

NOVEL ION-IMPRINTED POLYMER AS A TOOL FOR SELECTIVE DETERMINATION OF Sb^{III} IN NATURAL WATERS

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Abstract

A novel Sb^{III}-imprinted polymer was synthesized via radical copolymerization of methacrylic acid and trimethylolpropane trimethacrylate in the presence of 2-mercapto-N-(2-naphthyl)acetamide as a chelating ligand forming the functionality of specific binding sites. The extent of ligand incorporation in the active centres was evaluated by elemental analysis and found to be 73.6%. The IIP was utilized as a sorbent material for selective solid-phase extraction of Sb^{III} in drinking waters after optimization of sorption and desorption processes in a batch mode. Excellent separation of Sb^{III} and Sb^V was accomplished at pH 8 followed by elution of Sb^{III} with 0.5 M thiocarbamide. Analytical procedure for non-chromatographic speciation and determination of Sb^{III} was developed demonstrating very good precision (RSD 7–11%) and recoveries between 97–105%. This procedure enabled up to 25-fold preconcentration and completely met the requirements of EU legislation for the quality of water intended for human consumption.

Key words: antimony, speciation, ion-imprinted polymer, solid-phase extraction

Introduction. Antimony is a chemical element that occurs in the environment as a result of natural and anthropogenic processes and its biogeochemical

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cycle is nowadays sufficiently characterized. Toxicological profiles and bioaccumulative properties of particular Sb species are well known – the inorganic chemical forms are much more harmful than organic species, especially the lower oxidation state Sb^{III} [1,2]. In this sense, reliable knowledge about Sb speciation is essential taking into account significant differences between toxicity and bioavailability of trivalent and pentavalent forms.

Solid phase extraction (SPE) is one of the most preferred methods for separation and preconcentration due to the low reagents consumption, high enrichment factors, performance simplicity and fastness, but its applicability in non-chromatographic speciation analysis strongly depends on the chemical properties of the sorbents used [3]. Modelling and synthesis of suitable materials, enabling selective recognition and retention of the target chemical species, still attract researchers' attention because the structure and functionality of the sorbents have a crucial role in the development of reliable methods for speciation analysis [4]. Various smart materials such as nanosized metal oxides [5–7], single and multi-walled carbon nanotubes [8,9], ion-imprinted polymers and hybrid sorbents [10–12] have been utilized for efficient separation and preconcentration of Sb^{III} or Sb^{V} from different matrices before their instrumental measurement.

Ion-imprinted polymers (IIPs) are considered versatile materials for highly selective SPE due to the binding sites, artificially created during the polymerization process with a size, geometry and functionality fully complementary to the imprinted ionic species. In this way, a strong ionic memory is generated, resulting in selective recognition and retention upon subsequent contact of IIP with the target ion. According to our knowledge, the reported studies related to preparation and application of Sb^{III} -IIPs are relatively few. Ion-imprinted polymer for determination and speciation of Sb^{III} in water and juice samples was synthesized in the presence of ammonium pyrrolidine dithiocarbamate as a ligand using styrene as a monomer and ethylene glycol dimethacrylate as a cross-linker [10]. The same synthesis procedure was used by JAKAVULA et al. [12] to produce a nanocomposite material (Fe_3O_4 coated with carbon nanofibres, SiO_2 and IIP) for magnetic SPE of Sb^{III} in water samples. Selectivity of the nanocomposite was investigated in the presence of $\text{Al}(\text{III})$, $\text{Cd}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Sn}(\text{IV})$, $\text{Zn}(\text{II})$ but not $\text{Sb}(\text{V})$. Here, we report the synthesis of novel Sb^{III} -imprinted polymer using methacrylic acid as a monomer, trimethylolpropane trimethacrylate as a cross-linking agent, 2-mercapto-N-(2-naphthyl)acetamide as a chelating ligand, and its further application for non-chromatographic speciation analysis of antimony in natural waters.

