

Preconcentration of Metal Ions Using Silica Gel 60 F₂₅₄

Svraka I., Memić M., Sulejmanović J., Muhić-Šarac T.

University of Sarajevo, Faculty of Science, Department of Chemistry, Zmaja od Bosne 33-35, 71000 Sarajevo, Bosnia and Herzegovina

Article info

Received: 9/4/2014
Accepted: 13/5/2014

Keywords:

SPE
AAS
heavy metals
silica gel
preconcentration

*Corresponding author:

E-mail: m_memic@yahoo.com
Phone: 00-387-33-279882
Fax: 00-000-00-0000000

Abstract: In this study, the use of a column packed with unmodified activated silica gel as sorbent for preconcentration of Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb prior to their analysis by flame atomic absorption spectrometry (FAAS) was described. Factors affecting the preconcentration of analytes such as pH, sample flow rate and volume from pure multielement aqueous solutions of known concentration, were determined. The recovery values of prepared samples of known concentration of analytes were: 87.7% (Cd), 94.3% (Co), 95.7% (Cr), 91.2% (Cu), 105.2% (Fe), 84.5% (Mn), 96.6% (Ni) and 101.7% (Pb), under the optimum conditions (pH; 9, sample flow rate; 6mL/min, preconcentration factor; 10). The adsorption capacity of unmodified silica gel for Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb was found to be 6.05, 11.54, 13.08, 10.70, 12.18, 12.38, 11.59 and 3.28 $\mu\text{mol/g}$ of adsorbent, respectively. Detection limits of the method were 4.3, 35.0, 58.2, 18.5, 37.1, 10.3, 38.8 and 55.0 $\mu\text{g/L}$ for Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb, respectively.

INTRODUCTION

Nowadays, the heavy metal pollution has become big problem in the world since the heavy metal in particular concentration can affect the human and living organism body (Budiman et al., 2009). Therefore, countries and communities have regulations about allowed metal ion levels in the environment. Due to these quotes, accurate determination of metal ion traces is an important field of analytical chemistry. One of the most frequently used instrumental techniques for determination of metal ion traces is flame absorption spectrometry (FAAS) due to the ease of operation and determination, low cost, high precision and selectivity (Budizak et al., 2003, Ngeontae et al., 2009, Maltez et al., 2008). Separational and preconcentrational procedures for enrichment of metal ion traces present in environmental samples are necessity before flame atomic absorption spectrometry (FAAS) determination. Reason for this pretreatment is high detection limit FAAS (or low instrumental sensitivity) and interfering effect of sample matrix constituents on analyte (Ngeontae et al., 2007, Ngeontae et al., 2009). Main techniques for preconcentration and separation used for heavy metal traces are solid phase adsorption, solvent extraction, membrane filtration, coprecipitation, ion exchange, flotation and electrochemistry deposition (Soylak et al., 2005, Budiman et al., 2009, Takahoglu et

al., 2009). For the last years, solid phase extraction (SPE) has become the most used technique for analysis of traces, mainly because it is unnecessary to use the hazardous solvents (Budiman et al., 2009). The basic principle of SPE is the transfer of analytes from the aqueous phase to the active sites of the adjacent solid phase (Dogan et al., 2007). The transfer is stimulated by the selection of optimal conditions in the system having three main components: water (liquid phase), analyte and sorbent. After sorption on solid phase, analyte is either desorbed by suitable solvent or the analyte with the sorbent is dissolved in a suitable solvent and then analysed. Advantages of SPE include: flexibility in selection of solid phase, low costs due to less reagent consumption, lack of emulsion, high preconcentration factor, sensitivity improvement, sampling in the field, no requirements of toxic solvents, speed, simplicity and automation ability (Budizak et al., 2003, Tokman et al., 2003, Ngeontae et al., 2007, Budiman et al., 2009, Costa et al., 2011). Silica gel can be used as a very successful adsorbing agent, due to its relative inertness, good adsorption or cation exchange capability, simple modification with chemical compounds, excellent swelling resistance in different solvents, high mechanical and thermal stability (Silva et al., 2004, Budiman et al., 2009, Khosravan, 2009). Likewise, chelating agents can be bound to silica with high stability or can be chemically

bound as a support which makes silica material more stable (Zougagh *et al.*, 2005). For this reason, silica modified using organic substances which contain donor atom as S, N, P and O are of great interest (Alghami, 2012). Solid materials, like silica, are extensively used due to the presence of high number of reactive hydroxylic groups on its surface. These groups enable bonding of organic molecules which contain Lewis bases that can coordinate metal ions in solution, which increases metal ions sorption (Goswami *et al.*, 2002, Tzvetkova, 2012). Among the many existing support, silica gel deserves special attention due to the fact that it is subject to chemical modification with functional compounds through of its silanol groups dispersed on the surface. The surface of silica gel is characterised by the presence of silanol groups, which are known to be weak ion-exchangers, causing low interactions, binding and extraction of ionic species (Dogan *et al.*, 2007). Guided by this idea, aim of this work was to investigate ability of using unmodified, activated silica gel as an adsorbent (in column system) for simultaneous determination of Cr, Cu, Co, Cd, Fe, Mn, Ni i Pb from aqueous samples using FAAS technique.

