



Separation and preconcentration of trace amounts of Cr(III) ions on ion imprinted polymer for atomic absorption determinations in surface water and sewage samples

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ABSTRACT

A new type of Cr(III)-imprinted polymer was prepared from Cr(III)-pyrrolidinedithiocarbamate complex, acrylamide functional monomer and ethylene glycol methacrylate cross-linking agent. The polymer was employed as a selective solid phase extraction material for separation of trace amounts of Cr(III) ions under dynamic conditions. The effects of the conditioning of imprinted polymer, conditions of Cr(III) retention and elution were studied. It was found that Cr(III) ions can be retained on tested sorbent with high efficiency and repeatability (87%, RSD = 3.2%) from a solution of pH 3.50–4.75. The quantitative elution of analyte was obtained with 0.2 mol L⁻¹ nitric acid solution. The retention of Cr(VI) ions on the polymer in the studied pH range (1.0–7.0) was at the level of 10–15%. The selectivity of prepared sorbent towards Cr(III) ions was good in the presence of Cu(II) and Ni(II) ions and worse in the presence of Fe(III) ions at a concentration higher than 0.5 µg mL⁻¹. The detection limit for Cr(III) obtained by electrothermal atomic absorption spectrometry (ETAAS) after preconcentration of 40 mL of sample on the polymer was 0.018 ng mL⁻¹. The developed separation method was successfully applied to the ETAAS determination of trace amounts of Cr(III) in tap and river water and municipal sewage.

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1. Introduction

Chromium, due to its specific chemical properties, is widely used in metallurgy for the production of steel, ferro- and nonferrous alloy, in industrial processes for electroplating, tanning and metal smelting, and in the chemical industry for production of paints and pigments. After processing, large quantities of Cr compounds are discharged into the environment that cause contamination of soil, surface and ground water [1,2]. Drinking water can be contaminated with chromium originating from the corrosion inhibitors used in water pipes and containers. According to European Council Directive 98/83/EC on the quality of water intended for human consumption, the maximum concentration of Cr in drinking water cannot exceed 50 µg L⁻¹.

Chromium is present in the environment at two common oxidation states, as compounds of Cr(III) and Cr(VI), which have different physicochemical, toxicological and biological properties. Chromium(III) is an essential micronutrient playing an important role in the metabolism of glucose as a component of glucose tolerance factor (CrGTF) as well as in the metabolism of some lipids, such as cholesterol. Chromium(VI) possesses toxic effect on humans, animals and plants. The exposure of living organisms to Cr(VI) compounds can lead to damage of skin, respiratory tract, kidneys and increases risk of lung cancer. The toxicity of chromate ions is connected with its strong oxidative potential and the possibility of free diffusion across the cell membranes [1,3].

The development of simple and reliable analytical procedures for chromium speciation in aqueous environmental samples is still required. The methods developed for the determination of chromium species are discussed in details in review papers [1,2,4]. Among them the most popular is coupling of solid phase extraction (SPE) and various spectrometric techniques (Table 1). The separation of Cr(III) and Cr(VI) ions by SPE is mostly performed by the application of functionalized sorbents. Often, one of the determined species is retained on the sorbent, while another one remained in the solution [5–15]. As the next step of the procedure, the form of chromium initially remaining in the solution, after reduction/oxidation step with a suitable agent (e.g. H₂O₂ [8,9], Na₂SO₄ [10], hydroxylamine in HCl [13]), is retained on the same sorbent. Such procedure enables the determination of both chromium forms as well as its total amount. Other strategy is based on the application of sorbent that presents selectivity in function of the separation conditions, e.g. the pH [16,17] or applied eluent [18]. The application of dual-column systems (constructed with the same sorbent or with different sorbents) for simultaneous retention of Cr(III) and Cr(VI) species is another option [19]. The examples of SPE methods used for the determination of Cr(III), Cr(VI) or both forms are presented in Table 1.

It is obvious that the properties of the sorbent material play a significant role in efficiency and selectivity of separation process. Recently the new sorbents, molecularly imprinted polymers (MIP) and ion imprinted polymers (IIP) have been introduced as selective materials for SPE [20,21]. The advantages of such materials are high recognition ability, stability, relative ease and low cost of preparation. The selectivity of the IIP arises mainly from the following factors: the specific interaction

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Table 1

Solid phase extraction methods for the separation and determination of Cr in environmental samples by spectrometric techniques.

