



Application of a metal ion-imprinted polymer based on salen–Cu complex to flow injection preconcentration and FAAS determination of copper

Stanisław Walas*, Anna Tobiasz, Marta Gawin,
Bartosz Trzewik, Marcin Strojny, Halina Mrowiec

Jagiellonian University, Faculty of Chemistry, ul. Ingardena 3, 30-060 Kraków, Poland

ARTICLE INFO

Article history:

Received 3 October 2007

Received in revised form 7 February 2008

Accepted 14 February 2008

Available online 10 March 2008

Keywords:

On-line preconcentration

Salen-based ion-imprinted polymer

Copper

Flow injection-flame atomic absorption spectrometry

ABSTRACT

A new Cu(II)-imprinted polymer (Cu-IIP) for preconcentration of copper by liquid–solid extraction via flow injection technique has been proposed. Cu-IIP was obtained by copolymerization of salen–Cu(II) complex with styrene and divinylbenzene using suspension polymerization technique. Granules fraction of 60–80 μm in diameter was used as a microcolumn packing. Cu(II) sorption was proved to be the most effective from solutions of pH 7, whereas similar elution effectiveness was observed when applying as eluents hydrochloric or nitric acid in the concentration range of 0.5–10% (v/v). The system exhibited good long-term stability and acid resistance. Batch sorbent capacity was found to be 0.11 mmol g^{-1} of a dry polymer. Enrichment factor (EF) for 30 s loading time was 16. Preconcentration of Cu(II) and potentially interfering metal ions is strongly pH dependent. Examination of Cu(II) sorption in the presence of Pb(II), Cd(II), Zn(II) and Ag(I) showed significant influence of cadmium and zinc ions only and that was for the interferent concentrations above 0.5 mg L^{-1} (Cu-IIP mass of ca. 35 mg). The interference effect was reduced with the sorbent mass increase. Fe(III) and Mn(II) ions, present in treated tap water in relatively high concentrations, did not interfere. Effective pH adjusting of the loaded solution in on-line mode, when applying diluted Clark–Lubs buffering solution, allowed accurate copper determination in tap water (compared to graphite furnace atomic absorption spectrometry, GFAAS) using standard addition or combination calibration method.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Sensitivity of many popular analytical techniques, e.g. flame atomic absorption spectrometry (FAAS), is generally insufficient for trace analysis [1], therefore analyte preconcentration is required. Flow methods are universal tools for sample pretreatment, including preconcentration of analyte preceding its subsequent determination [2,3]. They improve selectivity of the analytical method and provide flexibility of enrichment factors appropriate for given analytical needs.

Although FAAS is generally a specific determination method, introducing a preconcentration step may lead to interferences in this stage due to sorbents insufficient selectivity. For that reason new packing materials are still being proposed and examined. Recent achievements in this field have been summarized in a review by de Pereira and Arruda [4]. Ion-imprinted polymers (IIPs), based on the idea of molecular imprinting technique, have attracted much attention as selective sorbents for preconcentra-

tion of metal ions [5–8]. In ion imprinting it is a metal ion which serves as a template. The choice of a complexing ligand is of great importance here, as it directly influences selectivity of the sorbent. Also the coordination geometry and the coordination number of a metal ion together with the charge and the size of the ion play an important role in obtaining selective IIPs [9]. Ion-imprinted polymers have already found various applications, e.g. in separation, preconcentration and purification processes with regard to metal ions including transition elements [10], actinides [11], lanthanides [12] and noble metals in diverse matrices [13].

Shiff bases may be perspective complexing ligands for ion imprinting purposes due to their complexing abilities towards heavy metals. They have been applied both as reagents in simple spectrophotometric determinations [14] and as modifying agents for various sorbents [15–17]. Among Shiff bases especially salens have been used for forming organometallic complexes but to the authors' knowledge they have not served as complexing ligands for IIPs yet.

Here we present a salen-based copper-imprinted polymer for on-line flow injection microcolumn preconcentration of Cu(II). The system was coupled with flame atomic absorption spectrometer in order to improve the sensitivity of copper determination.

* Corresponding author. Fax: +48 12 634 05 15.

E-mail address: walas@chemia.uj.edu.pl (S. Walas).

