

A Sustainable Methodology to Extract Bismuth from Secondary Sources

Maria C. Hespanhol,¹*,^{a,b} Pamela R. Patrício,^{b,c} Luis H. M. da Silva,^b
Silvia J. R. Vargas,^{a,b} Teresa C. S. Rezende^b and Raquel A. Campos^b

^aGrupo de Análises e Educação para a Sustentabilidade (GAES), Departamento de Química,
Centro de Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa (UFV),
Av. P. H. Rolfs s/n, 36570-900 Viçosa-MG, Brazil

^bGrupo de Química Verde Coloidal e Macromolecular (QUIVECOM), Departamento de Química,
Centro de Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa (UFV),
Av. P. H. Rolfs s/n, 36570-900 Viçosa-MG, Brazil

^cDepartamento de Ciências Exatas e da Terra, Universidade do Estado de Minas Gerais (UEMG),
Av. Olegário Maciel, 1427, 36500-000 Ubá-MG, Brazil

Bismuth is a critical metal broadly used in cosmetic, medicine and metallurgy. However, its scarcity in Earth's crust may impair further applications. An alternative is to recover bismuth from secondary sources. In this work, a methodology to extract bismuth from safety valves of discharged gas cylinders is proposed. Extraction and purification of bismuth were carried out using aqueous two-phase systems (ATPS) prepared with poly(ethylene oxide) polymer or poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) copolymer (L35) and electrolytes (NaNO₃, NH₄NO₃, sodium citrate or Na₂SO₄). The influence of iodide extractant concentration, tie-line length, electrolyte nature and polymer hydrophobicity on the bismuth extraction behavior were evaluated. Bismuth was significantly recovered in the absence of extractant, and its extraction depends on the ATPS composition, macromolecule and electrolyte nature. After three consecutive extractions bismuth was obtained with high purity (94.7%), resulting on a recovery of 38.5 g of bismuth per 1.00 kg of fusible plug, using L35 + NH₄NO₃ + H₂O ATPS, without any extractant.

Keywords: bismuth, urban mining, aqueous two-phase system, critical metal, domestic waste, green separation

Introduction

Bismuth is considered a critical metal,¹ because it has a low occurrence in the Earth's crust. However, it is mostly demanded by the cosmetic, pharmaceutical and metallurgical industries, mainly because of two reasons: low toxicity and low melting point.²⁻⁶ The low toxicity of bismuth renders it more friendly to the environment and human beings, therefore enabling its ample use in the production of medicine, makeup and metallic alloys.^{2,3,5,7-11} Its low melting point is also associated with its green nature, favoring the preparation of more sustainable metallic alloys that melt at relatively low temperatures.¹² Such alloys are employed in safety devices and systems for the detection and extinction of fires.^{9,12}

The high demand for bismuth has created a problem

for the industries because of the limited distribution of the metal in the Earth's crust. It is mainly obtained as a byproduct in the processing of other metallic ores, such as lead, copper, tungsten, tin and molybdenum.^{13,14} Besides, China and Laos have dominated the export market of processed bismuth, since these countries produce 82 and 12%, respectively, of all bismuth that is consumed in the world.¹⁴ Because of this, countries like Brazil and the USA, among many others, depend highly on the importation of bismuth for the fabrication of different products, due to the small amount of bismuth that can be found in their soils.^{14,15}

One possible solution to overcome the lack of bismuth in several countries is to recover it from secondary sources, such as domestic and industrial residues, since the concentration of bismuth is much higher than that typically found in nature.¹⁶ However, the viability of this alternative process requires the development of techniques for the purification of bismuth from such secondary sources.

*e-mail: mcarmohespanhol@gmail.com, mariacarmo@ufv.br

It is a substantial scientific and technological challenge, because of the necessity to combine technical efficiency with economic feasibility and environmental safety.

Based on these questions, this study aimed to develop an efficient method to extract bismuth from safety valves of discharged gas cylinders using aqueous two-phase systems (ATPS). The high percentage of bismuth in these valves (as high as 50% in weight) and the massive consumption of bottled gas in the world, makes this material a potential candidate as a secondary source of bismuth.

Extraction and purification of bismuth were investigated in different ATPS composed by poly(ethylene oxide) polymer (PEO2000) or poly(ethylene oxide) polymer or poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) copolymer (L35) and electrolytes (NaNO_3 , NH_4NO_3 , $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ or Na_2SO_4). The extraction behavior of bismuth was evaluated and optimized based on the following experimental parameters: ATPS-forming electrolyte, ATPS-forming macromolecule and tie-line length (TLL).

The ATPS proposed for the separation, and further purification assays can be applied in scale-up.^{17,18} Moreover, the ATPS are both environmentally and economically sustainable, since their main component is water and the other components are nontoxic, cheap, biodegradable and recyclable.¹⁹⁻²¹

Experimental

Materials

All chemicals used in this investigation were analytical grade. Deionized water produced by a Millipore Corp. deionizer (Massachusetts, USA) was used in the preparation of all solutions. The ATPS was prepared with macromolecule: triblock copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), denoted as L35, with an average molar mass of 1900 g mol^{-1} , or poly(ethylene oxide) with an average molar mass of 2000 g mol^{-1} , denoted as PEO2000. Both macromolecules and the bismuth salt $\text{BiN}_3\text{O}_4 \cdot 5\text{H}_2\text{O}$ were purchased from Aldrich (Wisconsin, USA). The chemicals NaNO_3 , Na_2SO_4 , KI, sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$), $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were supplied by Vetec (Rio de Janeiro, Brazil). HNO_3 and NH_4NO_3 were acquired from Merck (Darmstadt, Germany). The fusible plugs used as safety valves in gas cylinders were acquired in local Brazilian markets.

