

New Analytical Methodology for Sb(III) Traces Quantification as Emergent Contaminant in Drinks Packaged PET Samples by Solid Surface Fluorescence

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Abstract

Emerging contaminants constitute a set of substances that are released into the environment for which regulations are currently not established for their environmental monitoring, being antimony one of them. A new methodology for Sb(III) traces monitoring by solid surface fluorescence is proposed. The metal was complexed with alizarine (Az) as fluorophore reagent in alkaline medium in presence of the bile salt sodium cholate. To isolate the analyte of matrix constituents, a preconcentration/separation strategy on filter paper was introduced prior to determination step. The solid surface fluorescence was measured $\lambda_{em} = 450$ nm and $\lambda_{exc} = 363$ nm using a solid sampler holder. Under optimal conditions, the limits of detection and quantification of proposed methodology were 0.08 and 0.24 $\mu\text{g}\cdot\text{L}^{-1}$, respectively, showing a linear range from 0.24 to 304.4 $\mu\text{g}\cdot\text{L}^{-1}$ with good sensitivity and adequate selectivity. It was applied to the Sb(III) traces determination present in drinking water and beverages samples packaged in polyethylene terephthalate (PET) bottles widely consumed in Argentina. The combination of a preconcentration step on common filter paper and the inherent sensitivity of photoluminescent methods have permitted to achieve sensitivity similar to atomic spectroscopies using a lower price instrument typical in control laboratories. Precision and accuracy were tested with excellent agreement. Results were truenessed by ETAAS with satisfactory concordance.

Keywords

Emerging Contaminants, Antimony Traces, Alizarine, Solid Surface Fluorescence, Waters and Beverages

1. Introduction

One of the most relevant fields of Analytical Chemistry is the metal traces quantification with clinical and toxicological impact. The development of faster, safer and ecological extraction procedures is associated to traces analysis. It is in this context that new surfactants extraction schemes have been proposed as ecological procedures in replacement of traditional liquid-liquid extraction [1]. Surfactants are non-volatile and non-flammable substances that allow to carry out a safer sample handling and to obtain quantitative analytes recuperations. These surface-active compounds have been used in cloud point extraction (CPE), which has shown to be a powerful and very useful extractive technique [2] [3].

Surfactant mediated extractions (SME), also known as cloud point (CPE), coacervate, aqueous two phase surfactant or supramolecular extractions, among others, have become a popular approach to enrich and/or recover metal ions as well as organic compounds from aqueous (or solid) matrices [4] [5] [6] [7]. SME can be employed for samples with complex matrices due to the possibilities of manipulating and chemically modifying the matrix during the phase separation preconcentration step.

Solid phase extraction (SPE) is an alternative rapid, simple, more environmentally-friendly, and economic pre-concentration step, which has advantages over the traditional liquid-liquid extraction. SPE followed by Electro thermal atomic absorption (ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) or mass spectrometry inductively coupled plasma (ICP-MS) determination step has shown to be suitable for traces metals analysis [8] [9].

Investigators are interested in improving the selectivity of the sorbents used in SPE. Several solid materials, such as silica gel, exchange resins, aluminum oxide, poly (vinylalcohol), C18 membranes, cyclodextrines, filter papers, and nylon membranes, among others, have been successfully employed as solid supports [10].

Emerging contaminants constitute a set of substances that are released into the environment for which regulations are currently not established for their environmental monitoring [11]. Antimony (Sb) has recently been incorporated into this group of substances due to this element is present in polyethylene terephthalate (PET) recipients in which drink waters, fruit juices, soft drinks are commercialized [12].

Bach *et al.* in 2012, published a critical review of chemicals found in PET bottled waters and their toxicological assessment, where Sb was noted as clearly migrating from the PET plastic into the water [13]. If good, it can be demonstrated that several conditions increase the possibility of Sb migration (low pH, outdoor sunlight irradiation, in-car storage, cooling, heating and microwave treatment) [13] [14] [15], however, no conclusive information has been offer respect to the incidence of each particular factor. Clearly, only a small fraction of the antimony in PET plastic bottles is released into the water. Even so, the use of alternative

types of plastics that do not leach antimony should be considered [14].

Antimony trioxide is used as a catalyst in the manufacture of PET plastics [3] [4] containing > 100 mg/kg of Sb. These facts have caused the highest levels of human exposure to Sb, up to 10 $\mu\text{g}\cdot\text{L}^{-1}$ [16].

The growing popularity of bottled waters, as well as the use of PET bottles during the last four decades replacing gradually PVC and glass bottles, increases the severity of this emerging contaminant. Sb exhibits marked toxicity causing damages to human health, depending on different factors such as feeding and occupation. Among the pathologies linked to exposure to this metal, we can mention: gastrointestinal, cardiac and pulmonary disorders, eye and skin irritation, among others [17].

