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Article

Vortex-Assisted Ionic Liquid-Based Liquid-Phase Microextraction: A Simple, Low-Cost, and Environmentally Friendly Method for Speciation of Antimony in Water

Luana B. Santos[a,b] ***and Valfredo A. Lemos***[*,a,b]

[a]*Programa de Pós-Graduação em Química, Universidade Estadual do Sudoeste da Bahia,*
Campus de Jequié, 45206-510 Jequié-BA, Brazil

[b]*Programa de Pós-Graduação em Química, Universidade Federal da Bahia,*
Campus Universitário de Ondina, 40170-280 Salvador-BA, Brazil

A sensitive method is proposed to determine antimony species using vortex-assisted ionic liquid-based liquid-phase microextraction and digital imaging colorimetry. Sb^{III} forms a ternary complex with 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol, ascorbic acid, and iodide in an acid medium. The acceptor phase consists of the ionic liquid 1-butyl-3-methylimidazole hexafluorophosphate, dispersed in the aqueous solution with a vortex stirrer. After centrifugation, Sb^{III} was determined directly in the rich phase. Sb^{V} can also be measured by converting to reduced species. The method presented a limit of detection of 1.4 and 4.2 μg L^{-1} and an enrichment factor of 360. The precision (relative standard deviation) of the method is 7.0%. The procedure was applied to the speciation of antimony in river water and mineral water samples. Some results were compared with those obtained by electrothermal atomic absorption spectrometry (ET AAS). The method is an attractive alternative for determining antimony species, considering the aspects of green analytical chemistry.

Keywords: liquid phase extraction, antimony, digital image colorimetry, speciation

Introduction

Antimony is a cumulative toxic element whose compounds are widely used in various industrial applications.[1,2] Some antimony compounds, such as antimony trioxide (Sb_2O_3), are catalysts for synthesizing polyethylene terephthalate (PET). PET containers store drinking water, beverages, and condiments as raw materials in food packaging. Some researchers[1-5] have studied the contamination of water packed in PET bottles evaluating the leaching of Sb from the polymeric material to the water. The factors that influence the Sb content in water have also been studied. Thus, the development of robust and reliable methods for determining antimony species in water and food has been required.

Preconcentration techniques are essential for obtaining low limits of detection in the determination of many substances. Extraction techniques have been widely used for this purpose, such as liquid-phase extraction (LPE),[6,7] solid phase extraction (SPE),[8,9] and cloud point extraction (CPE),[8] among others. The formation of stable complexes between the antimony and some pyridylazo and thiazolylazo compounds has been the basis of procedures involving these techniques.[10-15]

Liquid-phase microextraction (LPME) has reduced or eliminated some disadvantages of the classical technique (LPE), such as using large amounts of reagents and consequent waste management, operating time, tedious procedures, and risk to the operator, among others. Many approaches to LPME have been described in the literature, such as single-drop microextraction (SDME),[16] hollow-fiber liquid-phase microextraction (HF-LPME),[17] and dispersive liquid-liquid microextraction (DLLME).[18] DLLME methods are based on the dispersion of the extraction solvent into fine microdroplets. The cloudy mixture formed increases the surface area between the extraction solvent and the aqueous phase. A dispersive solvent is necessary.[19-22] In some LPME techniques, the dispersion of the extraction solvent can be performed in other ways, such as vortex agitation, ultrasound, pressure variation, and controlled temperature, among others, eliminating the use of dispersive solvent. These approaches have given rise to several microextraction techniques, such

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*e-mail: vlemos@uesb.edu.br
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as pressure variation in-syringe dispersive liquid-liquid microextraction (PV-IS-DLLME),[23] ultrasound-assisted dispersive liquid-phase microextraction (UA-DLPME),[24] air-assisted dispersive liquid-phase microextraction (AA-DLPME),[25] temperature-controlled dispersive liquid-phase microextraction (TC-DLPME),[26] and VA-DLPME (vortex-assisted dispersive liquid-phase microextraction).[27,28]

