



Antimony Traces Water Monitoring Using Surfactant Sensitized Solid Phase Extraction and Solid Surface Fluorescence

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Abstract

Antimony (Sb) is a nonessential metal to life and is currently considered an emerging contaminant due to its increasing presence in the environment and its toxic effects on humans, plants, and animals. Human activities such as mining, smelting, and burning of fossil fuels, along with the minerals erosion and waste, release antimony into soil and water, posing a serious threat to ecosystems and public health. The objective of this study was to evaluate trace levels of Sb(III) in water samples from the northern and central regions of Argentina using a novel methodology. Sb(III) was complexed with the fluorophore 1,4-dihydroxy-9,10-anthraquinone (quinizarin, QZ) followed by solid-phase extraction using filter paper pretreated with hexadecyltrimethylammonium bromide (HTAB). The analyte was subsequently quantified by solid surface fluorescence ($\lambda_{em} = 575$, $\lambda_{exc} = 490$). At optimal experimental conditions, the calibration curve was linear from 2.69 to 4.6×10^5 ng·L⁻¹ of Sb(III) ($R^2 = 0.9983$) with a detection limit of 1.22 ng·L⁻¹ and a quantification limit of 2.69 µg·L⁻¹. Samples of mains, natural and bottled (untreated) water from 10 Argentine provinces were successfully analyzed, with an average recovery close to 100%. Solid-phase extraction demonstrated efficacy in removing potential interfering ions. Reproducibility (inter-day precision) was evaluated over 5 days, performing five daily determinations, and the CV obtained was 0.37. The results were validated using electrothermal atomic absorption spectrometry (ETAAS) with good agreement. The new methodology has a low operating cost, is easy to implement, and does not require organic solvents. The sensitivity and selectivity achieved through solid-phase extraction make it a suitable alternative to conventional techniques for determining traces of Sb(III).

Subject Areas

Analytical Chemistry

Keywords

Antimony, Solid-Phase Extraction, Solid Surface Fluorescence, Water Samples

1. Introduction

Antimony (Sb), as an element, has been known since ancient times and has been used by many civilizations for different purposes. It is classified as a heavy metal, since it has a specific density of more than 5 gr/cm³ [1], and it has adverse effects on the health and physiology of living organisms [2]. Sb is a metalloid that is often combined with other metals to form hardened alloys used in lead-acid batteries, solder, sheet metal, pipes, metal bearings, castings, and munitions. Furthermore, exposure to Sb can come from air, water (tap water, bottled water, and contaminated natural water sources), soil, as well as from cosmetics and older medications (Figure 1). Various factors, such as environmental persistence and mobility, cause this element to accumulate in the environment, endangering ecosystems and sources of drinking water for extended periods.

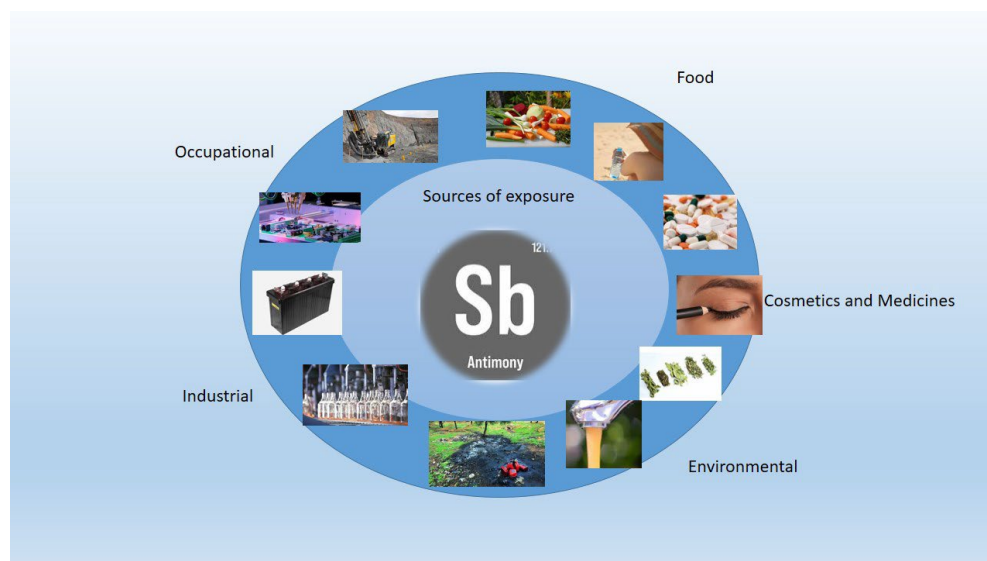


Figure 1. Main sources of exposure to Sb(III).

Commonly, it forms compounds with a valence state of (III) or (V) that have applications in products including polyethylene terephthalate water bottles and fire retardants applied to fabrics [3]. It exists in four valence states: 0, -3, +3, and +5. Most absorbed Sb is excreted rapidly through the urine and feces. Elimination and the route of excretion depend on the type of Sb compound. Urinary excretion

is higher for pentavalent than for trivalent Sb compounds, whereas gastrointestinal excretion is higher for trivalent than for pentavalent Sb. Some data on humans, as well as on animals, indicate that a small part of absorbed and retained Sb may have a long biological half-life, especially in the lung. After acute or chronic oral or parenteral exposure to Sb, the highest concentrations are found in the thyroid, adrenals, liver, and kidney [4] [5].

Both heavy metals and metalloids pose a particular danger to human health as they are non-biodegradable and therefore prone to accumulate in biological systems. In recent years, concern about Sb exposure has focused on potential mutagenic and carcinogenic risks [4].

