



Polymeric ion-imprinted nanoparticles for mercury speciation in surface waters



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ABSTRACT

Selective sorption and enrichment of Hg(II) were achieved by polymeric ion-imprinted nanoparticles, prepared by copolymerization of methacrylic acid (functional monomer), trimethylolpropane trimethacrylate (cross-linking agent), 2,2'-azo-bis-isobutyronitrile (initiator) and Hg(II) complexes with chelating agent 1-pyrrolidinedithiocarboxylic acid. The particles were characterized for their morphology, composition and structure by using AFM, FTIR and elemental analysis. Extraction efficiency and selectivity of ion imprinted sorbent toward Hg(II) were studied by batch procedures. Two distinct adsorption sites were identified on the surface of the polymeric nanoparticles through Scatchard analysis performed. Adsorption process was characterized by Langmuir isotherm model. Solid phase extraction procedure was developed for Hg speciation and determination in surface waters. The accuracy of the proposed speciation scheme was confirmed by the analysis of certified reference material. Limits of quantification achieved ($0.015 \mu\text{g L}^{-1}$ for Hg(II) and $0.02 \mu\text{g L}^{-1}$ for methylmercury) and RSD values (7–12% for both species) completely satisfy requirements of European legislation for monitoring of surface waters.

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1. Introduction

Mercury and its compounds are considered as one of the most toxic and harmful environmental pollutants and according to the European legislation are identified as priority hazardous substances [1]. It is well known that toxicity and mobility of Hg strongly depend on its chemical form. Mercury can naturally exist in several chemical forms with different properties but the main species to be identified and determined in surface waters are inorganic mercury (Hg(II)) and methylmercury (CH_3Hg^+). The latter is more hydrophobic, so it can easily cross biomembranes and be accumulated by living cells. Generally, methylmercury is much more toxic than inorganic Hg and can be naturally formed in the processes of biomethylation mediated by activities of microorganisms in aquatic systems. Due to the significant differences between toxicity, bioavailability and mobility of Hg(II) and CH_3Hg^+ , speciation analysis is an actual research topic of modern analytical chemistry.

In real unpolluted environmental samples total Hg content is usually very low, for surface waters, typical concentrations are in the range of ng to $\mu\text{g L}^{-1}$. Leopold et al. have summarized several recent reports, where levels of total Hg in uncontaminated natural waters are between 0.03 and 90 ng L^{-1} , while methylmercury ranges from 1 to 40% of total Hg concentration [2]. Due to their low concentrations and the influences of coexisting substances in real water samples, development of analytical procedures for reliable and accurate determination and speciation of

Hg at ng L^{-1} levels is still an analytical challenge. A large number of techniques for determination and speciation of Hg have been developed commonly based on chromatographic [3–7] or non-chromatographic separations followed by highly sensitive instrumental detection [8–12]. Nevertheless, sample pretreatment prior to measurement is often demanded due to the extremely low Hg concentrations or matrix interferences observed. Solid-phase extraction (SPE) is a widely used analytical procedure for preliminary separation and preconcentration of the toxic elements which offers several advantages such as performance simplicity, low solvent consumption, minimization of sample volumes, fast separation of phases without emulsion formation, high enrichment factor, good reproducibility and flexibility [13,14]. Relatively low selectivity of conventional sorbents used is the main disadvantage of this approach. During the last years ion-imprinted polymers (IIPs) have received much attention as selective sorbents [15] as they permit simultaneous preconcentration and speciation of target ions. IIPs are synthetic materials with artificially generated recognition sites able to specifically rebind a target chemical species. In brief, the synthesis of IIPs involves several stages: (i) complexation of a template species (metal ions or their complexes with specific ligands) with functional monomers, (ii) copolymerization of these monomers around the template with the help of a cross-linking agent in the presence of an initiator, and (iii) leaching out of the template which leaves behind binding sites that are complementary in size and shape to the imprinted species. High selectivity of IIPs is explained by the polymer memory effect toward the metal ion interaction with a specific ligand, coordination geometry, metal ion coordination number, ion charge, and size [15,16]. Numerous studies on IIPs and their application for selective

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preconcentration and separation of metal ions have been reported [17–19] including Hg(II)-imprinted ones [10,20–24].