In VA-DLPME procedures, the extraction solvent is dispersed in the aqueous solution with a vortex stirrer, promoting emulsification. The solvent droplets formed in the emulsification quickly extract the component from the donor phase due to the large surface area obtained. The technique has low cost, short extraction time, and ease of operation.[29-31]

Several methods employing LPME describe the use of ionic liquids (IL).[7,32-35] IL presents several advantages over conventional solvents. Some of the main benefits are the almost non-existent vapor pressure and the ability to solubilize organic, inorganic, and polymer compounds.[36] The search for environmentally friendly solvents and sustainable chemical processes is a priority between the principles of green chemistry and green analytical chemistry, and IL is an alternative to environmentally harmful organic solvents.[7,37-39]

Methods based on digital images have been widely used in analytical chemistry, allowing the development of fast, accurate, and low-cost analytical methodologies.[40-45] Digital images can be obtained from different imaging devices, including digital cameras, webcams, scanners, microscopes, and mobile phones.[23,46-50] Sensors present in image capture devices, such as CCD (charge-coupled device) and CMOS (complementary metal-oxide-semiconductor), can convert the intensity of incident radiation into an analog electrical signal. This signal is converted to a digital value stored in bits and pixels arranged in an array, similar to the RGB model.[40] The most common color space on capture devices is RGB (R: red, G: green, and B: blue). RGB has been widely used in quantifying solutions and immobilized substances using digital image processing and specific software that allows extracting colorimetric information by selecting the areas of interest in an image.[43] The photographs are processed and analyzed with image processing software.

This work proposes a method for determining antimony species in water samples using microextraction in the dispersive liquid phase based on vortex-assisted ionic liquid-based liquid-phase microextraction (VA-IL-LPME) and digital imaging spectrometry (DIC). A rapid, low-cost, and environmentally correct approach to antimony speciation is proposed.

Experimental

Apparatus

A Quimis model Q400AS pH meter (Diadema, Brazil) was used for pH measurements. The dispersion of the solvent in the aqueous phase was performed using a Lab Dancer (Ika, Campinas, Brazil) stirrer vortex. The capture of the digital images was performed in a system consisting of a box (32 × 23 × 8 cm) of medium-density fiberboard of white color to avoid the effects of reflection and the influence of external light. The lighting control inside the box was made using a lamp of LEDs (light-emitting diode) (6W) in white color, positioned at the top of the box, to guarantee uniformity and incidence of light and reproducibility of the image during measurements. The digital images of the system were recorded in a multifunctional portable microscope (Supereyes model B007, Shenzhen, China). A PerkinElmer (Shelton, USA) spectrometer model AAnalyst 400 equipped with an HGA 900 graphite atomizer was used to compare the results. An SP Labor centrifuge (model SP-32 T, Presidente Prudente, Brazil) was used to accelerate the decanting of the enriched phase.

Reagents and solutions

The glassware used in the procedure was previously decontaminated with 10% m v^{-1} nitric acid solution (Merck, Darmstadt, Germany) for 24 h and rinsed with deionized water. All reagents used were analytical grade. Solutions were prepared with ultrapure water processed by an Elga Purelab Classic model system. Hydrochloric acid 37% m v^{-1} (Merck, Darmstadt, Germany), ascorbic acid (Synth, Diadema, Brazil), potassium iodide (Synth, Diadema, Brazil), chloroform (Synth, Diadema, Brazil), trichloroethylene (Synth, Diadema, Brazil), carbon tetrachloride (Synth, Diadema, Brazil), and 1-butyl-3-methylimidazole hexafluorophosphate ([C_4MIM][PF_6]) (Sigma-Aldrich, São Paulo, Brazil) were used in the procedure. Solutions of 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (Br-PADAP) purchased from Sigma-Aldrich, São Paulo, Brazil, was prepared by dissolving the appropriate amount of commercial reagent in ethanol. Working antimony solutions (1000 µg mL^{-1}) were prepared from Sb_2O_3 (Vetec, Rio de Janeiro, Brazil) and $SbCl_5$ (Sigma-Aldrich, São Paulo, Brazil) dissolved in 15.0 mL of hydrochloric acid and diluted adequately in deionized water.