EXPERIMENTAL

Instrumentation

Instruments used for the experimental part of this work were: Atomic absorption spectrometer, AA240FS, Varian, pH-meter, CG 841 Schott – GERATE GmbH, analytical balance (± 0.1 mg), Mettler, Toledo, Dyer, Bodalec and Havoic apparatus, type SE – 10. A glass column (150 mm height and 8 mm internal diameter) packed with unmodified activated silica gel was used for preconcentration of metals.

Chemicals and reagents

During the experimental work, the following chemicals were used: standard solutions of Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb of CertiPur grade; Merck, Germany. Other chemicals were of p.a. grade: HNO₃, Carlo Erba, Milano, NaOH and Na₃PO₄·12H₂O, Alkaloid, Skopje, HCl and KH₂PO₄, Semikem, Sarajevo, while Na₂B₄O₇·10H₂O, KH-phthalate and silica gel 60 F₂₅₄ were purchased from Merck, Germany.

Activation of silica gel

50 g of silica gel was added to 125 mL (1:1) of hydrochloric acid. The mixture was maintained at reflux (70-80 °C) for 6 h. After cooling, the mixture was filtered off and washed with redistilled water until no chloride appeared in the washing. The activated silica was first dried at room temperature for 48 h and then in a dryer at 110 °C for 5 h.

General procedure

The columns were sealed with small portion of glass wool, previously treated with HNO₃, to prevent material losses. Then, the columns were packed with 500 mg of activated silica gel, washed with redistilled water and conditioned with appropriate buffer solutions. Subsequently, 0.1 mg/L standard solutions of Cd(II), Cr(III), Co(II), Cu(II), Fe(III), Mn(II), Ni(II) i Pb(II),

were prepared by appropriate dilution of 1000 mg/L single element atomic absorption standard solution and adjusting the pH at the optimum value. The volume of 100 mL of solutions containing previously mentioned multielement metal ions were passed through the column at a flow rate of 2 mL/min. Adsorbed analytes were eluted with 7 mL of 1 mol/L HNO₃ (Venkatesh *et al.*, 2004) in a volumetric flask of 10 mL. Then, the columns were washed with redistilled water (3 mL) so that the final volume of sample prior to analysis by FAAS- fast sequential technique was adjusted to 10 mL. 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

Effect of pH

One of the most important factors in a liquid-solid adsorption procedure is the pH of the aqueous phase (Matoso *et al.*, 20003). Therefore, the effect of pH on the preconcentration of trace metals on unmodified activated silica was investigated over the pH of 5 to 10 by passing 0.1 mg/L of solutions containing Cd(II), Cr(III), Co(II), Cu(II), Fe(III), Mn(II), Ni(II) and Pb(II), applying the general procedure. The experimental results shown in Figure 1 indicated that the recovery values at pH 5 were very low (<10%) for 7 of 8 investigated metal ions. The only exception is iron, with a recovery of 74.3%. According to the results shown in Figure 1 it can be concluded that the pH of 6, 7 and 8 were more satisfactory, but not quantitative for all investigated metal ions, because the best recovery of 79.9% was noted for Pb(II) ions. The exception again is recorded for iron with 101.2% at pH 6 and 94.8% at pH 8. Furthermore, it can be observed that the pH 9 was optimal for the simultaneous determination of Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb ions with best recovery values recorded for Cd (87.7%), Cr (91.0%), Cu (95.9%), Mn (89.6%) and Pb (105.2%). At pH 10 a decrease in recovery values were observed for most of metal ions, probably due to hydrolysis with formation of metal hydroxides. Therefore, as a compromise between recovery values and sample pH for the adsorption of analytes on the surface of activated unmodified silica, pH 9 was chosen in subsequent work.

