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Review article

Strategies of sample preparation for speciation analysis of inorganic antimony using hydride generation atomic spectrometry

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ABSTRACT

This paper reports a review about strategies developed for speciation analysis of inorganic antimony employing spectroanalytical techniques.
Generally, the speciation analysis of inorganic antimony is performed in two steps. Antimony(III) is quantified in the presence or absence of citrate, which acts as masking agent for antimony(V). Total antimony is determined after reduction of antimony(V) to antimony(III) using L-cysteine, iodide, thiourea or bromide as reducing agents. Applications and limitations of the procedures used for extraction of the antimony species in liquid and solid matrices have been summarized and discussed. Hydrochloric acid, sulfuric acid and EDTA solutions are the extracting agents more employed for this purpose. Also a brief discussion on the antimony hydride generation is made. Inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS) are the detection techniques more often used in speciation analysis of inorganic antimony. Advantages and drawbacks of coupling of high-performance liquid chromatography (HPLC) with HG AAS, HG AFS and ICP-MS are also discussed.
Procedures involving solid phase extraction, liquid–liquid extraction, cloud point extraction and slurry sampling in methods developed for speciation analysis of antimony are summarized and presented including tables with analytical parameters. Most of the proposed methods were established using solid phase extraction because of the advantages of this separation technique. The literature review reports the period from 2003 to 2013.

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1. Introduction

1.1. Occurrence and use

Antimony is a chemical group VA element known since ancient times which is found in nature mainly as the sulfide mineral (stibnite) [1]. The more ancient industrial applications include alloys prepared for use in solders, bullets and plain bearings. Nowadays, this metalloid is widely employed in brake linings, as additive in the vulcanization process of rubber in the fire industry and several other applications [2–5]. Antimony as organic compounds is used for the preparation of many flame retardants. In the biomedical field, antimony compounds are used as therapeutic agents in parasitic diseases as *Leishmanisis* and *Bilharziasis* [6]. Antimony is found in nature mainly as sulfide stibnite (Sb_2S_3). China has large mines of this metalloid and it has been the largest producer of antimony and its compounds. As a consequence of antimony mining activity, the widespread antimony contamination is prevalent in areas like Xikuangshan (XKS) in Hunan Province, China [7–11].

1.2. Antimony toxicity

The toxicity of antimony and its compounds has been of concern worldwide [12]. The World Health Organization (WHO) [13] and United States Environmental Protection Agency (EPA) [14] establish as maximum admissible concentration of antimony in drinking waters the values of 20 and 6 μg L^{-1}, respectively. Generally, inorganic antimony is more toxic than organic antimony, being that the trivalent species is 10 times more toxic than pentavalent species. This is because antimony(III) shows a high affinity for red blood cells and sulfhydryl groups of cell constituents, while erythrocytes are almost impermeable to antimony(V) [1]. Element antimony is more toxic than its salts. Exposure to antimony and its compounds causes irritation of the respiratory tract, leading to pneumoconiosis. Antimony also can induce other health problems such as: dermatitis, keratitis, conjunctivitis, suppuration of the nasal septum and gastritis [6]. There is no confirmation for carcinogenicity of antimony (III) compounds in humans; however, a research work showed that antimony trioxide and antimony trisulfide have been causes of lung tumors in rats [6]. The International Agency for Research on Cancer has classified antimony trioxide as possibly carcinogenic to humans (Group 2B) [15]. Generally, antimony compounds are 10 times less toxic than arsenic compounds, but it depends also in the oxidation state and chemical structure [1]. Exposure of 9 mg of antimony per cubic meter of air for a long time causes irritation of eyes, skin, and lungs. Respiration of humans with 2 mg of antimony per cubic meter of air can cause problems with the lungs (pneumoconiosis) and heart (altered electrocardiograms), stomach pain, diarrhea, vomiting and stomach ulcers [16]. A study proposed the detoxification of antimony by selenium using paddy rice under hydroponic conditions [17]. In the last years, considering the toxicity of antimony, several research investigations have studied the migration of this element from polyethylene terephthalate (PET), which is the polymer most used for storage of foods and beverages including drinking water [18–20]. Antimony as trioxide (Sb_2O_3) is the main catalyst employed for PET synthesis [21].

