \pm 1.93$ | 95.6 |
| | 20 | | $102 \pm 2.37$ | 102 |

Notes: [a]Mean $\pm$ SD, $n = 8$.

of calibration graph was up to $160 \, \mu g \, L^{-1}$. The limit of detection (three times the SD of the blank signal, divided by the slope of the calibration graph) for the proposed preconcentration method (with preconcentration factor 20) for vanadium (V) was $0.11 \, \mu g \, L^{-1}$.

In previously published papers concerning the determination of vanadium after SPE preconcentration, similar analytical features were obtained. Nukatsuka *et al.* [8] developed methods for the selective determination of vanadium (IV) and vanadium (V). vanadium (IV) and vanadium (V) were converted into their respective complexes by reaction with Chromazurol B and *N*-cinnamoyl-*N*-2,3-xylylhydroxylamine, respectively. These complexes were pre-concentrated on an anion exchange resin and determined by ETAAS independently. The detection limit for both methods was $0.02 \, \mu g \, L^{-1}$ for a 40 mL sample solution. Recoveries of vanadium (IV) or vanadium (V) were 99.2–109% with a SD less than 6%. Minelli *et al.* [10] trapped both vanadium (IV) and vanadium (V) species on a strong anion exchange column (SAX) loaded with $Na_2EDTA$, then selectively eluted the vanadium (IV) species using a solution containing $Na_2EDTA$, tetrabutylammonium hydroxide and isopropanol, and was subsequently determined by ETAAS. The detection limits were $1 \, \mu g \, L^{-1}$ for both species, when a 10 mL sample was eluted through the column. The recovery of vanadium (IV) was 95% or better.

### 3.2 *Preconcentration of chromium (VI) in water samples by SPE*

3.2.1 *Optimisation of the SPE procedure*

In order to obtain quantitative and selective retention of chromium (VI) ions, the preconcentration procedure was optimised for various analytical parameters, including the pH of the sample solution as well as concentration and volume of elution solution. The optimal conditions for preconcentration of Cr (VI) were studied by using 25 mL of spiked sample solutions containing $4 \, mg \, L^{-1}$ of Cr (VI) or Cr (III), nitric acid as elution solution and flow rate of $3 \, mL \, min^{-1}$.

To study the influence of the pH value on selective extraction of chromium (VI) ions, a series of spiked solutions containing $4 \, mg \, L^{-1}$ Cr (III) or Cr (VI) adjusted to pH values in the range 3–6.5 (with the acetic acid and/or sodium acetate solutions) were used. As Figure 2 indicates, Cr (VI) is practically completely retained on the sorbent at pH = 5.5, while the Cr (III) is not significantly adsorbed at this pH value. Therefore, this pH value of the sample solution was selected as the optimum.

To examine the effect of the concentration and volume of elution solution on retention of chromium (VI) ions, series of spiked solutions containing $4 \, mg \, L^{-1}$ Cr (VI) at pH = 5.5 were used. The experiments were performed using various concentrations of nitric acid from 0.5 to $4 \, mol \, L^{-1}$ (Figure 3) and volumes from 1 to 15 mL (Figure 4). The concentration $3 \, mol \, L^{-1}$ of nitric acid and 11 mL elution volume was found to be optimum and they were selected for further experiments.

3.2.2 *Application of the optimised SPE procedure to water samples*

In order to study the applicability of the developed SPE method to the concentration of chromium (VI), three different spiked synthetic solutions containing $2 \, mg \, L^{-1}$ of Cr (VI) (solution A), $4 \, mg \, L^{-1}$ of Cr (VI) (solution B) and mixture of $2 \, mg \, L^{-1}$ of Cr (VI) and $2 \, mg \, L^{-1}$ of Cr (III) (solution C) were used. The pH of all solutions was adjusted to 5.5 and
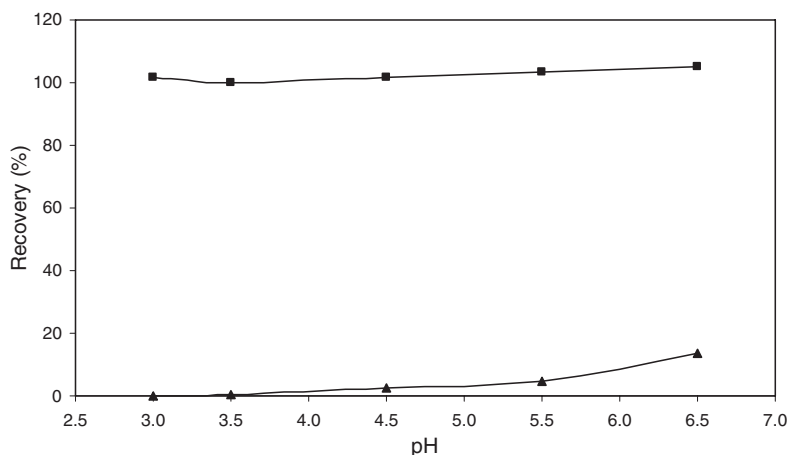
Figure 2. Effect of pH on the selective SPE of Cr (VI) (■) and Cr (III) (▲) (4 mg L$^{-1}$ of each species) on Chromabond NH$_2$ columns.



