

Research Article

Simultaneous Preconcentration and Determination of Co(II), Cr(III), Fe(III), Mn(II), Ni(II) and Pb(II) by FAAS using Silica Gel Modified with Niobium(V) oxide

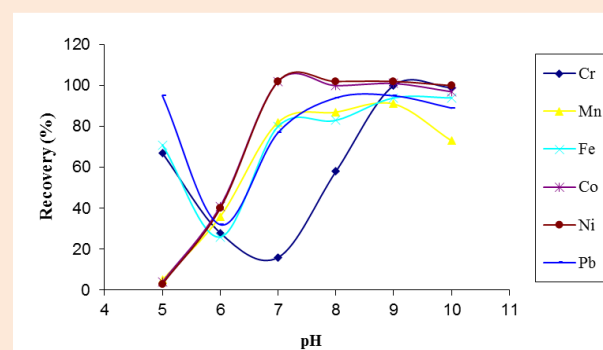
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Abstract

An analytical method using silica gel chemically modified with niobium(V) oxide for preconcentration of Co(II), Cr(III), Fe(III), Mn(II), Ni(II) and Pb(II), in a column system was described. The optimal experimental conditions were established. The sorption capacity has been found to be 64.48, 57.70, 68.04, 54.61, 64.75 and 14.48 $\mu\text{mol g}^{-1}$ for Co(II), Cr(III), Fe(III), Mn(II), Ni(II) and Pb(II), respectively, with the preconcentration factor of 25. Detection limits of the method for chromium(III), cobalt(II), iron(III), manganese(II), nickel(II) and lead(II) were 8.47, 3.16, 9.54, 3.67, 4.24 and 6.20 $\mu\text{g L}^{-1}$, respectively. The accuracy of the method was checked with certified reference material (NIST CRM 1-266YP). The application of this modified silica gel to preconcentration trace Cr(III), Co(II), Fe(III), Mn(II), Ni(II) and Pb(II) of two water samples gave high accurate and precise results with recoveries > 96%.

Keywords: silica, niobium(V) oxide, preconcentration, trace metals, FAAS

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Introduction

In recent years, the significance of metal quantification at the $\mu\text{g/g}$ (ppm), ng/g (ppb) and pg/g (ppt) comprises one of the most important targets in analytical chemistry. This interest is also demonstrated in different areas such as biology, geology and medicine [1-4]. The direct determination of trace metal ions from natural water is limited and difficult when its concentration is too low to be determined directly, it's very difficult to achieve accurate, reliable and sensitive results, therefore, separation and preconcentration step is often necessary prior to analysis [5]. The most representative preconcentration technique for trace analysis is considered to be solid phase extraction (SPE) [6]. Compared with traditional solvent extraction techniques, SPE has several advantages, including: flexibility, low cost because of reagents, absence of emulsion, speed and simplicity, sampling in the field, safety with respect to hazardous samples, higher preconcentration factors, stability and re-usability of solid phase, ease of automation [7-10]. The availability of different types of sorbents are some of the important advantages of SPE technique [11], not only providing an improvement in detection limits but also reducing the interference from matrix [12]. Silica gel is one of the most used supporting materials for various chelating agents. It shows faster metal ion-exchange kinetics, excellent swelling resistance in different solvents, ease of surface modification with analytical reagent and better mechanical strength than most chelating resins, so silica gel modified by chelating reagents has gained growing interest in recent years [9]. On the other hand, for inorganic functionalized silica, a few of studies of metal ion adsorption properties have been described in the literature [13]. Suleiman and co-workers [8] investigated adsorption behaviours of Co, Cr, Cu, Mn, Ni and Zn on manometer-sized zirconium dioxide microcolumn. Costa and co-workers [14] investigated the adsorption studies of Cd(II) onto $\text{Al}_2\text{O}_3/\text{Nb}_2\text{O}_5$ mixed oxide dispersed on silica matrix by on-line method, while Budizak and co-workers [15] describe the application of $\text{Nb}_2\text{O}_5\text{-SiO}_2$ for Cd and Co preconcentration using flow system analysis. Furthermore, Maltez and co-workers [16] developed an analytical work for determination of trace

metals in environmental samples using a FI on line preconcentration system with niobium(V) oxide grafted on silica gel surface. As can be seen, there are few of papers that describe the use of Nb₂O₅-SiO₂ as a material for preconcentration of metal ions and most of them described the FI on line method and there are no results for the preconcentration of Cr, Mn and Fe. Therefore, the main objective of this study is to investigate the adsorption behaviour of Co(II), Cr(III), Fe(III), Mn(II), Ni(II) and Pb(II) in water samples in the presence of other metal ions on Nb₂O₅-SiO₂, optimize the experimental conditions and propose a new preconcentration method for heavy metals using a column (150 mm x 5 mm) packed with silica modified with niobium(V) oxide prior to determination by FAAS of river water samples.

