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Improvement of copper FAAS determination conditions via preconcentration procedure with the use of salicylaldoxime complex trapped in polymer matrix

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ABSTRACT

The paper presents application of a new resin dedicated to copper(II) flow-injection on-line preconcentration prior its flame atomic absorption spectrometric (FAAS) determination. The new sorbent, obtained by suspension polymerization technique, was styrene-divinylbenzene copolymer modified with 5-dodecylsalicylaldoxime-copper(II) complex. In flow mode leaching of initially imprinted Cu(II) ions from polymer beads was effective with 1% (v/v) nitric acid, however for elution of ions retained on the sorbent during the loading process sufficient efficiency was obtained for 0.5% (v/v) nitric acid. The most effective copper(II) sorption was observed within sample pH ca. 6.3 at flow rate 7.5 mL min^{-1}. Furthermore, preconcentration studies of Cu(II) ions realized in the presence of popular foreign ions like Cd(II), Pb(II), Zn(II), Ni(II), Mn(II), Co(II) did not reveal significant interference. The expected effect of Cu(II)-imprinting was confirmed by higher tolerance level for interferents ions concentration for the new sorbent than for the control polymer. It was found that alkaline metals ions and humic acid had the most relevant influence on copper(II) uptake. Accuracy of the evaluated method was assessed for analysis of water samples (tap and mineral water, river water, artesian water) and certified water reference materials compare them to results obtained by inductively plasma mass spectrometry. The satisfactory relative error values obtained with use of standard addition calibration method, confirms the feasibility of this method for Cu(II) determination in water samples. Application of 120 s sorption time enabled to obtain 74-fold enrichment factor and limit of detection (3σ) equal to 0.4 μg L^{-1}.

1. Introduction

Copper is classified as biogenic element playing a significant role in photosynthesis, metabolism of nitrogen compounds or regulation of RNA and DNA transcription process. About 30 enzymes containing copper ion are known in animal organism, e.g. ceruloplasmin, cytochrome oxidase, tyrosinase, hemocyanine [1]. Except for natural sources like weathering of soil and mining operations, copper is released to environment also from anthropogenic ones: fertilizers, wood preservatives, fungicides, algicydes or corrosion of water delivery system made of copper. Increasing amount of copper compounds in environment is especially dangerous for water plants, fish and invertebrates which accumulate copper in organism and as the lower food chain link transfer copper to higher trophic levels increasing its uptake. Long-term exposition to high copper concentrations causes gastrointestinal or liver symptoms in humans [2]. Therefore, application of methods to control trace amounts of copper in environment is necessary.

Flame atomic absorption spectrometry (FAAS) as one of the most popular and relatively cheap technique for metal determination frequently exhibits insufficient detection limit to be applied to copper determination in water samples. Therefore, on-line preconcentration step preceding the determination, realized especially via solid phase extraction (SPE) in a flow mode, is often recommended. The main advantages of SPE technique are: the possibility to increase analyte/matrix (macrocomponent) ratio which results in lowering the detection limit of the determination method, as well as elimination or reduction of a probable interferent effect due to simplification of the sample matrix. Application of a flow injection system leads to: (i) enhancement in number of preconcentration cycles, which results from working in non-equilibrium conditions, (ii) increase in preconcentration factor, (iii) reduction of chemicals and sample consumption, (iv) gives possibility to use of nontoxic (inorganic) eluent and obtain higher repeatability of analysis. Moreover, wide variety of sorbent materials offers opportunity to adjust proper preconcentration conditions, adequate for the type of analyte and the sample. Among other sorbents: resins, silica gel, cellulose, carbon materials and biosorbents are frequently used [3]. Due to generally low selectivity of simple sorbent materials, chemical and physical modification of their structure with selective reagents are often employed.

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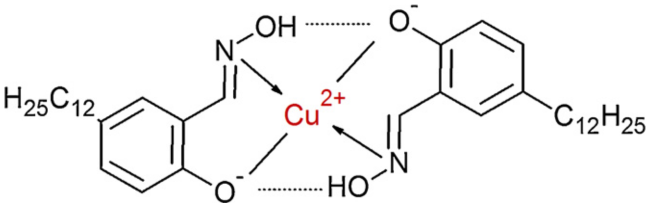

Fig. 1. Structure of 5-dodecylsalicylaldoxime copper(II) complex.

