

1-1-2016

## A novel ion-imprinted polymeric sorbent for separation and determination of chromium(III) species in wastewater

BARBARA LESNIEWSKA

IWONA JAKUBOWSKA

ELZBIETA ZAMBRZYCKA

BEATA GODLEWSKA - ZYLKIEWICZ

Follow this and additional works at: <https://journals.tubitak.gov.tr/chem>

 Part of the [Chemistry Commons](#)

---

### Recommended Citation

LESNIEWSKA, BARBARA; JAKUBOWSKA, IWONA; ZAMBRZYCKA, ELZBIETA; and ZYLKIEWICZ, BEATA GODLEWSKA - (2016) "A novel ion-imprinted polymeric sorbent for separation and determination of chromium(III) species in wastewater," *Turkish Journal of Chemistry*. Vol. 40: No. 6, Article 6.

<https://doi.org/10.3906/kim-1606-34>

Available at: <https://journals.tubitak.gov.tr/chem/vol40/iss6/6>

This Article is brought to you for free and open access by TÜBİTAK Academic Journals. It has been accepted for inclusion in Turkish Journal of Chemistry by an authorized editor of TÜBİTAK Academic Journals. For more information, please contact [academic.publications@tubitak.gov.tr](mailto:academic.publications@tubitak.gov.tr).

## A novel ion-imprinted polymeric sorbent for separation and determination of chromium(III) species in wastewater

Barbara LEŚNIEWSKA, Iwona JAKUBOWSKA, Elżbieta ZAMBRZYCKA,  
Beata GODLEWSKA-ŻYŁKIEWICZ\*

Department of Analytical Chemistry, Faculty of Biology and Chemistry, University of Białystok, Białystok, Poland

Received: 11.06.2016

Accepted/Published Online: 11.10.2016

Final Version: 22.12.2016

**Abstract:** A new chromium(III) ion-imprinted polymer (IIP) was prepared from a Cr(III)-nicotinate complex (template), acrylamide (functional monomer), and ethylene glycol dimethacrylate (cross-linking agent) using 2,2'-azobisisobutyronitrile as the radical initiator. IIP was characterised and used as a selective sorbent for the solid-phase extraction of Cr(III) ions. The conditions for dynamic separation of Cr(III) on IIP were optimised. Cr(III) ions are selectively retained on the sorbent in a pH range from 9 to 10 and can be eluted with 4 mol L<sup>-1</sup> acetic acid. Cr(III) ions were determined by flame atomic absorption spectrometry (FAAS) with a detection limit of 0.08 μg mL<sup>-1</sup>. The method was successfully applied to determine Cr(III) species in wastewater and reference material RES 25.2 with a reproducibility of 1.8%–3.4%.

**Key words:** Chromium, speciation analysis, ion-imprinted polymers

### 1. Introduction

Chromium is a toxic element to microorganisms, plants, animals, and humans. In 2015 chromium was classified as one of the six pollutants posing a major threat to human health.<sup>1</sup> Estimates suggest that it affects the health of 16 million people, especially in low- and middle-income countries. Chromium exists in the environment in two stable oxidation states: hexavalent [Cr(VI)] and trivalent [Cr(III)]. Chromium(III) was postulated as an essential nutrient taking part in carbohydrate and lipid metabolism, but nowadays many studies have shown that its role is controversial.<sup>2,3</sup> Supplementing organisms with different Cr(III) complexes does not have an effect on most blood, biochemical, morphological, and haematological parameters.<sup>4</sup> The mutagenic and carcinogenic effect of chromium(VI) on animals and humans has already been proved.<sup>5–7</sup> The toxicity of chromium manifests itself in the development of debilitating, life-threatening diseases and in death.

The aforementioned metal enters the environment from natural sources, such as the leaching of rocks, deposition of atmospheric aerosols, and run-off from topsoil. However, significant quantities of chromium are introduced into the atmosphere, soil, and water systems from various anthropogenic sources.<sup>8,9</sup> Worldwide emission of chromium is high, e.g., in 2009 in EU countries it was estimated at 333 t (336 t in 2013),<sup>10</sup> while in China it was estimated at 192,000 t and the number is still growing (8% per year).<sup>11</sup> The main sources of chromium emission into the atmosphere are coal combustion, oil combustion, iron and steel production, and cement production.<sup>8,11</sup> Chromium can enter ground and surface waters with discharges of wastewater

\*Correspondence: bgodlew@uwb.edu.pl

from nonferrous metal mining, stainless steel production, and the leather tanning and dressing industry. The chromium concentration in wastewater is in the range of 3–30 mg L<sup>-1</sup> for Cr(VI) and 5–100 mg L<sup>-1</sup> for total chromium, but much higher values have also been observed (e.g., 1800–3200 mg L<sup>-1</sup> in wastewater from electroplating factories<sup>12</sup>). According to governmental regulations in Poland, the maximum concentration of chromium in sewage that can be introduced into water or soil must be below 0.05–0.50 mg L<sup>-1</sup> of Cr(VI) and 0.5–1.0 mg L<sup>-1</sup> of the total chromium, depending on the type of industry.<sup>13</sup> Speciation analysis of chromium in wastewater samples is currently indispensable in order to assess its risk to humans.

