AMERICAN RESEARCH JOURNALS
An Academic Publishing House

Levels of Trace Antimony (III) in Water Samples with Single Drop Micro-Extraction using BPHA-[C$_4$mim][PF$_6$] System followed by Graphite Furnace Atomic Absorption Spectrometry Compared to other Analytical Methods

Abraha Gebregewergis

Ethiopian Institute of Agricultural Research, Kulumsa Agricultural Research Center, P.O.BOX 489, Asella, Food Science and Nutrition Research Process, Ethiopia.

ABSTRACT

Antimony is a chemical element with symbol Sb (from Latin: stibium) and atomic number 51. Antimony is can be released naturally from the earth's crust and so is found in soils, natural water bodies and sediments. The toxicity of antimony is a function of the water solubility and the oxidation state of the antimony species under consideration.

Several analytical techniques have been used for the determination of antimony species in various samples. Considering the poor sensitivies of flame atomic absorption spectrometry and UV-visible spectrophotometry, the more limited condition of hydride generation atomic fluorescence spectrometry and the expensive price and analysis cost of inductively coupled plasma mass spectrometry, graphite furnace atomic absorption spectrometry is an efficient alternative to determine amounts of antimony. Despite the high sensitivity of GFAAS, it is still necessary to use separation techniques that allow pre-concentration of antimony species, due to the complex matrix interferences and the low concentration of antimony species in water sample.

After a series of analysis of optimization conditions, an excellent accuracy, precision and lower limit detection were obtained by this method. The relative standard deviation of the 0.5 µg·L⁻¹ Sb (III) was 4.2% (n = 6). The detection limit and the enrichment coefficient of Sb (III) were 0.01 µg·L⁻¹ and 112, respectively. Single Drop Micro-extraction using BPHA-[C$_4$mim][PF$_6$] system followed by Graphite Furnace Atomic Absorption Spectrometry is simple, effective and environment-friendly way to determine the trace concentration of Sb (III) in water samples compared to the other methods.

KEYWORDS: *Antimony; Graphite Furnace Atomic Absorption Spectrometry (GFAAS); Single Drop Micro-extraction (SDME); Water sample.*

INTRODUCTION

Antimony is a chemical element with symbol Sb (from Latin: stibium) and atomic number 51. It was named after the Greek words anti and monos to mean a metal not found alone. It is a lustrous gray metalloid and found in nature mainly as the sulfide mineral stibnite (Sb$_2$S$_3$). Antimony compounds have been known since ancient times and were powdered for use as medicine and cosmetics, often known by the Arabic name, *Kohl* (Al-Ashban et al., 2004). Metallic antimony was also known, but it was erroneously identified as lead upon its discovery. It is used in a wide variety of alloys, especially with lead in battery plates, and in the manufacture of flame-proofing compounds, paint, semiconductor devices, and ceramic products. Antimony is a poor conductor of heat and electricity, it is stable in dry air and is not attacked by dilute acids or alkalis.

Antimony can be found free in nature, but is usually obtained from the ores stibnite (Sb$_2$S$_3$) and valentinite (Sb$_2$O$_3$). Nicolas Lémery, a French chemist, was the first person to scientifically study antimony and its compounds. He published his findings in 1707. Antimony makes up about 0.00002% of the earth's crust (Wilson et al., 2004). The industrial methods for refining antimony are roasting and reduction with carbon or direct reduction of stibnite with iron.

ANTIMONY IN THE ENVIRONMENT

Antimony occurs naturally in the environment. But it also enters the environment through several applications by

humans. Antimony is an important element in the world economy. Annual production is about 50,000 tons per year, with virgin materials coming mainly from China, Russia, Bolivia and South Africa. World reserves exceed 5 million tons. The abundance of antimony in the Earth's crust is estimated to be 0.2 to 0.5 ppm, comparable to thallium at 0.5 ppm and silver at 0.07 ppm. Even though this element is not abundant, it is found in more than 100 mineral species. More frequently it is found in the sulfide stibnite (Sb$_2$S$_3$) which is the predominant ore mineral (Wilson et al., 2004). In groundwater, sources of antimony also include plumbing materials, mining wastes, manufacturing effluent, leaching of fertilizers, leaching of landfills, and fossil fuel combustion products. The most common source of antimony in drinking-water appears to be dissolution from metal plumbing and fittings. The form of antimony in drinking-water is a key determinant of its toxicity, and it would appear that antimony leached from antimony containing materials would be in the form of the antimony(V) oxo-anion, which is the less toxic form (Sundar and Chakravarty, 2010).