About 40 years ago independently Wulff and Klotz proposed a new method of obtaining selective sorbents called imprinted polymers. Over the past two decades the idea of imprinted polymers has been developed and gained immense popularity both for molecules and metal ions, assuring high sorption selectivity obtained thanks to the presence of the analyte: molecule/ion complex (or its analog) during the synthesis process [4,5]. Leaching of the template ion/molecule from the obtained sorbent provides active cavities retaining spatial geometry of template (molecular/ion imprint). As for ion imprinted polymers (IIPs) three basic synthesis methods may be distinguished, namely: (i) covalent binding of an ion complex with a polymer body, (ii) surface imprinting or (iii) complex trapping inside the polymer matrix [6].

A few papers presenting copper-imprinting idea was published so far. Application of typical chelating ligands like pyridylazoresorcinol (PAR) [7,8], vinylopirydyne [9,10] or chinione compounds [11–13] are reported. Among them the lowest detection ($0.06\,\mathrm{mg\,L^{-1}}$) limit was obtained for polymethacrylic beads imprinted with Cu-PAR complex [7] while electrothermal atomic absorption spectrometer was chosen as a detection system. All above mentioned investigations show application of sorbent for off-line systems and describing parameters were estimated in equilibrium conditions.

Here we present a new polymeric sorbent with styrene-divinylbenzene matrix for which selectivity enhancement towards Cu(II) ions was obtained via of 5-dodecylsalicylaldoxime copper(II) complex (Fig. 1) trapping. The proposed chelating reagent is the main component of a commercial liquid-ion exchanger LIX 622® widely applied to metallurgical purification of copper from unwanted contaminants, exhibiting excellent selectivity towards Cu(II) especially in strong acidic conditions. The newly obtained polymer was exploited in flow-injection copper(II) preconcentration step on-line with FAAS determination.

2. Materials and methods

2.1. Apparatus

Preconcentration and determination steps were realized on-line with the use of a flow-injection system FIAS 400 and a flame atomic absorption spectrometer AAnalyst 300 (both Perkin Elmer, USA). The flow system was equipped with a homemade Plexiglass® column (5 mm × 3 mm or 30 mm × 3 mm) filled with a portion of ca. 20 mg of the examined polymer and Tygon® red-red tubings 1.14 mm i.d. were employed for propelling liquids. The setup worked under common computer software AA WinLab (Perkin Elmer, USA). Copper was determined under conditions recommended by the manufacturer. Analytical signals registered in the form of peak height were measured at 324.8 nm wavelength with deuterium background correction. Nebulizer aspiration flow rate was set at about $7\,\mathrm{mL\,min^{-1}}$.

Elmetron (Zabrze, Poland) CPI-551 pH-meter was used for pH measurements. ICP MS Elan DRC-e (Perkin Elmer, USA) was applied for reference measurements.

Scanning electron microscope JEOL JSM-7500F was applied for investigation of the morphology of the sorbent surface. The images were obtained with the use of brass stubs and sputter coated with chrome on accelerating voltage of 15 kV.

IR spectra analysis was performed with the use of Bruker Equinox 55 spectrometer, while thermogram was obtained with Mettler Toledo TGA/SDTA 851e analyzer.

2.2. Reagents and solutions

For polymerization purposes pure styrene (S) and 55% divinylbenzene (DVB) (Aldrich, USA) were applied. Pure 1,2-dichloroethane and azobisisobutyronitrile (AIBN) from Aldrich were used as a porogen and polymerization initiator, respectively. Domestic gelatin was employed as the protecting colloid. Commercial liquid ion exchanger LIX 622® (Henkel, Germany) containing 5-dodecylsalicylaldoxime as the main component was applied for copper(II) chelatation.

All eluents: nitric acid, hydrochloric acid and sulphuric acid and copper sulfate pentahydrate were analytical grade purchased form Merck (Darmstadt, Germany). Deionized water after reversed osmosis was used to prepare all solution. The laboratory glassware was kept overnight in 1% (v/v) nitric acid and afterwards rinsed by deionized water. Standard stock solutions of heavy metal ions were prepared from Titrisol® standards supplied by Merck.

Britton-Robinson buffers were prepared by mixing acidic buffer base containing $0.04\,\mathrm{mol\,L^{-1}}$ acetic acid (Merck), $0.04\,\mathrm{mol\,L^{-1}}$ phosphoric acid, $0.04\,\mathrm{mol\,L^{-1}}$ boric acid (POCh, Gliwice, Poland) with $0.2\,\mathrm{mol\,L^{-1}}$ sodium hydroxide (POCh, Gliwice, Poland) in appropriate ratios.

Certified reference materials EnviroMAT waste water EU-H-3 and ground water ES-H-2 both supplied by SCP Science (Canada) were applied to evaluate the method accuracy.