Different separation methods coupled with species nonspecific detection techniques, such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS), were proposed for chromium speciation analysis in environmental samples. Among them, as has been reported in review papers, chromatography,<sup>14,15</sup> liquid–liquid extraction,<sup>16–18</sup> and solid-phase extraction (SPE)<sup>19–21</sup> are the most extensively used. Nowadays, flow systems based on SPE have been recognised as excellent tools for the automation of sample pretreatment, including separation and/or preconcentration of chromium species.<sup>22</sup> Different sorbents have been used for chromium speciation analysis in wastewater (Table 1). Different chromium forms are retained on commercially available sorbents<sup>23</sup> or sorbents functionalised with reagents containing anion or cation exchange functional groups,<sup>24</sup> chelating groups,<sup>25–27</sup> microorganisms,<sup>28</sup> or as organic complexes on sorbents possessing adsorptive properties.<sup>28,29</sup> The need for more selective systems has resulted in the development of sorbents of a new generation, such as ion-imprinted polymers (IIPs). The selectivity of IIPs arises mainly from specific interaction between the ligand and metal ion, the coordination geometry, and the coordination number of the metal ion, as well as the charge and size of the metal ion.<sup>30</sup> So far, several complexes of Cr(III), such as Cr(III)-methacryloylhistidine,<sup>31</sup> Cr(III)-3-(2-aminoethylamino)propyltrimethoxysilane,<sup>32</sup> Cr(III)-polyethyleneimine,<sup>33</sup> Cr(III)-polyvinyl alcohol/sodium alginate,<sup>34</sup> Cr(III)-pyrrolidinedithiocarbamate,<sup>35</sup> Cr(III)-dithizone,<sup>36</sup> and Cr(III)-8-hydroxyquinoline;<sup>37</sup> or Cr(VI), such as Cr(VI)-4-vinylpyridine<sup>38,39</sup> or Cr(VI)-2-vinylpyridine,<sup>40</sup> were imprinted into a polymeric matrix. Most papers have reported on the synthesis of IIP and on studies of their adsorptive properties in a batch mode.<sup>31–34,38–40</sup> Some polymers were tested for separation of chromium species from real samples,<sup>32,36,39,40</sup> but only two of them were applied in dynamic procedures for their separation from wastewater.<sup>35,37</sup>

The aim of our work was to prepare a new selective polymeric sorbent with an imprinted Cr(III)-nicotinate complex for the separation of chromium(III) ions. The Cr(III) ion-imprinted polymer was prepared by precipitation polymerisation using acrylamide as the functional monomer, ethylene glycol dimethacrylate as the cross-linking agent, and 2,2'-azobisisobutyronitrile as the radical initiator. IIP was tested as a sorbent in the dynamic SPE procedure and applied for selective separation of Cr(III) from wastewater prior to being determined by FAAS.

## 2. Results and discussion

Cr(III)-nicotinate complexes are not well characterised since they are insoluble in water and other common solvents. Both the formula and structure of the complexes depend on the molar ratio of the reagents (Cr to nicotinic acid) and on the conditions (temperature, acidity) used during the synthesis reaction.<sup>41</sup> In this paper, the Cr(III) nicotinate complex (Cr(nic)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(OH)·H<sub>2</sub>O)<sup>42,43</sup> was imprinted into the polymeric structure of IIP by noncovalent bonds.

**Table 1.** Solid-phase extraction methods for the separation and determination of chromium(III) in wastewater and river water samples by FAAS technique.

Sorbent	Determined form of the analyte	Sample		Eluent/FR, mL min <sup>-1</sup>	LOD, ng mL <sup>-1</sup>	RSD, %	Analysis time per sample (10 mL)/ sorbent stability	Analysed sample	Ref.
		pH	FR, mL min <sup>-1</sup>						
Graphene	Cr(III)-8HQ	8	2	2 mL of 2 mol L <sup>-1</sup> HNO <sub>3</sub> / 2 mL min <sup>-1</sup>	0.5	4.3	21 min/50 cycles	Tap and river water	29
Chromosorb 108	Cr(III)-dithizonate	8	5	10 mL of 2 mol L <sup>-1</sup> HNO <sub>3</sub> in acetone/ 5 mL min <sup>-1</sup>	0.8	1.4–5.8	8 min + evaporation of eluent	River and seawater	23
XAD-4 functionalised with maleic acid	Cr(III) and Cr(VI) after reduction	5	2-4	40-45 mL of 1 % H <sub>2</sub> O <sub>2</sub> + 1 mol L <sup>-1</sup> NH <sub>3</sub> aq/ 2 mL min <sup>-1</sup>	-	0.2%	30 min/20 cycles	Synthetic wastewater and seawater	24
<i>Bacillus sphaericus</i> loaded Diatom SP-850	Cr(III) and Cr(VI) after reduction	5	5	10 mL of 1 mol L <sup>-1</sup> HCl/ 5 mL min <sup>-1</sup>	0.5	<5%	15 min	Tap, spring, sea-, and wastewater	28
Chelating resin with azophenolcarboxylate group	Cr(III) and Cr(VI)	5	1.5	20 mL of 4.0 mol L <sup>-1</sup> HCl/ 0.5 mL min <sup>-1</sup>	0.6 0.9	0.3–2.9 0.5–2.1	47 min/unstable in NaOH and mineral acids	Industrial wastewater	26
NDSA resin	Cr(III) and Cr(VI)	6.5	0.5	10 mL of 4.0 mol L <sup>-1</sup> HCl/ 0.5 mL min <sup>-1</sup>	30*	0.3–1.0	45 min	Industrial wastewater	27
XAD-16 modified with acetyl acetone	Cr(III)	5-7	1.0	5 mL of 2 mol L <sup>-1</sup> HNO <sub>3</sub> / 0.5 mL min <sup>-1</sup>	20	2%	20 min	Wastewater	25
**IIP:Cr(III)-dithizonate-SBA-15	Cr(III)	6	6 min in US	1.2 mL of 2 mol L <sup>-1</sup> HCl/ 2 min	0.06	1.9–3.8	10 cycles	River water	36
IIP: Cr(III)-8-HQ-St-DVB	Cr(III)	9	1	0.3 mL of 0.1 mol L <sup>-1</sup> HNO <sub>3</sub> /1 mL min <sup>-1</sup>	2.1	0.5–3.4	11 min/170 cycles	Tap water, municipal wastewater	37
IIP: Cr(III)-Nic-AA-EGDMA	Cr(III)	9	0.6	4 mL of 4 mol L <sup>-1</sup> CH <sub>3</sub> COOH/ 0.9 mL min <sup>-1</sup>	80	4.6–7.5	30 min/100 cycles	Municipal wastewater	This work