Sample preparation

Mineral water samples were purchased in commercial establishments in Jequié, Bahia, Brazil. Four samples of each brand of mineral water were acquired. River water samples were collected in the Contas River in Jequié, Bahia, Brazil. The samples were filtered through a quantitative porosity filter of 7-12 µm with vacuum filtration. After filtration, the water samples were submitted for pH measurement, and the preconcentration procedure was applied. All samples analyzed in this study presented pH in the range between 6.0 and 6.7.

Procedure for VA-IL-LPME

In a test tube containing 5.0 mL of an Sb^{III} solution, hydrochloric acid solutions (750.0 µL), ascorbic acid (250.0 µL), potassium iodide (1000 µL), and Br-PADAP (100.0 µL) were added in this order. Then, 120.0 µL of $[C_4MIM][PF_6]$ were added to the mixture. The system was taken to constant agitation in a vortex stirrer at 2500 rpm and then subjected to centrifugation for 5 min. The aqueous phase was discarded, and the reddish-rich-phase was photographed directly in the test tube. A schematic representation of the detection system is shown in Figure 1. The images were obtained directly in the test tube without the need to remove the enriched phase. The determination of total Sb was performed by promoting Sb^{III} reduction, using 1.0% m v^{-1} potassium iodide and 10.0% m v^{-1} ascorbic acid as reducing agents.[51,52] The Sb^{V} content was calculated by the difference between the quantity of total antimony and Sb^{III}.

The images were stored in JPEG format with a resolution of 96 dpi. The image size was 640 × 880 mm, and the bit depth was 32. A square region of interest (ROI) in a fixed position was defined using Chemostat software.[53] This program allows the acquisition of RGB data for all pixels in ROI. This information is organized into a color histogram, and the average value of each color channel, red (R), green (G), and blue (B), is calculated. The absorbance (A) is represented as A = –log (P/P_0) *versus* the concentration of the element, where P is the average value of channel R, G, or B measured by sample or standard solution, and P_0 is the average acquired value of analytical blank.

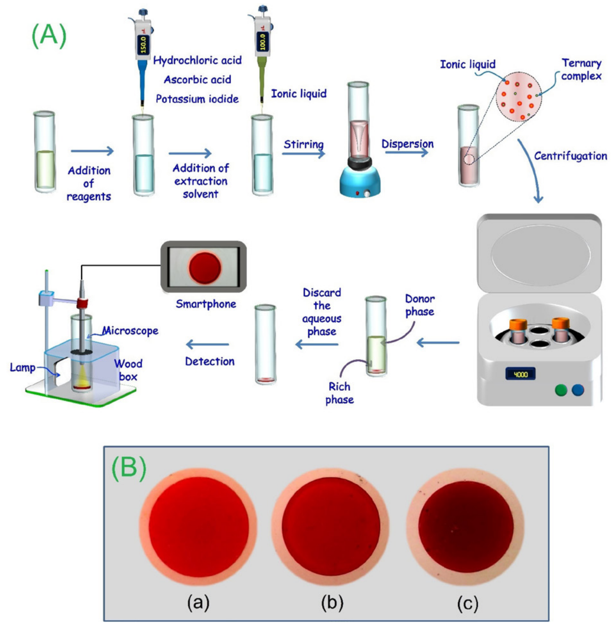

Figure 1. (A) Schematic representation of the system for the determination of antimony; (B) images of the rich-phase corresponding to solutions containing Sb^{III} at (a) 0.0; (b) 5.0; and (c) 50.0 µg L^{-1}.

