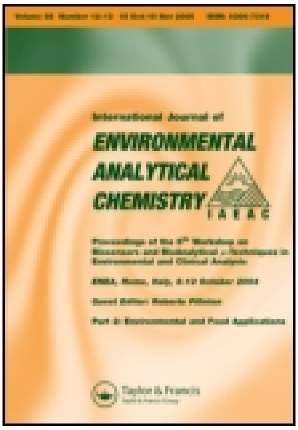

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Chemically modified silica gel for selective solid-phase extraction and preconcentration of heavy metal ions

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Chemically modified silica gel for selective solid-phase extraction and preconcentration of heavy metal ions

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This paper describes our research on the synthesis of the sorbent with chemically bonded ketoimine groups, and, furthermore, using this sorbent in the SPE technique to extract and preconcentrate trace amounts of metal ions in water samples. Surface characteristics of the sorbent were determined by elemental analysis, NMR spectra for the solid phases (^{29}Si CP MAS NMR), and analysis of pore size distribution of the sorbent and nitrogen adsorption-desorption. The newly proposed sorbent with ketoimine groups was applied for the extraction and preconcentration of trace amounts of Cu (II), Cr (III) and Zn (II) ions from the water from a lake, post-industrial water and purified water unburdened back to the lake. The determination of the transition-metal ions was performed on an emission spectroscope with inductively coupled plasma ICP-OES. For the batch method, the optimum pH range for Cu (II) and Cr (III) extraction was equal to 5, and Zn(II)–to 8. All the metal ions can be desorbed from SPE columns with 10 mL of 0.5 mol HNO_3. The detection limits of the method were found to be 0.7 $\mu g\,L^{-1}$ for Cu (II), 0.08 $\mu g\,L^{-1}$ for Cr (III), and 0.2 $\mu g\,L^{-1}$ for Zn (II), respectively.

Keywords: chemically modified silica gel; heavy metal ions; solid-phase extraction

1. Introduction

Heavy metals such as chromium, copper, lead, nickel and zinc are toxic and harmful, even at a low concentration level. Such metal ions provoke several serious and ongoing problems related mainly to aquatic life, human beings and environmental pollution [1,2]. In order to overcome these problems, new separation and preconcentration methods of given analytes are necessary, particularly those applicable at trace levels of concentration.

A vast majority of real samples contain analytes that are at a concentration that is too low for direct instrumental injection. Preparing a sample by concentrating the species of interest prior to instrumental introduction is often necessary. Currently, solid-phase extraction (SPE) is the most widely used sample preparation method for many analytical techniques, including isolation and concentration of various analytes, and the clean-up of samples in pharmaceutical, clinical, environmental and food analysis [3–6].

Thus, the current research is oriented on developing new, improved sorbents, capable of determination of selected compounds from complex matrices [7].

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The following substrates were used to separate trace amounts of heavy metal ions from the water and other solutions: 3-aminopropyltriethoxysilane [8], propanethiol modified silica gel [9], mono- and bis-salicylaldehyde and naphthaldehyde Schiff's bases [10], octadecyl silica membrane disc [11], 8-hydroxyquinoline immobilised on fluorinated metal alkoxide glass [12], N-propylsalicylaldimine (IE11) [13], bis-1-hydroxy-9,10-anthinon-2-methyl sulfide [14], cyrconium fosfide [15], 1-(2-pirydilazo)-2-naphtol (PAN) [16], C_{18}-bonded silica extraction disks modified with a novel Schiff base 2,2′-[1,6-hexanediyl bis (nitriloethylidine)]bis-1-naphthol [17], functionalised silica gel (SG-ofloxacin) [18], octadecyl silica membrane disks modified with 5,5′-dithiobis(2-nitrobenzoic acid [19], octadecyl-bonded silica membrane disks modified with a S-N-containing Schiff base (bis-2-thiophenal propandiamine) [20], octadecyl silica membrane disks modified with an H_2Salphen (L) [21], diaminothiourea-modified silica gel [22] and pentathia-15-crown-5 [23], as well as some other compounds [24,25]. Main disadvantages of the above-mentioned methods are related to: (1) a dependency of the method efficiency on metal concentration; (2) several restrictions in experimental conditions (appropriate pH, temperature); and (3) limited stability of the formed chelate. In order to bypass the above-mentioned disadvantages, in this paper we propose a new sorbent modified with ketoimine groups. The main goal of our research is twofold. First, we propose new methods for the preparation and the determination of properties of new sorbent based on silica modified with ketoimine groups. Second, we demonstrate the usefulness of the proposed sorbent by the discussion of physico-chemical characteristics of the sorbent under study applied for the extraction and preconcentration of trace amounts of Cu (II), Cr (III), and Zn (II) ions from the water from a lake, post-industrial water and purified water unburdened back to the lake.