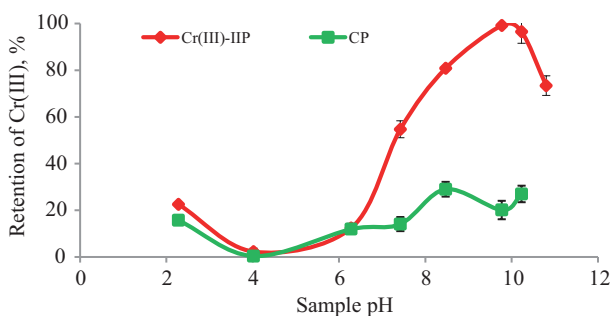
Notes: \* - sensitivity; \*\* - dispersive SPE with using ultrasonic bath (US) NDSA - polystyrene divinyl benzene copolymer functionalised with 2-naphthol-3,6-disulphonic acid; dithizonate-SBA-15 - mesoporous silica SBA-15 modified with dithizonate; IIP: Cr(III)-8-HQ-St-DVB - Cr(III)-8-hydroxyquinoline-imprinted poly(styrene-co-divinylbenzene).

## 2.1. Optimisation of the separation procedure of Cr(III) ions on IIP

Parameters influencing retention and elution of the analyte were initially optimised in order to evaluate the sorption properties of IIP toward Cr(III) ions.

### 2.1.1. Effect of pH on the retention of Cr(III)

The effect of pH of a sample on the retention of the analyte (10  $\mu\text{g}$  of Cr(III)) was tested in a pH range from 2 to 11 (adjusted with HCl or NaOH solution) (Figure 1). It is worth mentioning that nicotinic acid, depending on the pH of the solution, can exist in three protolytic forms, with  $\text{pK}_{a1}$  and  $\text{pK}_{a2}$  values equal to 2.01 and 4.72.<sup>44</sup> The lowest retention of chromium(III) on the polymer was observed at a pH range of 3–5 due to the lack of interaction between the analyte's cationic forms and the neutral form of the ligand. The efficiency of retention of Cr(III) ions on the IIP polymer increases at  $\text{pH} > 6$  and reaches a maximum at a pH range of 9–10. In such an environment chromium(III) may be present in forms of different charge, namely in cationic form as  $\text{Cr}(\text{OH})(\text{H}_2\text{O})^{2+}$ , in neutral form as  $\text{Cr}(\text{OH})_3$  ( $\text{pH}$  8.5–10), or in anionic form as  $\text{Cr}(\text{OH})_4^-$  (at  $\text{pH} > 9$ ).<sup>8</sup> We presume that single-charged anions, which are coordinated as ligands to hexacoordinated Cr(III) complexes, can be exchanged with the negatively charged carboxylic group of nicotinic acid that is imprinted in the polymer. Therefore, retention of the analyte is the effect of the analyte's interaction with the anionic form of nicotinic acid as well as of the presence of specific cavities on the imprinted particles. The retention of Cr(III) ions on the control polymer (CP) at the studied pH range was below 30%, probably due to unspecific bonding of the analyte on the polymeric matrix.



**Figure 1.** Effect of sample pH on Cr(III) retention on IIP and CP (sample: 10  $\mu\text{g}$  of Cr(III), pH: 9, flow rate: 0.6 mL  $\text{min}^{-1}$ ).

### 2.1.2. Effect of the sample's flow rate on the retention of Cr(III)

The influence of the sample's flow rate (from 0.3 to 0.9 mL  $\text{min}^{-1}$ ) on the retention of chromium(III) on the polymer was insignificant. However, the small size of the polymeric particles caused problems with sample throughput. It was found that conditioning of the sorbent with 0.1% sodium lauryl (dodecyl) sulphate (SDS) solution as well as adding SDS to the sample improved the sample's flow through the column due to a reduction in surface and interfacial tension. Hence, ultimately a sample flow rate of 0.6 mL  $\text{min}^{-1}$  was used in subsequent studies.