Results and Discussion

Extraction solvent

The extraction efficiency is related to the proper choice of solvent. This substance should have some characteristics, such as low solubility in the aqueous phase and high extraction capacity for the components. Chloroform, trichloroethylene, carbon tetrachloride, and $[C_4MIM][PF_6]$ were tested as acceptor phases. As shown in Figure 2, chloroform, trichloroethylene, and $[C_4MIM][PF_6]$ provided similar results. Then, the ionic liquid was selected for further studies due to its potential to meet various environmental, health, and safety characteristics that differentiate it from conventional solvents. These characteristics make the solvent quite suitable for the criteria established by green chemistry.

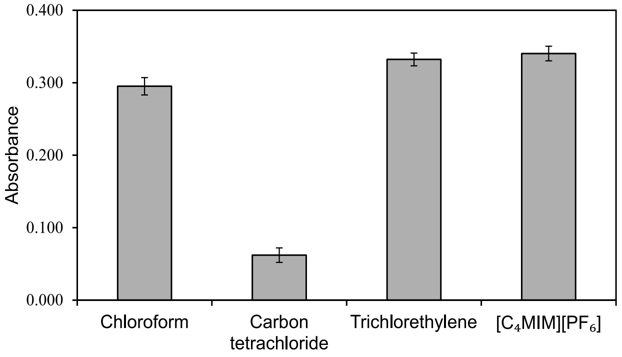

Figure 2. Influence of extraction solvent on Sb^{III} preconcentration by VA-IL-LPME. Experimental conditions: concentration of Sb^{III}, 50.0 µg L^{-1}; amount of extraction solvent, 100.0 µL; stirring time, 30 s; amount of Br-PADAP, 7.50×10^{-6} mol L^{-1}; amount of hydrochloric acid, 0.20 mol L^{-1}; amount of ascorbic acid, 2.0 mol L^{-1}; amount of iodide, 0.25 mol L^{-1}.

Amount of extraction solvent

In microextraction methods, the amount of the extraction solvent controls the volume of the rich phase and the extraction efficiency. The effect of the extraction solvent volume was studied in the range of 50.0 to 170.0 µL. According to Figure 3, the extraction solvent volume of 50.0 µL provided low analytical signals due to an insufficient acceptor phase. Volumes between 70.0 and 150.0 µL provided near average signals, although the smallest volumes in this range resulted in lower accuracy. When volumes above 150.0 µL were used, a decrease in signal was also observed due to excessive dilution. Based on these results, 120.0 µL of $[C_4MIM][PF_6]$ was chosen as the volume of extraction solvent for the subsequent studies.

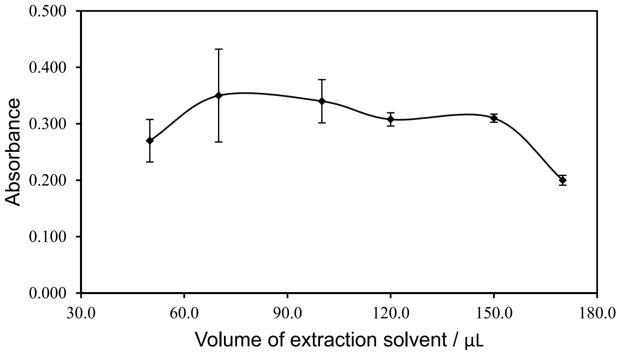

Figure 3. Influence of the amount of extraction solvent on Sb^{III} preconcentration by VA-IL-LPME. Experimental conditions: concentration of Sb^{III}, 50.0 µg L^{-1}; extraction solvent, $[C_4MIM][PF_6]$; stirring time, 30 s; amount of Br-PADAP, 7.50×10^{-6} mol L^{-1}; amount of hydrochloric acid, 0.20 mol L^{-1}; amount of ascorbic acid, 2.0 mol L^{-1}; amount of iodide, 0.25 mol L^{-1}.