2.3. Preparation of 5-dodecylsalicylaldoxime copper(II) complex

Saturated solution of copper sulfate prepared by dissolving 0.5 g copper sulfate pentahydrate in 5 mL of deionized water was shaken for about 5 min with a mixture of 2.5 mL LIX 622® in 2.5 mL dichloroethane and then the phases were left to separate. Afterwards bottom blue-black organic phase containing complex of copper(II) 5-dodecylsalicylaldoxime (LIX-Cu(II)) was isolated and used for subsequent synthesis.

2.4. Synthesis of Cu-imprinted polymer (IIP-LIX-Cu(II))

Modified sorbent beads were prepared via normal suspension polymerization as follows. First, dispersion medium consisting of gelatin (2.6 g), sodium chloride (0.35 g) and water (125 mL) was prepared in a round-bottom flask and thermostatted at 75 °C. Then, organic phase composed of: LIX-Cu(II) complex solution (0.8 mL), 1,2-dichloroethane (10 mL), AIBN initiator (0.35 g), styrene (7.0 mL) and divinylbenzene (3.0 mL) was added dropwise. The mixture was purged with argon for 5 min and mechanically stirred with 650 rpm for 5 h. The obtained beads were filtered, thoroughly washed with hot water and dried in a vacuum dryer.

Not-imprinted polymer (control polymer, CP) was prepared as a reference sorbent in similar polymerization procedure, however instead of 0.8 mL LIX-Cu complex, 0.8 mL LIX 622® dissolved in 0.8 mL 1,2-dichloroethane was utilized.

Scanning electron characteristic was made for both imprinted and control polymers. An example of micrograph obtained for IIP-LIX-Cu(II) sorbent at a 500-fold magnification is showed in Fig. 2. For both polymers particles were of spherical shape and diameters mainly in range of 30–50 µm.

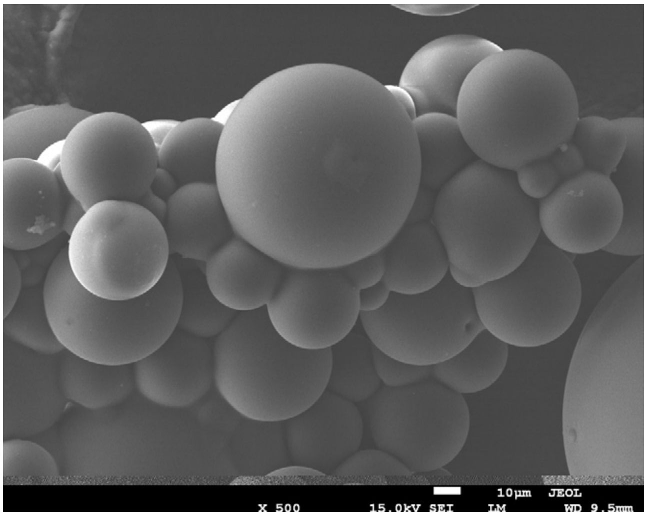

Fig. 2. Scanning electron micrograph of IIP-LIX-Cu(II) beads.

FTIR spectra of obtained imprinted microbeads relevant broad absorption band at 3453 cm^{-1} caused by stretching vibrations of –OH groups, however for non-imprinted polymer low frequency shifting (ca. 13 cm^{-1}) was observed that indicate formation of complex via O-atom. The observed at 1600 cm^{-1} medium intensive bands can be connected with C=C stretching vibrations from aromatic ring. Stretching asymmetric –CH_3 vibrations occurred at 2960 cm^{-1} as well as stretching symmetric –CH_2 2842 cm^{-1} from aliphatic chain. TGA analysis confirm stability of the proposed sorbent up to 440 °C.

2.5. On-line preconcentration procedure

The flow system utilized in preconcentration procedure consisted of two peristaltic pumps for loading the sample and eluent, a column filled with the examined polymer and a two-positional valve. Schematic representation of the applied system is showed in Fig. 3. The program controlling FIAS 400 included five steps: tubes prefilling (1 s), tubes filling (30 s), sample loading (30 s in the optimized procedure), elution (30 s) and the final stop pumps step (1 s). Ten seconds before the valve position was changed into “inject”, the second pump was activated in order to propel the eluent directly to FAAS and establish the base signal. Absorbance was measured for 12 s and peak high was read as the analytical signal. During the optimization study 18 mg of the sorbent was used as the column filling, while for subsequent copper determination in natural samples the sorbent mass was increased to 138 mg. Each new portion of the imprinted polymer after being packed in the column was washed several times in flow mode with 1% nitric acid to remove copper ions from active sites.