Materials and methods. Synthesis of IIP. The ion-imprinted polymer was synthesized via radical copolymerization of methacrylic acid (MAA, 2.2 mmol) as a functional monomer and trimethylolpropane trimethacrylate (TMPTMA, 1.0 mmol) as a cross-linking agent. Azobisisobutyronitrile (AIBN) was used as an initiator. The process was carried out in acetonitrile (solvent, 25.0 mL) for 24 h at

60 °C in the presence of 0.15 mmol Sb^{III} as a template ion and 2-mercapto-N-(2-naphthyl)acetamide (thionalide, 0.30 mmol) as a chelating ligand. The template Sb^{III} ion was introduced into the reaction mixture by adding 1.8 mL solution with concentration 10.0 mg/mL. The synthesized Sb^{III}-imprinted polymer was filtered, washed twice with acetonitrile and distilled water and then the template ion was removed from the polymer matrix by several sequential elution steps (6 M HCl, 2 M HNO₃ and 0.5 M tartaric acid). Finally, IIP was washed with acetonitrile and dried at room temperature. In order to evaluate sorption properties of polymer matrix toward the target analyte Sb^{III}, non-imprinted polymer (NIP) was prepared following the same procedure, but in absence of template ion and thionalide.

Characterization of IIP and NIP. The extent of incorporation of chelating ligand was evaluated by elemental analysis (C, H, N, S) performed on analyzer EURO EA 3000, EuroVector SpA. The shape of IIP and NIP particles was determined by a scanning electron microscope (SEM, JEOL JSM-5500).

Sorption study. Extraction efficiency of the IIP and NIP was studied in a batch mode. The influence of pH on the sorption of target analyte Sb^{III} was investigated in the range pH 3–10. Aqueous solutions, containing 5 µg/mL Sb^{III}, were prepared and pH was adjusted to desired value by adding of ammonia or buffer solution. All pH measurements were done with pH-meter Mettler Toledo, SevenCompact S220. Then, portions of 50 mg IIP or NIP were mixed with 10 mL of the model solution of Sb^{III} at different pH value and shaken for 60 min. Finally, samples were centrifuged for 15 min at 5500 rpm on EBA 20 DJB Labcare, supernatants were removed and concentrations of Sb were measured by ICP OES Varian Vista MPX. Degrees of sorption were calculated as follows:

$$D_S(\%) = \frac{A_i - A_{\text{eff}}}{A_i} \times 100,$$

where A_{eff} (µg) is the amount of Sb^{III} in the supernatant solution after SPE with IIP, A_i (µg) is the total amount of Sb^{III} added to samples.

Selectivity. The aim of this experiment was to evaluate the degree of Sb^V sorption under the optimal conditions for the specific retention of Sb^{III}. Aqueous solutions with pH 8 and volume of 10.0 mL, containing 5 µg/mL Sb^V or Sb^{III}, were added to portions (50 mg) of the ion-imprinted polymeric sorbent. Three parallel samples for both antimony species were prepared and sorption was conducted for 60 min on an electrical shaker. After centrifugation concentrations of Sb^{III} and Sb^V in the effluents were measured by ICP OES and the extraction efficiency of the IIP toward target (Sb^{III}) and competitive (Sb^V) species was evaluated.

Elution. Several acids at different concentration levels, such as hydrochloric, nitric, tartaric and citric, were tested as potential eluents. In addition, desorption of Sb^{III}, based on competitive complexation, was also investigated by treatment of IIP with solutions of thiocarbamide, EDTA and cysteine. All experiments were

done after loading the sorbent with 50 µg Sb^{III} under optimal conditions followed by treatment with 10.0 mL of each eluent for 60 min on an electrical shaker. Degree of elution (D_E %) was defined as follows:

$$D_E(\%) = \frac{A_{el}}{A_i - A_{eff}} \times 100,$$

where A_{el} (µg) is the amount of Sb^{III} in the eluate, A_i (µg) is the total mass of Sb^{III} added to samples, A_{eff} (µg) is the amount of Sb^{III} in the supernatant solution after sorption.

Analytical application. Water samples with volume 50.0 mL were mixed with sorbent particles (50 mg in each sample) and retention of Sb^{III} was accomplished for 40 min on an electric shaker. After centrifugation (5500 rpm), the supernatants were discarded and elution was performed for 35 min with 2.0 mL 0.5 M thiocarbamide. Finally, Sb^{III} was measured in the eluate solutions by ICP-OES.