The reference methods for quantifying Sb traces are atomic spectrometry, among them we can mention: graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), mass spectrometry inductively coupled plasma (ICP-MS), atomic generation of hydride fluorescence spectrometry (HG AFS) [18] [19] [20] [21] [22]. However, in many cases, the low levels of toxic metal are incompatible with instrumental sensitivity. Added to this, high prices and expensive instrumental inputs constitute a major constraint for many control laboratories.

In our laboratory, we have developed new analytical methodologies for quantification of several toxic metals in biological (urine, saliva, blood) and food samples (beverages, wine, cereals) using different extraction strategies and analyte-complexation followed by the subsequent quantification by molecular fluorescence [3] [7] [23] [24].

The aim of this work is to offer an alternative analytical method for Sb quantification in drinking waters and beverages samples in PET packed by solid surface fluorescence (SSF), based on the formation of a fluorescent association with the fluorophore alizarin (Az).

2. Material and Methods

2.1. Instruments

A Shimadzu RF-5301 PC spectrofluorometer (Shimadzu Corporation Analytical Instrument Division, Kyoto, Japan) equipped with a 150 W Xenon lamp and solid sample holder with a GF-UV35 filter was used for SSF measurements.

Measurements of Sb were performed with a Shimadzu Model AA-6800 Atomic Absorption Spectrometer (Tokyo, Japan) equipped with a deuterium background corrector, EX7-GFA electrothermal atomizer and ASC-6100 auto-sampler. L'vov graphite tubes (Shimadzu, Tokyo, Japan) was used in all experiments. Antimony hollow-cathode lamps (Hamamatsu, Photonics K., Japan) were employed as radiation sources. Wave length used was 217.6 nm (Slit Width: 0.5 nm). The ETAAS temperature program for Sb quantification in samples is shown in **Table 1**.

Table 1. ETAAS operating conditions and furnace temperature program for Sb quantification.

Step	Temperature (°C)	Ramp (°C·s ⁻¹)	Hold (s)	Argon Gas Flow (L·min ⁻¹)
Drying	150	20	-	0.1
	250	-	10	0.1
	600	10	-	1.0
Pyrolysis	600	-	10	1.0
	600	-	3	0.0 ^a
Atomization	2400	-	2	0.0 ^a
Cleaning	2500	-	2	1.0

^a = data acquisition.

Adjustments of pH were carried out using Orion Expandable Ion Analyzer pH-meter (Orion Research, MA, USA) Model EA 940 with a combined glass electrode.

Blue ribbon filter papers (FP) (Whatman, England) 2 - 5 µm pore size and 4.5 cm diameter were used in sorption studies.

2.2. Reagents

Stock solutions of Sb(III) were prepared by dilution of 100 µg·mL⁻¹ standard solution plasma-pure (Leeman Labs, Inc., Hudson, NH, USA). The standard stock solution was stored in a glass bottle at 4°C in the dark. Lower concentration standards were obtained weekly by dilution of the stock solutions.

Solution of 1,2-dihydroxyanthraquinone (Alizarin, Az) 1 × 10⁻³ mol·L⁻¹ (E-Merck, Darmstadt, Germany) was prepared by dissolving appropriate amounts of the reagent in ethanol (Sigma Chemical Co., St. Louis, MO, United States) and was kept in the refrigerator (4°C) for one week.

Tris-(hydroxymethyl)-aminomethane (Mallinckrodt Chemical Works, St Louis, USA) 1 mmol·L⁻¹, sodium tetraborate (Merck & Co., Inc.) 1 mmol·L⁻¹, potassium phthalate acid (Merck & Co., Inc.) 1 mmol·L⁻¹ and acetic acid/acetate (Mallinckrodt Chemical Works) buffer solutions were prepared.

Surfactant solution of sodium dodecyl sulfate (SDS, Tokyo Kasei Industries) 2 × 10⁻² mol·L⁻¹, sodium cholate (NaC) (C₂₄H₃₉NaO₅, Sigma Chemical Co.) 1 × 10⁻² mol·L⁻¹ and cetyltrimethylammonium bromide (CTAB) (Chuo-Ku, Tokyo, Japan) 1 × 10⁻² mol·L⁻¹ were prepared using an adequate weight of reagent and dissolving them in ultrapure water.

2.3. Sample Collection and Treatments

The samples of mineral waters, flavored waters and drinks were purchased in supermarkets and chosen taking into account the most consumed by the Argentine population. Samples were selected taking into account the main products consumed by segments of the population with different dietary requirements

due to their age and lifestyle. In order to guarantee representative samples, a randomize strategy sampling was used; three examples of the same brand for each product were acquired. Entire products were homogenized and reserved for sample preparation. Mineral water, flavored waters (grapefruit flavors, tropical fruits, lemonade and apple flavor), beverages (cola drink, lemon drink, tonic water and hydrating drinks) were diluted and directly analyzed for Sb(III) quantification.