Equipment

A Metrohm pH-meter (model 827) was used to

measure the pH of all solutions. Samples were weighed in a Shimadzu analytical balance (model AY 220), with an uncertainty of $\pm 0.0001 \text{ g}$. The ATPS was kept at $25.0 \pm 0.1 \text{ }^\circ\text{C}$ in a Marconi water bath (model MA 184). In order to favor phase separation, a Thermo Scientific centrifuge (model Heraeus Megafuge 11R) was employed. The metal concentration was assessed with a flame atomic absorption spectrometer (FAAS; fabricated by Varian, model AA240) and/or a microwave-induced plasma atomic emission spectrometry (MP-AES; fabricated by Agilent Technologies Inc., model 4100). The operational conditions used in the FAAS and MP-AES assays are presented in Tables S1 and S2 (Supplementary Information (SI) section).

Preparation of the ATPS for extraction

The composition of each used ATPS ($\text{L35} + \text{NaNO}_3 + \text{H}_2\text{O}$),²² ($\text{L35} + \text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$),²³ ($\text{L35} + \text{C}_6\text{H}_5\text{Na}_3\text{O}_7 + \text{H}_2\text{O}$),²² ($\text{L35} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$)²⁴ and ($\text{PEO2000} + \text{NaNO}_3 + \text{H}_2\text{O}$)²⁵ were obtained from literature, together with their corresponding TLL.

An aqueous solution of $0.100 \text{ mol L}^{-1} \text{ HNO}_3$ ($\text{pH} = 1.00$) was used as a solvent for the preparation of stock solutions of macromolecule and electrolyte, whose concentrations are presented in Table 1. All ATPS was prepared to mix 2.00 g of the macromolecule stock solution with 2.00 g of the electrolyte stock solution.

Table 1. Concentrations of the stock solutions of macromolecules (M) and electrolytes (E) for the preparation of ATPS

ATPS	TLL / % (m/m)	M / % (m/m)	E / % (m/m)
$\text{L35} + \text{NaNO}_3 + \text{H}_2\text{O}$	46.3	100 ^a	29.3
$\text{L35} + \text{NaNO}_3 + \text{H}_2\text{O}$	50.9	100 ^a	30.8
$\text{L35} + \text{NaNO}_3 + \text{H}_2\text{O}$	56.2	100 ^a	32.4
$\text{L35} + \text{NaNO}_3 + \text{H}_2\text{O}$	61.3	100 ^a	34.1
$\text{L35} + \text{NaNO}_3 + \text{H}_2\text{O}$	62.5	100 ^a	36.2
$\text{L35} + \text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$	50.4	100 ^a	46.9
$\text{L35} + \text{C}_6\text{H}_5\text{Na}_3\text{O}_7 + \text{H}_2\text{O}$	48.2	100 ^a	14.3
$\text{L35} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	46.8	100 ^a	11.0
$\text{PEO2000} + \text{NaNO}_3 + \text{H}_2\text{O}$	41.2	63.2	51.0

^aPure copolymer. ATPS: aqueous two-phase systems; TLL: tie-line length; M: macromolecule; E: electrolyte; L35: poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) copolymer; PEO2000: poly(ethylene oxide) polymer.

Effect of the amount of extractant agent on the recovery of bismuth

The $\text{L35} + \text{NaNO}_3 + \text{H}_2\text{O}$ ATPS, TLL = 46.3% (m/m) was used to investigate the influence of the quantity of

extractant added on the recovery of bismuth ions. Work solutions of an iodide (I^-) extractant agent were prepared by adding different amounts of the potassium iodide (0.86, 4.30, 8.60, 17.2 and 34.5 μmol) to L35 [100% (m/m)]. Work solutions of Bi^{III} (concentration ranging between 9.00 and 108 mg kg^{-1}) were prepared by dissolving Bi^{III} in the NaNO_3 stock solution [29.3% (m/m)]. In a centrifuge tube, 2.00 g of Bi^{III} work solution were mixed with 2.00 g of the iodide work solution. The tube was manually stirred for 3 min, centrifuged at $10000 \times g$ for 15 min and then kept in a water bath at 25.0 °C for 10 min. After these steps, the system separated in two clear phases, named as the upper phase (UP) and the bottom phase (BP). Aliquots of UP and BP were collected and diluted 10 times to determine the concentration of bismuth by FAAS (Table S1, SI section). The extraction percentage of bismuth (E_{Bi}) in all experiments was obtained by equation 1:

$$E_{\text{Bi}} (\%) = \frac{n_{\text{Bi}}^{\text{UP}}}{n_{\text{Bi}}^{\text{T}}} \times 100 \quad (1)$$

where $n_{\text{Bi}}^{\text{UP}}$ is the molar amount of bismuth in the upper phase and n_{Bi}^{T} is the total molar amount of bismuth in the system. All experiments were carried out in triplicate.

Effect of the ATPS-forming electrolyte on the recovery of bismuth

The ATPS formed by L35 + NaNO_3 + H_2O [TLL = 46.3% (m/m)], L35 + NaNO_3 + H_2O [TLL = 50.9% (m/m)], L35 + NH_4NO_3 + H_2O [TLL = 50.4% (m/m)], L35 + $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ + H_2O [TLL = 48.2% (m/m)] and L35 + Na_2SO_4 + H_2O [TLL = 46.8% (m/m)] were used to study the effect of the ATPS-forming electrolyte on the recovery of bismuth.