It is for this reason that it is necessary to have simple and precise analytical methodologies that allow the quantification of Sb in complex samples. Today, the most commonly analytical methods for Sb are atomic spectroscopies: atomic fluorescence spectrometry [6], inductively coupled plasma mass spectrometry [7]-[9] and inductively coupled plasma optical emission spectroscopy [9]. Although these methodologies are characterized by high precision and reproducibility, the equipment used is expensive and requires high maintenance. Among the less common methodologies are radiochemical methods [10] and UV-vis spectrophotometry; the former are difficult to access due to the need for highly complex security laboratories; the latter, while widely useful in routine laboratories due to their safety and relatively low instrument cost, often prove to be less selective for the analysis of complex samples, being necessary to introduce a previous cleaning treatment [11] [12].

In this sense, molecular fluorescence offers interesting analytical characteristics due to its high sensitivity and adequate selectivity, combined with its instrumental availability. Although not all substances possess native fluorescence, its applicability is feasible if an appropriate derivatization reaction is used [13] [14].

This work proposes the Sb(III) traces determination by solid surface fluorescence. The QZ fluorophore is used as chelant reagent of analyte; the product is retained on filter paper treated with HTAB cationic surfactant and the solid support is presented to spectrofluorimeter for spectroscopic measure by solid phase fluorescence. The experimental variables that influence on preconcentration and measurement steps will be studied and optimized. The new methodology will be applied to Sb(III) traces quantification present in argentinian water samples. Given the toxicity of Sb(III), we have focused our determination on this valence state. However, our goal in the future is to adapt the new method for the analysis of total antimony (e.g., after a pre-reduction step).

2. Experimental

2.1. Chemicals and Apparatus

Reagents

Stock solutions of Sb(III) were prepared by dilution of 100 $\mu\text{g}\cdot\text{mL}^{-1}$ 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 1,4-Dihydroxyanthraquinone, also called quinizarin (QZ) 1×10^{-3} mol·L⁻¹ (E-Merck, Darmstadt, Germany) was prepared by dissolving appropriate amounts of each reagent in ethanol (Sigma Chemical Co., St. Louis, MO, United States) and were kept in refrigerator (4 °C) for two weeks.

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

Potassium dihydrophosphate (2×10^{-2} mol·L⁻¹—Biopack, Buenos Aires, Argentina), solution was prepared (1×10^{-2} mol·L⁻¹). This solution was adjusted to the desired pH, with aqueous HCl (Merck, Darmstadt, Germany) or NaOH (Mallinckrodt Chemical Works) using a pH meter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA) Model EA 940.

Hexadecyltrimethylammonium bromide (HTAB, 1×10^{-4} - 1×10^{-6} mol·L⁻¹, Sigma-Aldrich, St. Louis, USA) and Sodium Dodecyl Sulfate (Sigma-Aldrich, St. Louis, USA) surfactants.

The stability of solutions was checked by spectrophotometric measurements. All used reagent were analytical grade.

2.2. Apparatus

All spectrofluorimetric measurements were made using a Shimadzu RF-5301 PC spectrofluorophotometer equipped with a 150 W Xenon lamp and devices for solid supports. Instrument excitation and emission slits both were adjusted to 3/5 nm. ($\lambda_{em} = 575$, $\lambda_{exc} = 490$).

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 autosampler. 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**.

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.

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
Pyrolysis	600	10	-	1.0
	600	-	10	1.0
	600	-	3	0.0 ^a
Atomization	2400	-	2	0.0 ^a
Cleaning	2500	-	2	1.0

^a = Data acquisition.

2.3. Sample Collection and Treatments

The proposed methodology was applied to the analysis of 25 samples of tap, and mineral bottled water from the northern and central regions of Argentina.

The samples of mineral waters were purchased in supermarkets and chosen taking into account the most consumed by the Argentine population in these specific regions of the country. 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 sampling strategy was used; three examples of the same brand for each product were acquired. Entire products were homogenized and reserved for sample preparation. Mineral and tap water were diluted and directly analyzed for Sb(III) quantification.

2.4. General Procedure

A 500 μL QZ solution ($1 \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}$), Sb (III) sample/standard (0.28, 0.56 and $0.82 \mu\text{g}\cdot\text{L}^{-1}$), 100 μL Potassium dihydrophosphate ($0.1 \text{ mol}\cdot\text{L}^{-3}$), pH 7.5 were placed in a volumetric flask. The mixture was diluted to 5 mL with ultrapure water and was filtrated across pretrated with HTAB blue ribbon filter 250 μL ($1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) in 5 mL of ultrapure water 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 2**).

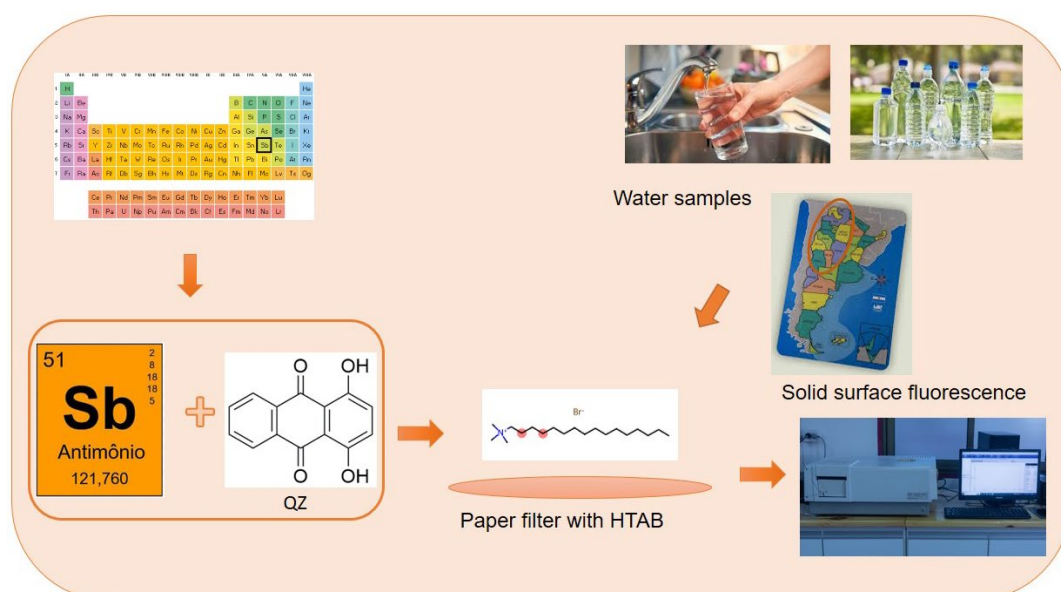


Figure 2. Representative outline of the general procedure.