2.6. Sample preparation

The proposed method was tested for determination of copper(II) in the following types of water: tap water, artesian well water, river water, snow water and bottled mineral water. After being collected all samples were refrigerated until used. Tap water was analyzed without additional preparation. Mineral water was sonicated for 5 min before analysis. Artesian, snow and river water were filtered through 0.45 μm cellulose acetate membrane filters (Sartorius, Goettingen, Germany). Prior to analysis, sample pH was adjusted to 6.3 with the use of 2 mL Britton-Robinson buffer for 50 mL of a sample.

3. Results and discussion

3.1. Elution conditions

To ensure the highest sorbent capacity and preconcentration effectiveness two kinds of eluents were tested. The first one (called preliminary eluent) was responsible for elution of Cu(II) ions built into the polymer matrix during the imprinting process. The second one was employed for elution of copper(II) ions retained on sorbent during the loading step. Eluents selection was based on two criteria: sorption capacity dependent on the number of active sites freed during the polymer washing and leaching effectiveness which is strongly affected by the kind and concentration of an eluent. Therefore, elution effectiveness of nitric, hydrochloric and sulfuric acid in both processes was tested for different acid concentrations, taking into account signals obtained for 0.3 mg L^{-1} copper(II) solution loaded onto the column each time using a new portion of the sorbent.

No important differences in elution effectiveness were observed among the tested acids, therefore nitric acid as the most popular for sample preservation was chosen for further applications. In the range of preliminary eluent concentrations from 1 to 20% (v/v) effectiveness of Cu(II) removal was almost the same. Proper eluent concentration was tested within the range of 0.5–10% (v/v). In this case it was observed that decrease in acid concentration increased the signal of about 27%. The detailed data is presented in Table 1. Finally, 1% and 0.5% (v/v) nitric acid was chosen as preliminary and proper eluent, respectively.

Effectiveness of elution process is also influenced by the eluent flow rate – generally low values are preferred in order to obtain quantitative elution. However, in on-line flow injection flame atomic absorption spectrometry (FI-FAAS), signal value depends also on aspiration flow rate of the nebuliser (typically >5 mL min^{-1}). As a compromise, the eluent flow rate was adjusted to the preferred

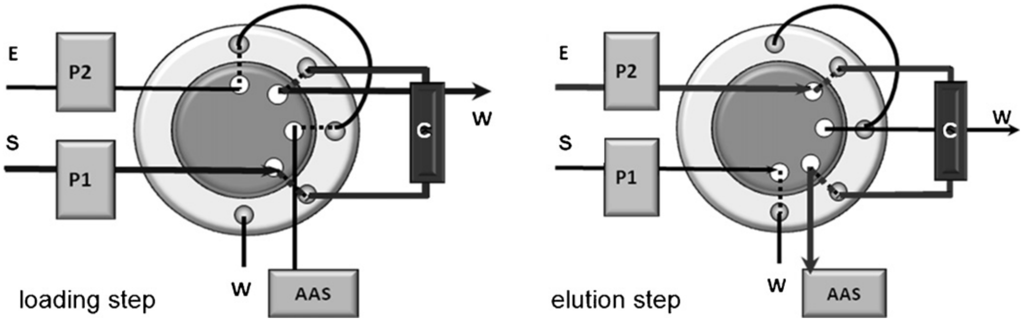

Fig. 3. Flow-injection system for on-line copper(II) preconcentration and determination: E – eluent, S – sample, P1, P2 – peristaltic pump, C – column filled with sorbent, W – waste.

Table 1
Influence of eluent concentration on analytical signal.

Preliminary eluent	Proper eluent	Average absorbance	RSD [%]
1% HNO_3	1% HNO_3	0.100	4.00
5% HNO_3		0.096	3.13
10% HNO_3		0.095	2.11
20% HNO_3		0.098	4.08
1% HNO_3	0.5% HNO_3	0.105	2.86
	1% HNO_3	0.095	2.11
	5% HNO_3	0.090	2.22
	10% HNO_3	0.083	3.61

RSD – relative standard deviation (5 replicates).

nebulizer uptake of the applied spectrometer (7 mL min^{-1}). At this eluent flow rate the elution effectiveness amounted to about 80%.