### 2.1.3. Optimisation of elution

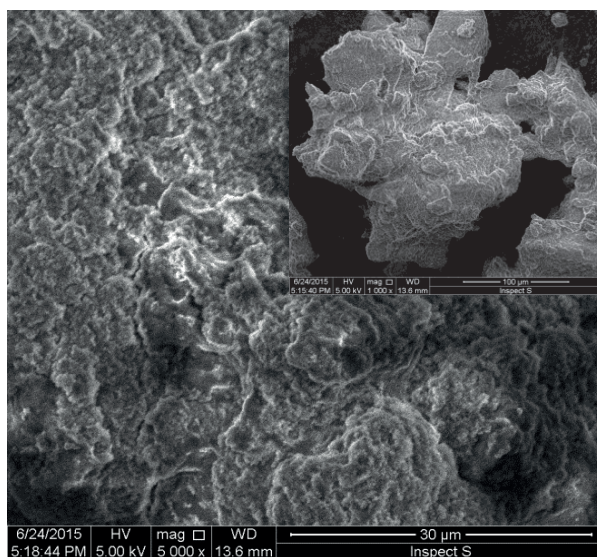
The efficiency of elution of Cr(III) ions from the polymeric sorbent was studied using acetic acid ( $\text{CH}_3\text{COOH}$ ) as a complexing agent ( $\log \beta_1 = 4.63$ ). Solutions of acetic acid (4 mL) in a concentration range from 0.5 to 4

mol L<sup>-1</sup> were tested independently for desorption of Cr(III) from the column at a flow rate of 0.9 mL min<sup>-1</sup>. It was found that the efficiency of elution of Cr(III) ions increased from 73% to 94% along with an increasing concentration of the stripping agent from 0.5 mol L<sup>-1</sup> to 4 mol L<sup>-1</sup>. The reason for this is that the nitrogen atoms of nicotinic acid are protonated in such a strong acid solution and have lost their ability of coordination with heavy metals. Moreover, the carboxylic group of nicotinic acid is also protonated. The influence of the eluent's volume on the elution efficiency of Cr(III) was studied in the range of 1–4 mL. It was found that 4 mL of 4.0 mol L<sup>-1</sup> CH<sub>3</sub>COOH was necessary for quantitative elution of Cr(III).

Retention of Cr(VI) ions on IIP and CP polymers at pH 9 was below 20%. It was observed that more than 90% of Cr(VI) retained on IIP was removed with 2 mL of Milli-Q water, which indicates nonspecific sorption of this ion on the sorbent. However, a small amount of Cr(III) (5%–7%) was also eluted with Milli-Q water. Hence, in order to improve the selectivity of the procedure we decided to rinse the column with water before elution of the Cr(III) ions. This additional step allowed us to remove most of the Cr(VI) ions from the column. Under optimised conditions, the efficiency of Cr(III) retention on IIP evaluated for 6 subsequent cycles was 93.7 ± 3.8%; the efficiency of elution was 94.7 ± 4.2%. The recovery of Cr(III), defined as the ratio of the mass of analyte determined in the eluent to the mass of analyte loaded on the column, was 88.6 ± 2.6%.

## 2.2. Characteristics of polymers

SEM images of IIP and CP polymers show that their particles have an irregular cauliflower shape sized 100–200 μm. The surface of the particles is very rough and porous (Figure 2). Nitrogen sorption analysis was carried out using approximately 0.3-g portions of polymers degassed for 24 h at 80 °C. The surface area of the imprinted and control polymers was derived from adsorption isotherms using the Brunauer–Emmett–Teller (BET) method. The BET surface area was 340 m<sup>2</sup> g<sup>-1</sup> for IIP and 358 m<sup>2</sup> g<sup>-1</sup> for CP, the pore volume was 0.23 cm<sup>3</sup> g<sup>-1</sup> for IIP and 0.24 cm<sup>3</sup> g<sup>-1</sup> for CP, and the pore diameter was 1.3 nm for IIP and 1.33 nm for CP.



**Figure 2.** SEM image of a IIP surface particle, 5000 × magnification; upper right-hand corner, 1000 × magnification.

In order to determine the sorption capacity of IIP and CP towards Cr(III) ions, the standard solution of Cr(III) (7 μg mL<sup>-1</sup>) was passed through columns filled with 25 mg of IIP or CP under optimised conditions.

Successive fractions of effluent (2 mL) were collected and examined to determine the chromium level. The sorption capacity was evaluated on the basis of the maximum volume of standard solution for which the analyte was still quantitatively retained (>80%). The sorption capacity was calculated at 4.5 mg g<sup>-1</sup> for IIP and 1.8 mg g<sup>-1</sup> for CP.

The polymer was subjected to numerous loading and elution operations in order to check the stability of the sorbent in the flow procedure. Reproducible results were obtained for more than 100 successive sorption–desorption cycles, indicating good stability of IIP. The prepared material was characterised by much longer reusability than other Cr-imprinted polymers.<sup>32,34,36,38,39</sup>

### 2.3. Selectivity study

The influence of metal ions commonly present in environmental samples (Cu(II), Ni(II), Mn(II), and Co(II)) was studied regarding selectivity of IIP towards Cr(III). For that purpose, solutions containing equivalent amounts of Cr(III) and competitive metal (Me) ions (5 μg mL<sup>-1</sup>) were passed through columns filled with IIP and CP. The concentration of the analyte and the metal ions in the effluent was measured by FAAS. The distribution coefficient (D), selectivity coefficient of Cr(III) ions (α), and relative selectivity coefficients were calculated using the following equations:

$$D = (C_0 - C_f)/C_f \times (V/m) \quad (1)$$

$$\alpha = D_{Cr(III)}/D_{Me} \quad (2)$$

$$\alpha' = \alpha_{IIP}/\alpha_{CP}, \quad (3)$$

where C<sub>0</sub> and C<sub>f</sub> were the initial and final concentrations of Cr(III) or competitive Me ions in the solution [μg mL<sup>-1</sup>], V – volume of the solution [mL], m – mass of sorbent [g].