Experimental

Materials and Reagents

Atomic absorption spectrometer, Varian Model AA 240 FS flame, equipped with hollow cathode lamps for Co, Cr, Fe, Mn, Ni, and Pb were run under the conditions recommended by the manufacture. Deuterium lamp background correction was used for the absorption measurements. The pH measurements were carried out using a pHs-CG 841 digital pH meter (Schott-GERATE GmbH, Germany) supplied with a combined electrode. The infrared spectra were obtained as KBr pellets on a Perkin Elmer BX FT-IR Fourier transform infrared spectrophotometer (Perkin Elmer, United States). A glass column (150 mm height and 5 mm internal diameter) packed with niobium(V) oxide modified silica gel was used for preconcentration of metals.

Reagents of analytical and spectral purity were used for all experiments and redistilled water was used throughout. In order to prevent metal contamination, the laboratory glassware was kept overnight in a 10% (v/v) nitric acid solution. The silica gel for column chromatography 60 F₂₅₄ (70-230 mesh) and the niobium(V) oxide (Nb₂O₅) were purchased from Merck (Germany). Chromium, cobalt, iron, manganese, nickel and lead standard solutions were prepared daily by appropriate dilution of a 1000 mg L⁻¹ single element atomic absorption standard solution (Merck, Germany) of metal ions. Buffer solution were prepared by mixing in adequate ratios, as follows: 0.05 mol L⁻¹ KH₂PO₄ and 0.1 mol L⁻¹ NaOH (pH 5), 0.05 mol L⁻¹ KH₂PO₄ and 0.1 mol L⁻¹ NaOH (pH 6), 0.054 mol L⁻¹ KH₂PO₄ and 0.005 mol L⁻¹ Na₂HPO₄ · 12H₂O (pH 7), 0.05 mol L⁻¹ KH₂PO₄ and 0.1 mol L⁻¹ NaOH (pH 8), 0.013 mol L⁻¹ Na₂B₄O₇ · 10H₂O and 0.1 mol L⁻¹ HCl (pH 9), 0.013 mol L⁻¹ Na₂B₄O₇ · 10H₂O and 0.1 mol L⁻¹ NaOH (pH 10).

Preparation of silica gel modified with niobium(V) oxide

The modification of silica gel with niobium(V) oxide was prepared as described by Silva and co-workers [13]. About 10 g of sublimed NbCl₅ was suspended in 150 mL of carbon tetrachloride and 20 mL of dry ethanol was slowly added. The mixture was stirred at room temperature for 50 min in a dry nitrogen atmosphere, until complete dissolution of the solid. Then, 37.5 g of activated silica gel was added to the solution and refluxed for 10 h at a temperature between 343 K and 353 K. The resulting solid material, silica modified with niobium(V) oxide was then washed with anhydrous ethanol and first dried for 2 h at 343 K in oven and then dried for another 2 h under vacuum at 413 K. The dry material was hydrolyzed by immersing the solid in redistilled water. After removing all chloride ions with redistilled water, the material was then filtered and dried in an oven at 423 K for 5 h.

General procedure

A total of 500 mg of silica gel modified with niobium(V) oxide were packed in the glass columns. Sample solution containing 0.1 mg L⁻¹ of metal ion Cr(III), Co(II), Fe(III), Mn(II), Ni(II) and Pb(II) was adjusted to the desired pH value with corresponding buffer solution. Then, 100 mL of the solution containing the above mentioned multi element metal ions was passed through the column at a flow rate of 2 mL min⁻¹. The sorbed ions were eluted with 7 mL of 1 mol L⁻¹ HNO₃ in a volumetric flask of 10 mL. Then, the columns were washed with redistilled water (3 mL) such that the final volume of sample was adjusted to 10 mL prior to analysis by flame atomic absorption spectrometry. During the process of data analysis, all values obtained were corrected by subtracting the values of the procedural blank. Data are given as the mean of three replicates.