3.2. Effect of loading solution pH on sorption efficiency

Complex formation is often pH depended, therefore first of all influence of sample pH on Cu(II) sorption was investigated. A set of copper(II) standard solutions (0.3 mg L^{-1}) of growing pH (adjusted by addition of 2 mL of appropriate Britton-Robinson buffer to 50 mL of sample) was prepared and analyzed. Copper in particular solutions was determined with 30 s loading time and column filled with 18 mg of sorbent. The measured signal grow with sample pH increase up to about 6.2, then reached plateau up to pH about 6.4 and went down at higher pH values. In further experiments, pH of each loading solution was adjusted to ca. 6.3.

3.3. Sample flow rate and sorption efficiency

Another important parameter influencing loading step effectiveness is sample flow rate. In the performed experiment sample (0.3 mg L^{-1} copper(II)) volume was set constant (4 mL) via proper adjustment loading time and the flow rate. The obtained signal exhibited high stability within the whole tested flow rate range (4–10 mL min^{-1}), therefore in further experiments sample flow rate of 7.5 mL min^{-1} was applied which ensured high sample throughput and moderate sample consumption.

In the next step, sorption effectiveness was evaluated on the basis of copper mass balance. The set experiment conditions were as follows: initial copper(II) concentration 20, 100, 200, 300 μg L^{-1}; sample pH 6.3; loading time 30 s; sorbent mass 18 mg. Aliquots of initial solution and final solution after passed thought the column were analysed by ICP MS technique. The obtained results indicated sorption, with efficiency ca. 79–93%. Also elution efficiency was calculated based on mass balance between copper retained on sorbent and copper eluted from column. Here the efficiency was slightly lower, ranging from 79 to 86%.

Application of a preconcentration step with the use of the new sorbent increased the obtained analytical signal when compared to direct copper FAAS determination. This fact may be illustrated with enrichment factor (EF) calculated as a ratio of FI-FAAS calibration slope to FAAS slope [14]. Calibration curves ($EF = 0.64t_s - 3.01$; $R = 0.998$) were created for 10 and 15 μg L^{-1} copper(II) standard solutions loaded onto the sorbent for 30 up to 180 s. EF values increased linearly with loading time elongation and for typical loading time values: 30, 60 and 180 s equalled 16, 35 and 74, respectively. Consumptive index (CI) values calculated as:

$$CI = \frac{V_s}{EF}\ [mL] \tag{1}$$

where V_s stands for sample volume required to obtain a unit of EF, were 0.23, 0.21 and 0.30 mL, respectively.

Since enrichment factor depends on the loading time, EF values are often recalculated into concentration efficiency factor CE which allows to compare effectiveness of preconcentration cycle for different systems, taking into account the total time required for analysis. CE can be found as:

$$CE = EF \cdot f\ [min^{-1}] \tag{2}$$

where f is sampling frequency (0.65, 0.49, 0.25 for 30, 60 and 180 s loading time, respectively) [min^{-1}].

For the discussed preconcentration procedure CE values calculated for 30 and 60 s loading time were 10.4, 17.31 and 18.5, respectively.

3.4. Kinetic models and sorption capacity

Time required to reach sorption equilibrium was estimated in a closed-circuit mode. 10 mL aliquots of 0.3 mg L^{-1} copper(II) standard solution were pumped through the column in a closed-circuit for 15, 30, 60, 90 or 120 min and subsequently initial and final copper concentrations were determined by FAAS. Then, the amounts of copper(II) retained on the sorbent were calculated. The data indicate that 30 min loading time was necessary for 90% sorption efficiency. Further extension of the contact time up to 120 min provided 95% sorption efficiency. For sorption capacity evaluation the contact time was set at 30 min.

Two models of reaction kinetics were applied to examine copper(II) sorption kinetics on the new polymeric material:

- Pseudo-first-order:

$$\log(Q_e - Q_t) = \log(Q_e) - \frac{kt}{2.303} \tag{3}$$

- Pseudo-second-order:

$$\frac{t}{Q_t} = \frac{1}{k_2 \cdot Q_e^2} + \frac{1}{Q_e}t \tag{4}$$

where Q_t is the amount of analyte adsorbed onto the sorbent after time t [mg g^{-1}], Q_e stands for the amount of analyte adsorbed onto the sorbent at equilibrium time [mg g^{-1}], k and k_2 are constants for pseudo-first order [min^{-1}] and pseudo-second order [g min^{-1} mg^{-1}] reactions, respectively and t is the sorption time [min].

The data shown in Table 2 point at pseudo-second order kinetic model for the examined reaction, therefore probably interaction between the analyte and the sorbent was the limiting step for this sorption process.