Bi^{III} work solutions with concentrations of 9.00, 18.0, 27.0, 36.0, 72.0, 90.0 and 108 mg kg^{-1} were prepared by dissolving the bismuth salt in the following electrolyte stock solutions: NaNO_3 [29.3% (m/m)], NaNO_3 [30.8% (m/m)], Na_2SO_4 [11.0% (m/m)], NH_4NO_3 [46.9% (m/m)] or $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ [14.3% (m/m)]. In a centrifuge tube, 2.00 g of the bismuth work solution were mixed with 2.00 g of L35. Again, the tube was manually stirred for 3 min, centrifuged at $10000 \times g$ for 15 min and then kept in a water bath at 25.0 °C for 10 min, after which two clear phases were formed. Aliquots of UP and BP were collected and diluted 10 times to determine the concentration of bismuth by FAAS (Table S1, SI section), then calculating E_{Bi} with equation 1. All experiments were carried out in triplicate.

Effect of the hydrophobicity of the ATPS-forming macromolecule on the recovery of bismuth

The extraction behavior of bismuth was evaluated in systems with distinct macromolecules [L35 + NaNO_3 + H_2O , TLL = 46.3% (m/m) and PEO2000 + NaNO_3 + H_2O , TLL = 41.2% (m/m)]. Bi^{III} work solutions with concentrations of 9.00, 18.0, 27.0, 36.0, 72.0, 90.0 and 108 mg kg^{-1} were prepared by dissolving the bismuth salt in the stock solutions of the NaNO_3 electrolyte at concentrations of 29.3 or 51.0% (m/m). In centrifuge tubes, two different systems were prepared. First, 2.00 g of the PEO2000 63.2% (m/m) stock solution were mixed with 2.00 g of the Bi^{III} work solution in NaNO_3 51.0% (m/m). Then, 2.00 g of the L35 stock solution were mixed with 2.00 g of the Bi^{III} work solution in NaNO_3 29.3% (m/m). Again, the tube was manually stirred for 3 min, centrifuged at $10000 \times g$ for 15 min and then kept in a water bath at 25.0 °C for 10 min, after which two clear phases were formed. Aliquots of UP and BP were collected and diluted 10 times to determine the concentration of bismuth by FAAS (Table S1, SI section), then calculating E_{Bi} with equation 1. All experiments were carried out in triplicate.

Effect of the ATPS composition on the recovery of bismuth

The L35 + NaNO_3 + H_2O ATPS in different TLL [46.3, 50.9, 56.2, 61.3 and 62.5% (m/m)] was used to study the effect of the ATPS composition on the recovery of bismuth.

Bi^{III} work solutions with concentrations of 9.00, 18.0, 27.0, 36.0, 72.0, 90.0 and 108 mg kg^{-1} were prepared by dissolving the bismuth salt in the stock solutions of the NaNO_3 electrolyte at different concentrations: 29.3, 30.8, 32.4, 34.1 and 36.2% (m/m). In a centrifuge tube, 2.00 g of the bismuth work solution were mixed with 2.00 g of L35. Again, the tube was manually stirred for 3 min, centrifuged at $10000 \times g$ for 15 min and then kept in a water bath at 25.0 °C for 10 min, after which two clear phases were formed. Aliquots of UP and BP were collected and diluted 10 times to determine the concentration of bismuth by FAAS (Table S1, SI section), then calculating E_{Bi} with equation 1. All experiments were carried out in triplicate.

Leaching of the fusible plug sample

The fusible plug sample was previously cleaned and dried, and the initial mass (12.0 g) was measured in the analytical balance. The plug was added with 39.7 mL of a 7.00 mol L^{-1} HNO_3 solution to a two-neck round-bottom flask. The mixture was heated at 70 °C for 80 min with a heating mantle. After cooling, the mixture was filtered

out, and the leachate was collected as a clear solution. The leachate was diluted 2000 times to determine the amount of bismuth, copper, lead, cadmium and tin using an MP-AES (Table S2, SI section) with the help of a multi-element analytical curve [coefficient of determination (R^2) ≥ 0.999]. All experiments were carried out in triplicate. This leachate without dilution was stored for future bismuth purification using ATPS.

Recovery and purification of bismuth from the fusible plug

The recovery of bismuth was carried out by three consecutive extraction steps using ATPS. For the first extraction step, 4.21 g of the leachate, 4.20 g of L35, 4.93 g of NH_4NO_3 and 1.75 g of a 0.100 mol L^{-1} HNO_3 solution were mixed in a centrifuge tube. Then, the tube was manually stirred for 3 min, centrifuged at $3000 \times g$ for 15 min and kept in a water bath at $25.0 \text{ }^\circ\text{C}$ for 10 min. After that, it was obtained two clear phases. This system was then named ATPS1. For the second extraction step, 5.00 g of the UP of the ATPS1 were transferred to a new centrifuge tube. In this tube, 0.0330 g of L35, 2.47 g of NH_4NO_3 , and 2.49 g of a 0.100 mol L^{-1} HNO_3 solution were added. The tube was manually stirred for 3 min, centrifuged at $3000 \times g$ for 15 min and kept in a water bath at $25.0 \text{ }^\circ\text{C}$ for 10 min. So, it was obtained two clear phases. This system was named ATPS2. Finally, in the third extraction step, it was transferred 2.00 g of the UP of ATPS2, 0.013 g of L35, 0.970 g of NH_4NO_3 and 1.00 g of a 0.100 mol L^{-1} HNO_3 solution to another centrifuge tube. This final system was manually stirred for 3 min, centrifuged at $3000 \times g$ for 15 min and kept in a water bath at $25.0 \text{ }^\circ\text{C}$ for 10 min. Then, it was obtained two clear phases. This system was then named ATPS3. Aliquots of the UP and BP of ATPS1, ATPS2 and ATPS3 were collected and adequately diluted to determine bismuth, copper, lead, cadmium and tin by FAAS or MP-EAS (Tables S1 and S2, SI section). All experiments were carried out in triplicate.