Results and Discussion

Characterization

The Fourier Transform Infrared (FT-IR) spectrum of activated (—) and modified silica (—) are shown in **Figure 1**. In the range 4000-2500 cm^{-1} , the spectra of both samples exhibit a broad band assigned to the symmetric and asymmetric O-H stretching vibration of silanol groups and to the remaining adsorbed water [17], while the band at ca. 1630 cm^{-1} is assigned to the water bending mode [9, 18, 19]. Then, the spectrum of activated silica treated at 383 K shows the characteristic bands at 1119, 1086, 802 and 471 cm^{-1} of fused quartz. The band at wave number 1119 cm^{-1} corresponds to the longitudinal optic mode (LO) of the asymmetric stretching vibration of Si-O-Si bond and that at 1086 cm^{-1} to the transversal optic mode (TO) [17]. The bands at 802 cm^{-1} and 471 cm^{-1} resulted from Si-O-Si vibrations [4, 17]. In addition, the spectrum of activated silica shows an adsorption band at 975 cm^{-1} due to the Si-OH stretching vibration. Comparing the two spectra and considering the number and intensities of the bands it can be concluded that only small differences are observed between them. The band at 1086 cm^{-1} shifted to higher wave number values, ca. 1102 cm^{-1} , for sample with niobium added. This band is attributed to the asymmetric stretching vibration of the Si-O-Si bond [9] and the shifting to higher wave numbers is due to higher density of the material structure [17], suggesting that the band is influenced by the amount of Nb_2O_5 . The infrared spectra indicate that the SiO_2 network is only slightly disturbed by the presence of metal oxide, suggesting that Nb_2O_5 is dispersed on the matrix.

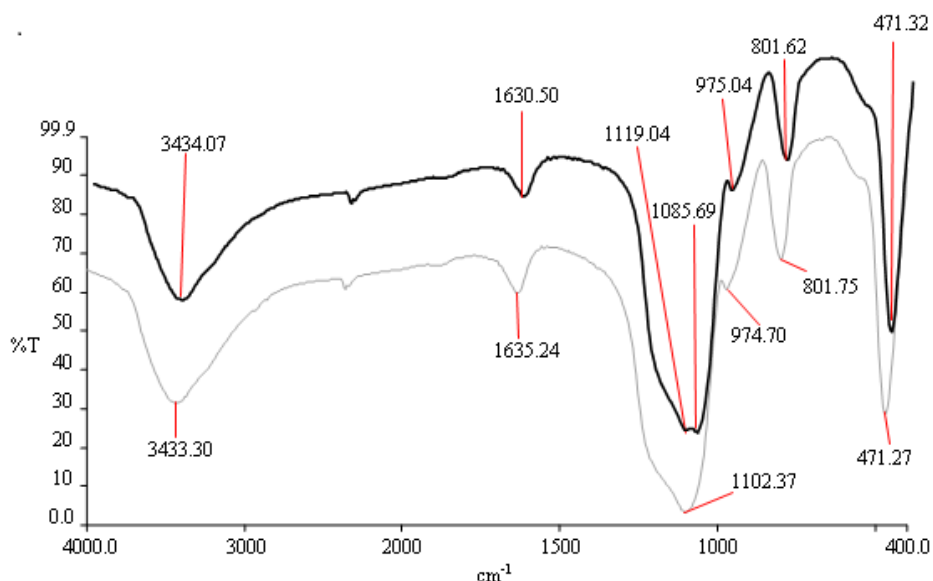


Figure 1 Infrared spectra of activated SiO_2 (—) and modified silica $\text{SiO}_2\text{-Nb}_2\text{O}_5$ (—).

Influence of sample pH

The reactions between Co(II), Cr(III), Fe(III), Mn(II), Ni(II) and Pb(II) and the adsorbent ($\text{Nb}_2\text{O}_5\text{-SiO}_2$), which works as a cationic exchanger, can be influenced by changes in the pH value. In order to optimize this parameter, the effect of the pH on metal ion sorption onto $\text{Nb}_2\text{O}_5\text{-SiO}_2$ was investigated by passing buffered solutions containing 0.1 mg L^{-1} of metal ions at different pH (5-10), applying the general procedure and the results are shown in **Figure 2**.