Sorbent	Determined form of analyte	Sample		Eluent/FR, mL min ⁻¹	Detection technique	LOD, ng mL ⁻¹	Analyzed sample	Ref.
		pH	FR, mL min ⁻¹					
Amberlite XAD-4	Cr(VI)-1,5-diphenylcarbazide	1	1–4	15 mL of acetone–2.5 mol L ⁻¹ H ₂ SO ₄ /2 mL min ⁻¹	UV–VIS	6.0	Tap and well water, electroplating wastewater	[6]
Dowex M 4195	Cr(VI)	2	5	10 mL of 4 mol L ⁻¹ NH ₃ /5 mL min ⁻¹	FAAS	1.94	Tap and river water, electroplating water	[8]
MWCNT	Cr(VI)-PDC	2	5	1 mol L ⁻¹ HNO ₃ in acetone/5 mL min ⁻¹	FAAS	0.90	River, waste and tannery water	[9]
Diaion HP-2MG ^a	Cr(VI)-PDC	4	10 min	1 mL of conc. HNO ₃ /30 min	ETAAS	0.03	Mineral water and salinas	[10]
XAD-4 functionalized with maleic acid	Cr(III) and Cr(VI) after reduction	5	2–4	20–25 mL of 1% H ₂ O ₂ + 1 mol L ⁻¹ NH ₃ /2 mL min ⁻¹	FAAS		Synthetic wastewater and sea water, coal CRM-1632	[11]
Activated carbon	Cr(III)	5	15	50 µL of 1.0% HNO ₃ /0.2 mL min ⁻¹	FI-ETAAS	0.003	Drinking water	[12]
Muromac A-1	Cr(III) and Cr(VI) after reduction	4	6	2 mol L ⁻¹ HCl + 2 mol L ⁻¹ HNO ₃ /6 mL min ⁻¹	FAAS	2.0	Estuarine and sea water	[13]
Chromosorb 108	Cr(III)-dithizone and Cr(VI) after reduction	8	5	10 mL of 2 mol L ⁻¹ HNO ₃ in acetone/5 mL min ⁻¹	FAAS	0.75	Tap, river and sea water, tomato leaves SRM 1573a	[14]
<i>Bacillus sphaericus</i> loaded Diaion SP-850-	Cr(III) and Cr(VI) after reduction	5	5	10 mL of 1 mol L ⁻¹ HCl/5 mL min ⁻¹	FAAS	0.50	Tap, spring, sea and waste water	[15]
Chelating resin with azo-phenolcarboxylate group	Cr(III) and Cr(VI)	5	1.5	20 mL of 4.0 mol L ⁻¹ HCl/0.5 mL min ⁻¹	FAAS	0.60	Waste water	[16]
NDSA resin	Cr(III) and Cr(VI)	6.5	0.5	10 mL of 4.0 mol L ⁻¹ HCl/0.5 mL min ⁻¹	FAAS		Waste water	[17]
SAX cartridge	Cr(III)-EDTA ⁻ and Cr(VI)	4.7	3–4	5 mL of 0.1 or 0.5 mol L ⁻¹ NaCl/5 mL min ⁻¹	ETAAS	0.07 0.19	Soil and SRM 2709	[18]
poly(EDMA-MAH-Cr(III)) imprinted polymer ^a	Cr(III)	7	30 min	10 mL of 0.1 mol L ⁻¹ succinic acid/2 h	FAAS	1.20	Model solutions	[22]
AAPTS-imprinted silica gel	Cr(VI) or Cr(III) and Cr(VI)	2	2	0.5 mL of 1 mol L ⁻¹ HNO ₃ /1 mL min ⁻¹	ICP-MS	0.004 0.008	Lake, tap and well water	[23]
Poly(VP-HEMA)-Cr(VI) imprinted polymer ^a	Cr(VI)	4	40 min	0.1 mol L ⁻¹ formic acid/2 h	UV–VIS		Synthetic waste water	[24]
Cr-PDC-AA imprinted polymer	Cr(III)	4	1	4 mL of 0.2 mol L ⁻¹ HNO ₃ /1 mL min ⁻¹	ETAAS	0.018	Tap and river water, municipal sewage	This work

