

Non-chromatographic speciation analysis of antimony in water samples assisted by vinylimidazole-based polymeric sorbent

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A functional polymeric material was synthesized *via* precipitation copolymerization of vinylimidazole and trimethylolpropane trimethacrylate and used as a sorbent for selective separation and determination of Sb(V) and Sb(III). The extraction efficiency of the newly synthesized material toward Sb(III) and Sb(V) was studied in batch mode. In weakly acidic aqueous solutions, at pH 5–6, Sb(V) was entirely retained on the polymeric sorbent, while Sb(III) remained in the supernatant. Quantitative elution of Sb(V) was accomplished with 1 mM diammonium hydrogen citrate for 30 min. An analytical procedure for non-chromatographic speciation and determination of inorganic antimony was developed. Concentrations of the target Sb(V) and the non-extractable Sb(III) were measured by ICP-OES with limits of quantitation of 4.2 µg/l and 3.4 µg/l, respectively. The method showed good accuracy, high precision, and applicability to low-mineralized waters, enabling up to 25-fold preconcentration of Sb(V).

Keywords: antimony, speciation analysis, solid-phase extraction, polymeric sorbent

INTRODUCTION

Antimony in aquatic environments primarily exists in two oxidation states: the trivalent Sb(III) and the pentavalent Sb(V). These species have quite different chemical behaviors, toxicities, and environmental dynamics [1]. In general, Sb(III) is more toxic than Sb(V), but it can be found in deep waters or sediments where oxygen concentrations are low, while Sb(V) is more stable under oxidizing conditions, typically found in well-oxygenated surface waters. Understanding the chemistry of antimony in aquatic environments is crucial for managing its impact on ecosystems and human health. Speciation analysis, defined as the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample [2], offers many tools for monitoring Sb species distribution in waters.

Solid-phase extraction (SPE) is a widely preferred technique for preconcentration and isolation of trace elements from environmental samples. This method is particularly useful in the determination of antimony species in water samples due to its efficiency, selectivity, and ability to handle complex matrices. Often considered the core of the SPE procedure, the used sorbent material has a great impact on the extraction efficiency because the retention of the target analyte strongly depends on its surface properties [3, 4]. As regards SPE-based speciation analysis of antimony, various sorbents such as carbon nanotubes [5, 6], nanosized titanium dioxide [7, 8], and ion-imprinted polymers [9–11]

have been successfully used in the separation and preconcentration of particular Sb species. A huge variety of polymeric materials also find numerous applications as reliable and effective adsorbents in non-chromatographic speciation analysis of antimony and other chemical elements in biological, environmental, and food samples [12]. The choice of polymer depends on the specific application and the target compounds to be adsorbed. The polymeric material plays a crucial role in analytical and separation processes because the extraction efficiency and selectivity are dependent on the active functional groups. Polyurethane foam loaded with bromopyrogallol red [13], polymer-supported ionic liquid [14], and polystyrene oleic acid imidazole polymer [15] have been utilized for selective retention and determination of particular Sb species. Here, we report on the preparation of a vinylimidazole-based polymeric material and its application as a sorbent for non-chromatographic speciation analysis of inorganic antimony in water samples.

EXPERIMENTAL

Materials and methods

All reagents were of analytical grade or high purity. Antimony (III) chloride ($\text{SbCl}_3 \geq 99.0\%$, Merck) and potassium hexahydroxoantimonate (KSb(OH)_6 , Merck) were used for the preparation of stock solutions of Sb(III) and Sb(V), respectively, with concentration of each species 500 µg/ml. The concentration of Sb species was measured by an

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inductively coupled plasma-optical emission spectrometer equipped with glass cyclonic-action spray chamber with glass concentric nebulizer (ICP-OES, Varian Vista Pro) under optimal instrumental parameters (wavelength for Sb: 206.834 nm; plasma gas flow rate: 22 l/min; auxiliary gas flow rate: 2 l/min; nebulizer gas flow rate: 1.1 l/min). The pH was measured with pH-meter Mettler Toledo, SevenCompact S220 (Greifensee, Switzerland). A centrifuge EBA 20 (DJB Labcare Ltd., Newport Pagnell, UK) was used for the separation of sorbent particles from the liquid phase.

The extent of linkage of vinylimidazole in the polymer was evaluated by elemental analysis (C, H, N) performed on analyzer EURO EA 3000 (EuroVector SpA, Italy). The shape of the polymeric particles was determined by a scanning electron microscope (SEM, JEOL JSM-5500 Tokyo, Japan). Specific surface area and pore size distribution were measured through nitrogen adsorption-desorption isotherms at 77 K using a Brunauer-Emmett-Teller (BET) analyzer (Quantachrome NOVA 1200e, Quantachrome, Boynton Beach, FL, USA).