According to the results shown in Figure 2, the maximum retention for cobalt(II) and nickel (II) occurred within the pH range 7-10, chromium (III) and iron (III) within the pH range 9-10, manganese at pH 9, while lead can be successfully adsorbed at pH 5, 8 and 9. Therefore, pH 9 was selected for subsequent work because it represents an adequate compromise between extractions of all investigated metals.

Effect of sorbent amount

Determination of sorbent amount is an important factor for quantitative sorption of the analytes from the solution. In order to estimate the optimum adsorbent ($\text{Si-Nb}_2\text{O}_5$) quantity, the recoveries of Co(II), Cr(III), Fe(III), Mn(II), Ni(II) and Pb(II) ions were examined by using 100 mg, 250 mg and 500 mg of adsorbent following the general procedure at

pH 9. The results shown in **Figure 3** indicate that quantitative recoveries (> 90%) for all investigated metals were achieved with the adsorbent amount of 250 mg and 500 mg, except for manganese and lead which quantitative recovery occurs only by the sorbent amount of 500 mg. For further studies, 500 mg of the sorbent was used for preconcentration of metals.

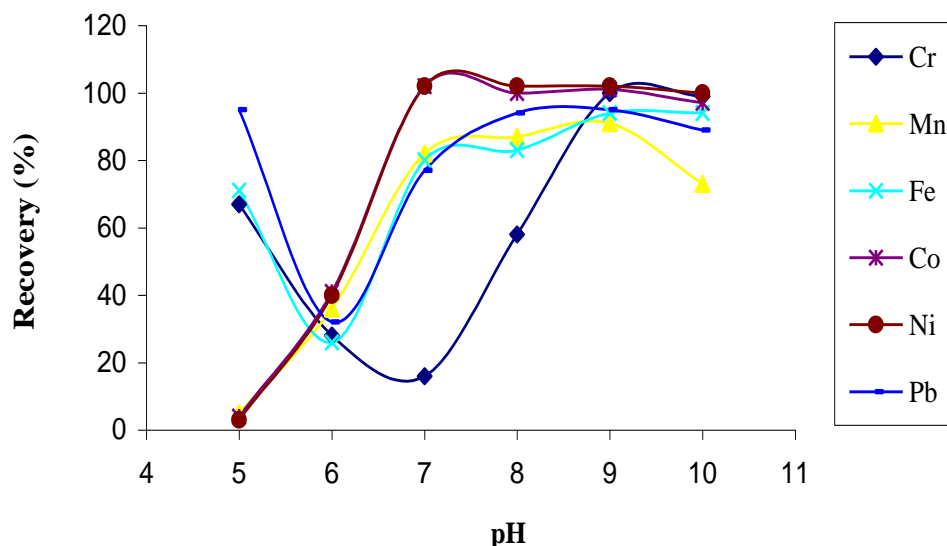


Figure 2 Effect of pH on the recovery of Co(II), Cr(III), Fe(III), Mn(II), Ni(II) and Pb(II) ions

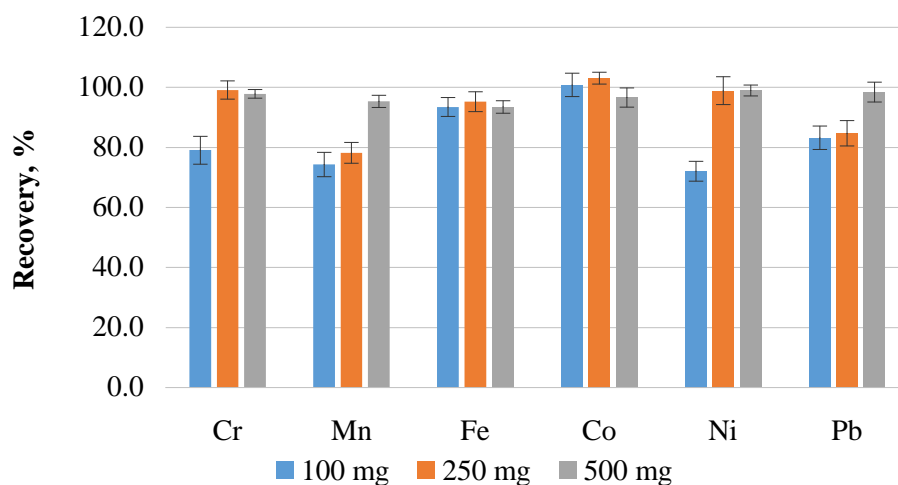


Figure 3 Effect of sorbent amount on the recovery of 0.1 mg L⁻¹ Co(II), Cr(III), Fe(III), Mn(II), Ni(II) and Pb(II) ions