Closed-circuit system was also applied to estimate the maximum equilibrium sorption capacity of the new material. In this case, 6 mL aliquots of copper(II) solutions within the concentration range in the 5–140 mg L^{-1} were loaded onto a column filled with 18 mg of the sorbent for 30 min. Afterwards, initial and final copper concentration was measured by ICP MS. Sorption capacity was found from the following equation:

$$Q = \frac{[(C_0 - C) \cdot V]}{m}\ [mg\ g^{-1}]\ \text{ or }\ [mmol\ g^{-1}] \tag{5}$$

where C_0 and C are the analyte initial and equilibrium concentrations [mg L^{-1}], V stands for the sample volume [L^{-1}] and m is the sorbent mass [g^{-1}].

Two most popular sorption isotherms were considered, namely:

- Langmuir isotherm:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L \cdot Q_{max}} \tag{6}$$

- Freundlich isotherm:

$$\log Q_e = \log K + \frac{1}{n} \log C_e \tag{7}$$

Table 2
Estimated isotherms and kinetic model parameters for Cu(II) sorption on IIP-LIX-Cu(II)..

Sorption kinetic equations					
Pseudo-first-order $y = -0.025x - 0.875$			Pseudo-second-order $y = 9.083 + 14.6$		
Q_e [mg g^{-1}]	k [min^{-1}]	R	Q_e [mg g^{-1}]	k_2 [g min^{-1} mg^{-1}]	R
0.133	0.058	0.903	0.110	5.651	0.999

Sorption isotherm equations					
Langmuir isotherm			Freundlich isotherm		
$y = 0.555x + 19.74$			$y = 0.474x - 0.824$		
Q_{max} [mg g^{-1}]	K_L [L g^{-1}]	R	K [mg g^{-1}] [L mg^{-1}]$^{1/n}$	n	R
1.801	0.028	0.995	0.150	2.109	0.993

where Q_{max} stands for maximum sorption capacity [mg g^{-1}], C_e is the analyte concentration at equilibrium [mg L^{-1}], K_L is Langmuir constant [mL mg^{-1}], K represents Freundlich constant [mg g^{-1}] [L mg^{-1}]$^{1/n}$ and n is dimensionless constant related to adsorption intensity. While the first equation describes creation of analyte monolayer onto the sorbent surface and is applicable to sorbents characterized with homogenous active sites, Freundlich isotherm is adequate for sorption process on heterogeneous surfaces. The obtained isotherm parameters shown in Table 2 indicate that Cu(II) sorption process on the new polymer is equally well described by both models. The maximum sorption capacity calculated from Langmuir isotherm was 1.8 mg g^{-1}.

3.5. *Sorbent stability test*

Application of a particular sorbent in routine analysis is often dependent on its stability. Durability the proposed polymer was evaluated on the basis of absorbance repeatability of 80 consecutive measurements. Preconcentration cycles were performed for copper(II) concentration of 0.3 mg L^{-1} and pH 6.3. Regression equation obtained for absorbance vs. number of cycle was expressed by the slope of 0.0001 and relative standard deviation (RSD) of absorbance mean value amounted ca. 10^{-5}, which indicates lack of systematic signal change and good stability of the sorbent.

3.6. *Interference effect study*

Selectivity of the obtained polymer was examined in five steps. Firstly, potential interferents to Cu(II) sorption were selected. In this step some main water components (Ca, Mg) and heavy metal ions co-exiting with copper(II), at two concentration levels: 0.2 and 1.0 mg L^{-1}, were determined by FAAS and FI-FAAS with preconcentration at pH 6.3 using 18 mg of sorbent and 30 s loading time. Because relevant preconcentration were observed for cadmium, lead, nickel, silver, cobalt, manganese, calcium and magnesium, the sorption process and influence of the mentioned above elements on copper determination were studied more in detail in further steps.

Secondly, influence of loading solution pH on sorption effectiveness of the particular heavy metal ions was examined (Fig. 4). Since sensitivity of FAAS determination of the chosen elements varies significantly, the results were presented in the form of enrichment factor EF vs pH. Because no significant difference in optimal pH value for Cu(II) sorption compared to other metal ions was found, allowing to differentiate sorption efficiency by this factor, it was finally decided to set loading solutions pH at 6.3 as this value was previously found to be optimal for Cu(II) sorption.

