

Reliable Quantification of Total Antimony in Environmental Samples by Atomic Absorption Spectrometry Methods

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Abstract

Antimony, a widely utilized element in industrial applications, poses a pollutant of emerging concern. To assess its environmental impact, reliable quantification in various complex matrices is of great importance. Even in speciation analysis, the determination of accurate total concentrations is the first step to obtain reliable results in this research field.

This article provides an overview of total antimony quantification methods using atomic absorption spectrometry (AAS), namely flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), and hydride-generation atomic absorption spectrometry (HG-AAS), all of which involve direct analysis. To ensure reliable results, the experimental conditions must be systematically optimized for each of method. The text delves into a discussion of the most crucial experimental parameters and their impact on achieving accurate and precise quantification.

Keywords: antimony, environmental samples, flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry, hydride-generation atomic absorption spectrometry

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I. Introduction

Antimony (Sb) is a toxic metalloid that finds widespread use in various industries. Its applications span across the production of ceramics, glass, batteries, pigments, pyrotechnics, ammunition, adhesives, and flame retardants [1]. Moreover, it is utilized in specialized fields, such as production of pump sealants, semiconductors, bipolar vacuum tubes, and infrared detectors [2]. The diverse array of industries relying on antimony underscores the essentiality of its mine production.

According to a report by WorldAtlas, the global mine production of antimony has fluctuated in the last decade, reaching a peak of 178,000 metric tons in 2011 and dropping to 111,000 metric tons in 2021 [3]. As a result of mining activities as well as other anthropogenic activities, significant amounts of Sb are released into the environment each year, leading to elevated concentrations in various environmental compartments [4-7]. Growing concerns about the potential adverse impacts of Sb on both natural ecosystems and human health have prompted the development of new analytical procedures to reliably quantify this element [8].

To quantify Sb, several methods are available. Electrochemical methods [9], predominantly anodic stripping voltammetry (ASV), and spectrometric methods [10], such as atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS), are widely employed for this purpose. Among the spectrometric methods, AAS stands out for its widespread accessibility in both research and routine laboratories, making it one of the most frequently employed methods.

II. Atomic absorption spectrometry

Atomic absorption spectrometry (AAS) is a powerful analytical method where gaseous atoms absorb electromagnetic radiation at a specific wavelength, resulting in a measurable signal. This absorption signal is directly proportional to the concentration of free atoms within the optical path. By utilizing this principle, AAS enables precise and sensitive quantification of various elements in a sample, making it a valuable tool in environmental analysis, biological research, and numerous other fields.

In AAS, two primary atomization modes are utilized: flame mode and electrothermal mode. Flame atomic absorption spectrometry (FAAS) mostly involves the use of a premixed combustion flame containing a

mixture of fuel and oxidant gas. The most commonly utilized mixtures consist of air and acetylene or nitrous oxide and acetylene.

FAAS is known for its relatively low sensitivity, which restricts its direct quantification capabilities for Sb in most environmental samples. As a result, this method is typically employed only when a preconcentration procedure is applied as a pre-treatment step to enhance sensitivity for Sb quantification.

In electrothermal atomic absorption spectrometry (ETAAS), atomization occurs within a small tube, also known as a furnace, which is heated by an electric current. The sample size introduced into the furnace is typically small, ranging from 5-100 μ L. Subsequently, the sample undergoes a series of precisely controlled heating steps. These sequential stages are essential to achieve the following objectives: first, to thoroughly dry the sample; second, to eliminate a significant portion of the sample matrix, and finally, to achieve rapid atomization of the element of interest within a fraction of a second.

Most ETAAS instruments utilize a graphite atomizer. Nonetheless, graphite has certain drawbacks such as carbide formation, wall degradation, and analyte diffusion through its porous surfaces. To overcome these limitations, pyrolytically coated and totally pyrolytic graphite tubes have been developed as alternative solutions. These advanced graphite tube variants offer enhanced protection to the inner surface, allowing for increased durability and the ability to withstand more firing cycles.