In our previous work, the silica modified with ketoimine groups was successfully applied for the determination of trace amounts of bisphenol-A (BPA) in mineral water and powder milk samples [26–28]. In this new research, we use the fact that ketoimine groups bonded to the silica surface are capable of complexation of transition metals. The newly proposed sorbent with ketoimine groups was applied for the preconcentration of trace amounts of heavy metal ions. These metals are extremely important for several biological processes; however, their levels in some cases may cause serious diseases [29].

2. Experimental

2.1 *Apparatus and reagents*

Elemental analysis was performed on 2400 CHN Elemental Analyzer (Perkin-Elmer, Norfolk, USA). NMR (Nuclear Magnetic Resonance) spectra for the solid phases (^{29}Si CP MAS NMR) were taken using spectrometer 300 MSL (Bruker, Rhenstteten, Germany). IR (InfraRed) spectra were taken using spectrophotometer Bruker IFS 113 V (Bruker, Rhenstteten, Germany) by the use of the KRS5/FTIR technique. Scanning conditions were as follows: wave number range from 4000 to 500 cm^{-1}; resolution 2 cm^{-1}. Nitrogen adsorption/desorption isotherms at the temperature of liquid nitrogen were obtained with ASAP 2010 sorptometer (Micrometrics, Narcross, GA, USA). Determination of the concentration of Cu (II), Cr (III), and Zn (II) was performed on a spectrophotometer VISTA-MPX with inductively coupled plasma (VARIAN ICP, Australia) and ICP MS (VARIAN Analyst, Australia). A Bakerbond SPE (Solid Phase Extraction) vacuum manifold was used for the elution of SPE columns.

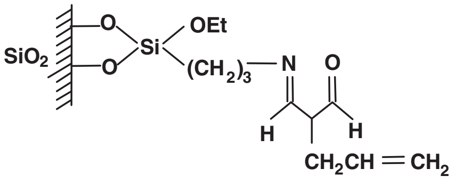


Figure 1. Structure of chemically bonded sorbent synthesized.

2.2 *Chemicals and materials*

Silica gel (Baker Analyzed^{R}) was purchased from J.T. Baker. 3-pentano-2,4-dione derivatives, which were used for the modification of the silica surface, were obtained from the Metalorganics Department of the Adam Mickiewicz University, Poznań, Poland. Solvents used for the modification reactions (xylene and hexane – analytical grade) were purchased either from POCh (Gliwice, Poland), or Fluka (Buchs, Switzerland). Copper, chromium and zinc stock standard solutions $1000\,\mu g\,mL^{-1}$ were purchased from Merck. Nitric acid and HCl of analytical reagent grade were purchased from Fluka.

2.3 *Modification procedure*

A quantity of 5 g of dry silica was immersed in a mixture of anhydrous xylene and 3-aminopropyltriethoxysilane. The mixture was boiled for 12 h in a vessel equipped with a reflux condenser. The contents were continuously stirred and carefully protected against the moisture. Unreacted silane was extracted with xylene and hexane in a Soxhlet apparatus. After that the whole system was dried under vacuum and finally subjected to the so-called 'end capping' reaction [30] with hexamethyldisilazane in order to deactivate free silanol groups remaining at the silica surface.