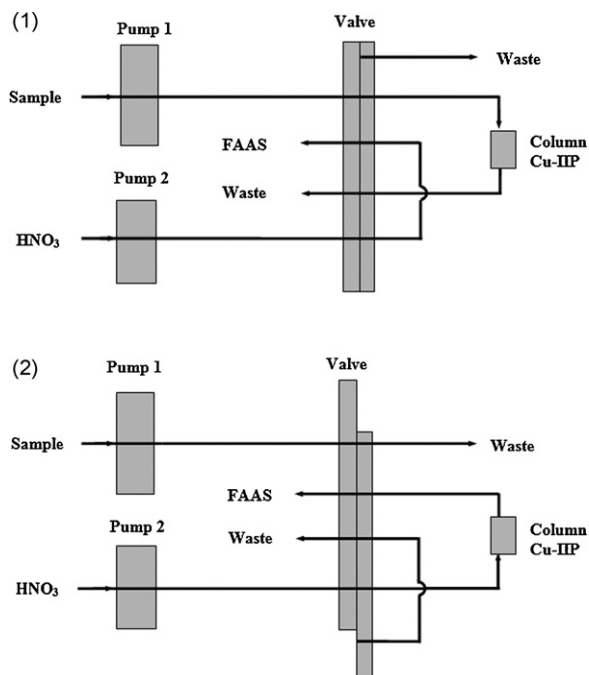


Fig. 1. A scheme of the flow injection preconcentration system FIAS 400: valve positions for sorption (1) and elution (2) step.

2. Experimental

2.1. Apparatus

PerkinElmer FIAS 400 flow injection system coupled with AA-analyst 300 flame atomic absorption spectrometer was applied. Air/acetylene flame was used and copper was determined at the wavelength of 324.8 nm. Deuterium background correction was applied in all measurements. Fig. 1 illustrates the on-line flow injection preconcentration system coupled with FAAS with the use of a capillary of 16 cm in length. FIAS 400 preconcentration system comprises two peristaltic pumps, a two-positional valve and a preconcentration column. Two TYGON R3607 red-red pump tubes (I.D. 1.14 mm) were applied for both pumps in most of the experiments. Only for on-line pH adjusting one yellow-blue tube (I.D. 1.52) and one red-red tube were used for pump 1.

Elmetron (Zabrze, Poland) CPI-551 pH-meter was used for pH measurements.

For GFAAS analyses SpectrAA Zeeman 220 (Varian) was applied.

NMR, IR spectra and elemental analysis were performed with the use of Bruker Avance II 300 MHz spectrometer, Bruker Equinox 55 spectrometer and EuroEA 3000 Elemental Analyzer, respectively.

Scanning electron microscope (SEM), ZEISS Leo 435 VP was applied to take microphoto of obtained microbeads.

2.2. Reagents and solutions

For organic synthesis of salen–Cu complex: 97% allyl bromide, Aldrich (Milwaukee, USA), ethylenediamine pure for analysis, Aldrich (Milwaukee, USA), salicylaldehyde pure, Aldrich (Milwaukee, USA), copper acetate pure for analysis, Merck (Darmstadt, Germany) were used. During polymerization process pure styrene and 55% divinylbenzene, Aldrich (Milwaukee, USA) were applied. All solvents were of pure for analysis grade.

Standard stock solutions (1 g L^{-1}) of copper, lead, cadmium, cobalt, nickel, chromium, manganese, iron, mercury, magnesium,

silver and zinc were prepared from Merck (Darmstadt, Germany) Titrisol solutions. Standard solutions were prepared by dilution of the stock solutions with deionized water. Eluent solutions (0.5; 1.0; 5.0 and 10.0% (v/v)) were prepared by dilution of concentrated nitric and hydrochloric acid, pure for analysis, Merck (Darmstadt, Germany). Deionized water after reversed osmosis was used throughout the work, also for preparation of blanks.

Britton–Robinson and Clark–Lubs buffer solutions were prepared according to Ref. [18]. In the former case, the buffers were prepared by mixing acidic solution (a mixture of 0.04 mol phosphoric acid, 0.04 mol boric acid and 0.04 mol acetic acid per litre) with 0.2 mol L^{-1} sodium hydroxide solution in appropriate ratios. In the latter case, 0.1 mol L^{-1} KH_2PO_4 solution and 0.1 mol L^{-1} NaOH were the buffer components.