A comparison of the selectivity coefficients for the Cr(III) ions on the IIP and CP showed that the α values for IIP were greater than for CP (Table 2). The values of the relative selectivity coefficients were in the range of 1.6 to 3.7, which indicates that Cr(III) ions can be selectively removed from aqueous samples even in the presence of other metal ions.

**Table 2.** Selectivity parameters of IIP towards Cr(III) ions in the presence of competitive ions (sample: 10 μg of Cr(III) + 10 μg of other metal ion).

Metal ion Me	Distribution ratio, <i>D</i> , mL g <sup>-1</sup>		Selectivity coefficient, <i>α</i>		Relative selectivity coefficient, <i>α'</i>
	Cr(III)	Me	IIP	CP	
Co(II)	969	313	3.1	1.7	1.8
Mn(II)	516	138	3.7	1.0	3.7
Cu(II)	576	113	5.1	3.1	1.6
Ni(II)	310	125	2.5	1.1	2.3

The IIP polymer was tested for the separation of Cr(III) and Cr(VI) ions. For that purpose, solutions containing different concentrations of Cr(III) and Cr(VI) ions were loaded on the column, then the column was rinsed with 2 mL of Milli-Q to remove the Cr(VI) ions, and Cr(III) was eluted and determined by FAAS. Good recovery of Cr(III) (Table 3) indicates that the method can be used for the separation of Cr(III) from Cr(VI) species.

**Table 3.** Recovery of Cr(III) from a mixture of Cr(III) and Cr(VI) ions on IIP (sample: pH 9, eluent: 4 mL of 4 mol L<sup>-1</sup> CH<sub>3</sub>COOH, mean value ± SD, n = 3).

Model sample	Found mass of Cr(III) ± SD, μg	Recovery of Cr(III) ± SD, %
9.95 μg of Cr(III)	8.82 ± 0.26	88.6 ± 2.6
10.28 μg of Cr(III) + 10.2 μg of Cr(VI)	8.30 ± 0.14	80.8 ± 1.4
10.28 μg of Cr(III) + 50.1 μg of Cr(VI)	8.16 ± 0.04	79.4 ± 0.4

#### 2.4. Method validation and application

Analytical performance of the method was evaluated under optimised experimental conditions. Repeatability of the separation process of Cr(III) ions on IIP obtained for 6 subsequent cycles was apparent as relative standard deviation (RSD) and was equal to 2.9%. The calibration graph of Cr(III) was prepared by loading 4 mL of standard solutions of Cr(III) at a concentration range from 1 to 10 μg mL<sup>-1</sup> on the column and its elution with 4 mL of 4 mol L<sup>-1</sup> CH<sub>3</sub>COOH. The calibration graph was linear up to 8 μg mL<sup>-1</sup>, giving the following regression equation:  $y = 0.032x - 0.001$  ( $r^2 = 0.991$ ). The limits of detection (LOD) and quantification (LOQ) of the method were calculated according to the IUPAC recommendation<sup>45</sup> at  $LOD = 3 SD_{blank}/a$ , and  $LOQ = 10 SD_{blank}/a$ , where  $SD_{blank}$  is a standard deviation of the absorbance of a blank sample subjected to the separation procedure, while  $a$  is a slope of the calibration graph. The LOD obtained for 10 successive analytical cycles was 0.08 μg mL<sup>-1</sup>, while LOQ was 0.24 μg mL<sup>-1</sup> for 10 mL of a sample.

Applicability of the method was tested for different volumes of samples (2–10 mL) of different concentrations (1–8 μg mL<sup>-1</sup>). It was found that recovery of the analyte from 10 mL of 1 μg mL<sup>-1</sup> solution was 77.7 ± 4.8% (n = 3), whereas from 5 and 10 mL of 2.5 μg mL<sup>-1</sup> solution it was 100.4 ± 4.0% and 107.1 ± 5.5% (n = 3), respectively.

The reference material (RM) of municipal wastewater RES 25.2 was used to study the accuracy of the method. This reference material possesses a certified property value of the total chromium concentration, but we confirmed, using the method based on ion exchange chromatographic (IC) separation of chromium forms coupled with their determination by ICP-MS,<sup>46</sup> that it contains Cr(III) ions only. An accurate determination of the chromium content in this material by FAAS is impossible due to the significant influence of matrix constituents on the chromium signal (the recovery was only 55% of the certified value). The recovery of chromium obtained by the standard addition method increased to 84%, but this result still shows the presence of matrix interferences. Our basic studies concerning the effect of potential matrix components on the analytical signal of chromium measured directly by the FAAS technique showed that the presence of nickel(II), copper(II), and manganese(II) ions in a concentration range of 5–200 mg L<sup>-1</sup> changed the absorbance of chromium by 2%–12%. A more significant effect was observed in the presence of Fe(III) and Co(II) ions, as the decrease in the Cr signal was in the range 30%–40%. It is evident from these results that accurate results of determining Cr in complicated samples may be obtained only after chemical separation of the analyte from the interfering matrix. The recovery of Cr(III) from RM after its separation on IIP was 89.9 ± 3.1%, n = 6, which confirmed the accuracy of the developed procedure.