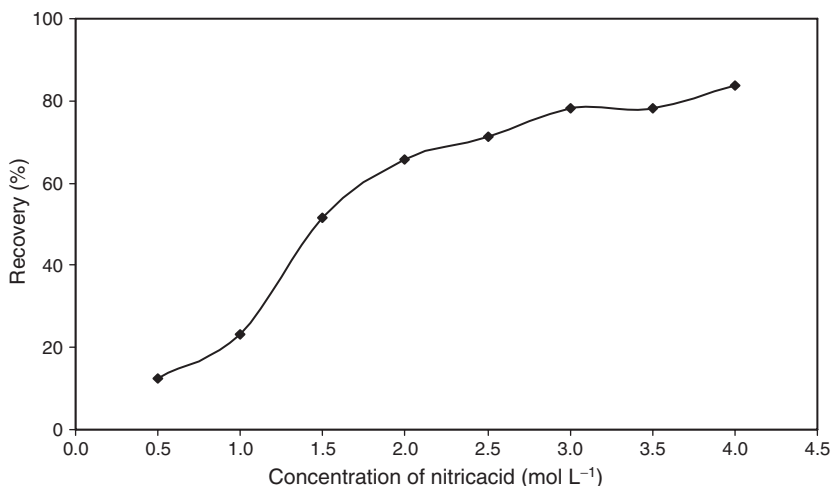Figure 3. The effect of the concentration of elution solution by SPE procedure on the recovery of Cr (VI) (4 mg L$^{-1}$) (elution volume was 6 mL).

the concentration of Cr (VI) was analysed by FAAS. The obtained results are shown in Table 3, from which it is clear that FAAS method in conjunction with presented SPE preconcentration procedure can be used for selective determination of Cr (VI).

Developed method was used to the selective preconcentration and determination of hexavalent chromium in different spiked water samples (drinking water and synthetic river water). The obtained results are given in Table 4. A good agreement was obtained between the added and determined chromium (VI) concentrations. The recovery values for preconcentration factors 5, 10 and 20 were in the range of 95.9–103%. These values show that the presented method can be applied for the preconcentration and determination of hexavalent chromium in real water samples.
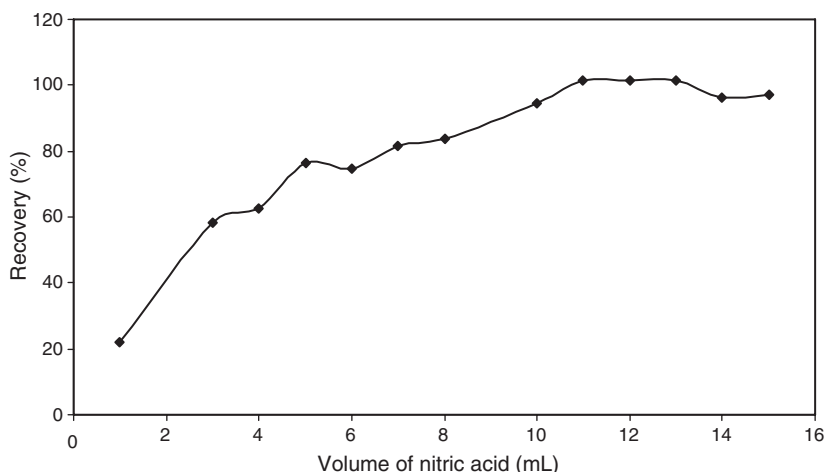
Figure 4. The effect of the volume of elution solution by SPE procedure on the recovery of Cr (VI) ($4\,mg\,L^{-1}$) (concentration of elution solution was $3\,mol\,L^{-1}$).