2.5. Interferences Study

Different amounts of foreign ions, which may be present in samples, (1/100, 1/10, 1/500 and 1/1000 Sb(III)/interferent ratio) were added to the test solution containing $0.28 \mu\text{g}\cdot\text{L}^{-1}$ 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 of 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 0.100 mL of water samples were spiked with increasing amounts of Sb(III) (0.28 and 0.56 $\mu\text{g}\cdot\text{L}^{-1}$). Antimony contents were determined by proposed methodology.

2.8. Precision Study

The repeatability (within-day precision) of the method was tested for water samples replicate samples ($n = 6$) spiked with 0.28 and 0.56 $\mu\text{g}\cdot\text{L}^{-1}$ 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

To evaluate the presence of antimony in natural and bottled drinking water samples from the specific region under study, a complex was formed, and given its low concentrations, a separation/preconcentration step was necessary. A solid-phase extraction (SPE) stage was introduced before the instrumental determination of Sb(III) using SSF. SPE offers a dual benefit: firstly, it allows for the preconcentration of the analyte, thanks to its retention in a small area of the solid support, and secondly, it improves selectivity by isolating the analyte from the complex matrix of the sample, eliminating potential 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.

Quinizarin is an organic compound, specifically a dihydroxyanthracenone (1,4-dihydroxyanthracenone), primarily used as a dye [15]. It has a deep orange color and various applications, including as an intermediate in the synthesis of other dyes, coloring fuels, and in research on organic electronic devices, as well as a pH indicator. Its planar structure allows it to absorb visible light, making it a fluorescent compound used as a sensor to detect and quantify certain ions [16]. In this case, it is used as a fluorophore for the quantification of Sb(III).

The concentration of the chelating agent was also studied by keeping the metal

concentration constant and varying the QZ concentration between 1×10^{-10} and 3×10^{-9} mol·L⁻¹. The concentration of 1×10^{-10} mol·L⁻¹ was selected as optimal, since it is high enough to guarantee an excess of QZ with respect to the expected Sb(III) content in the studied samples (Table 2 and Figure 3).

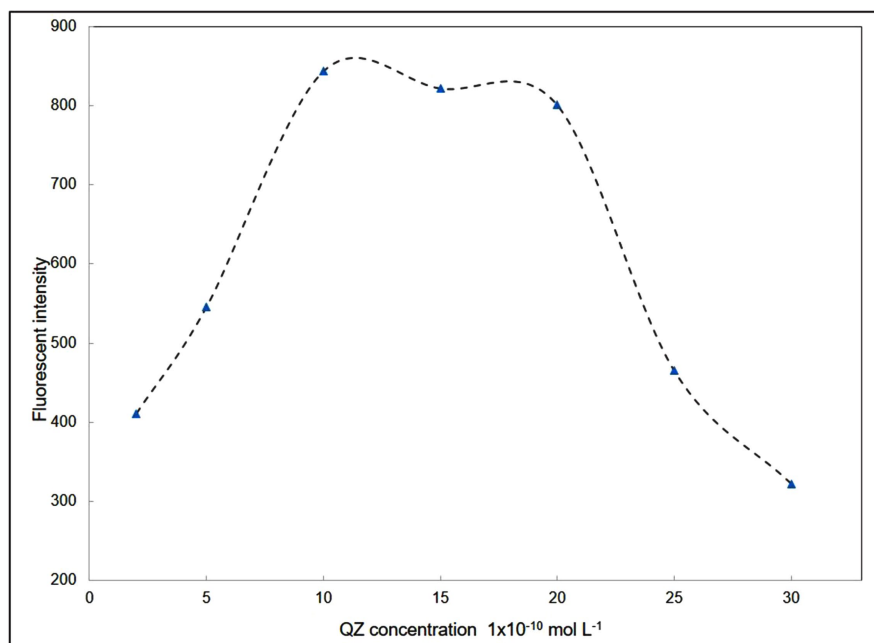


Figure 3. Optimization of Quinizarin (QZ) concentration.

Systems containing QZ solution and increasing concentrations of Sb(III) at pH 7.5 were prepared using potassium phosphate buffer. These systems were filtered through a solid support, dried at room temperature, and the SSF signal of each was determined using a solid sample holder. The SSF of the fluorophore was observed to increase in the presence of Sb(III) as the metal concentration increased.

The retention of the Sb(III)/QZ complex was studied using different solid supports. No retention of the Sb(III)/QZ complex or insufficient signal was observed on any of the supports tested (Table 2). The retention levels for each support analyzed were verified by measuring the SSF intensity at $\lambda_{em} = 575$ nm, using $\lambda_{exc} = 490$ nm. The best results in terms of sensitivity and reproducibility were obtained with blue ribbon filter paper. Therefore, this support was selected for subsequent tests.