For the analysis of Sb, the hydride generation (HG) can be employed as a sample pre-treatment technique to introduce the analyte into the atomizer. This technique involves the generation of volatile hydrides from the sample matrix through chemical reduction with a suitable reducing agent. Once formed, these hydrides are transported to the atomizer, where they undergo thermal decomposition, resulting in the formation of free atoms. The atomization step can be carried out in either a quartz tube heated by a flame or by an electric current, or a graphite furnace heated by an electric current. These methods are commonly abbreviated as HG-AAS and HG-ETAAS, respectively.

More detailed descriptions of the methods stated above can be found in interesting monographs [11-13] and reviews [14-16].

III. Quantification of antimony by flame atomic absorption spectrometry

The earliest article found in bibliographic databases that focuses on the quantification of Sb using FAAS dates back to 1977. In this work, Stauffer [17] demonstrated the quantification of total Sb in silica-rich geothermal waters. However, it is important to note that this method was not established on the direct quantification. Instead, the quantification of Sb was achieved after the oxidation of Sb(III) to Sb(V) and subsequent extraction into methyl isobutyl ketone (MIBK).

In another work, too poor sensitivity for direct quantification of Sb by FAAS (1.2-2.0 mg/L) was improved by a simple method using an inexpensive hydride generator with direct introduction into an air-acetylene flame through the nebulisation device of the spectrophotometer [18]. As a result of this procedure, an improved sensitivity level of 0.07 mg/L was achieved.

A procedure based on pulse-nebulization FAAS has demonstrated significantly lower limits of detection (LOD) compared to conventional FAAS for the direct quantification of trace elements, including Sb, in steel samples. This improvement in LOD was attributed to the capability of aspirating more concentrated sample solutions. For Sb analysis in solid steel, the LOD achieved using this method was 10 μ g/g [19].

Another enhanced method, known as the twin-spray method, has been developed for the direct quantification of antimony, bismuth, and mercury using FAAS [20]. This innovative approach resulted in significantly improved sensitivities under optimized conditions, with values 20, 30, and 70 times higher for antimony, bismuth, and mercury, respectively, compared to those achieved with conventional FAAS.

In the analysis of ores with relatively high Sb content, FAAS was utilized for direct quantification after decomposing the samples with aqua regia. The resulting sample solutions were aspirated into an air-acetylene flame adjusted to appropriate conditions [21]. In this specific application, a LOD of 20 μ g/g proved sufficient for accurate quantification of antimony in pyrite samples.

Anyway, looking back to the published procedures for the quantification of Sb by FAAS in real matrices, it becomes evident that the sensitivity of this method was inadequate for accurately quantifying trace concentrations of Sb in environmental samples. As a result, nowadays, FAAS is exclusively employed as a quantification method in combination with a suitable separation/preconcentration procedure. This approach has significantly enhanced the sensitivity of Sb quantification using FAAS, making it a valuable analytical tool for the measurement of trace amounts of antimony in diverse real-world samples.

IV. Quantification of antimony by electrothermal atomic absorption spectrometry

As mentioned above, electrothermal atomization is commonly performed in a graphite furnace. Following sample injection into the furnace, a series of precisely controlled heating steps ensues. Typically, the temperature program in ETAAS consists of four steps: drying, pyrolysis, atomization, and cleaning [15]. Due to the potential

loss of antimony from the graphite furnace at relatively low temperatures, especially when it is present in the form of chlorides, achieving thermal stabilization becomes a crucial criterion in developing a suitable procedure for reliable antimony quantification.