Synthesis of P-VIM sorbent

The polymeric sorbent (P-VIM) was synthesized via radical copolymerization of vinylimidazole (VIM, 3.0 mmol) as a functional monomer and trimethylolpropane trimethacrylate (TMPTMA, 1.0 mmol) as a cross-linking agent. 2,2'-Azo-bis-isobutyronitrile (AIBN) was used as an initiator and the process was carried out in acetonitrile (solvent, 50.0 mL) for 24 h at 60°C. The synthesized P-VIM particles were filtered, washed twice with acetonitrile and distilled water. Finally, the polymer was washed with acetonitrile and dried at room temperature.

Sorption studies

The extraction efficiency of P-VIM towards Sb species was studied in batch mode and evaluated by the degree of sorption. The influence of pH on the degree of sorption of both chemical species was investigated in the range of pH 2–9. Aqueous solutions containing 5 µg/ml Sb(III) or Sb(V) were adjusted to the desired pH value with additions of ammonia or nitric acid. Portions of 70 mg P-VIM were mixed with 10 ml of the prepared model solution of Sb(III) or Sb(V) at different pH values and shaken for 60 min. Finally, the samples were centrifuged for 10 min at 5800 rpm, the supernatants were removed, and concentrations of Sb were measured by ICP-OES. Degrees of sorption were calculated as follows:

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

where A_{eff} (µg) is the amount of Sb(III) or Sb(V) in the supernatant solution after SPE with P-VIM, A_i (µg) is the total amount of Sb(III) or Sb(V) added to samples.

Matrix effects

The aim of this experiment was to evaluate the degree of sorption of Sb(V) in the presence of competitive anions such as sulfate, hydrogen carbonate, carbonate, fluoride, chloride, etc. Tap and bottled waters with different total mineralization and known amounts of major anions were mildly acidified to pH 6 and spiked with 5 µg/ml Sb(V). About 70 mg of the P-VIM sorbent were added to three parallel 10.0 ml aliquots of each sample, and sorption was conducted for 25 min on an electrical shaker. The same experiment was also carried out for Sb(III). After centrifugation, concentrations of Sb(V) and Sb(III) in the supernatants were measured by ICP-OES and the degrees of sorption for both species were calculated.

Elution study

Several acids and aqueous solutions of ammonium salts at different concentration levels were tested as potential eluents. All experiments were done after loading the sorbent with 50 µg Sb(V) under optimal conditions, followed by treatment with 10.0 ml of each eluent for 60 minutes 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(V) in the eluate, A_i (µg) is the total mass of Sb(V) added to the samples, A_{eff} (µg) is the amount of Sb(V) in the supernatant solution after sorption.

Analytical procedure

Water samples with a volume of 50.0 ml were slightly acidified to pH 6, then mixed with sorbent particles (70 mg in each sample), and the retention of Sb(V) was accomplished for 25 min on an electric shaker. After centrifugation (40 min, 5500 rpm), Sb(III) was directly measured in the supernatants. The sorbent was washed with distilled water, and elution was performed for 30 min with 2.0 ml of 1 mM diammonium hydrogen citrate. Finally, Sb(V) was quantified in the eluate solutions by ICP-OES.

RESULTS AND DISCUSSION

Characterization of the polymeric sorbent

The new P-VIM sorbent material was synthesized by precipitation copolymerization of vinylimidazole and trimethylolpropane trimethacrylate in the presence of 2,2'-azo-bis-isobutyronitrile as an initiator and acetonitrile as a porogenic solvent. The fraction of vinylimidazole in the prepared polymer gel was evaluated by elemental analysis. The results obtained (11.73 wt.% N) indicate that the content of imidazole functional groups in P-VIM is 0.41 mmol. The SEM micrograph of the prepared polymer gel at 10 000× magnification (Fig. 1) shows that the particles have close to a spherical shape. The results from nitrogen adsorption-desorption isotherms studies showed that the values for the surface area (S_{BET}) and the total pore volume (V_{total}) are 5 m²/g and 0.01 m³/g, respectively. The average pore diameter (D_{average}) value for P-VIM particles was 8 nm, which confirms that they have a mesoporous structure.

Effect of pH and contact time on the extraction efficiency

The separation of Sb species in aqueous media is strongly dependent on the pH of the solution. At pH > 4, Sb(V) mainly occurs as a negatively charged [Sb(OH)₆]⁻ complex ion, while Sb(III) exists as a neutral molecule Sb(OH)₃ in a wide pH range (3–10) [16]. On the other hand, due to the low-basic properties of P-VIM [17, 18], it can be protonated at pH < 7 and thus be able to adsorb negatively charged species. Fig. 2 presents the calculated degree of sorption obtained at different pH values for both species. Quantitative sorption of the anionic Sb(V) was achieved at pH 5–6, mostly based on the electrostatic attraction, while the degrees of sorption for Sb(III) did not exceed 5% in the whole investigated pH range. Thus, at the optimal pH of 5–6 the newly synthesized P-VIM sorbent ensured excellent separation of inorganic Sb species. All further experiments were performed at the optimal pH values.