Surfactants play a crucial role in analytical chemistry, where they are used to modify the physical and chemical properties of solutions and interfaces, enabling improved performance in various analytical techniques. In spectroscopy (UV-Vis, fluorescence), their use in analyte solubilization and method sensitivity is particularly noteworthy. In our experience, we have previously used surfactants of different natures to improve the separation, extraction, and/or preconcentration of analytes of diverse nature in matrices of varying complexity, achieving satisfactory quantification [17]-[20]. In this particular case, tests were performed with two

surfactants: SDS (anionic surfactant) and HTAB (cationic surfactant).

Hexadecyltrimethylammonium bromide, also known as Cetyltrimethylammonium bromide, [21] is a quaternary ammonium compound widely used in various industrial and laboratory applications. It is an amphiphilic compound, meaning it has a polar “head” and a long, nonpolar “tail”. This structure allows it to reduce surface tension between different phases. It possesses a hydrophilic group with a net positive charge, which gives it a strong affinity for negatively charged surfaces.

In this case, it was the surfactant chosen to pretreat the FP, as it significantly improved the sensitivity of the proposed method. The concentration range studied was $1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ to $2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ with the optimal condition being $5 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ M. The blue ribbon filter paper, when treated with the cationic surfactant HTAB, showed a 5-fold improvement in the method’s sensitivity. The optimal surfactant concentration is shown in **Table 2** and **Figure 4**. As a possible hypothesis for the enhancement of the fluorescent signal caused by the surfactant, we propose that the interaction of the filter paper/HTAB/Sb(III) complex increases structural rigidity, favoring the enhancement of the fluorescent emission.

Therefore, the blue band filter paper was immersed in a solution of HTAB for 2 minutes, allowed to dry at room temperature, and then used for subsequent tests.

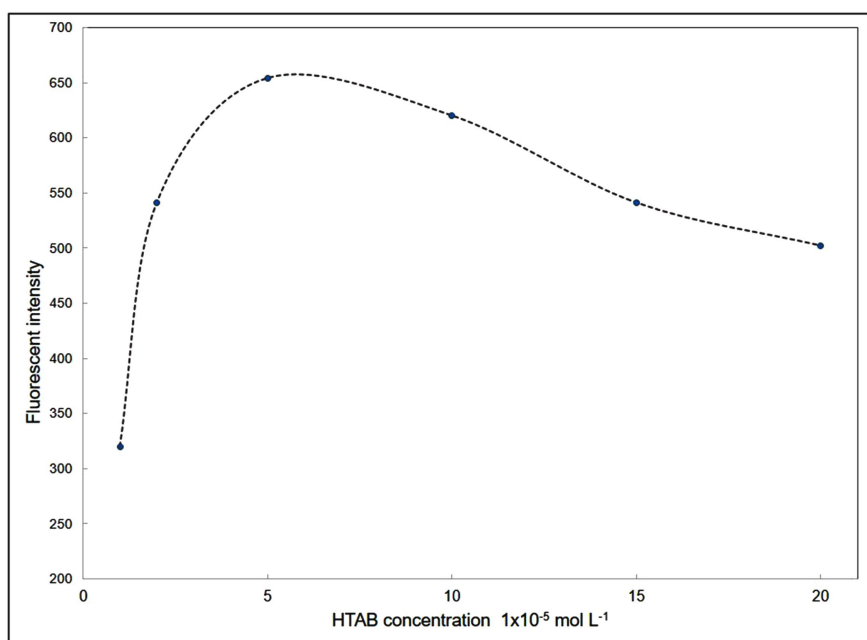


Figure 4. Optimization of HTAB concentration.

The pH is a critical factor in the formation and stability of metal complexes, as it determines the speciation of both the metal ion and the ligand in aqueous solution. Precise pH adjustment is essential to control and optimize the fluorescent intensity and achieve the quantification of Sb(III).

The pH value of the aqueous systems containing a constant concentration of

Sb(III) was adjusted between 3.5 and 10.5 by adding a suitable buffer solution. **Figure 5** shows the results of this study. The highest emission for Sb(III)/QZ was obtained at pH 7.5. Subsequently, the potassium phosphate buffer concentration was tested from $1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ to $2 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ to obtain the maximum fluorescent signal. A buffer concentration of $2 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ was chosen as optimal (**Table 2** and **Figure 6**).

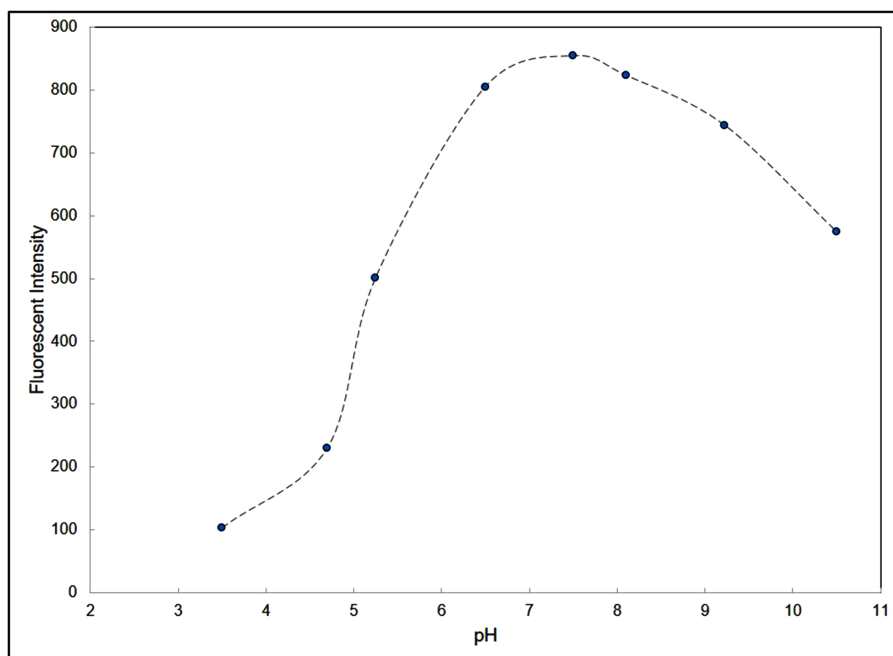


Figure 5. Influence of pH on the signal emission fluorescent of Sb(III) quantification.