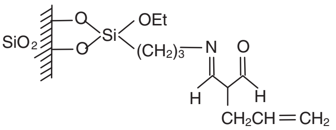
The second step was bonding of amino groups using an appropriate derivative of 3-pentano-2,4-dione. As previously, the reaction was performed under continuous stirring in anhydrous xylene and lasted 12 h. The system was protected against the moisture. The final product was extracted subsequently with xylene and hexane in a Soxhlet apparatus. Finally, silica was dried under vacuum.

The structure of chemically bonded sorbent synthesised is presented in Figure 1.

2.4 *Extraction procedure*

The general procedure for the extraction of Cu (II), Cr (III) and Zn (II) by means of the modified sorbent was as follows. The amount of 500 mg of the silica modified with ketoimine groups was placed in an SPE column. Before use, the system was conditioned, first in 8 mL of methyl alcohol, and further 8 mL of deionised water. The water samples were prepared with deionised water (100 mL) to contain 5 µg of Cu (II), Cr (III), and Zn (II). The pH value of sample solution was adjusted to a range of 4 to 8 with 0.1 mol KNO_3 and 30% (v/v) NH_4OH. Metal ions were eluted with 10 mL of 0.5 mol HNO_3 solution. The total concentration of Cu (II), Cr (III) and Zn (II) was determined by means of ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, for the optimisation process for column preconcentration) and ICP-MS method (in the analysis of the real samples).

Table 1. Physico-chemical properties of the sorbent under study.

	Elemental analysis, %			① $m^2\,g^{-1}$	② $\mu mol\,m^{-2}$	③ nm	④ $mL\,g^{-1}$
Sorbent	C	H	N				
Silica gel	0.05	0.99	–	552	–	6.18	0.88
	13.44	3.34	1.96	326	4.37	4.87	0.41

① Surface area, ② Surface concentration of silane, ③ Pore diameter and ④ Specific pore volume.

Blank samples were prepared in a similar way as described above, except that no metals were added. The results obtained for the blank samples were deducted from the corresponding results obtained for the samples under study.

3. Results and discussion

3.1 *Physicochemical properties*

To investigate physicochemical properties of the obtained packings, these packings were subjected to the elemental analysis, in order to determine total contents of carbon, hydrogen and nitrogen, and to estimate the specific surface area. The surface concentration of bonded siloxane molecules (denoted by α) in $\mu mol\,m^{-2}$ was calculated from the carbon content according to the following equation:

$$\alpha = \frac{\%C \cdot 10^6}{(100 \cdot n \cdot 12 - \ \%C \cdot M) \cdot S_{BET}}$$

where: $\%C$ denotes percentage of carbon contribution, n – number of carbon atoms in the molecule of bonded silane, M – molecular mass of the siloxane, and S_{BET} – specific surface area [$m^2\,g^{-1}$]. The results are presented in Table 1.

3.2 *^{29}Si CP MAS NMR spectra*

To examine the surface of the obtained sorbent, we used NMR technique for the solids (^{29}Si CP MAS NMR). ^{29}Si CP MAS NMR spectrum makes it possible to differentiate the silanols in the SiO_2 structure. Spectra ^{29}Si CP MAS NMR of the unmodified silica are presented in Figure 2a, while the spectra of the sorbent under study are presented in Figure 2b.

An analysis of these spectra confirms that a reaction of the synthesis took place at the silica surface. During this reaction, the geminal silanols were blocked. The distinct signal at −90.56 ppm for the spectrum of the unmodified silica is weaker for the modified silica. At the same time, the signal at −102.94 ppm is changed, and this fact proves that the isolated silanols are blocked as well. A clear signal at +12.52 ppm accompanied by the