Results and discussion. In the preparation process of the IIP (Fig. 1), thionalide was used as a chelating ligand for complex formation of Sb^{III} during polymerization and thus the target species was imprinted in the polymer matrix by non-covalent interactions. This approach, known also as trapping technique, is based on complex formation between template ion and non-polymerizing ligand which remains immobilized into the polymer matrix but not chemically linked to the polymer network. Such type of incorporation is usually due to H-bonding between the ligand and the functional monomer (Fig. 1). After removal of Sb^{III}, cavities with specific complementary size and functionality were formed. Incorporation of the ligand in these active centres was evaluated via elemental analysis. The results, expressed as a mean ± expanded uncertainty, showed (2.40 ± 0.13)% S and (3.48 ± 0.23)% N. It must be mentioned that (2.81 ± 0.15)% N was determined in NIP samples, which can be explained by inclusion of fragments from the initiator in the polymer structure. The calculated degree of incorporation of thionalide in the IIP was 73.6% and can be accepted as an evidence for successful synthesis of IIP with enough binding sites.

SEM was used to investigate the morphology and shape of IIP and NIP particles. As can be seen in Fig. 1(B), the non-imprinted polymeric particles have a size below 1 µm and shape close to the spherical, while the IIP is in the form of bigger aggregates of irregular particles.

Extraction efficiency, expressed as degree of sorption (D_S , %), is one of the main characteristics of SPE which is directly affected by pH. On the one hand, strong dependence of the sorption on pH is due to the protonation of thiol and carbonyl groups of the sorbent in acidic medium. On the other hand, distribution of particular chemical species of Sb in water systems is also pH dependent [13]. Extraction efficiency of the synthesized IIP was studied in the range pH 3–10 and the results are presented in Fig. 2.