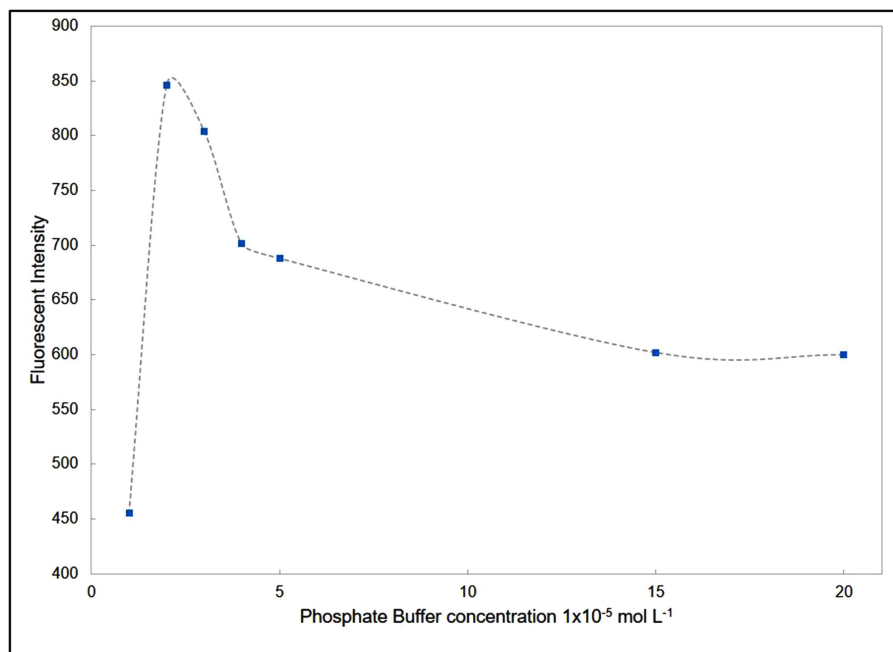


Figure 6. Optimization of phosphate buffer concentration.

Among the potential challenges of this approach are adapting it for applicability to more complex matrices (e.g., industrial wastewater) and studying the long-term stability of the analyzed complex on filter paper.

4. Analytical Parameters

Table 2 summarizes the studied experimental variables, the optimal values for separation/determination of Sb(III)/QZ on FP pretrated with HTAB and analytical parameters for the new proposed methodology. The limit of detection (LOD) was calculated as $3.3 s/m$ [22], 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 $R^2 > 0.9983$.

Table 2. Analytical parameters and Figures de Merit for Sb(III) determination.

	Parameters	Studied Range	Optimal conditions
Analytical parameters	Concentration QZ	$2 \times 10^{-10} \text{ mol}\cdot\text{L}^{-1} - 3 \times 10^{-9} \text{ mol}\cdot\text{L}^{-1}$	$1 \times 10^{-9} \text{ mol}\cdot\text{L}^{-1}$
	pH	3 - 11	7.5
	Potassium dihydrophosphate buffer	$1 \times 10^{-5} - 2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$	$2 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$
	Nature of solid support	Nylon, Acetate, Filter paper: black, white and blue ribbon	Blue ribbon Filter Paper
	Nature of surfactant	SDS and HTAB	HTAB
	HTAB concentration	$1 \times 10^{-5} - 1 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$	$5 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$
Figures of merit	LOD	-	$1.22 \text{ ng}\cdot\text{L}^{-1}$
	LOQ	-	$2.69 \text{ }\mu\text{g}\cdot\text{L}^{-1}$
	Linearity range	-	$2.69 \text{ to } 4.6 \times 10^5 \text{ ng}\cdot\text{L}^{-1}$
	R^2	-	0.9983

The analytical quality parameters obtained present advantages to highlight compared to other methods [6]-[9]: wide linearity range (5 orders of magnitude), LOD on the order of ppt, recovery percentages close to 100% which demonstrates good sensitivity, adequate selectivity and wide dynamic range without generating large economic costs or operational complexity as demanded by other equipment.

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. **Table 3** 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.

Table 3. Tolerance limits of selected interfering species in Sb(III) determination.

Inorganic Interferent/Sb(III) mole ratio	Interferent specie	
	Cations	Anions
1000:1	Na ⁺ , K ⁺ , Li ⁺ , Ca ²⁺ , Mg ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺ , Cd ²⁺ , Mn ²⁺ , Co ²⁺ , Fe ³⁺ , Al ³⁺ , As ³⁺	Cl ⁻ , NO ₃ ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻
500:1	Pb ²⁺ , Cr ³⁺	NO ₂ ⁻ , PO ₄ ³⁻
Organic Interferent/Sb(III) mole ratio	Interferent specie	
1000:1	Caffeine, theobromine, theophylline, nicotine and Atrazine	

5. Applications

The proposed method was applied to natural, tap, and commercially bottled water samples from northern and central Argentina to evaluate the population's potential exposure to this highly toxic substance. Increasing amounts of Sb(III) (from 0.26 to 0.58 µg·L⁻¹) were added to different sample aliquots. The results showed adequate precision (see **Table 4** and **Table 5**).

The repeatability of the assay was evaluated by repeating the analysis six times for each sample. **Table 4** and **Table 5** shows the recovery results. The results indicate that the proposed method is suitable for determining Sb(III) in the studied samples.

Table 4. Recovery studies Sb(III) determination in Tap Water sample.