In the third step maximum tolerable concentrations of interfering ions were estimated. The evaluation was carried out for two levels of copper(II): 0.2 and 0.4 mg L^{-1} and concentrations of interfering ions varying from 0 to 5 mg L^{-1}. Changes of analytical signal obtained for copper in the presence of particular ions were tested both for the imprinted and the control polymer. The imprinted polymer exhibited better tolerance to higher concentrations of most interferents than the control one, except for Pb(II) and Cd(II). Moreover, the concentrations to be tolerated are high enough (i.e. exceeding normal concentration level of the interferent in natural waters) to apply the method to copper(II) determination in many types of water. The detailed results of the interference study are presented in Table 3.

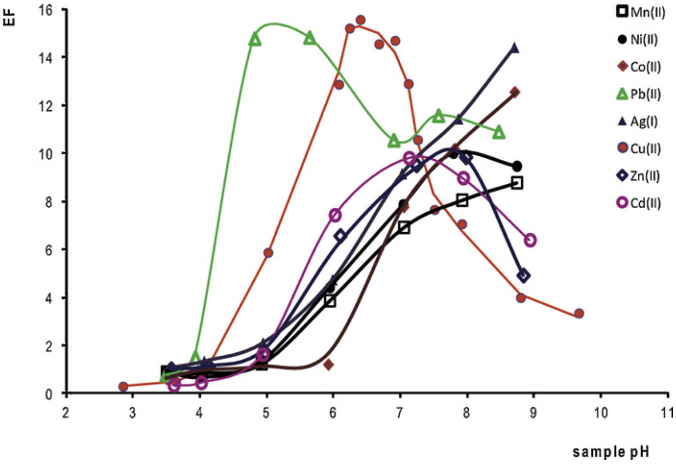

Fig. 4. Influence of loading solution pH on metal ions preconcentration with the use of IIP-LIX-Cu sorbent.

In some water samples humic substances, which strongly bind copper ions, can be present. Therefore, influence of humic acid on Cu(II) sorption process was also tested. The study was carried out for copper solutions of 0.04 mg L^{-1} containing different humic acid concentration and the experimental conditions were as follows: sorbent mass 18 mg; sample pH 6.3; sample flow rate 7.5 mL min^{-1} and loading time 60 s.

Table 3
Maximum tolerable concentrations of interfering ions in copper(II) preconcentration step.

Cu				Cd	Zn	Ag	Ni	Pb	Mn	Co
0.2	mg L^{-1}	IIP	max	1.0	2.0	5.0	5.0	0.1	5.0	5.0
		CP		1.0	1.0	1.0	1.0	0.1	2.0	1.0
0.4	mg L^{-1}	IIP	max	0.5	0.5	5.0	1.0	0.1	0.5	2.0
		CP		0.0	0.0	2.0	0.1	0.5	0.5	0.5

Table 4
Analytical results obtained for determination of trace copper(II) in different water samples with the use of the proposed method.

Sample	Δ [μg L^{-1}]	ICP MS	FI-FAAS, t_s 60 s		FI-FAAS, t_s 120 s	
		C_{Cu} [μg L^{-1}]	C_{Cu} [μg L^{-1}]	RE [%]	C_{Cu} [μg L^{-1}]	RE [%]
Artesian well water	–	3.9	3.7	−5.1	3.8	−2.6
Tap water 1	–	207.1	199.6	−3.6	–	–
Tap water 2	–	170.2	178.4	4.8	–	–
Żywiec Zdrój®	5	5.8	5.5	−5.2	5.6	−3.4
Snow water	–	4.9	4.8	−2.0	4.8	−2.0
EU-H-3	–	782.7	764.4	−2.3	766.5	−2.1
ES-H-2	–	660.3	625.1	−5.3	653.9	−1.0
Vistula river water	30	36.9	34.6	−6.2	–	–

t_s – sorption time; Δ – copper addition to water sample; C_{Cu} – concentration of copper(II).

Table 5
Analytical figures of merit for copper determination and on-line preconcentration step with the use of polymeric sorbents.

Sorbent (modification)	EF	CI [mL]	CE [min^{-1}]	Q [mmol g^{-1}]	DL [μg L^{-1}]	Technique	Reference
Styrene-divinylbenzene (functionalized with Cu-LIX 622®)	74	0.20	24.4	0.028	0.4	FAAS	This work
Amberlite XAD-2 (functionalized with 3,4-dihydroxybenzoic acid)	33	0.19	–	–	0.27	FAAS	[16]
Amberlite XAD-4 (functionalized with dihydroxybenzoic acid)	72	0.22	23.8	–	0.23	ICP OES	[15]
Amberlite XAD-4 (β-nitroso-α-naphthol)						FAAS	[17]
Impregnated	43	0.23	19.8	0.470	0.9		
Functionalized	44	0.23	20.2	0.369	0.7		
Styrene-divinylbenzene (functionalized with AEE)	21	0.63	8.7	0.330	1.1	FAAS	[18]
Styrene-divinylbenzene (functionalized with Cu-salen-OMe)	46	0.34	15.2	0.149	0.51	FAAS	[19]

AEE – (*S*)-2-[hydroxy-*bis*-(4-vinylphenyl)methyl]pyrrolidine-1-carboxylic acid ethyl ester; loading time: 120 s.