Notes: MWCNT—multiwalled carbon nanotube; NDSA—polystyrene divinyl benzene copolymer functionalized with 2-naphthol-3,6-disulfonic acid; poly(EDMA-MAH/Cr(III))—ion imprinted polymer with Cr(III)–methacryloylhistidine complex; AAPTS-imprinted silica gel—silica gel imprinted with Cr(III)-3-(2-aminoethylamino) propyltrimethoxysilane; poly(VP-HEMA)-Cr(VI) polymer—Cr(VI) imprinted poly(4-vinyl pyridine-co-hydroxyethyl methacrylate); Cr-PDC-AA imprinted polymer—ion imprinted polymer with Cr(III)-pyrrolidinedithiocarbamate complex; FAAS—flame atomic absorption spectrometry; ETAAS—electrothermal atomic absorption spectrometry; ICP MS—inductively coupled plasma mass spectrometry; UV–VIS—spectrophotometry.

^a Batch procedure; FR—flow rate.

of ligand with metal ion; the coordination geometry and the coordination number of metal ion; and the charge and size of metal ion. The commonly used ways of preparation of IIP is surface imprinting or trapping of non-vinylated chelating ligand via imprinting of binary/ternary mixed ligand complexes of metal ions with non-vinylated chelating agent and vinyl ligand [21].

This approach was also used to chromium speciation [22–24]. The Cr(III)-imprinted polymer was prepared by the suspension polymerization technique from the Cr(III)–methacryloylhistidine complex polymerized with ethylene glycol dimethacrylate [22]. Both chromium forms were simultaneously retained on that sorbent in a batch mode. The efficiency of sorption of each form was dependent on the solution pH. The highest sorption of Cr(III) ions on the imprinted beads was observed from the solution of pH 6 within 30 min. For desorption of Cr(III) ions the beads were stirred with 0.1 mol L⁻¹ succinic acid solution for 2 h. The silica gel imprinted with Cr(III)-3-(2-aminoethylamino)propyltrimethoxysilane was prepared by surface imprinting technique [23]. The Cr(III) ions were quantitatively retained on the sorbent from the solution of pH 6.5–8 and eluted with 1 mol L⁻¹ nitric acid solution, whereas Cr(VI) ions were sorbed at wider pH range (from 0.8 to 8). For speciation studies the authors proposed the separation of Cr(VI) ions at pH 2, and the retention of both chromium forms at pH >6.5. The Cr(III)-imprinted silica gel showed good tolerance to foreign ions. The anion imprinted polymer, Cr(VI)-poly(4-vinylpyridine-co-hydroxyethyl methacrylate), was prepared by bulk polymerization for the selective removal of Cr(VI) anions

from aqueous media [24]. The highest sorption of Cr(VI) ions on the imprinted beads was obtained from the solution of pH 4 within 40 min. Retained Cr(VI) anions were desorbed by 2 h treatment with formic acid solution.

It is known that in the reaction of ammonium pyrrolidine-1-carbodithioate (ammonium pyrrolidinedithiocarbamate–APDC) with Cr(III) and Cr(VI) ions different complexes are formed [25,26]. The (tris [pyrrolidine-1-dithioato-S,S']-Cr(III) complex, denoted here as Cr(III)-PDC, is a product of Cr(III) reaction with APDC. Two complexes: (bis [pyrrolidine-1-dithioato-S,S']-[pyrrolidine-1-peroxydithioato-O,S]-Cr(III) and, identical to the Cr(III)-PDC complex, (tris[pyrrolidine-1-dithioato-S,S']-Cr(III) are formed in the reaction of APDC with Cr(VI) ions. In all formed complexes chromium is present at +3 oxidation state.

In the present work our aim was to prepare the ion imprinted polymer based on the Cr(III)-PDC complex for selective separation of Cr(III) ions from aqueous solutions. It was expected that such polymer will have higher selectivity towards Cr(III) than to Cr(VI) ions, because the arrangement of functional groups in active sites formed in polymeric network would be complementary to the geometry of the Cr(III)-PDC complex and to the size of Cr(III) ions. In addition, a low efficiency of reduction of Cr(VI) ions on the surface of the polymer was expected. For the synthesis of IIP acrylamide (AA) as a functional monomer, chloroform as a porogen and ethylene glycol dimethacrylate (EGDMA) as a cross-linking monomer were used. The analytical properties of prepared polymer, called Cr-PDC-AA, and its usefulness for Cr(III) separation were studied in dynamic mode.

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