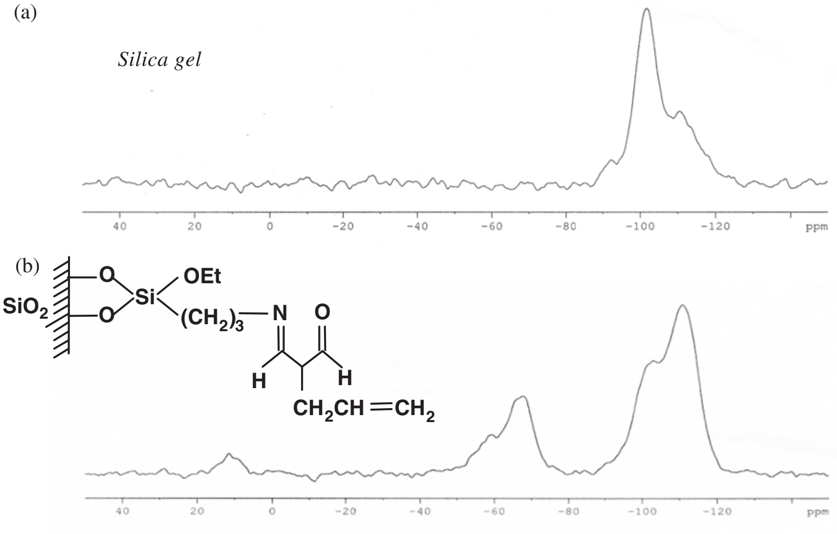


Figure 2. Spectra ^{29}Si CP MAS NMR of (a) the unmodified silica and (b) the sorbent under study.

signals at −59.9 to −67.61 ppm ($T_4 + T_4'$) points out the modification of the silica by trifunctional silane, and the ‘end capping’ process by the use of hexamethyldisilazane.

3.3 *FTIR spectra*

For the modified silica, the spectra were taken by the use of the FTIR (Fourier Transform Infrared Spectroscopy) method and KBr pellets. Due to the low concentration of the functional groups bonded to the silica surface, the intensity of the bands is low; however, some characteristic bands may be observed related with vibrations of given groups. In Figure 3, two spectra are presented, namely: a/for unmodified silica, and b/for the silica modified with ketoimine groups.

While interpreting the presented spectra, one may observe a presence of hydroxy groups (unmodified silica, Figure 3a). This presence is proved by stretching band OH at 3500 to 3434 cm^{-1}. This band is lowering after the modification (Figure 3b), which means that some surfaced silane groups were blocked. For the spectrum of the silica subjected to the second stage of the synthesis (Figure 3b), one may observe stretching C=O band at 1653 cm^{-1}, and stretching C=C band. This fact proves the presence of the ketoimino groups at the silica surface. In addition, the following bands may be observed: stretching C-H band (CH_2 groups) at 2937 cm^{-1}, and bending C-H band at 1568 cm^{-1}. The spectra taken, as well as the results obtained with other techniques, lead to the final conclusion: the silica was successfully modified with the given functional groups.

3.4 *Nitrogen adsorption/desorption isotherms*

The chromatographic materials should be free from micropores, i.e. those with diameters below 20 Å [31], because their presence slows mass transfer [32–36]. Figure 4 illustrates that this is the case of the sorbent under study.