Antimony is brittle, silvery-white metalloid with low thermal and electrical conductivity, displaying both metallic and non-metallic characteristics. It is a member of group 15 of the periodic table, one of the elements called pnictogens, and has an electronegativity of 2.05. In accordance with periodic trends, it is more electronegative than tin or bismuth, and less electronegative than tellurium or arsenic (Wieser, 2006).

Antimony is stable under ordinary conditions and is not readily attacked by air or water. It reacts with strong oxidizers, acids and halogenated acids. Generally, antimony is not used alone. It can be mixed with other metals to form antimony alloys or used to form antimony compounds. The most important compounds are antimony oxides, i.e. antimony trioxide and antimony pentoxide. Antimony trioxide is slightly soluble in water. Other less-important antimony compounds include antimony pentasulfide, antimony chloride, antimony potassium tartrate, antimony trichloride, antimony trisulfide and antimony hydride (or stibine).

Although the elemental form of antimony is relatively non-toxic (at low levels), certain antimony compounds (such as SbH$_3$ and Sb$_2$H$_3$) are highly toxic. If exposed to antimony at high levels, irritation to the lungs, eyes, and skin can occur. Even worse, inhaling antimony for long periods of time can result in severe damage to the lungs and/or heart. Antimony can be assimilated by inhalation of Sb salt or oxide dust, ingested with (contaminated) foods or fluids. Inhalation may occur in industrial areas where smelting or alloying is done (usually with copper, silver, lead, tin). Antimony is present in tobacco at about 0.01% by weight; about 20% of this is typically inhaled by cigarette smoking (Sundar and Chakravarty, 2010)).

APPLICATIONS OF ANTIMONY

Antimony is mainly used to form alloys (mixtures of metals), which are used for castings, bearings, metal sheeting and piping, pewter, solder and lead storage batteries. Antimony oxide is added to plastics and textiles to reduce flammability. It is also used as enamel for plastics, metals and glass and is added to paints and ceramics. Very pure antimony is used to make certain types of semiconductor devices, such as diodes and infrared detectors. Antimony is alloyed with lead to increase lead's durability. The ancient Egyptians used antimony in the form of stibnite for black eye make-up (Grund et al., 2006).

HEALTH RISKS OF ANTIMONY

The toxicity of antimony is a function of the water solubility and the oxidation state of the antimony species under consideration. In general, antimony (III) is more toxic than antimony (V), and the inorganic compounds are more toxic than the organic compounds, with stibine (SbH$_3$) being most toxic (by inhalation). Soluble antimony salts, exert a strong irritating effect on the gastrointestinal mucosa and trigger sustained vomiting. Other effects include abdominal cramps, diarrhea and cardiac toxicity (Sundar and Chakravarty, 2010). Antimony can enter the body by inhalation of air containing antimony, by ingestion of food or water containing antimony, or by dermal contact with antimony. The greatest concern with regard to the carcinogenicity of antimony compounds relates to the inhalation route. ATO has been found to be carcinogenic to experimental animals in inhalation studies and to cause direct lung damage following chronic inhalation as a consequence of overload with insoluble particulates (Sundar and Chakravarty, 2010).

GUIDELINES FOR ANTIMONY

The 8-hour time-weighted average (TWA) is set at 0.5 mg/m^3 by the American Conference of Governmental Industrial Hygienists and by the Occupational Safety and Health Administration (OSHA) as a legal permissible exposure limit (PEL) in the workplace. The National Institute for Occupational Safety and Health (NIOSH) has set a recommended exposure limit (REL) of 0.5 mg/m^3 as an 8 hour TWA (Makris, 2013). Antimony concentrations in fruit juice concentrates are somewhat higher (up to 44.7 µg/L of antimony), but juices do not fall under the drinking water regulations. The current WHO guideline value for Sb is 20 µg/L, the European Specific Migration Limit (SML) for antimony is 40 µg/L. The Japanese drinking water standard is 2 µg/L. The TDI proposed by WHO is 6 µg antimony per kilogram of body weight. The IDLH (immediately dangerous to life and health) value for antimony is 50 mg/m^3 (WHO, 2003).