Effect of sample flow rate

The quantitative retention of elements on the adsorbent depends on the flow rate of the sample solution. Therefore, it is very important to optimize it. The effect of sample flow rate on the retention of the studied metal ions on the SiO₂-Nb₂O₅ column was investigated by passing 100 mL of sample solution through the column and adjusting the flow rate within the range of 1-8 mL min⁻¹ under the optimum conditions of pH and sorbent amount. When the work was carried out with a preconcentration flow rate higher than 4 mL min⁻¹ the recovery value was decreased for Mn(II), Pb(II), and at flow rate of 8 mL min⁻¹ it decreases for Fe(III) and Cr(III), indicating that the kinetic of mass transfer of this metal ions towards the adsorbent sites is not so fast and depends on the flow rate (**Figure 4**). It can be mentioned, that the analyzed metals could be preconcentrated with quantitative recoveries (> 93%) by the flow rate between 2 mL min⁻¹ and 4 mL min⁻¹. Therefore, a flow rate of 4 mL min⁻¹ was selected as the optimum condition.

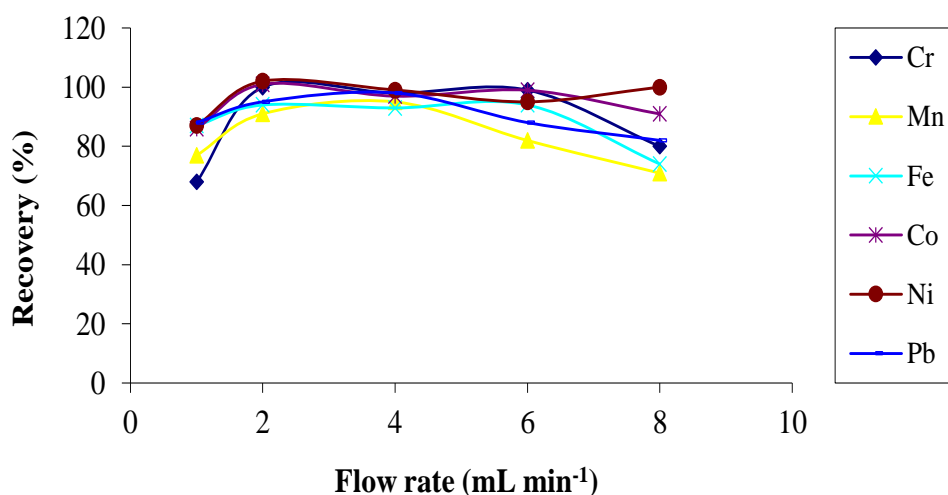


Figure 4 Effect of the sample flow rate on the retention of analytes on the $\text{SiO}_2\text{-Nb}_2\text{O}_5$ surface.

Effect of elution parameters

Several preconcentration papers employing modified silica gel use nitric acid as eluent [4, 10, 13]. Therefore, in this work, the elution of analytes from the column was tested using nitric acid solutions at different concentrations (0.5–3.0 mol L⁻¹). As shown in **Figure 5**, quantitative recoveries (> 90%) for the determination of Co, Cr, Fe, Mn, Ni, Pb were obtained with 1.0 mol L⁻¹ HNO₃. It can be mentioned that with increasing the eluent concentration a decrease in recovery value for all analyzed metals occur. Therefore, 1.0 mol L⁻¹ HNO₃ was used for all further experiments. The effect of the eluent volume on the recovery of investigated metal ions were also studied by keeping the HNO₃ concentration of 1.0 mol L⁻¹. The recovery percentage of metal ions increased by increasing the volume of HNO₃ up to 8 mL and remained constant afterwards. With 8 mL of 1 mol L⁻¹ nitric acid recoveries higher than 95% could be obtained. Therefore, 8.0 mL of eluent was used in the following experiments.