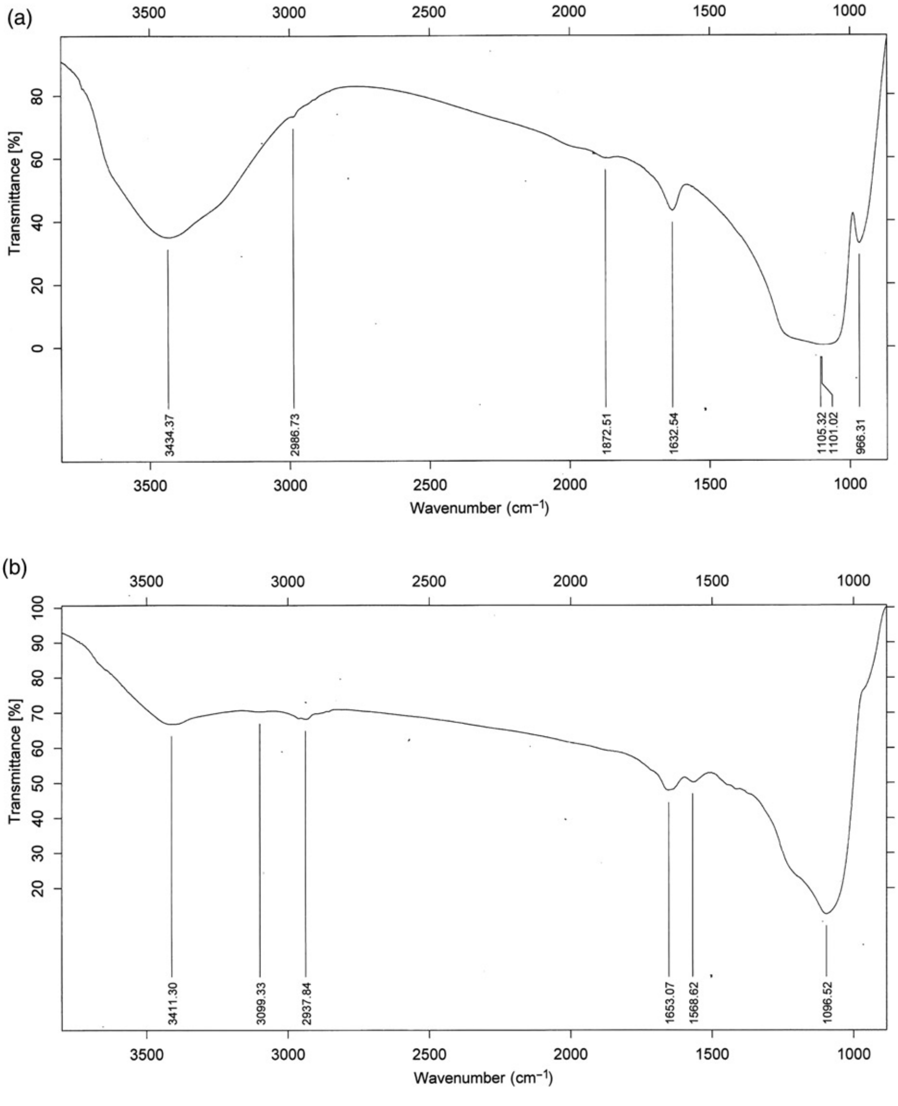


Figure 3. FTIR spectra of: (a) silica unmodified, and (b) modified with ketoimine groups.

The pore shape of the sorbent should, moreover, be homogeneous. Although this is not easy to verify, analysis of the shape of the hysteresis loop on the adsorption-desorption isotherm can give some information about pore structure.

The hysteresis loop shown in Figure 4 is almost vertical with almost parallel branches, thus it belongs to type H2 according to the IUPAC classification [31]. This type of hysteresis is usually associated with porous materials consisting of agglomerates or compacts of approximately uniform spheres as fairly regular array. Therefore, they have a relatively narrow pore size distribution.

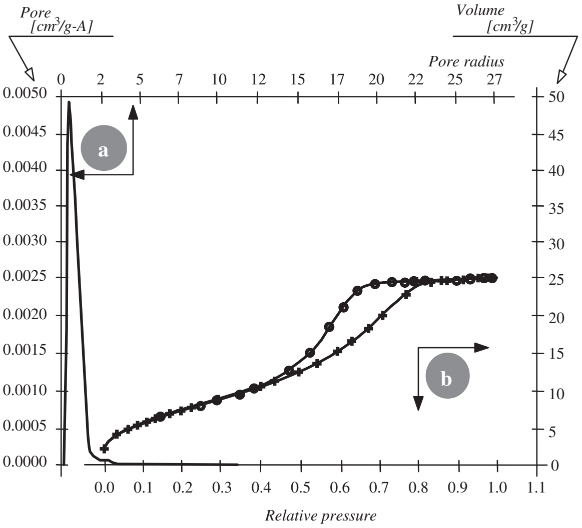


Figure 4. Pore size distribution of: (a) the silica support and (b) nitrogen adsorption/desorption isotherms, for the modified silica.

3.5 *Optimisation process for column preconcentration*

The column method was optimised for obtaining quantitative recovery of the analytes. Each of the optimum conditions determined was established while others were kept at the optimum value. Each condition was rechecked after optimising those remaining.