ANALYTICAL METHODS

Antimony can be determined by graphite furnace atomic absorption spectrophotometry (GFAAS), with a detection

limit of 0.8 µg/L (EPA Method 204.2). More sensitive determination is possible using inductively coupled plasma mass spectrometry, with detection limits of 0.1 µg/L in the presence of three other metals (ICI-Technology, 1996) and 0.02 µg/L (EPA Method 6020). Hydride-generation atomic absorption spectrometry (HGAAS) has been applied to determine trace antimony in such samples as water, atmospheric particulate, steel, geological, and biological materials. Although this technique is highly sensitive for determining hydride forming elements, introduction of a large quantity of water vapor into a heated quartz furnace results in deterioration of the furnace and reduces the sensitivity of the determination.

Several techniques including UV-visible spectrophotometry (Samadi-Maybodi and Rezaei, 2012), inductively coupled plasma mass spectrometry (Li et al., 2015), hydride generation atomic fluorescence spectrometry (Zhang et al., 2016), flame atomic absorption spectrometry (Nadiki et al., 2013) and electrothermal atomic absorption spectrometry (Lopez-Garcıa et al., 2017) have been used for the determination of antimony species in various samples. Considering the poor sensitivities of flame atomic absorption spectrometry and UV-visible spectrophotometry, the more limited condition of hydride generation atomic fluorescence spectrometry, and the expensive price and analysis cost of inductively coupled plasma mass spectrometry, graphite furnace atomic absorption spectrometry (GFAAS) is an efficient alternative to determinate trace and ultra-trace amounts of antimony. Besides the requirement of a relatively small injection volume, a partially eliminated matrix during the pyrolysis is another advantage of GFAAS. Despite the high sensitivity of GFAAS, it is still necessary to use separation techniques that allow pre-concentration of antimony species, due to the complex matrix interferences and the low concentration of antimony species in water sample.

Many miniaturized techniques such as homogenous liquid-liquid microextraction (Ghiasvand et al., 2005), solid phase extraction technology (Zhang et al., 2007), cloud point extraction (Gurkan et al., 2016), single drop microextraction (Mitani and Anthemidis, 2013), hollow-fiber liquid phase microextraction (Margul et al., 2013) and dispersive liquid phase microextraction (Yousefi et al., 2010) have been used as the processing methods of pre-concentration. Also, these methods have been applied to pre-concentration of antimony species. Compared with other methods, SDMM is a new and environmentally friendly sample pretreatment technology. It has the advantages of low cost, simple device, easy operation, very low amounts of organic solvent, and high enrichment efficiency. For its striking advantages, SDME was selected as the pre-concentration methods. Moreover, considering the toxicity and flammability of organic solvents, the ionic liquid of 1-butyl-3-methyl imidazolium hexafluorophosphate (C$_4$mimPF$_6$) has been employed in SDME because of its environmental friendliness.

Ionic liquids have been used as novel solvents for the extraction of metal ions at room temperature (Wen et al., 2011). Ionic liquid does not have detectable vapor pressure and it can avoid environmental and safety problems. Until now, few analytical applications of SDME method based on (C$_4$mimPF$_6$) for extraction and pre-concentration of Sb(III) have been reported. Thus, further studies in to the use of (C$_4$mimPF$_6$) in SDME are important in order to improve existing methods. In this seminar, a method for Sb(III) determination in water samples by SDME combined with GFAAS is described. BPHA and (C$_4$mimPF$_6$) were employed as complexing agent and extraction solvent, respectively. The SDME system was fully characterized through optimizations of the relevant variables influencing the extraction of Sb(III).

EXTRACTION METHODS

Extraction is the sample separation technique. It has various types such as liquid-liquid extraction, liquid-solid extraction, solid phase extraction, etc.

Liquid-Liquid Extraction (LLE)

LLE is based on establishment of distribution equilibrium of the analytes between two immiscible phases, an aqueous and an organic phase. The disadvantages of LLE are (i) consumption of large volumes of expensive and toxic solvents, (ii) difficult phase separations and (iii) low concentration factor.