Results and Discussion

Effect of the amount of extractant agent on the recovery of bismuth

It has been demonstrated that ATPS can be very effective in the extraction of metallic ions.²⁶⁻³⁰ The extraction procedures are usually conducted with the aid of an extractant agent, whose main function is to enhance the extraction of ions to the polymer-rich phase.³¹ Because of this, it is important to determine optimal conditions for the

use of such agent, with the choice of the most appropriate chemical and the selection of the best concentration, which can favor the extraction or separation of metals in a given sample.²⁹⁻³²

Bulgariu and Bulgariu³³ investigated the extraction behavior of bismuth in the ATPS formed by PEG1500 + $(\text{NH}_4)_2\text{SO}_4$ + H_2O , in the presence of four inorganic extractants (I^- , Br^- , Cl^- and SCN^-). The efficiency of extractants follows the order: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{SCN}^-$. Based on these results, in the present work, the extraction behavior of bismuth was investigated in a different system consisting of L35 + NaNO_3 + H_2O in the presence of the most promising extractant, I^- .

The values of E_{Bi} obtained when adding different amounts of iodide (I^-) extractant agent to the L35 + NaNO_3 + H_2O ATPS in the TLL = 46.3% (m/m), at $25.0 \text{ }^\circ\text{C}$ and pH 1.00 are presented in Figure 1. In the absence of I^- , E_{Bi} was $79.1 \pm 5.9\%$. When adding I^- at concentrations higher than $2.15 \text{ } \mu\text{mol}$, the value of E_{Bi} increased to approximately 98%.

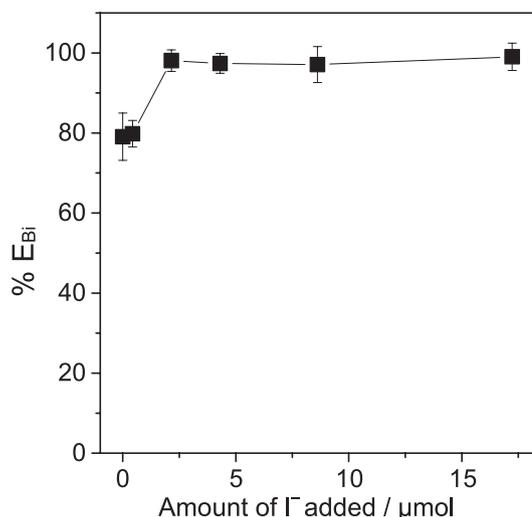


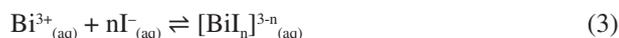
Figure 1. Effect of the amount of the iodide (I^-) extractant agent on the extraction percentage of bismuth (E_{Bi}) using the L35 + NaNO_3 + H_2O ATPS, with TLL = 46.3% (m/m), at $25.0 \text{ }^\circ\text{C}$ and pH = 1.00.

In aqueous solution, bismuth ions can undergo a series of hydrolysis reactions and polynucleation processes which justify the performance of the extraction procedures in the absence of extractant agents. In this case, E_{Bi} was as high as $79.1 \pm 5.9\%$. Investigations show that the species $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$ and $[\text{Bi}_6\text{O}_5(\text{OH})_3]^{5+}$ are favored in acidic media. Equilibrium between these species (equation 2) depends on the pH of the medium, which at low pH the compound $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot y\text{H}_2\text{O}$ ($y = 1$ or 4) is formed, and at slightly higher pH the compound $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ is formed.^{34,35}



Based on calorimetric measurements, da Silva and Loh³⁶ proposed that the UP of ATPS contains macromolecules and cations of the system-forming electrolyte adsorbed on the polymeric chain, generating a positively-charged surface (pseudopolycation) that interacts with negatively-charged species. Therefore, pseudopolycations found in the UP of L35 + NaNO₃ + H₂O ATPS must establish repulsive interactions with the bismuth cationic species that are also present in that phase. However, specific interactions among the bismuth polymorphous species and the macromolecule chain must overcome such repulsive phenomena.

The addition of small amounts of iodide to the ATPS increased the value of E_{Bi} due to the formation of anionic complexes between I⁻ and Bi^{III}, as indicated by equation 3:



High values of formation constants revealed that the complexes are stable ($\log K_1 = 3.63$, $\log K_4 = 14.95$, $\log K_5 = 16.80$ and $\log K_6 = 18.80$).³⁷ The transfer of bismuth species to the UP in the presence of iodide occurs because of electrostatic interactions between the bismuth anionic complexes and the pseudopolycations that are abundant in that phase. As these complexes are formed, they are transferred to the UP from the BP, a phenomenon which induces the formation of more complexes in the BP through equilibrium shifts. When adding iodide, the equilibrium is also shifted until reaching a saturation point, after which the addition of more iodide has no further effect on E_{Bi} . From 2.15 μmol of added iodide, the value of E_{Bi} was stabilized close to 98%. The relatively small increment in E_{Bi} in the presence of iodide, from ca. 79 to ca. 98%, demonstrates that it is not necessary to employ an extractant agent to obtain significant recovery of bismuth with ATPS. Besides being environmentally advantageous, the elimination of such an extractant agent reduces costs in the recovery of bismuth. For these reasons, further investigations in this work have been conducted without any extractant agent in the systems.