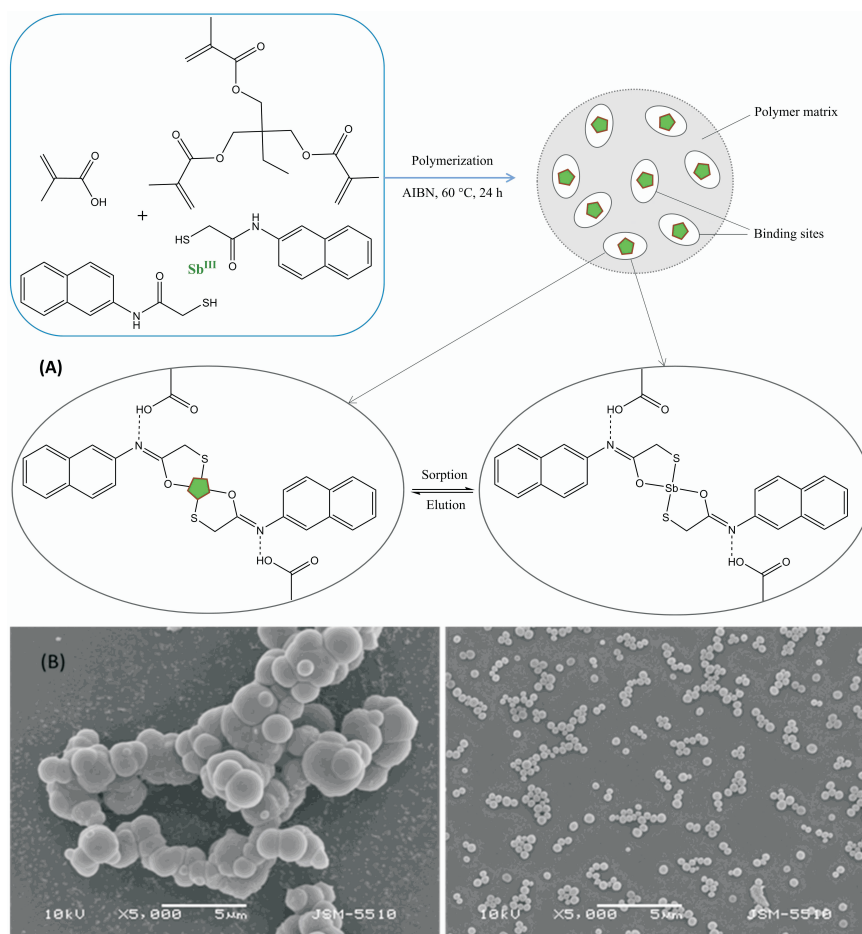


Fig. 1. (A) Preparation scheme of the IIP; (B) SEM images of the synthesized IIP (left) and NIP (right)

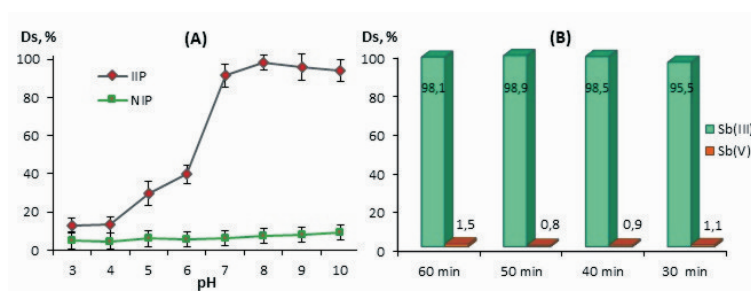


Fig. 2. Extraction efficiency of IIP and NIP at different pH values (A); Degrees of sorption for Sb^{III} and Sb^{V} (at pH 8) achieved after different contact time (B)

As was expected, at lower pH values extraction efficiency was immensely reduced (around 13%), slightly increased in weakly acidic media (pH 5–6) but did not exceed 40%. Significantly better retention of Sb^{III} was achieved at $\text{pH} > 7$. As can be seen in Fig. 2(A), degree of sorption sharply escalated in alkaline media and attained maximum value ($D_S = 98.1\%$) at pH 8. Based on the calculated degrees of sorption, pH 8 was selected as an optimal for quantitative retention of the target chemical species. From a practical view point, this can be accepted as a significant advantage because there is no need of considerable pH adjustment of real water samples before analysis. Furthermore, the low levels of non-specific sorption in weakly alkaline media (NIP, $D_S < 7\%$) confirmed the significant role of ion-imprinting in polymer matrix leading to formation of highly specific binding sites for effective sorption of Sb^{III} . Applicability of the IIP in the speciation analysis of antimony in water samples strongly depends on its selectivity toward the target Sb^{III} species. It was experimentally verified that excellent separation of Sb^{III} and Sb^{V} could be easily achieved at pH 8 because degree of sorption for Sb^{V} was below 1.5%. Additionally, time of sorption was optimized by reducing the process duration. As can be seen in Fig. 2(B), 40 min are completely enough for quantitative separation of both Sb species.

The choice of a suitable eluent is an important part of optimization of the extraction conditions, because the accuracy and reproducibility of the analytical procedure depend on the efficiency of desorption. The results obtained for all tested eluents are presented in Fig. 3. Antimony (III) is known to form tartrate complexes ($\lg \beta = 9.41$ [14]), but their thermodynamic stability is probably not high enough the sorbed analyte to be eluted quantitatively as a result of competitive complexation.

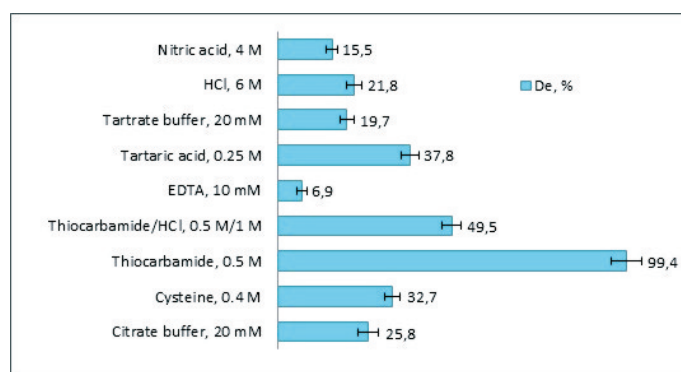


Fig. 3. Efficiency of different eluent solutions

In all cases, eluents aiming Sb^{III} desorption via tartrate complexation yielded unsatisfactory elution rates ($D_E < 40\%$), even at 120 min elution time. Almost identical results were obtained with a citrate buffer as an elution agent. EDTA was also tested as a possible eluent as it forms a very stable complex with Sb^{III}