3.5.1 *Effect of pH*

One of the most important features in a liquid-solid adsorption procedure is the pH value of the aqueous phase. The effect of pH on the SPE of Cu (II), Cr (III) and Zn (II) was studied in the range 4 to 8. The pH value of sample solution was adjusted to a range of 4 to 8 with 0.1 mol KNO_3 and 30% (v/v) NH_4OH. The solutions obtained were passed at a flow rate about 1 mL min^{-1}. The heavy metal ions were determined in the eluate and the recovery was calculated. The concentration of the metal ions in the eluate was determined by means of ICP-MS method. The results are shown in Figure 5. The curve illustrating the percentage of Cu (II), Cr (III) and Zn (II) adsorbed on the new sorbent at the different pH values of the model solution indicates that for pH ranging from 4 to 8 the recovery of Cu (II), Cr (III), and Zn (II) ions is quantitative in the range 5 to 6.

3.5.2 *Effect of the type and concentration of elution solutions*

We also examined the effect of concentration and type of eluting acids on the recovery, at pH 5 and weight 500 mg. For the elution we applied 0.5 mol and 1 mol HNO_3, as well 0.5 mol and 1 mol HCl. The obtained results are presented in Table 2. Taking into account these results, 0.5 mol HNO_3 was taken as an eluting acid for the subsequent experiments.

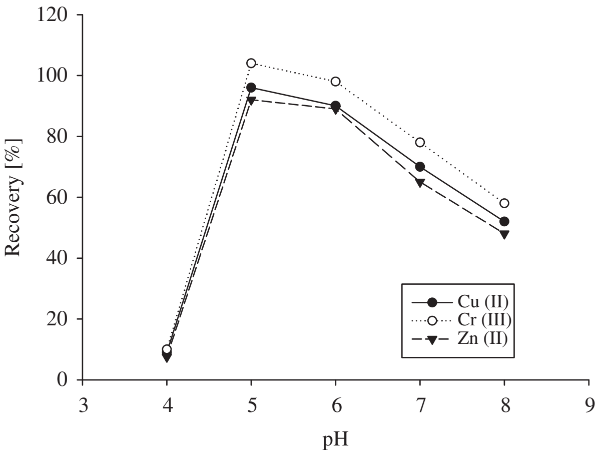


Figure 5. Effect of pH of sample solution on extraction efficiency of analytes Cu (II), Cr (III) and Zn (II).

Table 2. Effect of the type and concentration of elution solutions on the recovery of Cu (II), Cr (III), and Zn (II).

Element	Type of elution solution	Recovery* [%] for concentration 0.5 mol L^{-1}	Recovery* [%] for concentration 1 mol L^{-1}
Cu (II)	HCl	53 ± 4	65 ± 2
	HNO_3	97 ± 4	90 ± 3
Cr (III)	HCl	62 ± 2	73 ± 4
	HNO_3	100 ± 1	95 ± 3
Zn (II)	HCl	65 ± 2	70 ± 3
	HNO_3	96 ± 3	89 ± 2

*$\overline{x} \pm s$ ($n = 3$), $\overline{x}$: average value for three determinations; s, standard deviation.

3.5.3 *Effect of amount of solid phase*

The retention of the metal ion studied was examined at the optimum pH (pH 5) under certain circumstances (concentration 5 µg L^{-1}; sample volume 100 mL; flow rate 1 mL min^{-1}, elution solution 10 mL 0.5 mol HNO_3) in relation to the amount of solid phase, which was varied from 100 to 500 mg. The detected recovery of Cu (II) (Cr (III), Zn (II), respectively) was the following: 41% (30%, 28%) for the amount of the solid phase equal to 100 mg, 50% (36%, 39%) for 250 mg, and 97% (104%, 95%) for 500 mg (Figure 6). As may be seen, the recovery of the above-mentioned metals was the highest for the 500 mg of the sorbent. Therefore, 500 mg of solid phases were used in the subsequent experiments.