All the samples packed in PET were opened, half of the volume was discarded and they were left at rest (with lid) at room temperature, exposed to light and to ambient temperature changes for 6 months in total. The determinations of Sb (III) were carried out at times 0, 3 and 6 months of rest [25].

2.4. General Procedure

A 250 μL Az solution ($1 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$), Sb (III) sample/standard (0.36, 0.48 and $0.72 \mu\text{g}\cdot\text{L}^{-1}$), 100 μL sodium borate buffer ($0.1 \text{ mol}\cdot\text{L}^{-1}$, pH 10.7), and 100 μL NaC ($1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) were placed in a volumetric flask. The mixture was diluted to 10 mL with ultrapure water and was filtrated across blue ribbon FP using a vacuum pump and dried at room temperature. Sb(III) was determined on the solid support by SSF at $\lambda_{\text{em}} = 450 \text{ nm}$ and $\lambda_{\text{exc}} = 363 \text{ nm}$, using a solid sample holder (Figure 1).

2.5. Interferences Study

Different amounts of foreign ions, which may be present in samples, (1/1, 1/10,

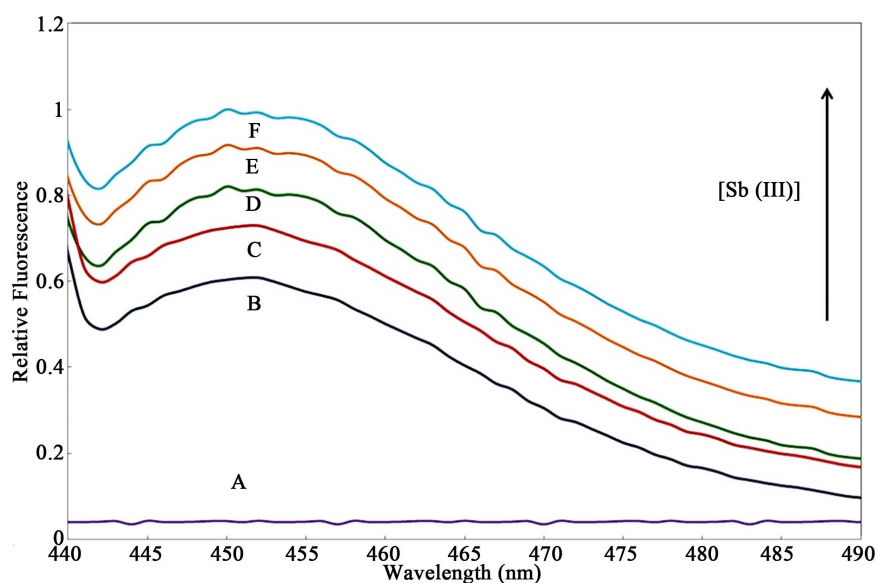


Figure 1. Solid surface fluorescence of Sb(III)/Az quantification. A: filter paper. B: filter paper with Az + NaC. C: Idem B with Sb(III) $0.36 \mu\text{g}\cdot\text{L}^{-1}$. D: Idem B with Sb(III) $0.48 \mu\text{g}\cdot\text{L}^{-1}$. E: Idem B with Sb(III) $0.60 \mu\text{g}\cdot\text{L}^{-1}$. F: Idem B with Sb(III) $0.72 \mu\text{g}\cdot\text{L}^{-1}$. Conditions: $\lambda_{\text{em}} = 450 \text{ nm}$; $\lambda_{\text{exc}} = 363 \text{ nm}$; $C_{\text{Az}} = 5 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$, $C_{\text{NaC}} = 2 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{buffer Sodium borate}} = 1 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, pH 10.7. Other experimental conditions are described under procedure.

1/50 and 1/100 Sb(III)/interferent ratio) were added to the test solution containing $0.60 \mu\text{g}\cdot\text{L}^{-1}$ Sb(III) and the General Procedure was applied.

2.6. Dilution Test

In order to establish the proper volume of each sample for realizing Sb(III) determination, several sample volumes were assayed. The adequate dilution for each sample was that signal which intensities fall into the linearity range of the developed methodology. Dilution test was assayed of 100 μL to 0.025 μL depending on the sample characteristics. These dilution factors were adopted for the following studies. Sb(III) contents were determined by the proposed methodology, employing the obtained volume samples through test dilution.

2.7. Accuracy Study

Volumes of 0.050 mL of water and beverages samples were spiked with increasing amounts of Sb(III) (0.36 and $0.72 \mu\text{g}\cdot\text{L}^{-1}$). Antimony contents were determined by proposed methodology.

2.8. Precision Study

The repeatability (within-day precision) of the method was tested for water and beverages samples replicate samples ($n = 4$) spiked with 0.36 and $0.72 \mu\text{g}\cdot\text{L}^{-1}$ of Sb(III) and metal contents were determined by proposed methodology.