The procedure was applied to an analysis of chromium in treated municipal wastewater. The samples were filtered through a 0.45 μm Supelco membrane filter, adjusted to pH 9 with sodium hydroxide and left for equilibration. However, as the concentration of Cr(III) in the analysed samples was below the LOQ of



the method, the samples were spiked with 12  $\mu\text{g}$  of Cr(III). The absence of the Cr(VI) form in the analysed samples was proved by the IC-ICP-MS method. The recovery of Cr(III) was in the range of 81%–90% (Table 4). Reproducibility of the separation procedure for different wastewater samples was below 3.5%. It confirmed that the developed SPE method using IIP is suitable for chromium speciation analysis in contaminated wastewater. A comparison of the analytical parameters of the developed method and previously published methods for analysis of chromium(III) in wastewater is summarised in Table 1. As can be observed, the developed method is characterised by good reproducibility, small consumption of reagents, and short analysis time.

**Table 4.** Recovery of Cr(III) from real samples on IIP (sample: 4 mL, pH 9, eluent: 4 mL of 4 mol L<sup>-1</sup> CH<sub>3</sub>COOH, mean value  $\pm$  SD, n = 3).

Sample	Added mass of Cr(III), $\mu\text{g}$	Found mass of Cr(III) $\pm$ SD, $\mu\text{g}$	Recovery of Cr(III) $\pm$ SD, %
Treated wastewater A <sup>(a)</sup>	12 $\mu\text{g}$	9.7 $\pm$ 0.3	80.8 $\pm$ 2.5
Treated wastewater B <sup>(b)</sup>	-	13.0 $\pm$ 0.5	87.4 $\pm$ 3.0
Treated wastewater B <sup>(b)</sup>	12.4 $\mu\text{g}$	24.2 $\pm$ 0.2	89.9 $\pm$ 1.6
Wastewater RES 25.2 <sup>(c)</sup>	-	6.2 $\pm$ 0.2	89.9 $\pm$ 3.1

<sup>(a)</sup>concentration of total chromium below LOD of the FAAS method

<sup>(b)</sup>concentration of Cr(III) determined by IC-ICP-MS: 3.72  $\mu\text{g mL}^{-1}$

<sup>(c)</sup>wastewater RES 25.2 - property value of Cr: 1.72  $\pm$  0.026  $\mu\text{g mL}^{-1}$ ; n = 6.

A new polymeric sorbent with imprinted Cr(III)-nicotinate complex synthesised in this work by precipitation polymerisation is characterised by good selectivity towards Cr(III) ions in the presence of Cr(IV) and other competitive ions, good capacity, and high stability during flow working conditions (more than 100 sorption–desorption cycles). The Cr(III) ions are selectively retained on IIP at pH 9 and quantitatively removed with 4 mol L<sup>-1</sup> of CH<sub>3</sub>COOH. The developed dynamic SPE procedure allows for selective separation of Cr(III) species from wastewater, which was confirmed by an analysis of the reference material.

### 3. Experimental

#### 3.1. Instrumentation

A Solaar M6 atomic absorption spectrometer (Thermo Electron Corporation, UK) with atomisation in an air-acetylene flame and deuterium background correction was used to determine the concentration of chromium. A chromium hollow cathode lamp (Photron, Australia) was operated at a 6 mA current. The measurements were done at  $\lambda = 357.9$  nm with a spectral bandpass of 0.5 nm.

The surface morphology of the polymers' particles was examined using an Inspect S50 scanning electron microscope (SEM) (Hitachi, USA). The polymers were coated under reduced pressure with a thin gold layer, which improved the secondary electron signal required for their topographic examination.

The infrared spectra of polymers by Fourier transform infrared spectroscopy (FTIR) were obtained using a Nicolet Magna IR 550 Series II FTIR spectrophotometer (Thermo Scientific, Japan). Pore-size distribution and specific surface area of the particles were determined via nitrogen adsorption/desorption according to the BET method using a Gemini VII 2390 surface area and porosity analyser (Micrometrics, USA).

A flow SPE system was used for chromium separation. The system consisted of a peristaltic pump Minipuls 3 (Gilson, France), PTFE tubing of i.d. 0.8 mm, and glass adsorption columns (i.d. 10 mm) filled with 25 mg of the polymeric sorbent. Both ends of the columns were blocked with PTFE membranes. An

inoLab pH Level 1 (WTW, Germany) pH meter equipped with an electrode SenTix 21 (WTW, Germany) was used for the pH measurements.

### 3.2. Reagents

A stock solution (20 mg mL<sup>-1</sup>) of Cr(III) as CrCl<sub>3</sub> was obtained from Merck (Darmstadt, Germany); a stock solution (1.001 mg mL<sup>-1</sup>) of Cr(VI) as K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Sigma Aldrich, Germany) was used. Chromium chloride (CrCl<sub>3</sub>·6H<sub>2</sub>O) was used for the syntheses of polymers, sodium hydroxide and hydrochloric acid were used for pH adjustment, and acetic acid was used as a desorption agent as supplied by POCh (Gliwice, Poland). Sodium lauryl (dodecyl) sulphate (SDS) was supplied by Sigma Aldrich (Munich, Germany). Solutions of copper(II), nickel(II), manganese(II), and cobalt(II) nitrates(V) and iron(III) chloride (Fluka, Buchs, Switzerland) were used for the interference studies. High purity deionised Milli-Q water (Millipore, USA) was used to prepare all of the solutions. All reagents were of analytical grade or higher.