Stirring time

A vortex agitator was used to promote the dispersion of the extraction solvent in the aqueous solution. This external energy source promotes a high efficiency in the mass transfer of the component. The stirring time required for displacement of the analyte from the aqueous phase to the extraction solvent was studied. The results can be seen in Figure 4. The time range investigated was 10 to 60 s. The analytical signal increases as a more significant amount of Sb^{III} is transferred to the acceptor phase. After 30 s, the absorbance remains constant. So, the 40 s was the period chosen for the stirrer of the system in the later experiments.

Amount of Br-PADAP

The influence of Br-PADAP concentration on the extraction and determination of Sb^{III} was evaluated at 2.15×10^{-6} to 1.42×10^{-5} mol L^{-1} range. According to the results observed in Figure 5, the analytical signal is maximum for concentrations greater than or equal to 7.16×10^{-6} mol L^{-1}. Concentrations of ligands lower than this value are not enough to complex all the Sb^{III} present in the medium so that a part of the element remains in the donor phase, impairing the extraction. Therefore, Br-PADAP solutions at a concentration of 7.50×10^{-6} mol L^{-1} were used in later experiments.

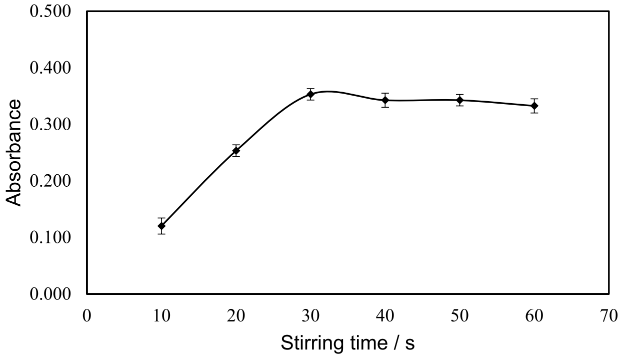

Figure 4. Influence of the agitation time on the preconcentration of Sb^{III} by VA-IL-LPME. Experimental conditions: concentration of Sb^{III}, 50.0 µg L^{-1}; extraction solvent, $[C_4MIM][PF_6]$; amount of extraction solvent, 120.0 µL; amount of Br-PADAP, 7.50×10^{-6} mol L^{-1}; amount of hydrochloric acid, 0.20 mol L^{-1}; amount of ascorbic acid, 2.0 mol L^{-1}; amount of iodide, 0.25 mol L^{-1}.

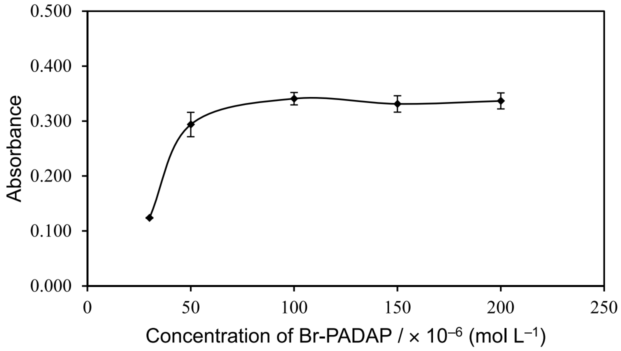

Figure 5. Influence of Br-PADAP concentration on Sb^{III} preconcentration by VA-IL-LPME. Experimental conditions: concentration of Sb^{III}, 50.0 µg L^{-1}; extraction solvent, $[C_4MIM][PF_6]$; amount of extraction solvent, 120.0 µL; stirring time, 40 s; amount of hydrochloric acid, 0.20 mol L^{-1}; amount of ascorbic acid, 2.0 mol L^{-1}; amount of iodide, 0.25 mol L^{-1}.