Effect of the ATPS-forming cation on the recovery of bismuth

The extraction percentage of metallic ions in ATPS normally depends on the nature of the cation of the ATPS-forming electrolyte.^{26,29,38,39} The contribution of the cation to the distribution of bismuth between phases of the ATPS can be viewed in Figure 2. Figure 2 shows the E_{Bi} as a function of bismuth concentration for the systems L35 + NaNO₃ + H₂O (TLL = 50.9% (m/m)) and L35 + NH₄NO₃ + H₂O (TLL = 50.4% (m/m)) at 25.0 °C, pH = 1.00, and in the absence of extractant agent.

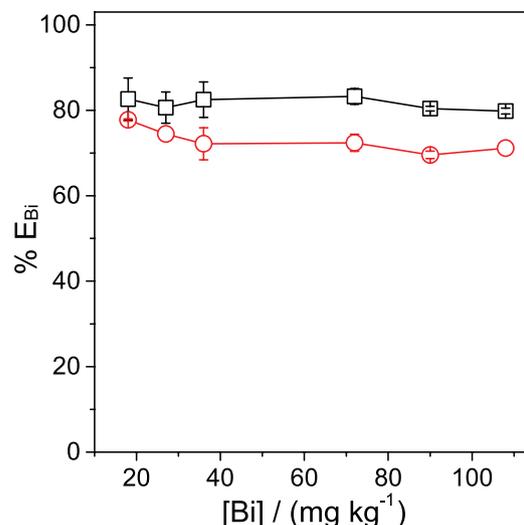


Figure 2. Effect of ATPS-forming cation on the extraction percentage of bismuth (E_{Bi}). ATPS: (□) L35 + NaNO₃ + H₂O (TLL = 50.9% (m/m)) and (○) L35 + NH₄NO₃ + H₂O (TLL = 50.4% (m/m)), at 25.0 °C, pH = 1.00, in the absence of extractant agent.

The ATPS formed with NaNO₃ was more efficient in the partition of bismuth from the BP to the UP than the ATPS formed with NH₄NO₃ within all the examined bismuth concentration range. ATPS formed with sodium cations promoted a maximal E_{Bi} of $83.2 \pm 1.9\%$, while ATPS formed with ammonium cations has a maximal E_{Bi} of $77.8 \pm 0.3\%$. Since these electrolytes have the same nitrate anion, one can describe the variation in E_{Bi} to the cation. Calorimetric investigations reported elsewhere³⁶ suggest that pseudopolycations formed with ammonium would be less positively charged than those formed with sodium cations. Therefore, the ATPS formed with NaNO₃ would be more efficient in repelling bismuth species, which would cause a decrease in their E_{Bi} when compared to those of ATPS formed with NH₄NO₃. However, the concentration of sodium cations in the UP of the L35 + NaNO₃ + H₂O ATPS is 13.19% (m/m), whilst the concentration of ammonium cations in the L35 + NH₄NO₃ + H₂O ATPS is 23.98% (m/m).^{22,23} The higher concentration of ammonium cations in the UP of the L35 + NH₄NO₃ + H₂O ATPS enhances repulsive interactions between the bismuth polymorphous cationic species and the pseudopolycations in this ATPS. As a consequence, the extraction of bismuth in the ATPS containing ammonium is a little lower than that promoted by the sodium-based ATPS.

Effect of the ATPS-forming anion on the recovery of bismuth

The contribution of the anion to the extraction of bismuth was also examined. Figure 3 shows the values of E_{Bi} as a function of bismuth concentration for ATPS with L35 and sodium salt with different anions (nitrate, sulfate

and citrate) in the TLL ca. 47% (m/m), pH = 1.00, 25.0 °C, and absence of extractant agent.

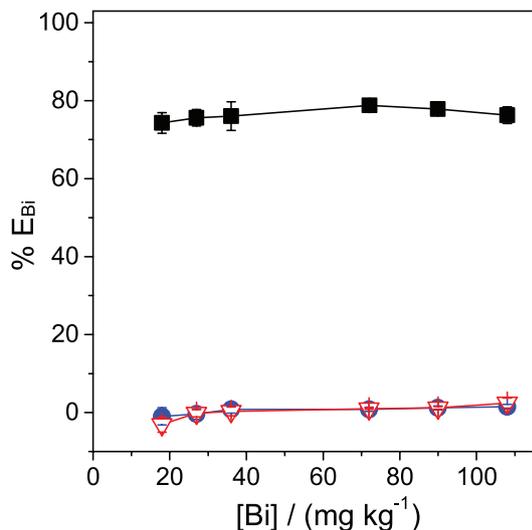


Figure 3. Effect of ATPS-forming anion on the extraction percentage of bismuth (E_{Bi}). ATPS: (■) L35 + NaNO₃ + H₂O (TLL = 46.3% (m/m)); (●) L35 + Na₂SO₄ + H₂O (TLL = 46.7% (m/m)) and (▽) L35 + C₆H₅Na₃O₇ + H₂O (TLL = 48.1% (m/m)), at 25.0 °C, pH = 1.00, in the absence of extractant agent.

As opposed to the effect of cation, the nature of the anion profoundly impacted the values of E_{Bi} . The maximal E_{Bi} for the ATPS formed with nitrate was $78.8 \pm 0.5\%$, while with sulfate and citrate the maximal E_{Bi} was only 1.49 ± 0.59 and $2.43 \pm 1.30\%$, respectively. ATPS formed with sulfate and citrate anions were less efficient in the extraction of bismuth because the formation of stable bismuth complexes with sulfate⁴⁰ and citrate⁴¹ is more favorable in the BP of the ATPS that is an electrolyte-rich phase.