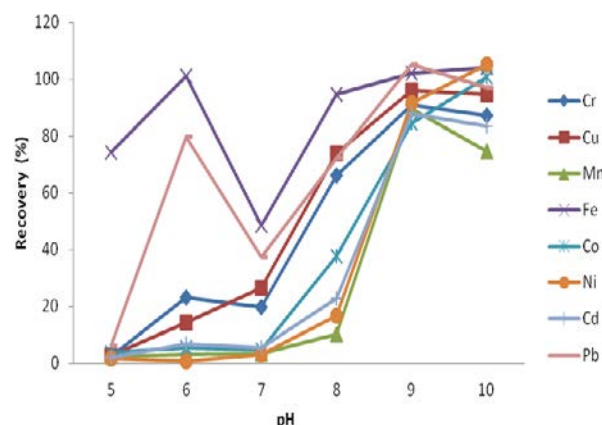


Figure 1: Effect of sample pH on the preconcentration of analytes on the unmodified silica.

Effect of sample flow rate

The sample flow rate is a very important operational parameter for the preconcentration efficiency and it determines the sample volume to be used (Maltez et al., 2008). The effect of sample flow rate on the retention of the studied metal ions on the activated silica gel was investigated by passing 100 mL of sample solution through the column and varying the flow rates between 1-6 mL/min. As it can be seen from Figure 2, the retention of Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb is not significantly affected by the flow rate, indicating that the sorption kinetics is very fast. The flow rate of 6 mL/min reduces the efficiency by 10% only for copper. Therefore, the flow rate of 6 mL/min was found to be suitable and quantitative for all investigated analytes and was used for all further experiments.

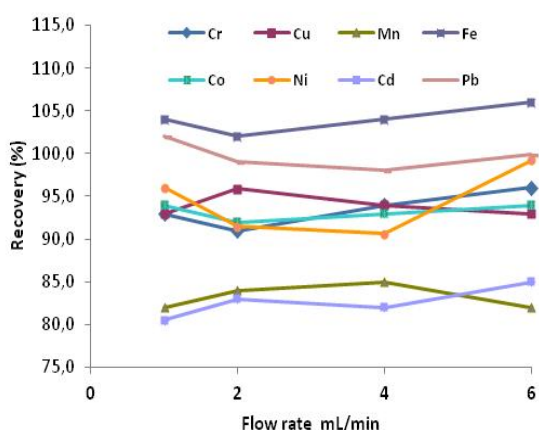


Figure 2: Effect of sample flow rate on the simultaneous retention of analytes on the unmodified silica surface. Other conditions: sample pH 9,500 mg of sorbent, analytes concentration of 0.1 µg/mL each.

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 silica (Suleiman et al., 2007). For this purpose, 100 mL, 250 mL, 500 mL and 1000 mL of sample solutions containing 0,1 µg/mL, 0,04 µg/mL, 0,02 µg/mL, 0,01 µg/mL, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb were passed through the column at the optimum flow rate. Recovery values as a function of sample volume at the optimum flow rate and mass of sorbent (500 mg) were shown in Figure 3. It can be seen that, with the increase of the preconcentration factor from 10 to 25, 50 and to 100 a decrease of 52%, 27% and 49% in recovery value occur for most of analyzed metals, respectively. According to the results from Figure 3, quantitative recoveries were obtained for the preconcentration factor of 10. Therefore, 100 mL of sample solution was selected as the optimum volume for the preconcentration of the analytes.

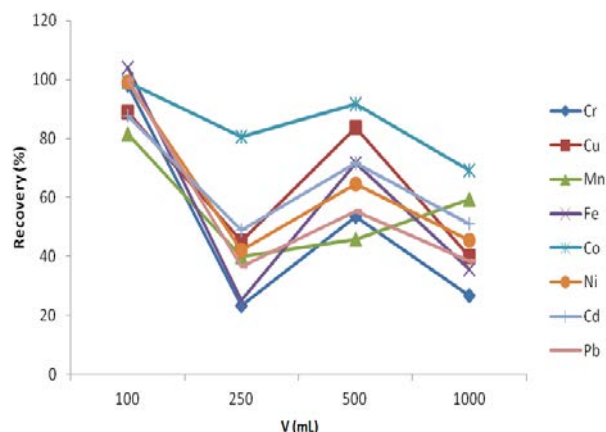


Figure 3: Effect of sample volume on the preconcentration of analytes in a column system.

Column capacity studies

The capacity of the column packed with 500 mg activated unmodified silica gel using the optimum conditions was studied by measuring the maximum quantity of the Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb ions sorbed on the non-modified silica surface. For this reason, increasing quantities of Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb were introduced into the column. It was possible to obtain quantitative recovery by using 0.5 mg of unmodified silica and up to 0.34 mg of Cd, Cr, Cu, Mn and Pb, Co, Fe and Ni. That means that the maximum adsorption capacity was 6.05, 11.54, 13.08, 10.70, 12.18, 12.38, 11.59 and 3.28 µmol/g of adsorbent for Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb, respectively.