Amount of hydrochloric acid

A three-part ionic coordination compound of blue-greenish coloration is formed between Sb^{III}, iodide, and 5-Br-PADAP.[10] In the medium of the extraction solvent, the complex presents reddish staining. The complex is produced in an acidic medium, which contributes significantly to the intensification of the color. In addition, the acid medium contributes to the increase of the reducing effect of ascorbic acid. Hydrochloric and sulfuric acid were tested, and both showed similar results. Next, the concentration of hydrochloric acid in the medium was studied between 0.08 and 0.60 mol L^{-1}. Figure 6 presents the results obtained. It is observed that acid solutions of concentrations between 0.20 and 0.40 mol L^{-1} enabled

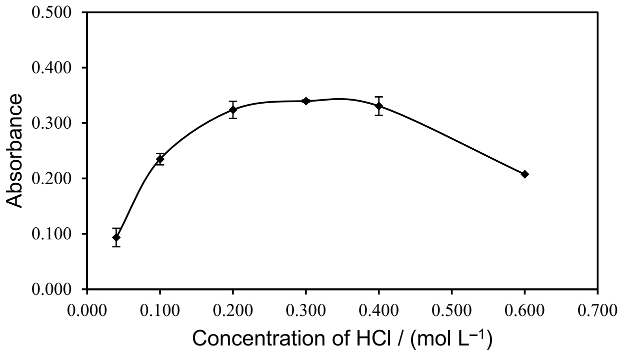

Figure 6. Influence of acid concentration on the Sb^{III} preconcentration by VA-IL-LPME. Experimental conditions: concentration of Sb^{III}, 50.0 µg L^{-1}; extraction solvent, [C$_4$MIM][PF$_6$]; amount of extraction solvent, 120.0 µL; stirring time, 40 s; amount of Br-PADAP, 7.50 × 10^{-6} mol L^{-1}; amount of ascorbic acid, 2.0 mol L^{-1}; amount of iodide, 0.25 mol L^{-1}.

the highest absorbance values. Thus, a concentration of 0.30 mol L^{-1} was established for the following experiments.

Amount of ascorbic acid

Ascorbic acid was used to prevent the release of iodine by any oxidizing species present in the medium. Thus, the introduction of ascorbic acid prevents the conversion of I$^-$ to I$_2$, which would decrease the amount of complex formed, besides affecting the color of the medium. The reducing agent concentration was studied between values 5.0 × 10^{-3} and 5.5 × 10^{-2} mol L^{-1}. According to Figure 7, the best results were obtained when acid solutions of 1.5 and 4.5 mol L^{-1} were used. Then, 2.0 mol L^{-1} HCl solutions were used in subsequent experiments.

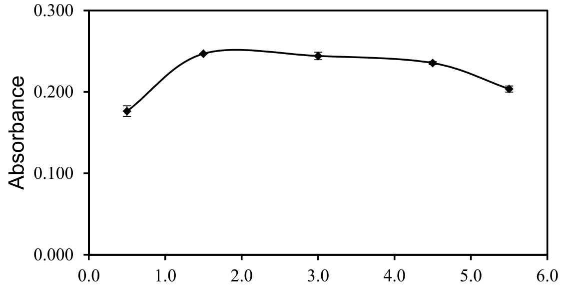

Figure 7. Influence of ascorbic acid concentration on Sb^{III} preconcentration by VA-IL-LPME. Experimental conditions: concentration of Sb^{III}, 50.0 µg L^{-1}; extraction solvent, [C$_4$MIM][PF$_6$]; amount of extraction solvent, 120.0 µL; stirring time, 40 s; amount of Br-PADAP, 7.50 × 10^{-6} mol L^{-1}; amount of hydrochloric acid, 0.30 mol L^{-1}; amount of iodide, 0.25 mol L^{-1}.

Amount of iodide

The amount of iodide is a critical condition because it directly influences the quantity of the extracted species. The anion should be added to the extraction medium to ensure the production of a significant amount of ternary complex formed between Sb^{III}, iodide, and 5-Br-PADAP. Potassium iodide was the salt used. The effect of iodide concentration was studied in 0.00 to 0.48 mol L^{-1}. The addition of a 0.24 mol L^{-1} potassium iodide solution was sufficient to obtain the maximum signal. A 0.25 mol L^{-1} iodide solution was then selected. The results are shown in Figure 8.