In order to better explore the contribution of the

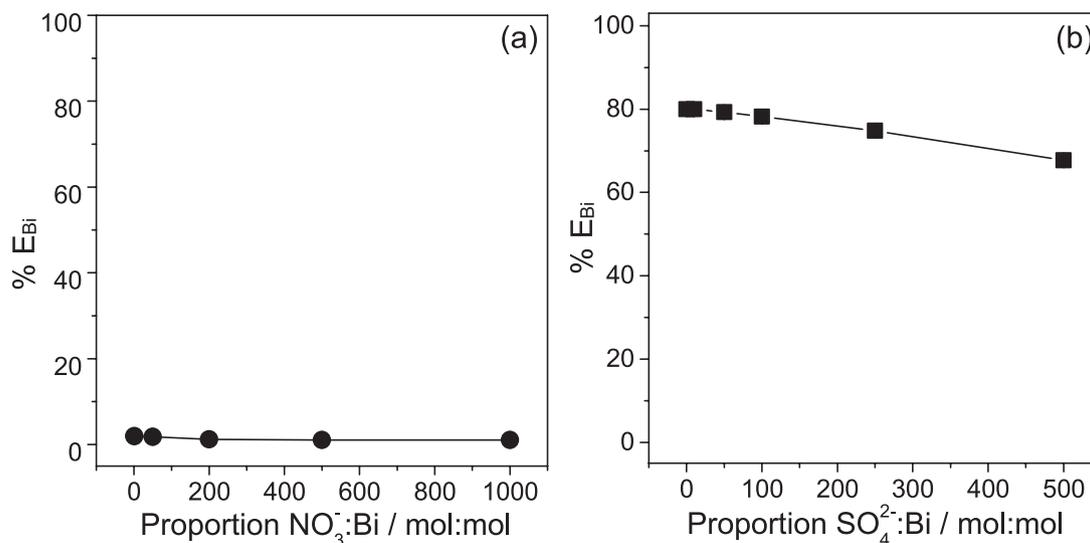


Figure 4. Extraction of bismuth in the presence of nitrate and sulfate ions. ATPS: (a) (●) L35 + Na₂SO₄ + H₂O (TLL = 46.7% (m/m)) in the presence of nitrate; (b) (■) L35 + NaNO₃ + H₂O (TLL = 46.3% (m/m)) in the presence of sulfate, at 25.0 °C and pH = 1.00.

anion to E_{Bi} , known amounts of nitrate were added to the L35 + Na₂SO₄ + H₂O ATPS (Figure 4a) and known amounts of sulfate were added to the L35 + NaNO₃ + H₂O ATPS (Figure 4b).

The addition of nitrate ions to the L35 + Na₂SO₄ + H₂O ATPS could not enhance the extraction of bismuth ($E_{Bi} < 2.00\%$). On the other hand, the continuous increment of sulfate ions to the system L35 + NaNO₃ + H₂O reduced E_{Bi} from $80.0 \pm 0.5\%$ in the absence of sulfate to $67.7 \pm 0.3\%$ when the [SO₄²⁻:Bi] molar ratio was 500:1. These data confirm the stability of bismuth sulfate complexes ($\log K_1 = 1.98$, $\log K_2 = 3.41$, $\log K_3 = 4.08$, $\log K_4 = 4.34$, $\log K_5 = 4.6$)⁴¹ and their preferential interaction with the components of the electrolyte-rich phase (BP). The ATPS formed with NaNO₃ in the absence of sulfate proved to be a more efficient system to extract bismuth.

Effect of the hydrophobicity of the ATPS-forming macromolecule on the recovery of bismuth

In this particular investigation, two macromolecules, L35 and PE02000, with different hydrophobicity were investigated. The NaNO₃ was selected as the ATPS-forming electrolyte because ATPS containing this sodium salt proved to be more useful to extract bismuth in previous studies. The ATPS formed with L35 is more hydrophobic because of the polypropylene oxide (PPO) and polyethylene oxide (PEO) segments of the macromolecule than PE02000, which is more hydrophilic because it contains only PEO segments.

Figure 5 shows the values of E_{Bi} as a function of bismuth concentration for the PE02000 + NaNO₃ + H₂O ATPS, TLL = 41.2% (m/m), and L35 + NaNO₃ + H₂O,

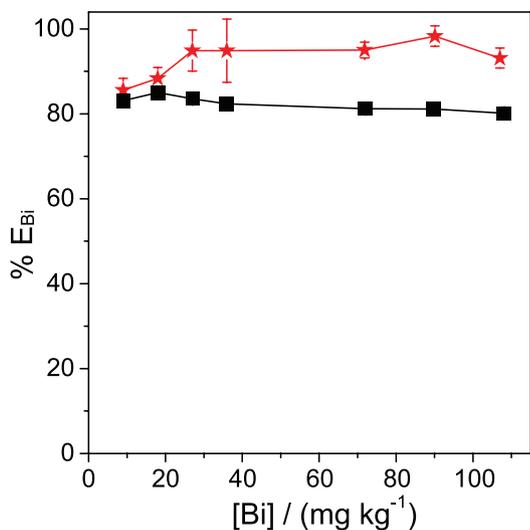


Figure 5. Effect of the hydrophobicity of the ATPS-forming macromolecule on the extraction percentage of bismuth (E_{Bi}). ATPS: (■) L35 + NaNO₃ + H₂O (TLL = 46.3% (m/m)); (★) PEO2000 + NaNO₃ + H₂O (TLL = 41.2% (m/m)), at 25 °C and pH = 1.00, in the absence of extractant agent.

TLL = 46.3% (m/m), at pH = 1.00, 25 °C, and absence of extractant agent.