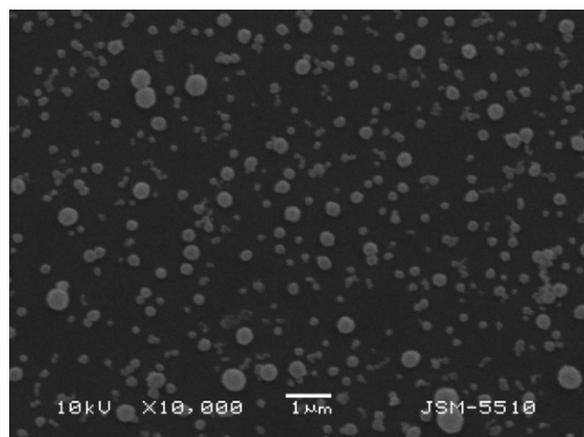


Fig. 1. SEM image of P-VIM particles.

The contact time was optimized by reducing the sorption duration starting from 60 min in 5 min steps. The degrees of sorption of Sb(V) were above 97% until the 25th minute and started to decline with lowering the time. Therefore, it can be concluded that 25 min are entirely sufficient for quantitative retention of Sb(V) at pH 5–6.

Effect of competitive ions

As was discussed in the previous section, retention of Sb(V) in a weakly acidic medium is most probably due to electrostatic attraction between positively charged P-VIM and negatively charged Sb(V). In this sense, naturally existing anions in water samples can considerably interfere with the SPE of the target analyte due to the competitive adsorption on P-VIM. Table 1 presents the values of D_s achieved after spiking 5 μg/ml Sb(V) in bottled mineral and tap waters with different concentrations of major anions and total mineralization (TM).

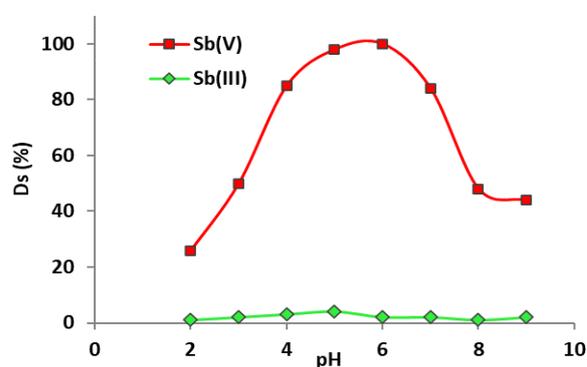


Fig. 2. Dependence of extraction efficiency on pH.

Table 1. Extraction efficiency of P-VIM towards Sb(V) in the presence of competitive ions (mean \pm standard deviation).

Sample	Competitive ions, mg/l					TM, mg/l	D_s , %
	Cl ⁻	F ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻		
Devin	3.5	4.0	20.6	85.4	24.0	255.0	52 \pm 3
Bankya	8.2	0.5	62.1	61.0	18.0	255.9	31 \pm 2
Gorna banya	2.54	0.15	19.96	7.93	36.01	146	64 \pm 3
Aqua viva	13.3	0.12	25	329	20	280	47 \pm 5
Hissar	10.39	2.96	27.57	131.19	32.33	317	42 \pm 4
Clever	< 2	< 1	< 5	< 20	< 50	< 50	99 \pm 3
Baldaran	2.30	< 0.1	3.29	< 20	< 50	90	96 \pm 3
Tap water	5.1	0.13	2.2	9.5	11.3	< 70	95 \pm 4

As was expected, a strong suppression of Sb(V) retention on the surface of P-VIM from co-existing ions was observed. The degrees of Sb(V) sorption varied between 31% and 99%. It is worth mentioning that all samples were preliminarily acidified in order to adjust pH to the optimal value (5–6), which partially reduces the impact of carbonates because of their conversion into carbon dioxide. On the other hand, at high levels of sulfates (e.g., Bankya water), the sorption of Sb(V) decreased to 31%. Much better extraction efficiency was achieved in waters with lower concentrations of sulfate and chloride. A quantitative sorption of Sb(V) was accomplished only in spring and tap waters with very low total mineralization (< 100 mg/l). For Sb(III), the degrees of sorption for all samples were less than 5%, which confirmed the ability of P-VIM sorbent to separate the two inorganic Sb species.