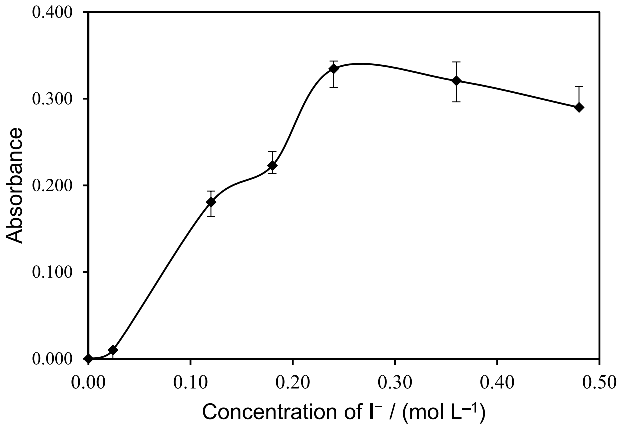

Figure 8. Influence of potassium iodide concentration on Sb^{III} preconcentration by VA-IL-LPME. Experimental conditions: concentration of Sb^{III}, 50.0 µg L^{-1}; extraction solvent, [C$_4$MIM][PF$_6$]; amount of extraction solvent, 120.0 µL; stirring time, 40 s; amount of Br-PADAP, 7.50 × 10^{-6} mol L^{-1}; amount of hydrochloric acid, 0.30 mol L^{-1}; amount of ascorbic acid, 2.0 mol L^{-1}.

Selectivity

The possibility of interference caused by some ions in the preconcentration was evaluated using 30.0 µg L^{-1} Sb^{III} solutions. Each species was added to these solutions, and the analytical signal was compared with those corresponding to the solution signal containing only antimony. A species was considered interfering when the analytical signal in its presence varies ± 10% about the absorbance of the element. The results are shown in Table 1. It is observed that the method is not affected by the presence of the species in the tested quantities.

Table 1. Study of the interference caused by some ions on the preconcentration of Sb^{III} by VA-IL-LPME

Species	Ratio species: Sb^{III}
Cl^{-1} and Na^{I}, Al^{III}, K^{I}, Pb^{II}, Cd^{II}, Cr^{III}, Cu^{II}, Fe^{III}, Mn^{II}, Ni^{II}, V^{V}, Zn^{II}, As^{III}	100
Co^{II}, Hg^{II}	50
Se^{IV}	25

Analytical features

The analytical performance of the method was evaluated under optimized conditions. Linear calibration ranges, calibration curve equation, limit of detection (LOD), and limit of quantification (LOQ) were calculated. The calibration curves were constructed to determine Sb^{III} at a 2.5 to 50.0 µg L^{-1}. The red channel was processed to obtain the analytical signals due to higher sensitivity than the green and blue channels. The calibration curve equation was obtained using the linear regression method, and it is presented in Table 2, where A is the absorbance signal, and C is the Sb^{III} concentration in µg L^{-1}. The limits of detection and quantification were calculated using the expressions LOD = 3δ/s and LOQ = 10δ/s, respectively, where δ is the standard deviation of eleven measurements of analytical blank and s is the slope of the analytical curve. The method's precision was calculated using a relative standard deviation (RSD) of eight 30.0 µg L^{-1} Sb^{III} solution measurements. The enrichment factor (EF) was obtained by calculating the ratio between the angular coefficient of the analytical curve and that relative to the direct measurement.[54,55]

Table 2. Analytical features of the method

Calibration graph	VA-IL-LPME	$A = 7.2 \times 10^{-3}\,C + 3.6 \times 10^{-3}$
	direct measurement	$A = 2.0 \times 10^{-5}\,C + 4.1 \times 10^{-3}$
Limit of detection / (µg L^{-1})	1.4	
Limit of quantification / (µg L^{-1})	4.2	
Precision / %	7.0	
Enrichment factor	360	

VA-IL-LPME: vortex-assisted ionic liquid-based liquid-phase microextraction; A: absorbance; C: concentration.