In the absence of chlorides, Sb can remain stable up to 900 °C [22, 23]. Higher pyrolysis temperatures can be used in the presence of chemical compounds containing Pt [24], Pd [23-28], Ir [24], Rh [29], Ni [30, 31], and Cu [30]. Voth-Beach and Shrader [32] utilized Pd in combination with reducing agents, such as ascorbic acid, hydroxylammonium hydrochloride, ammonium citrate, and a mixture of 5% H₂ in argon, to effectively stabilize antimony. A mixture containing palladium and magnesium nitrates has demonstrated its suitability as an effective chemical modifier for various elements, including antimony [33-35]. When using this modifier, a pyrolysis temperature of 1300 °C can be utilized. Another effective chemical modifier is glucose, which also stabilizes antimony up to 1300 °C [36]. Uncommon modifiers such as gluconic and tartaric acids can also be found in the published literature [37]. Dahl et al. [38] tested 13 different chemical modifiers and found that the mixed modifier containing Pd, Pt, Rh, and Ru yielded the best results for the thermal stabilization of antimony when ascorbic acid was used as the reducing agent. Tsalev et al. [39] investigated the thermal stability of some volatile elements (including Sb) and achieved satisfactory results using a mixed modifier containing palladium and tungsten. Niskavaara et al. [23] conducted a study investigating five chemical modifiers (HNO₃, Cu, Ni, Mo, and Pd) for Sb quantification in geological acid extracts and aqueous samples. Their research revealed that Pd yielded the most favorable results, even though the mixture of palladium and ascorbic acid effectively reduced interferences caused by iron. Cal-Prieto et al. [40] reported HNO₃ as the optimal modifier for determining Sb in similar sample types after evaluating five modifiers, namely HNO₃, H₂SO₄, NH₄H₂PO₄, Mg(NO₃)₂, and a mixture of Pd(NO₃)₂ and Mg(NO₃)₂. Additionally, some Pd-based modifiers like Pd, Pd+Zr, Pd+Zr+citric acid, Pd+W, and Pd+W+citric acid have been suggested for determining various elements with different volatilities, including Sb [41]. In these cases, superior outcomes were consistently obtained with mixed modifiers rather than using Pd alone. Another study by Morishige et al. [42] explored the use of several metallic chemical modifiers for Sb quantification by ETAAS. They investigated Pd, Mg, La, and Ni and concluded that Ni served as the most effective modifier due to its ability to form alloys with Sb, characterized by melting temperatures exceeding 1000°C. These findings highlight the significance of appropriate modifier selection to enhance accuracy in the quantification of Sb using ETAAS.

Based on our study [43], we conducted a comparison of pyrolysis curves for antimony using two different chemical modifiers: 0.2% (v/v) HNO₃ and palladium nitrate (15 µg of Pd in 10 µL). In the first case, we employed a pyrolysis temperature of 900 °C, whereas in the second case, a pyrolysis temperature of 1200 °C was utilized. Measurements in the presence of palladium nitrate yielded reliable results for antimony in soil samples of various origin.

While the sensitivity of ETAAS is indeed much better than that of FAAS, there are many cases where the concentrations of Sb are too low to be directly quantified in the analyzed matrix. This is especially evident in natural waters, where ultra-trace concentrations of this analyte are commonly found. However, reliable quantification can be attained by implementing a carefully optimized separation procedure, often involving extraction techniques [44]. Both, liquid-based and solid-based separation templates can be utilized for this purpose [45].

V. Quantification of antimony by hydride-generation atomic absorption spectrometry

Since the introduction of the hydride generation (HG) technique by Holak in 1969 [46], this technique has been studied by many authors.

The HG-AAS method consists of two main steps [47]. In the initial step, the hydride generation process liberates antimony from the sample solution, facilitated by the presence of a reducing agent. The subsequent step involves transporting the released hydride to the atomizer through the flow of an inert purge gas.

During the determination of antimony using hydride generation, the inorganic Sb(III) and Sb(V) species form stibine (SbH₃) with different reaction yields [48]. Under mild acidic conditions (pH > 2), only Sb(III) is efficiently reduced by tetrahydroborate to the required volatile stibine, whereas under strongly acidic conditions (pH < 1), Sb(V) is also converted into a volatile stibine [49]. Due to this fact, for total antimony quantification, the reduction of Sb(V) to Sb(III) using various methods is typically involved. These methods may include the use of potassium iodide alone [50, 51], potassium iodide in combination with ascorbic acid [52], or the employment of L-cysteine [53, 54].

For the selective quantification of Sb(III) in the presence of other antimony species, the addition of citric acid can be employed. However, achieving accurate results requires careful optimization of the citric acid concentration [51].