Analytical precision and detection limits

The precision of the method, evaluated as the relative standard deviation for solutions containing 1 mg/L Cd, Cr, Co, Cu, Fe, Mn, Ni and Pb were 3.14, 1.96, 4.60, 2.19, 4.91, 2.86, 2.64 and 1.42 %, respectively (n=12). Linear calibration graphs with correlation coefficients > 0.99 were obtained for all analyzed metals. The limit of detection (LOD) and limit of quantification (LOQ) for the eight metals were calculated as 3.3σ/S and 10σ/S, respectively, where S is the slope of the calibration curve and σ is the standard deviation of 12 consecutive measurements of the blank solution. Obtained results for R², LOD and LOQ are given in Table 1.

Table 1. Correlation coefficients (R²), limit of detection (LOD, µg/L) and limit of quantification (LOQ, µg/L)

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb
R²	0.997	0.992	0.998	0.998	0.995	0.995	0.990	0.997
LOD	4.3	35.0	58.2	18.5	37.1	10.3	38.8	55.0
LOQ	13.2	106.1	176.5	56.2	112.5	31.3	117.6	166.7

Experimentally obtained recovery values for the eight metals under the optimum conditions of pH, sample flow rate and volume were shown in Figure 4. The results show that the recovery values of prepared samples of known concentration of analytes were: 87.7% (Cd), 94.3% (Co), 95.7% (Cr), 91.2% (Cu), 105.2 % (Fe), 84.5 % (Mn), 96.6% (Ni) and 101.7% (Pb).

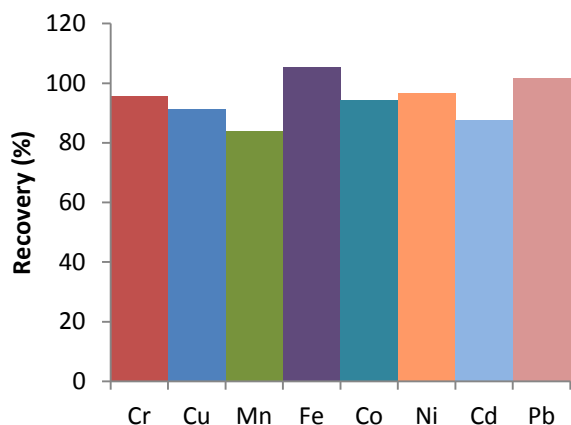


Figure 4: Results of recovery values after preconcentration on non-modified silica.

CONCLUSIONS

High values of recovery indicate that the activated silica gel 60 F₂₅₄ can be used as: (i) an excellent sorbent for preconcentration of Fe(III), Pb(II), Ni(II) and Cr(III); (ii) a good sorbent for preconcentration of Co(II) and Cu(II); (iii) a sufficient sorbent for preconcentration of Cd(II) and Mn(II) ions from aqueous samples, under the optimum conditions obtained by this study. The use of 500 mg of the unmodified silica gel allows the preconcentration of Co, Cr, Cu, Fe, Mn, Ni and Pb by a factor of 10. Non modified silica can be reused up to 12 times. In this system, sample preparation is simple and fast, and the elution step does not involve the use of organic solvents. The method detection limits improved under the optimal conditions in the column were adequate for FAAS.

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Summary/Sažetak

U ovoj studiji opisano je korištenje kolone punjene sa nemodificiranim aktiviranim silika gelom kao sorbentom za prekoncentriranje Cd, Co, Cr, Cu, Fe, Mn, Ni i Pb, neposredno pred njihovo određivanje plamenom atomskom apsorpcionom spektrometrijom (FAAS). Određeni su faktori koji utječu na prekoncentriranje analita iz čistih multielementnih vodenih rastvora poznate koncentracije i to pH, brzina protoka i volumen korištenog uzorka. Vrijednosti *recovery*-ja pripremljenih uzoraka metala poznate koncentracije su bile: 87.7% (Cd), 94.3% (Co), 95.7% (Cr), 91.2% (Cu), 105.2 % (Fe), 84.5 % (Mn), 96.6% (Ni) and 101.7% (Pb), pod optimalnim uvjetima (pH; 9, brzina protoka uzorka; 6 mL/min, prekoncentracioni faktor; 10). Adsorpcioni kapacitet nemodificiranog silika gela za Cd, Co, Cr, Cu, Fe, Mn, Ni i Pb je iznosio 6.05, 11.54, 13.08, 10.70, 12.18, 12.38, 11.59 and 3.28 $\mu\text{mol/g}$ adsorbenta, respektivno. Detekcioni limiti metode su bili 4.3, 35.0, 58.2, 18.5, 37.1, 10.3, 38.8 i 55.0 $\mu\text{g/L}$ za Cd, Co, Cr, Cu, Fe, Mn, Ni i Pb, respektivno.