2.3. Preparation of salen–Cu complex

The chelating ligand—salen was obtained in a three-step organic synthesis. Salicylaldehyde (0.33 mol) was dissolved in acetone (0.5 mL), then allyl bromide (0.35 mol) and potassium carbonate (55.7 g) were added to the solution. The mixture was heated under reflux for 3 h, then the solvent was removed using rotary evaporator and finally the residue was distilled under reduced pressure. The intermediate product (refractive index (RI) 1.557) was subsequently subjected to Claisen rearrangement by heating. Thus, obtained product (0.06 mol) (RI = 1.564) and ethylenediamine (0.03 mol) were dissolved in ethanol (110 mL) and heated under reflux for 2 min. Yellow crystals of salen were obtained and filtered. $^1\text{H NMR}$ (CDCl_3): δ = 13.52 (s, 1H, OH), 8.36 (s, 1H, CH=N), 7.19 (dd, J = 7.5, 1.8 Hz, 1H, H-3), 7.12 (dd, J = 7.5, 1.8 Hz, 1H, H-5), 6.82 (t, J = 7.5 Hz, 1H, H-4), 6.03 (ddt, J = 23.2, 10.5, 6.6 Hz, 1H, –CH=), 5.10 (ddd, J = 8.6, 3.6, 1.5 Hz, 1H, CH_2 =), 5.06 (t, J = 1.5 Hz, 1H, CH_2 =), 3.93 (s, 2H, N– CH_2), 3.74 (s, 3H, OCH_3), 3.44 (d, J = 6.6 Hz, 2H, CH_2). $^{13}\text{C NMR}$ (CDCl_3): δ = 166.7 (C=N), 158.9 (C-1), 136.6, 132.6, 129.7, 127.8, 118.3, 118.1, 115.6, 59.6 (CH_2 –N), 33.6 (CH_2 =). FT-IR (KBr, cm^{-1}): 3500 (ν (OH); broad), 1631 (ν (C=N)), 1448 (ν (C=C)), 912 (γ (=C–H); vinyl), 744 (γ (C–H); aromatic). Calculated for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2$ (%): C, 75.84; H, 6.95; N, 8.04. Analytically found: C, 75.70; H, 6.98; N, 8.14.

Complexation reaction was performed as follow: salen (2 mmol) was dissolved in ethanol (15 mL) and added to solution of copper acetate (2.4 mmol) in water (5 mL) upon stirring. Dark violet crystals of salen–Cu complex were obtained and filtered. FT-IR (KBr, cm^{-1}): 1624 (ν (C=N)), 1546 (ν (C=C); vinyl), 916 (γ (C–H); aromatic), 462 (ν (N–Cu)). Calculated for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_2\text{Cu}$ (%): C, 64.14; H, 5.38; N, 6.82. Analytically found: C, 64.65; H, 5.52; N, 6.89.

2.4. Preparation of copper(II)-imprinted polymer microbeads

IIP microbeads were prepared by suspension polymerization technique. The procedure was as follow: (i) dispersion medium was prepared by dissolving sodium chloride (0.3 g) and gelatine (2.1 g) in water (100 mL); (ii) salen–Cu complex (0.11 g) was dissolved in chloroform (11 mL) and subsequently mixed with styrene (7.5 mL) and divinylbenzene (1.5 mL); then benzoylperoxide (BPO) (0.5 g) was added as an initiator; (iii) both solutions were transferred to thermostatted reactor and mechanically stirred. The reactor temperature was kept constant at 90°C for 4 h. The scheme of the Cu-IIP preparation process is presented in Fig. 2.

Thus, obtained spherically shaped microbeads were separated from the polymerization medium, thoroughly washed with water and dried in a vacuum oven for 24 h. Control (non-imprinted) polymer was prepared in a similar way but salen ligand (0.10 g) was used instead of salen–Cu complex. Both imprinted and non-imprinted polymers were subsequently sieved and the fraction of

Download English Version:

<https://daneshyari.com/en/article/1243967>

Download Persian Version:

<https://daneshyari.com/article/1243967>

[Daneshyari.com](https://daneshyari.com)