Samples	Sb(III) added ^a (µg·L ⁻¹)	Proposed methodology		ETTAS validation	%RE ^d
		Sb(III) found ± CV ^c (µg·L ⁻¹)	Recovery ^b (%, n = 6)	Sb(III) found ± CV (µg·L ⁻¹)	
Tap water-San Luis					
1	-	1.23 ± 0.01	-		
	0.28	1.50 ± 0.07	99.19	1.25 ± 0.09	1.60
	0.56	1.77 ± 0.04	98.37		
2	-	1.55 ± 0.05	-		
	0.28	1.86 ± 0.06	101.94	-	-
	0.56	2.12 ± 0.05	100.64		
3	-	1.27 ± 0.03	-		
	0.28	1.53 ± 0.01	98.42	1.29 ± 0.18	1.55
	0.56	1.85 ± 0.04	101.57		
4	-	1.74 ± 0.07	-		
	0.28	2.03 ± 0.03	100.57	-	-
	0.56	2.31 ± 0.03	101.15		

Continued

	-	1.69 ± 0.05	-		
5	0.28	1.98 ± 0.02	100.60	1.68 ± 0.20	0.59
	0.56	2.25 ± 0.02	100.00		
Tap water-Salta					
	-	2.01 ± 0.05	-		
6	0.28	2.28 ± 0.04	99.50	-	-
	0.56	2.57 ± 0.03	100.00		
	-	2.33 ± 0.02	-		
7	0.28	2.60 ± 0.05	99.57	-	-
	0.56	2.91 ± 0.03	100.85		
	-	2.57 ± 0.03	-		
8	0.28	2.86 ± 0.07	100.39	-	-
	0.56	3.14 ± 0.04	100.39		
Tap water-Jujuy					
	-	1.89 ± 0.02	-		
9	0.28	2.16 ± 0.01	99.47	-	-
	0.56	2.43 ± 0.02	98.94		
	-	2.87 ± 0.06	-		
10	0.28	3.16 ± 0.06	100.35	-	-
	0.56	3.41 ± 0.01	99.30		
	-	2.54 ± 0.07	-		
11	0.28	2.84 ± 0.04	100.79	-	-
	0.56	3.08 ± 0.05	99.21		
Tap water-Other provinces					
	-	3.25 ± 0.05	-		
12	0.28	3.53 ± 0.05	100.00	-	-
	0.56	3.78 ± 0.01	99.07		
	-	0.98 ± 0.06	-		
13	0.28	1.25 ± 0.04	98.98	-	-
	0.56	1.55 ± 0.07	101.02		
	-	1.33 ± 0.08	-		
14	0.28	1.60 ± 0.04	99.25	-	-
	0.56	1.92 ± 0.02	102.25		
	-	1.67 ± 0.07	-		
15	0.28	1.98 ± 0.05	101.80	-	-
	0.56	2.25 ± 0.03	101.20		

1—(UNSL Campus-San Luis); 2—Northern Zone of the city of San Luis; 3—Southern Zone of the city of San Luis; 4—Potrero de los Funes-San Luis; 5—Nogoli-San Luis; 6—Salta Capital-Central Zone; 7—Salta-Cafayate; 8—Salta-Cachi; 9—Jujuy-Humahuaca; 10—Jujuy-Purmamarca; 11—San Juan Capital; 12—La Rioja Capital; 13—Tucumán-San Miguel de Tucumán; 14—Catamarca Capital; 15—Catamarca-Tinogasta.

Table 5. Recovery studies Sb(III) determination in Mineral Water sample.

Samples	Sb(III) added ^a ($\mu\text{g}\cdot\text{L}^{-1}$)	Proposed methodology		ETTAS validation	%RE ^d
		Sb(III) found \pm CV ^c ($\mu\text{g}\cdot\text{L}^{-1}$)	Recovery ^b (%, n = 6)	Sb(III) found \pm CV ($\mu\text{g}\cdot\text{L}^{-1}$)	
Mineral Water					
1	-	0.77 \pm 0.01	-		
	0.28	1.07 \pm 0.05	102.60	0.75 \pm 0.09	2.6
	0.56	1.32 \pm 0.07	98.70		
2	-	0.68 \pm 0.07	-		
	0.28	0.94 \pm 0.04	97.06	-	-
	0.56	1.23 \pm 0.04	98.53		
3	-	1.87 \pm 0.02	-		
	0.28	1.14 \pm 0.05		1.93 \pm 0.03	3.2
	0.56	2.42 \pm 0.03			
4	-	1.03 \pm 0.08	-		
	0.28	1.29 \pm 0.04	98.05	-	-
	0.56	1.61 \pm 0.01	101.94		
5	-	1.44 \pm 0.06	-		
	0.28	1.73 \pm 0.07	100.70	1.41 \pm 0.20	4.6
	0.56	2.02 \pm 0.05	101.39		
6	-	0.95 \pm 0.04	-		
	0.28	1.21 \pm 0.04	97.90	-	-
	0.56	1.48 \pm 0.05	96.84		
7	-	1.41 \pm 0.02	-		
	0.28	1.70 \pm 0.07	100.71	-	-
	0.56	1.96 \pm 0.04	99.30		
8	-	0.73 \pm 0.04	-		
	0.28	1.02 \pm 0.02	101.37	0.70 \pm 0.01	4.3
	0.56	1.31 \pm 0.06	102.74		
9	-	1.10 \pm 0.03	-		
	0.28	1.37 \pm 0.02	99.10	1.12 \pm 0.02	1.78
	0.56	1.64 \pm 0.07	98.20		
10	-	1.25 \pm 0.03	-		
	0.28	1.55 \pm 0.04	101.60	-	-
	0.56	1.80 \pm 0.01	99.20		