Application

The method developed was applied to determine antimony in river water and mineral water samples. The results are shown in Tables 3 and 4. The following equation was used for the calculation of recovery: $R(\%) = \frac{C - C_0}{m} \times 100$, where C is the concentration of Sb^{III} found without addition, C_0 is the concentration of Sb^{III} found with addition, and m is the amount of Sb^{III} added. The recovery values for the samples ranged from 92 to 104%, demonstrating the proposed applicability of the method. The *t*-test showed that the results obtained with the proposed methodology showed no significant difference at 95%. Table 5 compares the results obtained for the determination of total Sb using electrothermal atomic absorption spectrometry (ET AAS) and the proposed method. The values found by the proposed method are in agreement with those found using ET AAS.

Table 3. Results for Sb^{III} determination in water by the proposed method

Sample	Amount of Sb^{III} / (µg L^{-1})		Recovery / %
	Added	Found	
River water 01	0	5.6 ± 1.1	95
	30.0	34.2 ± 1.3	
River water 02	0	6.7 ± 0.1	92
	30	34.4 ± 2.4	
River water 03	0	13.5 ± 0.8	92
	30	41.3 ± 3.2	
River water 04	0	15.7 ± 2.9	101
	30	46.1 ± 3.6	
Mineral water 01	0	13.1 ± 0.7	93
	30	40.8 ± 0.8	
Mineral water 02	0	11.0 ± 1.1	102
	30	36.9 ± 3.3	
Mineral water 03	0	14.6 ± 0.9	91
	30	39.9 ± 1.4	
Mineral water 04	0	16.9 ± 2.1	–
Mineral water 05	0	12.0 ± 0.8	–
Mineral water 06	0	10.2 ± 1.2	–
Mineral water 07	0	18.7 ± 2.6	–
Mineral water 08	0	16.7 ± 0.8	–
Mineral water 09	0	14.5 ± 0.5	–
Mineral water 10	0	22.8 ± 1.1	–
Mineral water 11	0	14.7 ± 1.1	–
Mineral water 12	0	12.0 ± 2.1	–
Mineral water 13	0	15.1 ± 3.2	–

Table 4. Results for determination of Sb^{III} and Sb^{V} in water

Sample	Amount of Sb^{III} / (µg L^{-1})	Amount of Sb^{V} / (µg L^{-1})
River water 05	6.1 ± 0.7	2.6 ± 0.8
River water 06	6.0 ± 0.6	4.4 ± 1.1
Mineral water 14	9.2 ± 1.4	14.0 ± 2.1
Mineral water 15	8.3 ± 1.8	9.4 ± 1.3

Table 5. Results for determination of total Sb by ET AAS and the proposed method

Sample	Amount of total Sb		Error / %
	Proposed method	ET AAS	
River water 07	17.6 ± 1.1	18.7 ± 1.5	–5.9
River water 08	7.8 ± 0.8	7.2 ± 0.4	+8.3

ET AAS: electrothermal atomic absorption spectrometry.

Conclusions

The proposed method presented a simple, low-cost, and fast approach for the extraction and determination of the concentration of Sb^{III} and Sb^{V}. The procedure made it possible to determine trace species in mineral water and river water samples. The method is based on the principles of green chemistry, as it does not employ toxic or persistent solvents. On the contrary, the acceptor phase used is an ionic liquid, a solvent with several characteristics that differentiate it from conventional solvents. Among these properties, low toxicity, volatility, and vapor pressure can be cited as the ability to extract several species. The procedure also has the advantage of using small amounts of reagents and solvents, reducing waste generation. The association of VA-IL-LPME with DIC resulted in a method whose benefits make it an excellent alternative to determine antimony species in water samples. Other approaches to Sb speciation can be tested, such as inserting operations using flow injection or different types of LPME, such as SDME or headspace single-drop microextraction (HS-SDME). Work in this direction is being developed in this laboratory.

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