In the present study, spheric nanosized Hg(II)-IIP is synthesized via dispersion copolymerization using methacrylic acid (MAA) as a functional monomer, trimethylolpropane trimethacrylate (TMPTMA) as a cross-linking agent, 1-pyrrolidinedithiocarboxylic acid (PDC) as a non-polymerizable chelating agent and Hg(II) as a template ion. Size distribution, morphology and composition of ion-imprinted nanoparticles are defined by AFM, FTIR and elemental analysis. The extraction efficiencies and selectivities of the imprinted with Hg(II)-PDC complex (P(PDC-Hg)) polymeric nanoparticles and non-imprinted (blank) polymer P(B) are studied in a batch system. Analytical scheme for Hg speciation and enrichment in surface waters is developed based on the high selectivity of polymeric nanoparticles (P(PDC-Hg)) toward Hg(II). The versatility of proposed analytical method is confirmed by the analysis of certified reference material BCR®-505 Estuarine Water.

2. Experimental

2.1. Materials

Methacrylic acid (MAA), trimethylolpropane trimethacrylate (TMPTMA), 2,2'-azobisisobutyronitrile (AIBN), 1-pyrrolidinedithiocarboxylic acid ammonium salt (PDC), thiourea (TU) (Merck, Darmstadt, Germany), and acetonitrile (ACN) (Labskan, Dublin, Ireland) were used to prepare the Hg(II) ion-imprinted and non-imprinted polymer sorbents. Stock standard solutions for Hg were: inorganic Hg(II), stock standard solution for AAS, Trace CEPT™, 998 µg mL⁻¹ in 2 mol L⁻¹ HNO₃, (Sigma-Aldrich, USA). Methylmercury stock solutions (100 mg L⁻¹) were prepared by dissolving the appropriate amount of methylmercury(I) chloride (highly toxic, handle with care), PESTANAL®, analytical standard, Fluka (33368) in 5 mL of methanol and diluting to 100 mL with water. The exact concentration of this solution was defined against standards prepared from inorganic Hg(II). All stock solutions were stored in dark glass bottles at 4 °C. Working standard solutions for calibration were freshly (daily) prepared by successive dilution and contained reagents used for sample preparation or elution; e.g. 0.1 mol L⁻¹ thiourea in 0.1 mol L⁻¹ HCl. Reductant solutions of sodium tetrahydroborate(III) NaBH₄ (Merck) 0.04% (m/V) and 0.4% (m/V) in 0.1% (m/V) NaOH were prepared fresh daily and was used without filtration. The stock standard solutions for Cd(II), Cu(II), Fe(III), Pb(II), Mn(II), Ni(II) and Zn(II) (1000 µg mL⁻¹) were Titrisol, Merck (Darmstadt, Germany), in 2% HNO₃ (V/V).

All reagents were of analytical-reagent grade and all aqueous solutions were prepared in high-purity water (Millipore Corp., Milford, MA, USA).

For validation purposes a BCR®-505 Estuarine Water CRM stabilized with HNO₃ at pH 1.6, with 'Additional material information' value of 0.69 nmol kg⁻¹ was used.

2.2. Apparatus

CVAAS measurements were carried out with a Perkin Elmer AAnalyst 400 atomic absorption spectrometer (Perkin Elmer, USA) equipped with a MHS 15 Mercury Hydride System and an externally heated quartz tube atomizer at room temperature for inorganic Hg(II) and in air/acetylene flame for CH₃Hg⁺. The optimal instrumental parameters for Hg species determination include: pre-reaction purge time 7 s and post-reaction purge time 60 s. Solutions of NaBH₄ 0.04% (m/V) and 0.4% (m/V) were used as reductants for inorganic Hg(II) and CH₃Hg⁺ respectively.