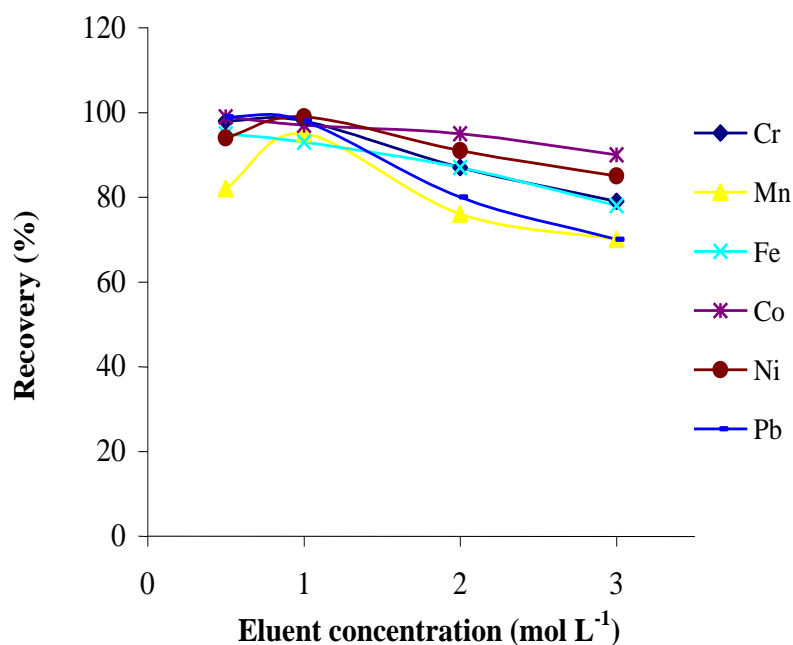


Figure 5 Effect of nitric acid concentration on the recovery of analytes from the column. Other conditions: 500 mg sorbent amount, pH 9, sample volume 100 mL, flow rate 4 mL min⁻¹, concentration of analytes 0.1 mol L⁻¹.

Effect of sample volume

In order to obtain a high or achievable preconcentration factor of very dilute analyte solutions from large volumes, it is imperative to determine the effect of sample volume on the retention of trace metals on modified silica [8]. For this purpose, 100, 250, 500 and 1000 mL of sample solutions containing 0.1 mg L⁻¹, 0.04 mg L⁻¹, 0.02 mg L⁻¹, 0.01 mg L⁻¹ Co, Cr, Fe, Mn, Ni, Pb ions were passed through the column under optimum conditions. The results are given in **Table 1**. As the reported recoveries show, the retention of all the metal ions examined was not affected by sample volume up to 250 mL, with recovery values higher than 93%. At higher sample volumes, the recovery decreased for Cr(III), Fe(III), Mn(II) and Pb(II).

Table 1 Effect of the sample volume on analyte recovery under the optimum conditions. (pH = 9, sorbent amount = 500 mg, sample flow rate = 4 mL min⁻¹, eluent volume and concentration = 8 mL 1 mol L⁻¹ HNO₃)

Sample volume (mL)	Recovery, %					
	Co	Cr	Fe	Mn	Ni	Pb
100	96.6 ± 3.2	97.8 ± 1.4	93.5 ± 2.1	95.3 ± 2.0	98.9 ± 1.8	98.4 ± 1.3
250	102.9 ± 1.1	100.9 ± 3.3	95.8 ± 3.4	94.3 ± 1.9	96.7 ± 2.3	98.1 ± 2.8
500	96.0 ± 3.5	71.6 ± 3.8	74.3 ± 2.1	75.3 ± 2.7	100.9 ± 2.0	74.9 ± 3.1
1000	95.3 ± 3.4	79.1 ± 4.3	72.1 ± 4.7	60.2 ± 2.2	92.7 ± 3.3	41.5 ± 3.6

Only, Co(II) and Ni(II) could be determined with the preconcentration factor 10, 25, 50 and 100. Therefore, 250 mL sample solution was adopted for the simultaneous preconcentration of analytes from sample solution. In this study, the final solution was 10 mL, so the preconcentration factor was 25 for all investigated metal ions.