2.9. Trueness

Sb(III) contents in water and beverages samples were determined by ETAAS, using operational conditions previously consigned in apparatus item.

3. Results and Discussion

Anthraquinones are the largest group of natural quinones and are the basis of a variety of natural colorants. Az is a mordant type dye and due to the $\alpha\text{-OH}$ group can react with metal ions forming complexes whose color vary with the cation nature and work conditions [26] [27].

To study the possibility of evaluating the content of antimony as a Sb(III)/Az association in drinking waters and beverages samples, due to the low concentration levels, a separation/preconcentration step is necessary. An extraction stage in solid phase (SPE) was introduced before the instrumental determination of Sb(III) by SSF. The SPE offers a double beneficial effect; on the one hand, it produces the preconcentration of the analyte, due to its retention in a small area of the solid support and, on the other, the selectivity is improved by isolation of analyte of the sample complex matrix, removing possible interferences.

To establish the best conditions to analyte quantification, the experimental parameters that influence the SPE procedure and the SSF determination were studied and optimized.

Systems were prepared containing Az solution and increasing concentrations

of Sb (III) at pH 10.7 using sodium borate buffer; they were filtered through solid support, dried to room temperature and SSF signal of each system was determined using a solid sampler holder. It was evidenced that the SSF of the fluorophore was exalted in the presence of Sb(III) as the concentration of the metal was increased.

Retention of the Sb(III)/Az association was studied using different solid supports. In any of the studied solid supports, the Sb(III)/Az was not retained or an adequate signal of system was not observed; in **Table 2**, the obtained results are shown. The retention levels for each analyzed support were verified by measuring SSF intensity at $\lambda_{em} = 450$ nm, using a $\lambda_{exc} = 363$. The best results regarding sensitivity and reproducibility were obtained using blue ribbon filter papers. Thereby, this support was selected to the following assays.

The next optimized parameter was the pH of the aqueous systems. The pH value of the aqueous systems containing a constant concentration of Sb (III) was adjusted between 2.5 and 12, by adding a solution of suitable buffer. **Figure 2** shows the results of this study. The highest emission for Sb(III)/Az was obtained at pH 10.7. Subsequently, the sodium borate buffer concentration was tested from 5×10^{-4} mol·L⁻¹ to 0.1 mol·L⁻¹ to obtain the maximum fluorescent signal. A buffer concentration of 1×10^{-4} mol·L⁻¹ was chosen as optimal.

Table 2. Study of retention of Sb(III)/Az on different types of membranes.

Type of Membrane	Observations
Cellulose acetate	
(Whatman)	Az retention: (+)
Pore size: 0.45 μ m	Sb(III) retention: (+/-)
Teflon	
(Millipore)	Az retention: (-)
Pore size: 1 μ m	Sb(III) retention: (-)
Mixed esters	
(Schleicher & Schuell)	Az retention: (+)
Pore size: 0.45 μ m	Sb(III) retention: (-)
Filter paper	
(S & S)	Az retention: (+/-)
Black ribbon	Sb(III) retention: (-)
Nylon	
(Millipore)	Az retention: (+)
Pore size: 0.45 μ m	Sb(III) retention: (-)
Filter paper	
(S & S)	Az retention: (+)
Blue ribbon	Sb(III) retention: (+)

Conditions: $\lambda_{em} = 450$ nm; $\lambda_{exc} = 363$ nm; $C_{Az} = 5 \times 10^{-7}$ mol·L⁻¹; $C_{NaAc} = 2 \times 10^{-5}$ mol·L⁻¹; C_{buffer} Sodium borate = 1×10^{-4} mol·L⁻¹, pH 10.7. Other experimental conditions are described under procedure.