Table 3. Recovery studies of chromium (VI) preconcentration in spiked synthetic solutions[a].

| Solution | Added Cr (III) ($mg\,L^{-1}$) | Added Cr (VI) ($mg\,L^{-1}$) | Determined Cr (VI) [b] ($mg\,L^{-1}$) | Recovery (%) |
|---|---|---|---|---|
| A[c] | 0 | 2 | $2.02 \pm 0.17$ | 101 |
| B[d] | 0 | 4 | $4.08 \pm 0.13$ | 102 |
| C[e] | 2 | 2 | $1.98 \pm 0.27$ | 98.9 |

Notes: [a]Cr (VI) was selective adsorbed onto the sorbent at pH 5.5, while Cr (III) is not adsorbed, [b]Mean $\pm$ SD, $n = 6$; [c]A-Spiked synthetic solution containing $2\,mg\,L^{-1}$ of Cr (VI), [d]B-Spiked synthetic solution containing $4\,mg\,L^{-1}$ of Cr (VI), [e]C-Spiked synthetic solution containing the mixture of $2\,mg\,L^{-1}$ of Cr (VI) and $2\,mg\,L^{-1}$ of Cr (III).

Table 4. Results for chromium (VI) preconcentration in spiked water samples.

| Sample | Preconcentration factor | Added Cr (VI) ($mg\,L^{-1}$) | Determined Cr (VI)[a] ($mg\,L^{-1}$) | Recovery (%) |
|---|---|---|---|---|
| Drinking water | 5 | 0.1 | $0.51 \pm 0.07$ | 103 |
| | 10 | | $0.98 \pm 0.11$ | 97.7 |
| | 20 | | $1.92 \pm 0.10$ | 95.9 |
| Synthetic river water | 5 | 0.1 | $0.49 \pm 0.08$ | 97.7 |
| | 10 | | $0.99 \pm 0.05$ | 99.0 |
| | 20 | | $1.94 \pm 0.11$ | 96.8 |

Notes: [a]Mean $\pm$ SD, $n = 6$.

The repeatability of the determinations was performed by three successive retention and elution cycles with $0.1\,mg\,L^{-1}$ Cr (VI) solution. The relative SDs were 5.21 and 5.67% in drinking and synthetic river water, respectively. The linear range of calibration graph was up to $5\,mg\,L^{-1}$ and the limit of detection (three times the SD of the blank signal divided by the slope of the calibration graph) for the proposed preconcentration method with preconcentration factor 20 for chromium (VI) was $11.7\,\mu g\,L^{-1}$.

The proposed procedure was compared with previously published methods. Narin *et al.* [17] developed method for preconcentration, speciation and determination of Cr (III), Cr (VI) and total chromium by FAAS. The procedure is based on the adsorption of Cr (III)–diphenylcarbazone complex on Amberlite XAD-1180 resins. After oxidation of Cr (III), the developed SPE system was applied to determine the total chromium and the Cr (III) content was calculated as the difference between the total Cr content and the Cr (VI) content. The detection limits for Cr (VI) and total chromium were 7.7 and $8.6\,\mu g\,L^{-1}$, respectively. Zemberyova *et al.* [20] used for the preconcentration and speciation of Cr (III) and Cr (VI) a strong anion exchange column (SAX). The detection limit was $44\,\mu g\,L^{-1}$ with a relative SD < 6%. The recoveries of Cr (VI) were in the range of 94–103%.

## 4. Conclusions

The solid phase extraction method has some advantages over the other preconcentration techniques, yielding a higher enrichment factor, higher efficiency and handling simplicity. In this work, the effective SPE methods were developed and used for the preconcentration and determination of vanadium (V) and chromium (VI) coupled with electrothermal and flame AAS detection, respectively. SPE using Chromabond® $NH_2$ columns was used for the selective preconcentration of vanadium (V) as its chelate with ARS and chromium (VI) ions. Present methods could be applied successfully to the analysis of trace concentrations of vanadium (V) and chromium (VI) in real water samples.

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