Solid Phase Extraction (SPE)

SPE process is based on distribution of analytes between solid sorbent packed in a cartridge and liquid sample which moves through the solid phase. Solid phase usually consists of small porous particles of silica with or without bonded organic phase, organic polymers and ion exchangers. The limitations of SPE are (i) clogging the pores of the solid phase, (ii) SPE needs at least 100 µL of the solvent and (iii) time consuming method due to several steps of operation.

MICROEXTRACTION

Microextraction is defined as an extraction technique where the volume of the extracting phase is very small and extraction of analytes is not exhaustive. In most cases only a small fraction of the initial analyte is extracted for analysis (Pourya Biparva and Amir Abbas Matin, 2012). There are different types of microextractions.

Solid Phase Microextraction (SPME)

SPME is a simple and efficient technique, which eliminates the necessity of using solvents. SPME fiber is quite sensitive to complex matrix such as plasma. With pulling the syringe plunger in, the fiber is protected in the needle and with pulling out; the fiber is exposed to the sample.

Liquid Phase Microextraction (LPME)

LPME is a solvent-minimized procedure, in which only several μL of solvent are required to concentrate analytes from various samples rather than hundreds of mL needed in traditional LLE. It is compatible with GC & HPLC. Extraction normally takes place into a small amount of a water-immiscible solvent from an aqueous sample containing analytes.

Single Drop Micro Extraction (SDME)

SDME is the process of transferring a dissolved substance from one liquid phase to another (immiscible or partially miscible) liquid phase in contact with it. In the single-drop microextraction (SDME) technique, extraction solvent has the form of one drop (1-8 μL) hence called single-drop microextraction. A microdrop of organic solvent, is suspended from the end of Teflon rod immersed in a stirred aqueous solution of the sample. The sample solution is stirred until equilibrium is reached, after which, the drop is retracted into the Teflon rod. Single drop micro extraction (SDME) has emerged as one of the simplest and most easily implemented forms of micro-scale sample cleanup and pre-concentration. An ordinary gas chromatography syringe is used to suspend micro liter quantities of extracting solvent either directly immersed in the sample, or in the headspace above the sample. The syringe is then used to inject the solvent and extracted analytes into the gas chromatography system for identification and/or quantitation (Xiaoshan et al, 2018). Advantages of the SDME include high selectivity, good quantitation, low detection limits, no carryover, higher upper limits of detection and minimal sample preparation. One of the biggest advantages is only one drop of a solvent instead of a SPME fiber is needed. Single-drop microextraction (SDME) has become more popular than other microextraction techniques because it is simple, cost-effective, easy to operate and nearly solvent-free. The technique has been employed successfully for trace analysis in environmental, biomedical and food applications. It is compatible with GC and HPLC, AAS and ICP.

The factors affecting SDME includes the following parameters. These are (i) the kind and volume of extraction solvent, (ii) extraction time, (iii) extraction temperature, (iv) salt addition, (v) pH adjustment and (vi) sample agitation. The disadvantages of SDME are (i) instability of the drop, (ii) small surface of the drop and (iii) slow kinetics of extraction

Dispersive Liquid-Liquid Microextraction (DLLME)

This technique uses μL volume of extraction solvent along with a few mL of dispersive solvents. A cloudy solution is formed when an appropriate mixture of extraction and dispersive solvents is injected into an aqueous sample containing the analytes of interest. Solutes are enriched in the extraction solvent, which is dispersed into the bulk aqueous solution. After centrifugation, analytes in the settled phase can be determined by using conventional analytical techniques. Extraction solvent must be immiscible with aqueous sample solution and disperser solvent must soluble in both of the extraction solvent and aqueous sample solution (Rivas et al., 2009).

The factors affecting DLLME are (i) the kind and volume of extraction solvent, (ii) kind and volume of dispersion solvent, (iii) extraction temperature, (iv) time and (v) salting out. Advantages of DLLME are low cost operation, simplicity, high recovery, high enrichment factor and very short extraction time. Disadvantages of DLLME are low selectivity, requires the use of three solvents, limited solvent choice and requires centrifugation.

GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY

Graphite furnace atomic absorption spectrophotometry (GFAAS) is an analytical technique designed to perform the quantitative analysis of metals in a wide variety of samples. In comparison to standard flame atomic emission or flame atomic absorption methods for the determination of metals at the trace and ultra-trace level, it is an approach that is particularly attractive. The major reasons include: (i) the capability of using relatively small volumes or masses of samples, (ii) it can allow the direct determination of solid samples with minimal sample preparation and (iii) it exhibits high sensitivity primarily because there are no flame gases to dilute the free gaseous atoms that are analyzed.

Table I. Graphite furnace atomizer temperature-rising program

Steps	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (mL.min^{-1})
Drying	120	10	15	250
Pyrolysis	600	5	20	250
Atomization	2000	0	5	0
Cleaning	2400	1	3	250

MATERIALS AND METHODS

Reagents

The experiment water was double distilled deionized water purified by Millipore. Potassium antimony tartrate, N-benzoyl-N-phenyl hydroxylamine (BPHA), sodium thiosulfate, hydrochloric acid, ammonia solutions oxine, dpy, dichloromethane trichloromethane, and 1-butyl-3-methyl imidazolium hexafluorophosphate ([C$_4$mim][PF$_6$]) were used. A 1000 mg·L^{-1} Sb(III) stock solution was prepared by

amounts of potassium antimony tartrate dissolved in double distilled deionized water. The pH of the Sb (III) stock solution was adjusted to 2.0 with 0.1 M hydrochloric acid and 0.1 M ammonia solution.

Instruments

Atomic absorption spectra were performed by a Perkin-Elmer 900T atomic absorption spectrometer equipped with transverse heated graphite atomizer, pyrolytic graphite coated tubes and an antimony hollow cathode lamp recommended by the manufacturer. In the whole operation, except for atomization mode, argon 99.99% was used as protective and purge gas, and the flow rate was 250 mL·min⁻¹. The pH of all solutions was measured by a pH meter. The stirring was performed by a magnetic stirrer. Some instrumental parameters of GFAAS were as follows: the lamp current was 10 mA, the wavelength was 217.6 nm, the spectral band pass was 0.7 nm. Table 1 shows graphite furnace atomizer temperature-rising program.

Preparation of Samples

All the water samples were filtered through a 0.45 μm pore size membrane filter to remove the suspended particulate matters and the pH of all the water samples was adjusted to 2.0 by using 0.1 M hydrochloric acid and 0.1 M ammonia solution. Water samples including bottled mineral water, river water (pH = 6.2, Beijiang River, Shaoguan, China), and tap water were collected locally. Each of the treated water samples was preserved for the later determination.

Process of Single Drop Microextraction

1.9 mL treated water sample or 1 μg·L⁻¹ Sb (III) standard solution and 100 μL of 1×10⁻⁴ M BPHA solution were added to a 5 mL vial. Micro-syringe with 5 μL of [C₄mim][PF₆] was positioned above the vial, and the needle was inserted through the septum. The tip of syringe needle was attached to a flared polytetrafluoroethylene tube. Then, the needle tip was immersed into the sample solution, and the micro-syringe was pushed slowly in order to make the micro-drop hang under the needle tip steadily. The time of the extraction was 6 min under the stirring rate of 600 rpm. After extraction, micro-drop was inhaled into the micro-syringe and injected into the graphite furnace atomic absorption spectrometer for analysis manually.

RESULTS AND DISCUSSION

Chelating Agent and Extraction Solvent

A chelating agent has a great influence on the extraction efficiency of Sb (III). Thus, a suitable chelating agent is very important. Figure 1 shows the pattern of the atomic absorbance of Sb (III) with different chelating agents (BPHA, Oxine, and Dpy) and their background absorbance. It was found that the absorbance signal of Sb (III) with the chelating agent of BPHA was stronger than others. Although

the absorbance signal of Sb (III) with Oxine was good, it had the stronger background interference. The absorbance signal of Sb (III) with Dpy had weaker signal compared with BPHA and Oxine. As a result, BPHA was selected as the chelating agent for SDME.