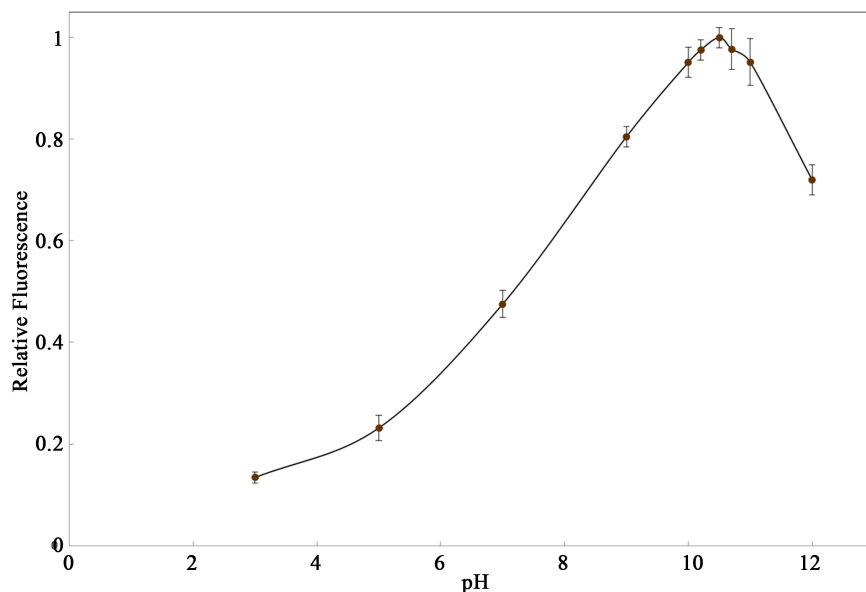


Figure 2. Influence of pH on Sb(III)/Az determination. Conditions: $\lambda_{em} = 450$ nm; $\lambda_{exc} = 363$ nm; $C_{Az} = 5 \times 10^{-7}$ mol·L⁻¹, $C_{NaC} = 2 \times 10^{-5}$ mol·L⁻¹; C_{buffer} Sodium borate = 1×10^{-4} mol·L⁻¹, $C_{(Sb(III))} = 0.60$ μ g·L⁻¹. Other experimental conditions are described under procedure.

The concentration of the chelating reagent was also studied keeping a constant concentration of the metal and varying the concentration of Az between 1×10^{-9} to 1×10^{-6} mol·L⁻¹. The concentration of 2.5×10^{-7} mol·L⁻¹ was selected as optimal, which is high enough to guarantee an excess of Az with respect to the expected Sb(III) contents in studied samples (Figure 3).

It is well known that the use of surfactants in molecular fluorescence provides some advantages that improve the determination of the analyte under study. In this way, micellar media have shown to be effective to minimize intermolecular interactions between the analyte and sample matrix constituents. Additionally, the photophysical properties of the fluorescent solutes can be altered in the micellar medium improving the fluorescent sensitivity [28].

Like traditional surfactant micelles, bile salt (BS) micelles present unique properties that can be used in chemical analysis and separation science applications; between others the ability to solubilize selectively solutes, alter the rate and equilibrium of chemical processes, modify the effective microenvironment such as polarity, viscosity and surface tension of bound solutes [29].

In contrast to synthetic surfactants (e.g. Triton X-110, Triton X-114, SDS), BS micellar solutions are much easier to work with since they are former and scatter light to lesser extent, which is beneficial in spectroscopic measurements [30]. The BS aggregation behavior is also different from that observed for synthetic surfactants. Namely, they exhibit a sequential aggregation pattern and their micelle aggregation number is typically much less than that of other micelles.

The effect of different surfactants in the SPE for the quantification of the Sb(III)/Az by SSF was studied. Obtained results put in evidence that the bile

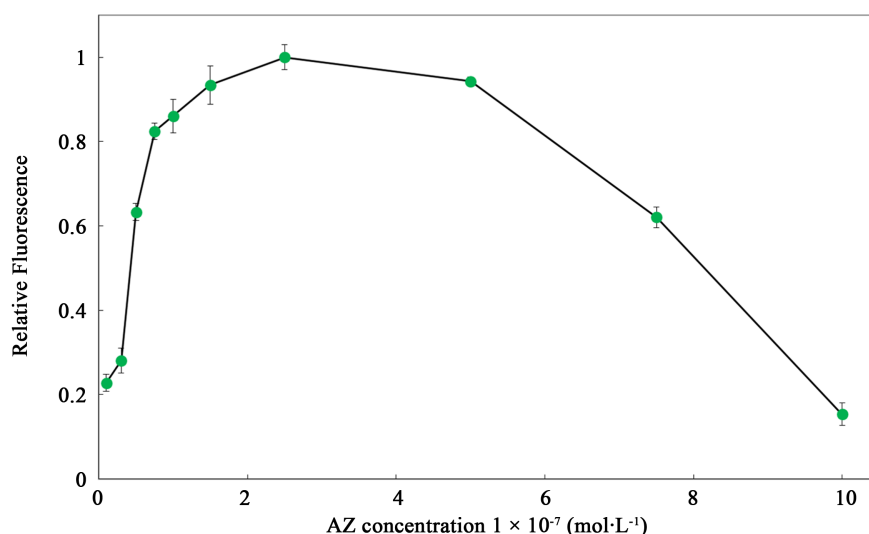


Figure 3. Effect of Az dye concentration on the Sb(III). Conditions: $\lambda_{\text{em}} = 450 \text{ nm}$; $\lambda_{\text{exc}} = 363 \text{ nm}$; $C_{\text{NaC}} = 2 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{buffer Sodium borate}} = 1 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, pH 10.7, $C_{\text{(Sb(III))}} = 0.60 \mu\text{g}\cdot\text{L}^{-1}$. Other experimental conditions are described under procedure.

salt NaC ($1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) increased the fluorescent intensity of Sb(III) association.