Comparison of sorption capacities

To determine the amount of analyte retained on the column, that is, the maximum quantity of the elements, which can be sorbed by SiO₂-Nb₂O₅, aqueous solutions of Co, Cr, Fe, Mn, Ni and Pb were passed through the column and the amount of the analyzed metals that was retained in this process was determined. In this case, the column containing 500 mg of modified silica was used and different volumes of metal solutions (0.1 mg L⁻¹) were passed through the column and the amount of the Co, Cr, Fe, Mn, Ni and Pb in the solutions was determined by FAAS. The sorption capacity of SiO₂-Nb₂O₅ compared with other sorbents is shown in **Table 2**.

Table 2 Comparison of sorption capacities (μmol/g)

Sorbent	Metal ion						Ref.
	Co	Cr	Fe	Mn	Ni	Pb	
Nanometer-sized ZrO ₂	25.45	25.00		23.66	66.45		[8]
Banana peel	28.85	32.70	30.44	30.94	28.97	8.21	[20]
Non modified silica gel	11.54	13.08	12.18	12.38	11.59	3.28	[21]
2,3-Dihydroxy Benzaldehyde (SiO ₂)					40	40	[22]
o-Dihydroxybenzene (SiO ₂)	175				178	82	[23]
Aminothioamido-anthraquinone (SiO ₂)	120				150	560	[24]
SiO ₂ -Nb ₂ O ₅	64.48	57.70	68.04	54.61	64.75	14.48	This work

The sorption capacity of Nb₂O₅ used for the preconcentration of Co, Cr, Fe, Mn, Ni and Pb was better than the capacity of banana peel, which is considered as an eco-friendly sorbent and then the capacity of nanometer-sized ZrO₂. Nevertheless, Nb₂O₅ has comparable capacity values to 2,3-Dihydroxy Benzaldehyde, while it exhibited a lower capacity when the silica gel was modified with aminothioamido-anthraquinone or with o-dihydroxybenzene. The most important is to mention that the capacity of SiO₂-Nb₂O₅ is much better than the capacity of non modified silica gel studied previously, which mean that the capacity is influenced by the amount of Nb₂O₅.

Effect of coexisting ions

The effect of common coexisting ions that might be adsorbed together with Cr(III), Co(II), Fe(III), Mn(II), Ni(II) and Pb(II) on SiO₂-Nb₂O₅ was investigated. In this experiments, solutions of 0.1 mg L⁻¹ of Cr(III), Co(II), Fe(III), Mn(II), Ni(II) and Pb(II) in the presence of interfering ions (Al(III), Bi(III), Ca(II), Hg(II), Mg(II), Na(I), Zn(II)) were analyzed according to the recommended procedure. An interfering specie was one whose amount introduced in the working solution changed more than ±10% the recovery value of the standard solution of each metal. The maximum concentrations of the foreign ions studied was 50 mgL⁻¹. The results showed showed that interferences by FAAS after preconcentration for various elements occurred only at concentrations higher than those given in brackets: Hg (10 mg L⁻¹) pose an interference on the determination of Mn, Ca and Mg (20 mg L⁻¹) increases the recovery for Mn and decreases the recovery for Pb, while Na (20 mg L⁻¹) increases the recovery for Cr and Mn. Al (20 mg L⁻¹) decreases the recovery for Cr, Fe and Pb. Bi (20 mg L⁻¹) pose an interference on the determination of Fe, Mn and Pb, while Zn (50 mg L⁻¹) showed an interference on Mn and Pb determination. These results demonstrate that present solid matrix could be used to enrich all the six metal ions (Cr(III), Co(II), Fe(III), Mn(II), Ni(II) and Pb(II)) simultaneously from natural water samples, as their common constituents at normal level do not adversely affect the sorption efficiency of the matrix for these metal ions.

Analytical precision and detection limits

Under the optimum conditions, nine portions of mixed standard solutions were enriched and analyzed simultaneously by following the general procedure. The precision of the method, evaluated as the relative standard deviation for solutions containing 0.1 mg L⁻¹ Co(II), Cr(III), Fe(III), Mn(II), Ni(II) and Pb(II) were 2.24, 1.32, 3.46, 1.21, 1.66 and 2.22 %, respectively. Linear calibration graphs with correlation coefficients >0.994 were obtained for all analyzed metals. The limit of detection (LOD) and of quantification (LOQ) for the six metals were calculated as three times and ten times the standard deviation of nine replicate measurements of blank sample, respectively, and the results are present in **Table 3**.