Elution study

The selection of a suitable eluent is an important step in optimizing the extraction conditions because the accuracy and precision of the analytical procedure strongly depend on the efficiency of desorption. Aqueous solutions of several ammonium salts were tested as eluents in an effort to achieve quantitative desorption of Sb(V) based on ion exchange. As can be seen from the results presented in Fig. 3, this approach was not effective because the degrees of elution were below 75%, even when doubly charged anions were used. The better results

achieved with ammonium carbonate are probably due to the deprotonation of imidazolium groups in the alkaline solution, leading to a higher release of the retained Sb(V). An attempt to improve the elution with 0.2 M (NH₄)₂CO₃ was made by increasing the contact time to 90 min, but the obtained elution degrees were still unsatisfactory ($D_E = 79\%$). A treatment of the loaded P-VIM particles with nitric, hydrochloric, and sulfuric acid (0.1 mol/l) was also tested, aiming to keep the sorbent surface positively charged while converting Sb(V) into the neutral molecule Sb(OH)₅ at pH < 2 [16]. This approach was also unsuccessful because the degrees of elution for all tested acids were below 65%.

Antimony (V) is known to form citrate complexes [19, 20], and that is why the next step was to investigate the desorption based on complex formation. Initially, citric acid solutions (0.1–0.5 mol/l) were studied as potential eluents and resulted in much higher desorption (90–95%), but the excellent elution was accomplished with a solution of diammonium hydrogen citrate. A possible reason for the superiority of the salt over the acid is that hydrogen citrate acts as a buffer, helping to maintain a weakly acidic pH in the solution, which is ideal for the complexation of citrate with Sb(V). Furthermore, the elution time optimization showed that a degree of elution D_E above 98% could be attained for at least 30 min using a hydrogen citrate solution.

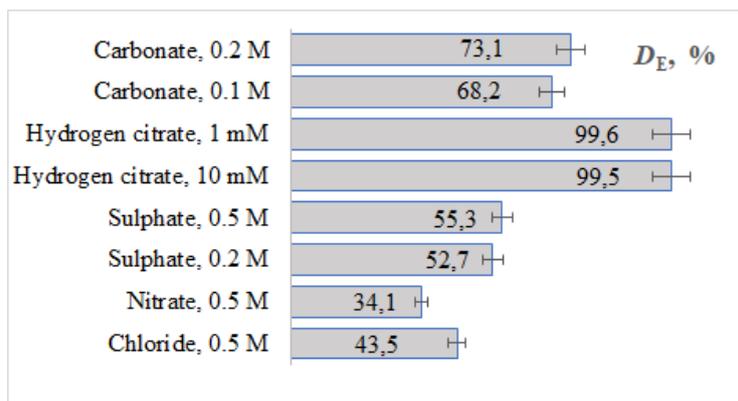


Fig. 3. Degree of elution (D_E) of different ammonium salts (60 min elution time).

Analytical procedure for speciation analysis of antimony

A non-chromatographic method for the determination of inorganic antimony species Sb(III) and Sb(V) in water samples with low mineralization was proposed based on their selective separation by using a newly synthesized sorbent P-VIM. The analytical procedure was developed following a well-known strategy for SPE-based speciation analysis [12], according to which the target species was retained on the sorbent while the non-target one remained in the supernatant solution. In this way, the non-extractable Sb(III) was directly measured in the supernatant after the sorption step, while Sb(V) was determined in the eluate solution after desorption.

The added/found method was applied to three spring waters with low mineralization (< 100 mg/l) spiked with 5 $\mu\text{g/l}$ Sb(V) and 5 $\mu\text{g/l}$ Sb(III). Each sample was run in triplicate. The calculated analytical recoveries were between 96 and 104%, relative standard deviations did not exceed 10%, which confirmed the good accuracy and precision of the developed procedure. The limits of quantitation (LOQ, 10σ criteria) for Sb(V) and Sb(III) were found to be 4.2 $\mu\text{g/l}$ and 3.4 $\mu\text{g/l}$, respectively. It should be emphasized that the proposed method provides not only quantitative separation of inorganic Sb species but also 25-fold preconcentration of Sb(V), which allows its determination at ppt-levels.

CONCLUSIONS

A polymeric sorbent containing vinylimidazole was synthesized and applied for non-chromatographic speciation analysis of inorganic antimony species. The excellent separation of Sb(V) and Sb(III) was achieved by quantitative sorption of the former at pH 5–6. A simple analytical procedure based on the determination of Sb(III) in the supernatant and Sb(V) in the eluate solutions was

developed. A considerable limitation of this non-chromatographic approach for Sb speciation analysis was the matrix interference by competitive anion sorption. The proposed method demonstrated good accuracy for surface and tap waters with low levels of total mineralization.

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