3.5.4 *Effects of matrix ions*

The effects of common coexisting ions on the adsorption of studied ions were investigated, respectively for the metals under study. In these experiments, different foreign ions were

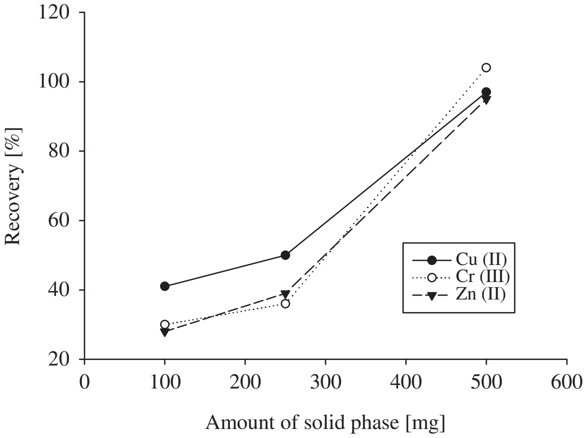


Figure 6. Effect of the amount of solid phase on the recovery of analytes Cu (II), Cr (III) and Zn (II).

added to equal quantities of the diluted mixed standard solutions, enriched and determined according to the general procedure. The results showed that such metals as Na and K do not have an influence to the separation and determination processes if concentration of these metals is low enough – up to 80 μg mL^{-1} for Na and 35 μg mL^{-1} for K, respectively. Ca and Mg show no influence while in concentration below 10 and 2.5 μg mL^{-1}, respectively.

3.5.5 *Detection limits of the proposed method*

In accordance with the definition of IUPAC, the detection limit of the method was calculated based on three times the standard deviation of eight runs of the blank solution. The detection limits (3σ) were found to be 0.7 μg L^{-1} for Cu (II), 0.08 μg L^{-1} for Cr (III) and 0.2 μg L^{-1} for Zn (II), respectively.

3.6 *Application*

The proposed sorbent was applied to preconcentrate and to determine a content of three heavy metal ions: Cu (II), Cr (III) and Zn (II), in the water from a lake, post-industrial water (i.e. water used for some activities in a factory) and purified water unburdened back to the lake. For the analysis of the water samples, the standard addition method was used. As shown in Table 3, the recovery values of the analytes were in the range 94 to 98%. The recovery results for both metals are presented in Table 3, with the confidence interval equal to 95% and relative error less than 1.23 to 4.26%. This fact demonstrates a suitability of the proposed sorbent with ketoimine groups for the preconcentration of Cu (II), Cr (III), and Zn (II) from water samples prior to ICP-OES analysis.

4. Conclusion

In this work new sorbent was proposed for the SPE method with chemically bonded ketoimine groups. A way of preparation and the physico-chemical properties of this

Table 3. Analytical results for the determination of Cu (II), Cr (III) and Zn (II) in water samples, after preconcentration.

Element	Pre-industrial water [μg L^{-1}]	Recovery [%]	Post-industrial water [μg L^{-1}]	Recovery [%]	Purified water [μg L^{-1}]
Cu (II)	0.81 ± 0.11 1.76 ± 0.06	95	0.97 ± 0.14 1.93 ± 0.05	96	BDL*
Cr (III)	0.05 ± 0.01 1.04 ± 0.04	99	0.10 ± 0.02 1.07 ± 0.03	97	BDL
Zn (II)	0.60 ± 0.02 1.54 ± 0.04	94	0.73 ± 0.01 1.69 ± 0.02	96	BDL

*BDL – below detection limit.

sorbent are presented. We had successfully synthesised a novel chemically modified silica gel and afterwards applied such obtained packings to solid-phase extraction and preconcentration of Cu (II), Cr (III), and Zn (II) by means of SPE and ICP-OES methods. Based on the obtained results, we proved that the new sorbent with ketoimine groups may be used for efficient preconcentration of the trace amounts of the above-mentioned heavy metals.

Careful determination of the conditions for the sorption and desorption for Cu (II), Cr (III), and Zn (II) ions allowed us to determine quantitatively these metals in the water samples. The water to be analysed was collected from a lake, as post-industrial water and purified water unburdened back to the lake from an electric plant. Unburdened water seems to be the richest source of Cu (II) and Cr (III) ions. As such water is subjected to contact with electric-plant equipment, including boilers, turbines and condensers; it contains not only transition metals, but also some other pollutants.

Purified water in turn contains a lower amount of Cu (II) and Cr (III) ions. Such water is extensively purified, to be used in refrigerating and thermal cycle. Purified water provokes no degradation of the equipment, both of chemical and mechanical nature.

Acknowledgements

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