According to this information, it is evident that careful control of the concentration of the reducing agent (mostly NaBH₄ or KBH₄) together with a suitable acid at an optimal concentration can lead to the development of a reliable procedure to quantify total antimony in the analyzed samples [55].

The pre-treatment procedure of separating antimony from the sample matrix in the form of a volatile hydride offers significant advantages. However, the presence of transition metals, such as Fe, Co, Ni, and Cu, in the sample can influence the hydride generation process when antimony is reduced using sodium tetrahydroborate, potentially leading to a reduction in the antimony analytical signal. It is worth noting that these interferences typically manifest at high metal concentrations, usually on the order of a few tens [56], which are much higher than the typical environmental concentrations. Therefore, in most environmental samples, the impact of these interferences on antimony quantification is minimal.

Furthermore, there is a possibility of interferences arising from other elements capable of forming hydrides, leading to the formation of binary systems in the gas phase. However, this issue can be mitigated by utilizing multielement standards, which enable accurate compensation and correction for any interference effects [57].

VI. Comparison of the AAS methods

As mentioned earlier, the sensitivity of FAAS is inadequate for accurately quantifying trace concentrations of Sb in most environmental samples. However, certain advantages of this method, such as fast and cost-effective analysis, remain important, especially when considering the financial aspect of the analysis. Consequently, FAAS continues to be employed as an effective quantification method in combination with a suitable separation/preconcentration procedure. This approach has significantly enhanced the sensitivity of Sb quantification using FAAS, rendering it a valuable analytical tool for measuring trace amounts of antimony in diverse environmental samples.

Conventionally, ETAAS has primarily served as a mono-elemental detection method. However, with the introduction of commercial multi-elemental instruments, it has become possible to simultaneously analyze several elements (typically ranging from 4 to 6) using multi-element hollow cathode lamps and new solid-state detectors [15]. Furthermore, a continuum light source system has been developed, eliminating the need for multiple lamps and providing improved background correction capabilities [58].

One great advantage of ETAAS lies in the significantly smaller sample volume required (tens of microlitres) compared to FAAS and HG-AAS methods. This feature makes ETAAS particularly beneficial when working with limited sample amounts.

HG-AAS significantly improves the limit of detection by a factor of 1000 or much more compared to FAAS, and by a factor of 10 or more compared to ETAAS. For instance, Nan et al. [59] provided information of LOD for antimony using ETAAS (0.25 µg/L) and HG-AAS (0.028 µg/L). Recently published LOD for direct antimony determination by FAAS can be found in the work published by Yazıcı et al. (2.7 mg/L). However, using a highly improved injection system in FAAS, they were able to improve the LOD to 47 µg/L [60]. All these values demonstrate that HG-AAS enables the quantification of ultra-trace antimony concentrations compared to the other two AAS methods.

Another advantage of HG-AAS is its ability to remove the analyte from the most common matrix interferences present in the original sample. Combining HG-AAS with flow injection analysis further enhances the speed of measurement and allows for the automation of the analysis. However, a pre-treatment procedure involving the reduction of Sb(V) to Sb(III) is necessary for accurate total quantification of antimony, which can be considered a slight drawback as it increases the overall analysis time required to obtain the final result.

VII. Conclusion

Of course, speciation analysis cannot be overlooked. It encompasses the detection of inorganic species like Sb(III) and Sb(V) as well as the identification and quantification of organic species, particularly methylated variants that are commonly found in analyzed samples. Speciation analysis is important due to the fact that antimony species exhibit diverse chemical, biological, and toxicological properties.

While research interest in antimony species was somewhat neglected in the past, there has been a significant increase in knowledge regarding the separation and quantification of antimony species in recent years. The literature now includes both chromatographic and non-chromatographic procedures to distinguish among the various antimony species present in diverse environmental matrices.

Anyway, it can be safely stated that determining the reliable total concentration of antimony is the first and most crucial step even in speciation analysis. Each quantification method capable of achieving this task must undergo careful optimization and verification of experimental conditions, including AAS methods.

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