4. Analytical Parameters

Table 3 summarizes the studied experimental variables, the optimal values for separation/determination of Sb(III)/Az on FP and analytical parameters for the new proposed methodology. The limit of detection (LOD) was calculated as 3.3 s/m [31], where s is the standard deviation of 10 successive means of the blank and m is the slope of the calibration curve (calibration sensitivity). The limit of quantification (LOQ) was calculated as 10 s/m . The range of linearity was evaluated by checking the linear regression coefficient (R^2) of the calibration curve. The linearity of the calibration curve was considered acceptable when $R^2 > 0.9998$.

Table 4 summarizes the main characteristics of calibration plot of proposed methodology and of other instrumental conventional methodologies for quantification of Sb(III) traces. These methods present high degree of accuracy and repeatability and a short time of analysis. However, in many cases the low levels of toxic metal are incompatible with instrumental sensitivity. Added to this, high prices and expensive instrumental inputs constitute a major constraint for many control laboratories.

The application of luminescent methods to antimony traces determination has shown several analytical advantages such as high sensitivity, proper selectivity and dynamic wide range when they have been associated to separation/preconcentration/sensitization steps. Additionally, the proposed methodology presents the advantage of a significant lowest standard deviation, the simplicity and low cost of equipment, versatility in sample application, as well as the low consumption of reagents. With regard to the disadvantages of the

Table 3. Optimal experimental conditions and analytical parameters for Sb(III)-AZ determination.

Parameters	Studied Range	Optimal Conditions
Type of membrane	Nylon, cellulose acetate, esters, teflon, filter paper	Filter paper (blue ribbon)
pH	3 - 12	10.7
Concentration buffer	1×10^{-2} - $0.1 \text{ mol}\cdot\text{L}^{-1}$	$1 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$
Concentration Az	1×10^{-9} - $1 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$	$2.5 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$
Concentration NaC	1×10^{-6} - $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$	$1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$
LOD	-	$0.08 \mu\text{g}\cdot\text{L}^{-1}$
LOQ	-	$0.24 \mu\text{g}\cdot\text{L}^{-1}$
LOL	-	$0.24 - 304.4 \mu\text{g}\cdot\text{L}^{-1}$
R ²	-	0.999

Table 4. Analytical parameters of methodologies for Sb(III) determination in samples of different nature.

Method	Comments	Reference
UA-IL-DLLME-ICP-OES	RSD = 2.1% - 2.5% LOD = $120 \mu\text{g}\cdot\text{L}^{-1}$ LOQ = $250 \mu\text{g}\cdot\text{L}^{-1}$ $r^2 = 0.9987$ Sample: beverages	[16]
ETAAS	Linear range = uninformed - 200 ppm Samples: solid of environmental interest	[17]
HG-AFS.	LOD = $0.28 \mu\text{g}\cdot\text{L}^{-1}$ LOQ = $0.96 \mu\text{g}\cdot\text{L}^{-1}$ RSD = 2.8% Sample: hair	[18]
ICP-MS	LOD = $0.01 - 0.03 \mu\text{g}\cdot\text{L}^{-1}$ RSD = 10% Sample: single whiskers	[19]
HG AFS	Linear range = $30 \text{ ng}\cdot\text{L}^{-1} - 10.0 \mu\text{g}\cdot\text{L}^{-1}$ RSD < 5% LOD = $9 \text{ ng}\cdot\text{L}^{-1}$ LOQ = $30 \text{ ng}\cdot\text{L}^{-1}$ Sample: natural water	[20]
This method	LOD = $0.08 \mu\text{g}\cdot\text{L}^{-1}$ LOQ = $0.24 \mu\text{g}\cdot\text{L}^{-1}$ Linear range = $0.24 - 304.4 \mu\text{g}\cdot\text{L}^{-1}$ R ² = 0.999 Sample: waters and beverages	-

method, we can mention the selectivity and the analysis time, which is not a time involved in a drying stage.

Interferences Study

The effect of foreign ions on the recovery of Sb(III) was tested. An ion was considered as interferent when it caused a variation in the SSF signal of the sample

greater than $\pm 5\%$. The assayed ions for interferences study were selected considering nature of the analyzed sample. **Figure 4** shows the obtained results for assayed ions. These results demonstrate that, at optimal experimental conditions, even large amounts of some common ions do not interfere with the determination of Sb(III) trace levels, confirming the selectivity of the developed method.

5. Applications

To establish the applicability of proposed method at real-world samples, it was applied to Sb(III) quantification in drinking waters and beverages samples packed in PET recipients. Different sample aliquots were spiked with increasing amounts of Sb(III) (0.36 to $0.72 \mu\text{g}\cdot\text{L}^{-1}$). The results obtained showed an adequate precision (see **Table 5** and **Table 6**).

Table 5. Recuperation studies by antimony determination in water samples packaged in PET bottles.