Nicotinic acid (3-pyridinecarboxylic acid), glycol ethylene dimethacrylate (EGDMA, 98%), and 2,2'-azobis(isobutyronitrile) (AIBN) were supplied by Sigma Aldrich. Acrylamide (AA), dimethyl sulfoxide (DMSO), and acetonitrile (ACN) were supplied by POCh.

Reference material from a wastewater treatment plant of urban origin RES 25.2 (Ielab Calidad, Spain) was used for the accuracy studies. The wastewater samples were delivered from a municipal sewage treatment plant (Bialystok, Poland).

### 3.3. Preparation of the chromium(III) imprinted polymer

The Cr(III)-nicotinate complex was prepared according to a procedure described elsewhere.<sup>42,43</sup> A hot solution of Cr(III) ions (2.5 mL, 1.16 mmol Cr(III) as CrCl<sub>3</sub>) was added to a hot solution of nicotinic acid (2.5 mL, 3.51 mmol). The mixture was adjusted to pH 4 with a diluted solution of NaOH and stirred for 120 min at 80 °C. This way a grey-blue complex with a molar ratio of Cr to nicotinate equal to 1:2 was formed. The solid complex was filtered, rinsed with water, and dried. The FT-IR (in KBr) spectrum of the Cr(III)-nicotinate complex was registered and the following characteristic bonds were observed:  $\nu_{asym}(-C=O)$  at 1630 cm<sup>-1</sup>,  $\nu_{sym}(-C=O)$  at 1440 cm<sup>-1</sup>,  $\nu(-C-N)$  at 1170 cm<sup>-1</sup>,  $\nu(-C=N)$  at 1560 cm<sup>-1</sup>, and  $\nu(-C-H)$  bands at 760 cm<sup>-1</sup>.

Next, 0.12 mmol of the Cr(III)-nicotinate complex (6.05 mg Cr) and 5.74 mmol of acrylamide (0.4046 g) were placed in a magnetically stirred glass polymerisation reactor, dissolved in 23 mL of dimethyl sulfoxide (DMSO), and mixed for 60 min. Then 0.30 mmol of AIBN (0.1 g) and 22.5 mmol of EGDMA (4.33 mL) previously dissolved in 23 mL of acetonitrile were added. The solution was purged with argon and precipitation polymerisation was carried out at 60 °C for 24 h at a constant stirring rate of 100 rpm. The obtained precipitate of polymer was rinsed with methanol-water solution (1:4, v/v) in order to remove the unreacted monomers, dried at 50 °C for 48 h, and sieved. The FT-IR (in KBr) spectrum of the polymer was registered and the following characteristic bonds were observed:  $\nu(-C=O)$  at 1727 cm<sup>-1</sup>,  $\nu(-C-O)$  at 1265 cm<sup>-1</sup>,  $\nu(-C-N)$  at 1149 cm<sup>-1</sup>,  $\nu(-C=N)$  at 1560 cm<sup>-1</sup>, and  $\nu(-C-H)$  bands at 752, 1452, 2954, and 2992 cm<sup>-1</sup>.

The fraction of particles with a size range of 200–300 μm was used for the experiments. The degree of chromium imprinted in the polymer was assessed at 82%. The polymers were treated with 2 mol L<sup>-1</sup> acetic acid to remove the imprinted Cr(III) ions. The control polymer (CP) was prepared in the same way but without the addition of Cr(III) ions.

## Acknowledgements

The authors kindly acknowledge the financial support of the Polish National Science Centre (DEC-2012/07/B/ST4/01581).