1—Bottled Mineral Water-Bottled in San Salvador de Jujuy; 2—Bottled Mineral Water-Brand Bottled in Salta; 3—Bottled Mineral Water-Brand Bottled in Catamarca; 4—Bottled Mineral Water-Brand Bottled in Santiago del Estero; 5—Bottled Mineral Water-Brand Bottled in Tucumán; 6—Bottled Mineral Water-Brand Bottled in Mendoza; 7—Bottled Mineral Water-Brand Bottled in Córdoba 1; 8—Bottled Mineral Water-Brand Bottled in Córdoba 2; 9—Bottled Mineral Water-Brand Bottled in San Luis 1; 10—Bottled Mineral Water-Brand Bottled in San Luis 2. ^aMean \pm standard deviation for six determinations. ^b% Recovery = 100 * (analyte concentration in fortified sample – analyte concentration in the unfortified sample)/analyte concentration added in the unfortified sample. ^cCoefficient variation = (SD/mean). ^d%RE (Percent relative error) = 100 \times (|measured value – actual value|)/actual value. Measured value: Sb(III) concentration obtained by applying the developed methodology. Actual value: Sb(III) concentration found by ETAAS.

Since certified materials were unavailable, to verify the accuracy of the proposed method, the samples studied were analyzed using electrothermal atomic absorption spectrometry (ETAAS), under the instrumental conditions indicated in **Table 1**. The results obtained for the replicated samples ($n = 6$) with the proposed method and the ETAAS technique were statistically compared (t-test), and no significant differences were observed ($p = 0.05$).

As previously mentioned, exposure to antimony can cause both acute and chronic toxic effects in the population, which is why drinking water is regulated in several countries worldwide. However, the maximum permissible concentration of antimony in mineral bottle water in Argentina is not explicitly established in the main regulations, as is the case for other contaminants. Nevertheless, a guideline value can be inferred indirectly through the National Guideline Levels for Water Quality, which indicate a limit of $1.5 \mu\text{g}\cdot\text{L}^{-1}$ for filtered water samples from surface sources and $1.2 \mu\text{g}\cdot\text{L}^{-1}$ for unfiltered water samples from groundwater sources [23].

On the other hand, in Argentina, the Argentine Food Code (CAA) establishes a maximum permissible limit for antimony in drinking water, but actual concentrations in the distribution network can vary. The Maximum Permissible Limit: The Argentine Food Code (Chapter XII, "Hydraulic Beverages") establishes a maximum limit of 0.02 mg/L (milligrams per liter) for antimony in drinking water [24]. All the samples analyzed are below this value; therefore, we can say that the current regulations are being met in our country.

6. Conclusion

The developed methodology proposes the determination of trace antimony based on the formation of the Sb(III)/QZ complex, employing solid-phase extraction as a preconcentration/separation strategy. This method has demonstrated effectiveness in real water samples from different sources: tap and mineral bottled. It constitutes an environmentally friendly alternative to traditional preconcentration methods, offering advantages such as lower cost (thanks to the use of filter paper as a solid support for analytical retention), ease of use in laboratories with limited resources (since the equipment is inexpensive), availability for installation in toxicological and environmental control laboratories, safety for the operator and the environment, the use of non-polluting solvents, and operational simplicity. The level of sensitivity achieved was comparable to that of atomic spectroscopies. The good tolerance to common components suggests high selectivity and versatility of the new method. Precision and accuracy were evaluated with good agreement. Given the toxicity of the metal studied, the need to minimize its presence in drinking water, and the lack of legislation regulating its content, we emphasize the importance of informing and raising awareness among the population about the precautions that must be taken to minimize exposure. Consuming water from reliable sources, protecting soil and air, and ensuring safety in the workplace make health a priority that must be addressed from various perspectives.

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Conflicts of Interest

The authors declare no conflicts of interest.

References

- [1] Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B. and Beeregowda, K.N. (2014) Toxicity, Mechanism and Health Effects of Some Heavy Metals. *Interdisciplinary Toxicology*, **7**, 60-72. <https://doi.org/10.2478/intox-2014-0009>
- [2] Periferakis, A., Caruntu, A., Periferakis, A., Scheau, A., Badarau, I.A., Caruntu, C., *et al.* (2022) Availability, Toxicology and Medical Significance of Antimony. *International Journal of Environmental Research and Public Health*, **19**, Article No. 4669. <https://doi.org/10.3390/ijerph19084669>
- [3] Boreiko, C.J. and Rossman, T.G. (2020) Antimony and Its Compounds: Health Impacts Related to Pulmonary Toxicity, Cancer, and Genotoxicity. *Toxicology and Applied Pharmacology*, **403**, Article ID: 115156. <https://doi.org/10.1016/j.taap.2020.115156>
- [4] Li, J., Zheng, B., He, Y., Zhou, Y., Chen, X., Ruan, S., *et al.* (2018) Antimony Contamination, Consequences and Removal Techniques: A Review. *Ecotoxicology and Environmental Safety*, **156**, 125-134. <https://doi.org/10.1016/j.ecoenv.2018.03.024>
- [5] Tylanda, C.A., Tomei Torres, F.A. and Sullivan, D.W. (2022) Antimony. In: *Handbook on the Toxicology of Metals*, Elsevier, 23-40. <https://doi.org/10.1016/b978-0-12-822946-0.00002-7>
- [6] Costa Ferreira, S.L., dos Anjos, J.P., Assis Felix, C.S., da Silva Junior, M.M., Palacio, E. and Cerda, V. (2019) Speciation Analysis of Antimony in Environmental Samples Employing Atomic Fluorescence Spectrometry—Review. *TrAC Trends in Analytical Chemistry*, **110**, 335-343. <https://doi.org/10.1016/j.trac.2018.11.017>
- [7] Li, P., Chen, Y., Hu, X. and Lian, H. (2015) Magnetic Solid Phase Extraction for the Determination of Trace Antimony Species in Water by Inductively Coupled Plasma Mass Spectrometry. *Talanta*, **134**, 292-297. <https://doi.org/10.1016/j.talanta.2014.11.026>
- [8] Gao, Y., Sturgeon, R.E., Mester, Z., Hou, X., Zheng, C. and Yang, L. (2015) Direct Determination of Trace Antimony in Natural Waters by Photochemical Vapor Generation ICPMS: Method Optimization and Comparison of Quantitation Strategies. *Analytical Chemistry*, **87**, 7996-8004. <https://doi.org/10.1021/acs.analchem.5b02001>
- [9] Adhikari, J., Chatterjee, D., Kundu, A.K. and Kulp, T.R. (2020) Optimisation of Laboratory Antimony Measurement Techniques for Environmental Samples. *Internationa-*