Sample	Sb(III) Added ($\mu\text{g}\cdot\text{L}^{-1}$)	Propose Methodology		ETTAS	RE%*
		Sb(III) Found \pm SD ($\mu\text{g}\cdot\text{L}^{-1}$)	Recovery (% , n = 4)	Sb(III) Found \pm SD ($\mu\text{g}\cdot\text{L}^{-1}$)	
	-	0.93 ± 0.03	-		
1	0.36	1.278 ± 0.02	98.71	-	-
	0.60	1.522 ± 0.07	99.14		
	-	0.77 ± 0.05	-		
2	0.36	1.134 ± 0.04	100.52	0.75 ± 0.09	2.60
	0.60	1.381 ± 0.03	101.43		
	-	1.88 ± 0.02	-		
3	0.36	2.231 ± 0.09	99.52	1.93 ± 0.03	2.59
	0.60	2.474 ± 0.07	99.68		
	-	1.32 ± 0.04	-		
4	0.36	1.685 ± 0.03	100.38	1.41 ± 0.04	6.38
	0.60	1.914 ± 0.03	99.55		
	-	0.65 ± 0.03	-		
5	0.36	1.008 ± 0.06	99.70	0.70 ± 0.001	7.14
	0.60	1.239 ± 0.08	98.31		
	-	1.13 ± 0.07	-		
6	0.36	1.476 ± 0.05	98.76	1.11 ± 0.03	1.77
	0.60	1.738 ± 0.04	100.70		
	-	1.06 ± 0.06	-		
7	0.36	1.431 ± 0.03	101.03	1.12 ± 0.02	5.36
	0.60	1.654 ± 0.02	99.43		
	-	1.45 ± 0.09	-		
8	0.36	1.807 ± 0.01	99.79	-	-
	0.60	2.055 ± 0.04	100.34		

*%RE = $100 \times (|\text{measured value} - \text{actual value}|) / \text{actual value}$. 1 - 8: mineral water samples of differences marks.

Table 6. Recuperation studies by antimony determination in drinks samples packaged in PET bottles.

Sample	Sb(III) Added ($\mu\text{g}\cdot\text{L}^{-1}$)	Propose Methodology		ETTAS	RE%*
		Sb(III) Found \pm SD ($\mu\text{g}\cdot\text{L}^{-1}$)	Recovery (%, n = 4)	Sb(III) Found \pm SD ($\mu\text{g}\cdot\text{L}^{-1}$)	
1	-	2.04 \pm 0.01	-		
	0.60	2.632 \pm 0.03	99.61	2.15 \pm 0.001	5.11
	0.72	2.748 \pm 0.05	99.41		
2	-	1.39 \pm 0.06	-		
	0.60	1.987 \pm 0.02	100.52	1.30 \pm 0.02	6.47
	0.72	2.105 \pm 0.08	101.43		
3	-	1.98 \pm 0.03	-		
	0.60	2.587 \pm 0.06	99.78	1.84 \pm 0.003	7.07
	0.72	2.703 \pm 0.06	100.15		
4	-	2.22 \pm 0.06	-		
	0.60	2.830 \pm 0.02	100.45	2.50 \pm 0.04	11.2
	0.72	2.943 \pm 0.07	100.13		
5	-	0.33 \pm 0.03	-		
	0.36	0.679 \pm 0.01	96.66	0.303 \pm 0.07	8.18
	0.48	0.803 \pm 0.04	97.87		
6	-	0.16 \pm 0.04	-		
	0.36	0.523 \pm 0.02	101.87	□	-
	0.48	0.644 \pm 0.05	102.50		
7	-	1.06 \pm 0.02	-		
	0.36	1.411 \pm 0.05	99.15	1.10 \pm 0.02	3.63
	0.48	1.537 \pm 0.01	99.72		
8	-	1.45 \pm 0.04	-		
	0.36	1.804 \pm 0.07	99.59	-	-
	0.48	1.919 \pm 0.07	99.24		
9	-	3.23 \pm 0.03	-		
	0.60	3.841 \pm 0.02	100.34	3.15 \pm 0.07	1.54
	0.72	3.955 \pm 0.09	100.15		
10	-	2.91 \pm 0.01	-		
	0.60	3.501 \pm 0.02	99.69	3.02 \pm 0.01	3.64
	0.72	3.647 \pm 0.03	100.58		

*%RE = $100 \times (|\text{measured value} - \text{actual value}|) / \text{actual value}$. 1 - 4: flavored water without carbonated (flavors: 1: grapefruit, 2: tropical fruits, 3: lemonade and 4: apple). 5 - 8: flavored water carbonated (flavors: 5: lemon-lime; 6: cola; 7: tonic and 8: orange). 9 and 10: hydrating drinks (flavors: 9: apple; 10: orange).