The maximal value of E_{Bi} obtained with the L35 ATPS was $85.0 \pm 0.5\%$, while for the PEO ATPS was $98.3 \pm 2.4\%$. The values of E_{Bi} are indicative that bismuth polymorphous cationic complexes preferably interact with the ethylene oxide (EO) segments of the macromolecules. Therefore, the lower amount of EO segments on the L35 molecule (50 wt.%) when compared to PEO2000 (100 wt.%) justifies the lower E_{Bi} of L35 ATPS. ATPS with L35 was selected to carry out further investigations and to develop the methodology to recover bismuth from the discharged safety valves of gas cylinders. As shown in Figure 6, when ATPS with L35 + NaNO₃ was used for bismuth recuperation from

the discharged safety valve the E_{Bi} was quantitative. Also, the choice of L35 is relevant to scale-up the extraction and separation process with no significant negative impact on its overall efficiency. Triblock copolymers are thermosensitive, presenting a lower cloud point temperature than PEO polymer.²³ Consequently, L35 macromolecules are easier to be recycled by the phase separation induced by the temperature increase.²³

Influence of the ATPS composition on the recovery of bismuth

Their intensive thermodynamical properties govern the distribution of a given solute between both ATPS phases. The TLL, associated with the ATPS composition, numerically expresses the difference between these properties, and can be calculated with equation 4:

$$TLL = [(C_M^{UP} - C_M^{BP})^2 + (C_E^{UP} - C_E^{BP})^2]^{1/2} \quad (4)$$

where C_M^{UP} and C_M^{BP} are the concentrations of macromolecule in the upper and bottom phase, respectively, and C_E^{UP} and C_E^{BP} are the concentrations of electrolyte in the upper and bottom phase, respectively. All concentrations in this work are expressed in % (m/m).

The bismuth extraction percentage was determined for different TLL with the L35 + NaNO₃ + H₂O ATPS (Figure 7).

The average E_{Bi} values obtained with TLL 46.3, 50.9, 56.2, 61.3 and 62.6% (m/m) were 76.5 ± 1.6 , 81.5 ± 1.4 , 88.4 ± 2.0 , 86.8 ± 2.9 and $86.3 \pm 3.6\%$, respectively. A slight increase in E_{Bi} is influenced with increasing TLL, reaching a plateau from TLL = 56.2% (m/m), regardless of the amount of bismuth added to the ATPS. Such extraction behavior

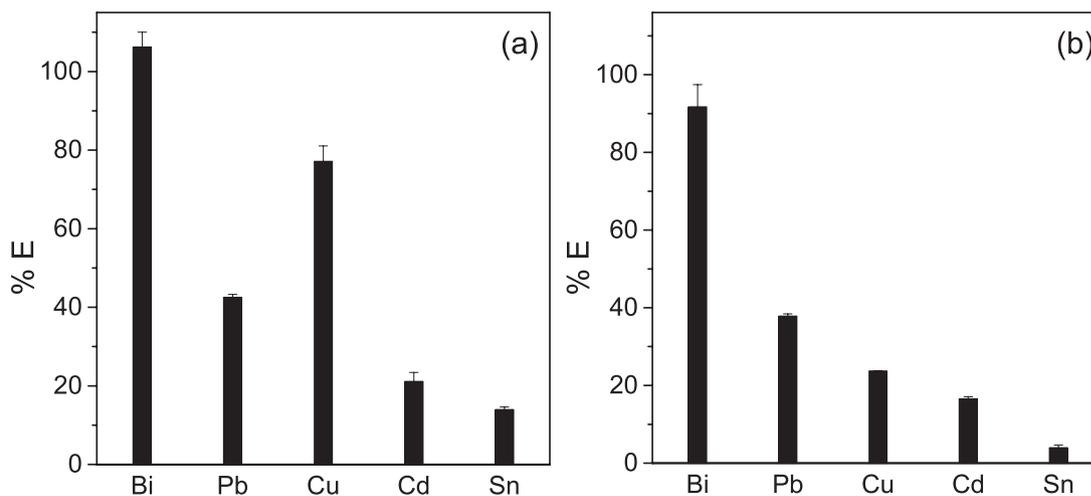


Figure 6. Extraction of metals found in the leachates of the fusible plugs of gas cylinders using ATPS. (a) L35 + NaNO₃ + H₂O, TLL = 62.6% (m/m) and (b) L35 + NH₄NO₃ + H₂O, TLL = 50.4% (m/m), at 25 °C, in the absence of extractant agent.

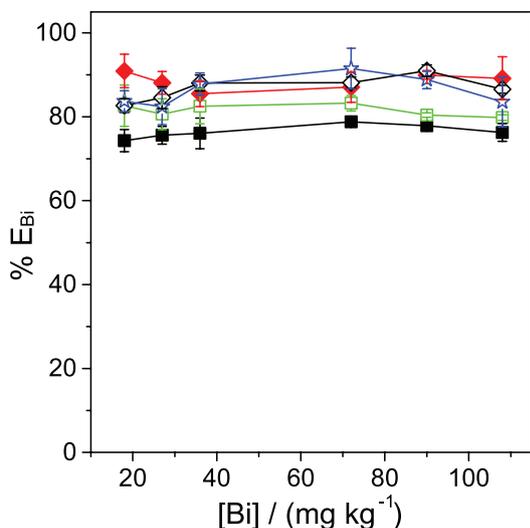


Figure 7. Effect of the tie-line length of the L35 + NaNO₃ + H₂O ATPS on the extraction percentage of bismuth (E_{Bi}). (■) TLL = 46.3% (m/m); (□) CLA = 50.9% (m/m); (♦) TLL = 56.2% (m/m); (◇) TLL = 61.3% (m/m); (☆) TLL = 62.6% (m/m), at 25 °C and pH = 1.00, in the absence of extractant agent.

is attributed to the increase in the difference between the intensive thermodynamically properties as TLL increases. The small variation in the concentration of NaNO₃ in the UP of the ATPS²² helps to justify the fact that E_{Bi} remains constant from TLL = 56.2% (m/m), with the formation of pseudopolycations that have similar charge densities.