1.3. Antimony species

The speciation analysis of antimony has been divided in two groups of species. The classical and conventional speciation involves evaluation of inorganic antimony, by the oxidation states trivalent and pentavalent. In inorganic speciation analysis the compounds commercially available used as standards are the sodium antimonyltartrate for Sb(III) and potassium hexahydroxyantimonate for Sb(V) [1]. The second group involves the organic antimony compounds in environmental and biomedical matrices, being mainly the methylated species such as: monomethylated methyl-stibonic acid [$MeSbO(OH)_2$], dimethylated dimethylstibinic acid [$Me_2SbO(OH)$], monomethylstibine [$MeSbH_2$] and dimethylstibine [Me_2SbH] [22,23]. In occupationally exposed human urine the antimony compound $(CH_3)_3SbCl_2$ (TMSb(V)) has been found [24]. Antimony is associated strongly with soil organic matter, with oxyhydroxides of iron, manganese and aluminum and also clay minerals. These interactions have been subjects for several studies because different antimony species can be formed with organic chelating and macromolecules [25–28].

1.4. Extraction procedures for speciation analysis of inorganic antimony

During the development of analytical methods for speciation analysis of antimony the detection step of the species is well established and consolidated, considering the spectroanalytical techniques: HG AAS, HG AFS, HG ETAAS, HG ICP-MS and HG ICP OES besides the couples of these with separation techniques such as: HPLC, GC and LC. However, the principal difficulty encountered in the speciation analysis of inorganic antimony is in the step of sample preparation (extraction of the antimony species). The volatile character of the antimony species and the impossibility of use of oxidizing acids are the major limitations encountered during the development of these procedures [29]. The sample pretreatment process in speciation analysis for liquid samples is relatively easier than for solid samples. Many methods have been established for speciation analysis of antimony in water samples. Generally, hydrochloric acid is the extracting agent frequently used for aqueous matrices.

De La Guardia et al. proposed a procedure of sample pre-treatment for speciation analysis of antimony and other metalloids in solid sample. This involves firstly an extraction step using 1 M hydrochloric acid solution and subsequently another extraction employing 0.1% (w/v) EDTA solution. This procedure has been used for quantification of antimony species in garlic [30], mushrooms [31] and ten types of cereals [32]. A method for determination of total antimony and antimony(III) in sediments by slurry sampling and HG AAS used a 4 M hydrochloric acid solution for extraction of antimony(III) and antimony(V) species [33]. During the speciation analysis of inorganic antimony in airborne particulate matter using slurry sampling and HG AAS the sample preparation was performed using a 4 M hydrochloric acid and a sonication step at room temperature [34]. For the speciation analysis of inorganic antimony in terrestrial plants, the samples were shaken in 0.1 M citric acid medium for 4 h and afterward sonicated by 1 h. The extract obtained was centrifuged and subsequently filtered. The supernatant was used for the determination of antimony(III) and antimony(V) employing HG-ICP OES [35]. In a method for speciation analysis of antimony in soil samples, the antimony extraction was performed using a 0.25 M oxalic acid solution (pH 1.3) [36]. Other authors have recommended the use of oxalic and citric acids for antimony extraction during speciation analysis of this metalloid in soil and sediment samples [37]. Gregori et al. evaluated the extraction efficiency of total antimony and the stability of antimony(III), antimony(V) and trimethylantimony(V) of four extraction procedures proposed for speciation analysis of antimony in algae and mollusk by HPLC-HG AFS. The authors tested water (at 25 and 90 °C), methanol, EDTA and citric acid. EDTA showed the best results considering the extraction yield for total antimony and the stability of three antimony species [38].

1.5. Analytical techniques for speciation analysis of antimony

Atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS) coupled to hydride generation (HG) are the detection techniques more employed for speciation studies of antimony. In the last years, HG AFS became more popular due to its great sensitivity for antimony determination at trace levels, wide dynamic range and low instrumental cost [39,40]. The major advantage of AFS compared to AAS is the greater sensitivity obtained because the fluorescence signal has a low background. The limits of detection found for antimony using AFS are comparable to those reported for ICP-MS. Also a number of other