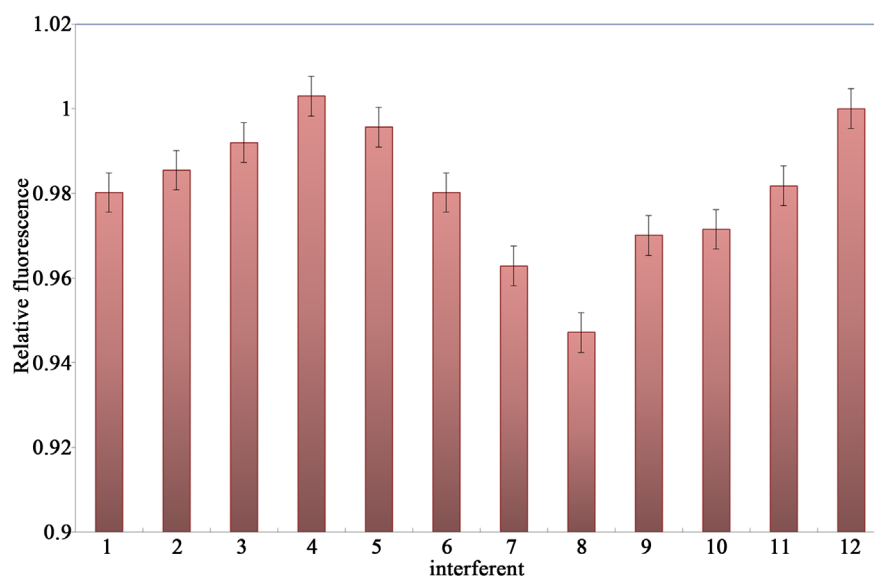


Figure 4. Study of cation interferences of Sb(III) quantification. %SDs (I-I) have been included for each interferent. Interferent/Sb(III)mole ratio (100/1). Conditions: $\lambda_{em} = 450$ nm; $\lambda_{exc} = 363$ nm; $C_{Az} = 5 \times 10^{-7}$ mol·L⁻¹, $C_{NaC} = 2 \times 10^{-5}$ mol·L⁻¹; C_{buffer} Sodium borate = 1×10^{-4} mol·L⁻¹, pH 10.7, $C_{(Sb(III))} = 0.60$ μ g·L⁻¹. Other experimental conditions are described under procedure. 1: Sb(III) = 0.60 μ g·L⁻¹; 2: Idem 1 in presence of Na (I); 3: Idem 1 in presence of K (I); 4: Idem 1 in presence of Mg (II); 5: Idem 1 in presence of Cd (II); 6: Idem 1 in presence of Pb (II); 7: Idem 1 in presence of Zn (II); 8: Idem 1 in presence of Ni (II); 9: Idem 1 in presence of Ca (II); 10: Idem 1 in presence of Tl (I); 11: Idem 1 in presence of Al (III); 12: Idem 1 in presence of Fe (III).

Repetitivity of the assay was evaluated by repeating the analysis four times for each sample. **Table 5** shows the recovery results achieved. The results obtained indicate that the proposed method is suitable for Sb(III) determination in studied samples.

As there are not Certified Materials available, to check the accuracy of the proposed method, studied samples were analyzed by electrothermal atomic absorption spectrometry (ETAAS), using the instrumental conditions cited in **Table 1**. Results obtained for replicate samples ($n = 4$) with proposed method and ETAAS technique were statistically compared (t-test) and no significant differences ($p = 0.05$, $DF = 3$) were observed.

Sbanalyte, which can have both acute and chronic toxicity effects, is regulated in drinking waters in different countries such as United States, Canada, Europe, and Japan at action levels ranging from 2 to 6 μ g·L⁻¹ [32]. Nevertheless, in our country, current legislation does not yet regulate antimony concentrations in beverages intended for human consumption.

6. Conclusion

Although atomic spectroscopies are the most important techniques for metal traces analysis, they require specialized and very expensive instruments. The continued importance and employment in work areas of Sb and its toxicity in environmental health has demanded the development of simple and rapid ana-

lytical methods for its determination. Developed methodology proposes the antimony traces determination based in the formation of the association Sb(III)/Az. Solid phase extraction strategy demonstrated efficacy to preconcentration/eliminate possible interferences. This method constitutes a green alternative to traditional preconcentration methods, showing advantages such as lower cost (associated with the use of filter paper as a solid support for the analyte retention), operator and environment safety, use of non-polluting solvents and operational simplicity. The level of sensitivity attained was comparable to those of atomic spectroscopies. The good tolerance at common constituents suggests high selectivity and versatility of the new method. Precision and accuracy were tested with excellent agreement. Results were truenessed by ETAAS with satisfactory concordance. The method developed was successfully applied to Sb(III) quantification in drinking water and beverages samples packaged in PET bottles widely consumed in Argentina. Considering the toxicity of the metal studied, the need to minimize its presence in drinking for human consumption and the absence of legislation that regulates the content of Sb, we emphasize the importance of informing and raising awareness among the population about the precautions to be taken once the PET containers are opened. Namely, consume in a short time, keep refrigerated until the contents of the package are finished and avoid direct exposure to sunlight.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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