3.7. *Application to copper determination in water samples*

The presented method of FAAS copper determination coupled with on-line FI preconcentration with the use of the proposed polymer was applied to analysis of tap water, artesian water, snow water, as well as fortified Vistula river water and Żywiec Zdrój® mineral water. In all copper determinations loading time was set at 60 or 120 s and 3-cm-long column filled with 138 mg of the sorbent was employed. Standard addition method was used for calibration. The obtained results listed in Table 4 indicate suitability of the new sorbent for preconcentration of copper(II) from water samples. Concentrations determined by FI-FAAS technique were compared with those obtained in parallel by ICP MS. The results expressed as relative error (RE, see Eq. (8)) indicate good agreement between the results.

$$\mathrm{RE} = \frac{c_{FI-FAAS} - c_{ICP\,MS}}{c_{ICP\,MS}} \times 100\% \qquad (8)$$

Limit of detection found as triple value of blank standard deviation (3σ) (limit of quantifications 6σ) for 60 and 120-s sample loading time amounted to 0.8 (2.4) and 0.4 (1.2) μg L^{-1}, respectively. Precision of the method expressed as relative standard deviations was below 5%. Linear range of the method was 0–0.2 mg L^{-1} and correlation coefficient was set 0.999.

Trueness of the method was evaluated by analysis of certified reference materials: waste water EU-H-3 and ground water ES-H-2. Copper content found in ES-H-2 was in good agreement with the CRM confidence interval, whereas for EU-H-3 the obtained results were within the tolerance level. The performed experiments confirm that proposed copper determination method is of practical value.

4. Conclusions

On-line preconcentration procedure realized with the use of the newly synthesized styrene-divinylbenzene polymer modified with Cu(II)-5-dodecylsalicylaldoxime complex was found to be a proper technique for improvement of FAAS determination parameters of copper in water samples. The proposed sorbent opens new possibilities for application of a popular liquid-ion exchanger: 5-dodecylsalicylaldoxime and merges the complexing agent's good selectivity towards copper ions with advantages of solid phase extraction procedure, e.g. easy phase separation, use of aqueous non-toxic solvents, flexible phases ratio adjustment and ease of automation. Especially the last feature allows to adapt easily on-line copper determination procedure.

Due to the utilized synthesis method, namely suspension polymerization the obtained sorbent exhibited good physical properties for on-line preconcentration, such as lack of swelling and spherical shape leading to low back-pressure. Simultaneously, the sorbent indicated excellent sorption long-term stability which enabled no less than 80 preconcentration cycles without any loss of sensitivity. The optimized parameters of preconcentration, like the kind and concentration of the eluent, sample and eluent flow rate, allowed to obtain relatively high sorption efficiency.

When compared to other polymers dedicated to copper(II) on-line preconcentration (Table 5), the presented sorbent: IIP-LIX-Cu offered excellent enrichment factor and concentration efficiency slightly better than those obtained for Amberlite XAD-4 functionalized with dihydroxybenzoic acid [15] and much higher than other presented [16–19]. Also the limit of detection obtained for IIP-LIX-Cu sorbent was well rounded.

Application of highly selective ligand like 5-dodecylsalicylaldoxime led to high selectivity of the sorbent towards copper compared to other heavy metal ions: Cd(II), Zn(II), Ag(I), Ni(II), Pb(II), Mn(II), Co(II). The sorbent tolerated higher concentrations of these ions than they typically occur in natural waters. Moreover, the imprinted polymer exhibited higher tolerance to interferents than the control (non-imprinted) one, which proves achieving ion imprinting effect. On the other hand, the performed experiments revealed calcium and magnesium ions as the most important interferents. Another significant factor influencing Cu(II) sorption was humic acid which has to be taken into consideration in analysis of some sorts of water (e.g. pond). This kind of samples require previous digestion step.

Application of the standard addition method to FI-FAAS determination of copper in natural water sample allowed to overcome the observed interferent effect and to obtain results with good precision and accuracy both for natural waters and certified reference materials.

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