Recovery and purification of bismuth from safety valves of gas cylinders (fusible plugs)

ATPS has been employed in the recovery and purification of bismuth from waste fusible plugs of gas cylinders. Fusible plugs are metallic alloys (Wood's alloy) composed mainly of bismuth, cadmium, lead and tin, covered with a copper casing.⁴² The plug + copper casing assembly underwent leaching treatment with nitric acid, whereby only the fusible plug was solubilized, and thereby separated from the copper casing. The concentration of metals in the fusible plug was determined as: Bi = 14.8 ± 0.6 g kg⁻¹; Pb = 10.8 ± 0.5 g kg⁻¹; Cu = 51.4 ± 0.9 g kg⁻¹; Cd = 1.60 ± 0.01 g kg⁻¹; and Sn = 0.255 ± 0.003 g kg⁻¹.

Figure 6 presents the extraction percentages (E) of these metals using the L35 + NaNO₃ + H₂O ATPS, TLL = 62.6% (m/m), and L35 + NH₄NO₃ + H₂O, TLL = 50.4% (m/m). The L35 + NaNO₃ + H₂O ATPS was more efficient, as already discussed earlier.

The presence of concomitant metals does not affect the E_{Bi} that is 106 ± 4%, but high extraction percentages are obtained for the concomitant metals: E_{Cu} = 77.1 ± 4.0%; E_{Pb} = 42.5 ± 0.8%; E_{Cd} = 21.1 ± 2.3%; and E_{Sn} = 14.0 ± 0.7%.

It compromises the purity of the recovered bismuth samples, which was only 26.1%. Similar behavior is observed when the L35 + NH₄NO₃ + H₂O ATPS is applied in the extraction of bismuth. In this case, E_{Bi} was 91.7 ± 5.7%, but the extraction percentages of Cu, Pb, Cd and Sn were lower: 23.7 ± 0.0, 37.9 ± 0.6, 16.6 ± 0.5 and 3.96 ± 0.67%, respectively. Therefore, bismuth could be recovered with a higher purity of 45.1% with this ATPS.

However, 45.1% purity is not an appropriate level for a given product to be available to the industrial production chain. As a consequence, three consecutive extraction procedures were carried out to obtain bismuth with higher purity. The extraction percentages (E) of all metals found in the fusible plug leachate after three consecutive steps are depicted in Figure 8 for the L35 + NH₄NO₃ + H₂O ATPS.

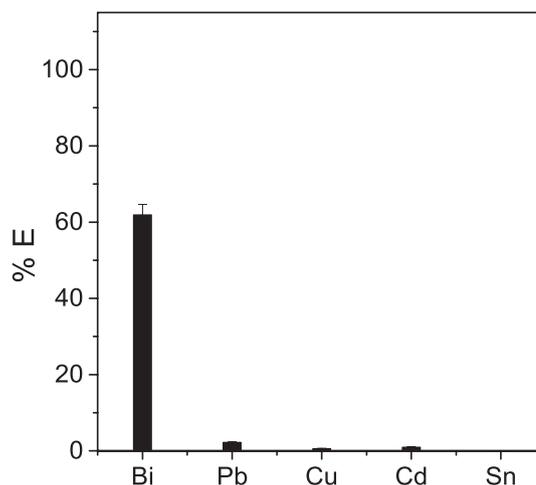


Figure 8. Extraction of metals found in the leachates of the fusible plugs of gas cylinders after three consecutive extraction steps using the L35 + NH₄NO₃ + H₂O ATPS, TLL = 50.4% (m/m) at 25 °C, in the absence of extractant agent.

It can be observed that, although E_{Bi} was reduced to 61.9 ± 2.1%, the bismuth was obtained with very high purity (94.7%), resulting from the recovery of 38.5 g of bismuth *per* 1.00 kg of the fusible plug.

Conclusions

In this work, it has been demonstrated that aqueous two-phase systems are useful for the extraction of bismuth from secondary sources without any extractant agent or organic solvents. The partition of bismuth to the macromolecule-rich phase (upper phase of ATPS) was governed by specific interactions between the bismuth species and the ethylene oxide group of the macromolecules. The nature of the ATPS-forming electrolyte, the nature of the macromolecule and the composition of the ATPS (expressed by the corresponding

TLL) significantly affect the recovery of bismuth. Although some investigated ATPS are useful to extract bismuth, the ATPS formed with L35 + NH₄NO₃ + H₂O and TLL = 50.4% (m/m), working at 25.0 °C in the absence of extractant agent, was the one that promoted the highest recovery of bismuth with high-purity (94.7%). This work is a pioneer in opening possibilities to implement ATPS in the extraction of such a critical metal as bismuth on a large scale. Therefore, it is possible to carry out urban mining operations to enhance the production of bismuth, with distinct environmental and economic advantages to society. The following environmental and economic advances have been reached: (i) the proposed methodology to obtain bismuth is green and economical, since the ATPS is composed mainly of water, also comprising other nontoxic, cheap, biodegradable and recyclable chemicals that are found in relatively low concentrations; (ii) the discharge of fusible plugs of gas cylinders could be diminished and even avoided, and at the same time some aggregate value would be granted to such discharged material; (iii) natural reserves could be preserved, because bismuth would not be acquired or extracted from the nature itself; (iv) countries with little or no potential to produce bismuth because of scarce natural sources would be more independent on the production and use of this critical metal.

Supplementary Information

Supplementary data are available free of charge at <http://jbcs.sbq.org.br> as PDF file.

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