($\lg \beta = 24.8$ [15]). Contrary to the expectations, the obtained elution rates are extremely low, which is probably due to some kind of steric hindrance (e.g. $\pi - \pi$ stacking) that block the effective contact of the large EDTA molecule with the active centres of the sorbent. An attempt was made to improve the elution with EDTA by increasing the time (120 min) and ensuring that the desorption process took place at a higher pH 9–10 in a buffered medium. However, in any case the elution efficiency of EDTA did not exceed 20%. Alternatively, the desorption of Sb^{III} has been studied with solutions of S-containing ligands such as cysteine and thiocarbamide. As can be seen in Fig. 3, quantitative elution was achieved using an aqueous solution of thiocarbamide (pH 5.5). The optimization of elution time showed that D_E above 97% might be achieved for 35 min.

Analytical application. Water samples (tap water, ground water with low and high mineralization) with volumes of 20 mL and 50 mL (Table 1) were spiked with 2 $\mu\text{g/L}$ Sb^{III} or 2 $\mu\text{g/L}$ Sb^{V} followed by pH adjustment with a few drops of ammonia solution (3 mol/L) and the SPE procedure was carried out under the optimal conditions. Each sample was run in three replicates. Elution was performed with 2.0 mL 0.5 M thiocarbamide and thus 10-fold and 25-fold pre-concentration was done before ICP-OES measurements. Results showed that 50 mL water sample might be used based on analytical recoveries for Sb^{III} between 97–105% (Table 1). It is worth mentioning that the larger sample volume (50 mL) required centrifugation for longer time (90 min) in order to ensure complete precipitation of the IIP and separation of the solid and liquid phase without any loss of sorbent material. In addition, for all samples recoveries for Sb^{V} is below 1% (Table 1). Furthermore, the achieved recoveries testified to the lack of significant matrix interferences, even in samples with high total mineralization (TM). The accuracy of developed analytical procedure for selective Sb^{III} determination was confirmed by added found method. Analysis of various tap and ground water samples for Sb^{III} content showed relative standard deviations (RSD) in the range 7–11% for the concentration range 1–20 $\mu\text{g/L}$. The limit of quantitation (10σ criteria) was found to be 1 $\mu\text{g/L}$. According to the EU regulations on the quality of waters intended for human consumption, the parametric value for antimony is de-

T a b l e 1
Analytical performance for Sb^{III} and Sb^{V} determination in tap and ground waters

Sample	Recovery, Sb^{III} %		Recovery, Sb^{V} %	
	20 mL	50 mL	20 mL	50 mL
Devin, TM 82 mg/L	98 ± 3	97 ± 3	< 1	< 1
Devin, TM 255 mg/L	103 ± 2	105 ± 2	< 1	< 1
Tap water	97 ± 2	101 ± 4	< 1	< 1

creed to be 10 µg/L [16]. The feasibility of the proposed method to analysis of real water samples, containing Sb^{III} at low ppb-levels, was experimentally confirmed.

Conclusions. Non-chromatographic method for determination of Sb^{III} in drinking waters was realized by selective SPE of the analyte with a novel ion-imprinted polymer as a sorbent followed by ICP-OES measurement. In the preparation process of the IIP, 2-mercapto-N-(2-naphthyl)acetamide was used as a chelating ligand resulting in an excellent extraction efficiency and selectivity toward Sb^{III}. The major advantages of the method developed are easy operation, fastness and low reagents consumption with no need of any additional sample pre-treatment. The reported procedure was applied to natural water samples demonstrating very good accuracy and reproducibility enabled 25-fold preconcentration of target chemical species Sb^{III}.

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