Table 3 Analytical figures of merit

	Co	Cr	Fe	Mn	Ni	Pb
Correlation coefficient, R ²	0.997	0.999	0.996	0.995	0.998	0.994
Limit of detection, µg L ⁻¹	3.16	8.37	9.54	3.67	4.24	6.20
Limit of quantification, µg L ⁻¹	10.54	27.89	31.80	12.25	14.14	2.68

Analysis of real samples

The proposed method has been applied to the determinations of Co(II), Cr(III), Fe(III), Mn(II), Ni(II) and Pb(II) in certified reference material (NIST CRM 1-266YP, Trace Metals I) and in two river water samples from Bosnia and Herzegovina: (i) Bosna river and (ii) Spreča river. The analytical results of the certified reference material in **Table 4** were in good agreement with the certified values.

Table 4 Analysis of certified reference material NIST 1-266YP (n=5), mean ± standard deviation

	Co	Cr	Fe	Mn	Ni	Pb
Certified values (mg L ⁻¹)	100 ± 0.50	100 ± 0.50	100 ± 0.50	100 ± 0.50	100 ± 0.50	100 ± 0.50
Values found (mg L ⁻¹)	99.4 ± 0.92	101.3 ± 1.18	97.6 ± 2.23	100.2 ± 0.62	99.3 ± 0.87	98.1 ± 2.39
Recovery (%)	103.1	99.5	97.4	100.5	103.1	97.6

For the analysis of river water samples, the standard addition method was used. Therefore at the optimum conditions, river water samples were passed through the column for preconcentration and determination of the target heavy metal ions. The analytical results given in **Table 5** and **Table 6** show that the recovery of spiked samples were in the range of 96.6-101.2%. Good agreement was achieved between the added and found concentrations of analytes using the

general procedure at optimum conditions for preconcentration. These results indicated good accuracy of the method. Therefore, Nb₂O₅-SiO₂ is suitable for preconcentration of Co(II), Cr(III), Fe(III), Mn(II), Ni(II) and Pb(II) from river water samples prior to FAAS analysis.

Table 5 Analytical results for the determination of spiked metal ions in Bosna river water

Metal ion	Added (mg L ⁻¹)	Founda (mg L ⁻¹)	Recovery (%)
Cr	0.04	0.0387 ± 0.0005	96.8
Co	0.04	0.0404 ± 0.0011	101.1
Fe	0.04	0.0403 ± 0.0015	100.7
Mn	0.04	0.0386 ± 0.0002	96.6
Ni	0.04	0.0389 ± 0.0005	97.2
Pb	0.04	0.0394 ± 0.0015	98.6

^aThe value following “±” is the standard deviation (n=6)

Table 6 Analytical results for the determination of spiked metal ions in Spreča river water

Metal ion	Added (mg L ⁻¹)	Founda (mg L ⁻¹)	Recovery (%)
Cr	0.04	0.0393 ± 0.0004	98.2
Co	0.04	0.0397 ± 0.0007	99.3
Fe	0.04	0.0405 ± 0.0011	101.2
Mn	0.04	0.0404 ± 0.0008	101.1
Ni	0.04	0.0392 ± 0.0006	98
Pb	0.04	0.0398 ± 0.0009	99.6

^aThe value following “±” is the standard deviation (n=6)

Conclusions

Silica gel modified with Nb₂O₅-SiO₂ showed to be a good system for simultaneous preconcentration of some heavy metal ions from water samples with atomic absorption determination. The proposed method shows good precision and accuracy for all analytes analyzed. The limits of detection obtained for Co(II), Cr(III), Fe(III), Mn(II), Ni(II) and Pb(II) were satisfactory for FAAS. It was found that there is no significant difference between the results achieved by the proposed method and the certified values or spiked water samples. The proposed methodology is simple, accurate and low cost. Satisfactory spiking recoveries within the range of 96.6-101.2% (preconcentration factor = 25) were achieved for the water samples, demonstrating the practical and usefulness of the procedure. It may be concluded that the method is an effective approach in preconcentration and determination of Cr(III), Co(II), Fe(III), Mn(II), Ni(II) and Pb(II) from the river water.

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Publication History

Received 25th May 2015
Revised 04th Jun 2015
Accepted 13th Jun 2015
Online 30th Jun 2015