The IR-spectra (4000–400 cm⁻¹) in KBr were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Scientific, USA).

For AFM imaging NanoScope Multi Mode V system (Bruker Inc., Germany) was used operating in tapping mode in air at room

temperature. Instrument setup, instrumental parameters and sample preparation procedure are described in Supplementary materials (Section S2.2).

Elemental analysis (C, H, N, S) were performed using a Euro EA CHNS-O elemental analyzer (EuroVector, Italy).

A microprocessor pH meter (Hanna Instruments, Portugal) was used for pH measurements.

2.3. Synthesis of the Hg(II) ion-imprinted and non-imprinted sorbents

The synthesis of Hg(II) ion-imprinted and non-imprinted polymer nanoparticles was adapted from the procedure reported by Dakova et al. [25]. The Hg(II)-IIP was prepared via a cross-linking dispersion copolymerization using MAA (1.8 mmol) as a functional monomer, TMPTMA (2.8 mmol) as a cross-linking agent, AIBN (52 mg) as an initiator, Hg(II) as a template ion (0.18 mmol), PDC as a non-polymerizable chelating agent (0.36 mmol) and acetonitrile (75 mL) as a solvent. The solution was saturated with dry nitrogen for 15 min and copolymerization was carried out at T = 60 °C for 24 h. The polymer particles obtained were recovered by centrifugation, washed with ACN to remove unreacted monomers and other ingredients. Mercury was removed from the sorbent by several, sequential elution steps using 4 mol L⁻¹ HNO₃ and 0.5 mol L⁻¹ thiourea in 0.5 mol L⁻¹ HCl as eluents. This procedure was repeated until the Hg concentration (template ions) in the eluate solution is below the LOQ as measured by CVAAS. Non-imprinted polymer sorbent (called P(B)) was synthesized in the same way as described above, in the absence of chelating agent and template ion. Reaction scheme for Hg(II)-IIP preparation is shown in Fig. S1 (Supplementary material).

2.4. Hg(II) sorption/desorption studies

The effects of solution pH, concentration and volume of the eluent, sorption and elution time on the degree of sorption and degree of elution of Hg(II) were evaluated by a batch procedure. Sorbent particles (50 mg) were added to an aqueous solution (10 mL) containing 5 ng Hg. The pH of this solution was varied in the range 1–8, using NH₄OH and HNO₃ solutions. After pH adjustment the solution was stirred with an electric shaker for 30 min and then centrifuged. In order to investigate the degree of Hg(II) sorption the supernatant was removed and analyzed by CVAAS as an effluente. The sorbent was washed with deionized water and Hg(II) was eluted from the sorbent particles by 2 mL of various reagents for 30 min. The degree of Hg elution was determined in the eluate solutions by CVAAS.

The kinetics of the Hg(II) sorption and desorption were investigated in a batch system. Ten milliliters of Hg solution (5 ng) was treated with 50 mg of Hg(II)-IIP particles at pH 7 for 5–40 min. The contents of metal ions in the effluente and eluate solutions after sorption and elution, respectively, were determined by CVAAS.

The degree of sorption (D_S %) of Hg(II) ions is defined as:

$$D_S\% = [(A_i - A_{\text{eff}})/A_i] \cdot 100, \quad (1)$$

where A_{eff} (µg) is the cation amount in the effluente solution after extraction by synthesized sorbents from a solution with a total cation amount A_i (µg).

The degree of elution (D_E %) of sorbed Hg(II) ions from loaded sorbent is defined as:

$$D_E\% = [A_{\text{el}}/(A_i - A_{\text{eff}})] \cdot 100, \quad (2)$$

where A_{el} (µg) is the amount of metal cations in solution after elution process.

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