- tional Journal of Environmental Analytical Chemistry*, **102**, 5033-5044.
<https://doi.org/10.1080/03067319.2020.1791325>
- [10] Wen, B., Zhou, J., Zhou, A., Liu, C. and Li, L. (2018) A Review of Antimony (sb) Isotopes Analytical Methods and Application in Environmental Systems. *International Biodeterioration & Biodegradation*, **128**, 109-116.
<https://doi.org/10.1016/j.ibiod.2017.01.008>
- [11] Frizzarin, R.M., Portugal, L.A., Estela, J.M., Rocha, F.R.P. and Cerdà, V. (2016) On-line Lab-in-Syringe Cloud Point Extraction for the Spectrophotometric Determination of Antimony. *Talanta*, **148**, 694-699.
<https://doi.org/10.1016/j.talanta.2015.04.076>
- [12] Yağmuroğlu, O. (2022) Accurate and Sensitive Determination of Sb(III) in Water Samples Using UV-VIS Spectrophotometry after Simultaneous Complexation and Preconcentration with Deep Eutectic Solvent/DTZ Probe-Based Liquid-Liquid Microextraction. *Environmental Monitoring and Assessment*, **195**, Article No. 191.
<https://doi.org/10.1007/s10661-022-10809-y>
- [13] Talio, M.C., Feresin, V., Muñoz, V.A., Acosta, M. and Fernandez, L.P. (2019) Nueva metodología analítica para la cuantificación de trazas de Sb(III) como contaminante emergente en muestras de bebidas envasadas en PET mediante fluorescencia de superficie sólida.
- [14] Talio, M.C., Acosta, M. and Fernández, L.P. (2019) Comparative Study of Antimony Exposition by Cigarettes and Alternatives of Tobacco Consumption. *Microchemical Journal*, **145**, 622-629. <https://doi.org/10.1016/j.microc.2018.11.028>
- [15] National Center for Biotechnology Information (2025) PubChem Compound Summary for CID 6688, Quinizarin.
<https://pubchem.ncbi.nlm.nih.gov/compound/Quinizarin>
- [16] Noushija, M.K., Shanmughan, A., Mohan, B. and Shanmugaraju, S. (2022) Selective Recognition and Reversible “Turn-Off” Fluorescence Sensing of Acetate (CH_3COO^-) Anion at Ppb Level Using a Simple Quinizarin Fluorescent Dye. *Chemistry*, **4**, 1407-1416. <https://doi.org/10.3390/chemistry4040092>
- [17] Alesso, M., Bondioli, G., Talío, M.C., Luconi, M.O. and Fernández, L.P. (2012) Micelles Mediated Separation Fluorimetric Methodology for Rhodamine B Determination in Condiments, Snacks and Candies. *Food Chemistry*, **134**, 513-517.
<https://doi.org/10.1016/j.foodchem.2012.02.110>
- [18] Silva, R.A., Talío, M.C., Luconi, M.O. and Fernández, L.P. (2012) Evaluation of Carbon Nanotubes as Chiral Selectors for Continuous-Flow Enantiomeric Separation of Carvedilol with Fluorescent Detection. *Journal of Pharmaceutical and Biomedical Analysis*, **70**, 631-635. <https://doi.org/10.1016/j.jpba.2012.06.031>
- [19] Talio, M.C., Kaplan, M., Acosta, M., Gil, R.A., Luconi, M.O. and Fernández, L.P. (2015) New Room Temperature Coacervation Scheme for Lead Traces Determination by Solid Surface Fluorescence. Application to Wines Produced in Argentina. *Microchemical Journal*, **123**, 237-242. <https://doi.org/10.1016/j.microc.2015.06.014>
- [20] Santarossa, D.G., Talio, M.C. and Fernández, L.P. (2016) Aluminium Traces Determination in Biological and Water Samples Using a Novel Extraction Scheme Combined with Molecular Fluorescence. *Microchemical Journal*, **129**, 274-280.
<https://doi.org/10.1016/j.microc.2016.06.026>
- [21] American Chemical Society (2023) Cetyltrimethylammonium Bromide.
<https://www.acs.org/molecule-of-the-week/archive/c/cetyltrimethylammonium-bromide.html#:~:text=I'm%20a%20surfactant%20and,surface%20Dac-tive%20and%20antiseptic%20properties>

- [22] Allegrini, F. and Olivieri, A.C. (2020) Figures of Merit. In: Brown, S., Tauler, R. and Walczak, B., Eds., *Comprehensive Chemometrics: Chemical and Biochemical Data Analysis*, 2nd Edition, Elsevier, 441-463.
<https://doi.org/10.1016/b978-0-12-409547-2.14612-8>
- [23] Desarrollos de niveles guia nacionales de calidad de agua ambiente correspondientes a antimonio. <https://www.argentina.gob.ar/sites/default/files/documento19.pdf>
- [24] The Argentine Food Code (Chapter XII, "Hydraulic Beverages").
<https://www.argentina.gob.ar/normativa/nacional/resoluci%C3%B3n-33-2023-394636/texto>