## References

1. The New Top Six Toxic Threats: A Priority List for Remediation World's Worst Pollution Problems 2015. Document prepared by Pure Earth and Green Cross Switzerland ([http://www.worstpolluted.org/docs/WWPP\\_2015\\_Final.pdf](http://www.worstpolluted.org/docs/WWPP_2015_Final.pdf)).
2. Sterans, D. M. In *The Nutritional Biochemistry of Chromium(III)*; Vincent, J. B., Ed. Elsevier: Amsterdam, the Netherlands, 2007, pp. 57-70.
3. Vincent, J. B. *Dalton Trans.* **2010**, *39*, 3787-3794.
4. Staniek, H.; Krejpcio, Z.; Wieczorek, D. *Biol. Trace Elem. Res.* **2016**, *171*, 192-200.
5. Chromium Hexavalent Compounds, In *Report on Carcinogens (RoC)*, 13th Edition, National Toxicology Program, US Department of Health and Human Services, 2014, CAS No. 18540-29-9.
6. IARC, Monographs on the evaluation of carcinogenic risks to humans. Chromium, nickel and welding. WHO International Agency for Research on Cancer, IARC: Lyon, France. 1990, *49*, 49-214.
7. Hoet, P. In: *Handbook of Elemental Speciation II: Species in the Environment, Food, Medicine & Occupational Health*, Cornelis, R.; Crews, H.; Caruso, J.; Heumann, K. G. Eds., John Wiley & Sons, Ltd.: Chichester, UK. 2005, pp. 135-157.
8. Kotaś, J.; Stasicka, Z. *Environ. Poll.* **2000**, *107*, 263-283.
9. Dahl, B.; Thatoi, H. N.; Das, N. N.; Pandey, B. D. *J. Hazard. Mater.* **2013**, *250-251*, 272-291.
10. European Union emission inventory report 1990–2013 under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) EEA, Technical report No 8/2015, ISSN 1725-2237.
11. Cheng, H.; Zhou, T.; Li, Q.; Lu, L.; Lin, C. *PLoS ONE* **2014**, *9*, e87753.
12. Yilmaz, S.; Türe, M.; Sadikoglu, M.; Duran, A. *Environ. Monit. Assess.* **2010**, *167*, 235-242.
13. Ordinance of the Minister of Environment concerning the conditions for spreading sewage into the water or soil, and on substances particularly harmful to the aquatic environment. *Official Journal* **2006**, *137*, 984, pp. 9787-9820.
14. Ščančar, J.; Milačič, R. *J. Anal. At. Spectrom.* **2014**, *29*, 427-443.
15. Sarica, D. Y.; Türker, A. R.; Erol, E. *J. Sep. Sci.* **2006**, *29*, 1600-1606.
16. Hemmatkhan, P.; Bidari, A.; Jafarvand, S.; Milani Hosseini, M. R.; Assadi, Y. *Microchim. Acta* **2009**, *166*, 69-75.
17. Meeravali, N. N.; Madhavi, K.; Kumar, S. J. *J. Anal. At. Spectrom.* **2011**, *26*, 214-219.
18. Ünsal, Y. E.; Tüzen, M.; Soylak, M. *Turk. J. Chem.* **2014**, *38*, 173-181.
19. Pyrzyńska, K. *Trends Anal. Chem.* **2012**, *32*, 100-110.
20. Namieśnik, J.; Rabajczyk, A. *Crit. Rev. Environ. Sci. Technol.* **2012**, *42*, 327-377.
21. Pyrzyńska, K. *Inter. J. Environ. Anal. Chem.* **2012**, *92*, 1262-1275.
22. Trzonkowska, L.; Leśniewska, B.; Godlewska-Żyłkiewicz, B. *Crit. Rev. Anal. Chem.* **2016**, *46*, 305-322.
23. Tuzen, M.; Soylak, M. *J. Hazard. Mater.* **2006**, *129*, 266-273.
24. Yalcin, S.; Apak, R. *Anal. Chim. Acta* **2004**, *505*, 25-35.
25. Memon, J. R.; Memon, S. Q.; Bhangar, M. I.; Khuhawar, M. Y. *J. Hazard. Mater.* **2009**, *163*, 511-516.
26. Pramanik, S.; Dey, S.; Chattopadhyay, P. *Anal. Chim. Acta* **2007**, *584*, 469-476.
27. Mondal, B. C.; Das, D.; Das, A. K. *Talanta* **2002**, *56*, 145-152.
28. Tuzen, M.; Uluozlu, O. D.; Soylak, M. *J. Hazard. Mater.* **2007**, *144*, 549-555.

29. Chang, Q.; Song, S.; Wang, Y.; Li, J.; Ma, J. *Anal. Methods* **2012**, *4*, 1110-1116.
30. Rao, T. P.; Daniel, S.; Gladis, J. M. *Trends Anal. Chem.* **2004**, *23*, 28-35.
31. Birlik, E.; Ersöz, A.; Açikkalp, E.; Denizli, A.; Say, R. *J. Hazard. Mat.* **2007**, *140*, 110-116.
32. Zhang, N.; Suleiman, J. S.; He, M.; Hu, B. *Talanta* **2008**, *75*, 536-543.
33. An, F.; Gao, B. *Desalination* **2009**, *249*, 1390-1396.
34. Chen, J. H.; Chen, G. P.; Liu, Q. L.; Ni, J. C.; Wu, W. B.; Lin, J. M. *Chem. Eng. J.* **2010**, *165*, 465-473.
35. Leśniewska, B.; Godlewska-Żyłkiewicz, B.; Wilczewska, A. *Z. Microchem. J.* **2012**, *105*, 88-93.
36. Jashmidi, M.; Ghaedi, M.; Dashtian, K.; Hajati, S. *RSC Advances* **2015**, *5*, 105789-105799.
37. Leśniewska, B.; Trzonkowska, L.; Zambrzycka, E.; Godlewska-Żyłkiewicz, B. *Anal. Methods* **2015**, *7*, 1517-1526.
38. Bayramoglu, G.; Arica, M. Y. *J. Hazard. Mat.* **2011**, *187*, 213-221.
39. Ren, Z.; Kong, D.; Wang, K.; Zhang, W. *J. Mater. Chem. A* **2014**, *2*, 17952-17961.
40. Pakade, V.; Cukrowska, E.; Darkwa, J.; Torto, N.; Chimuka, L., *Water SA* **2011**, *37*, 529-537.
41. Cooper, J. A.; Anderson, B. F.; Buckley, P. A.; Blackwell, L. F. *Inorg. Chim. Acta* **1984**, *91*, 1-9.
42. Pham, T. H. N.; Aitken, J. B.; Levina, A.; Lay, P. A. *Inorg. Chem.* **2014**, *53*, 10685-10694.
43. Evans, G. W.; Pouchnik, D. J. *J. Inorg. Biochem.* **1993**, *49*, 177-197.
44. Szabłowicz, M.; Kita, E. *Transition Met. Chem.* **2005**, *30*, 623-629.
45. Inczedy, J.; Lengyel, T.; Ure, A. M.; Gelencser, A.; Hulanicki, A. *Compendium of Analytical Nomenclature*. 3rd ed. IUPAC, Blackwell Science: Oxford, UK, 1998.
46. Tonoshima, M.; Sakai, T.; Jones, C. Low-level speciated analysis of Cr(III) and Cr(VI) using LC(IC)-ICP-MS. Application note 5990-9366EN, Agilent Technology 2012.