A suitable extraction solvent is also important for SDME. The density of the extraction solvent can be supposed to be higher than water so that it could keep the drop stable. CH₂Cl₂, CHCl₃, and [C₄mim][PF₆] were evaluated as the extraction solvents. Each extraction solvent was dealt with via three different chelating agents, and then the method of SDME-GFAAS was applied to determine the amounts of Sb (III), and the results are shown in Table 2. Whatever the chelating agent is, [C₄mim][PF₆] always had the strongest signal. Figure 2 described the atomic absorbance of Sb (III) in different extraction agents (CH₂Cl₂, CHCl₃, and [C₄mim][PF₆]) with BPHA as the chelating agent and their background absorbance. Therefore, [C₄mim][PF₆] was selected as the extraction solvent for SDME.
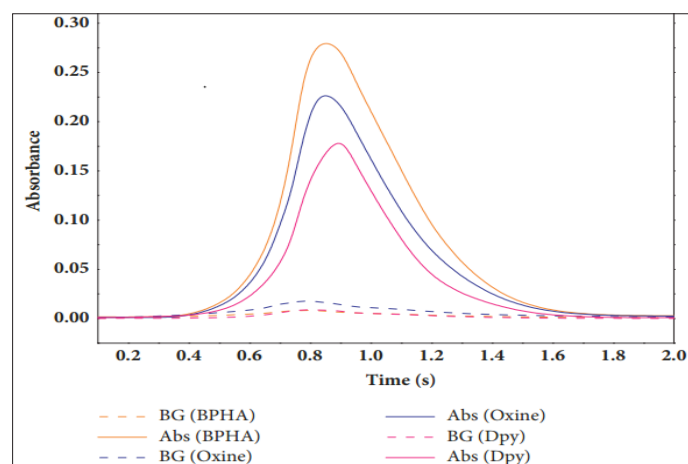

Figure 1. The atomic absorbance of Sb (III) with different chelating agents such as BPHA, Oxine, and Dpy and their background absorbance. BG: background absorbance without Sb (III); Abs: absorbance.
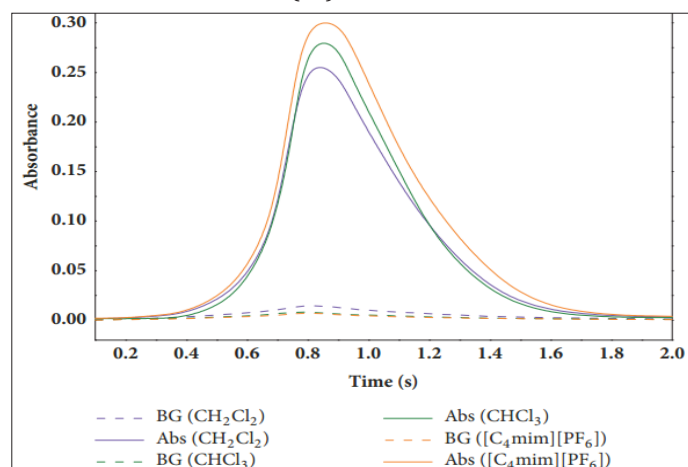

Figure 2. The atomic absorbance of Sb (III) in different extraction solvents such as CH₂Cl₂, CHCl₃, and [C₄mim][PF₆] and their background absorbance; BG: background absorbance without Sb (III); Abs: absorbance.

Table II. The atomic absorbance of three chelating agents in three different extraction solvents

Chelating agent	Extraction solvent		
	CH$_2$Cl$_2$ (Abs.)	CHCl$_3$ (Abs.)	[C$_4$mim][PF$_6$] (Abs.)
Oxine	0.287	0.274	0.294
Dpy	0.158	0.143	0.176
BPHA	0.322	0.355	0.364

Optimization of Single Drop Microextraction Conditions

pH

The pH of the solution played an important role in the formation of metal chelate and the influence of the stability of chemicals. Also, it could affect the extraction of Sb (III) in the BPHA-[C4mim][PF6] system. The effect of pH was studied in the range 1.0 to 6.0 and the results are shown in Figure 3. The absorbance signals of Sb (III) are high and less variable in the range of 1.0-6.0. Considering that there may be interferences due to the competitive complexation reaction of other metal ions when the pH value was at a high level, pH = 2.0 was chosen for the further study.
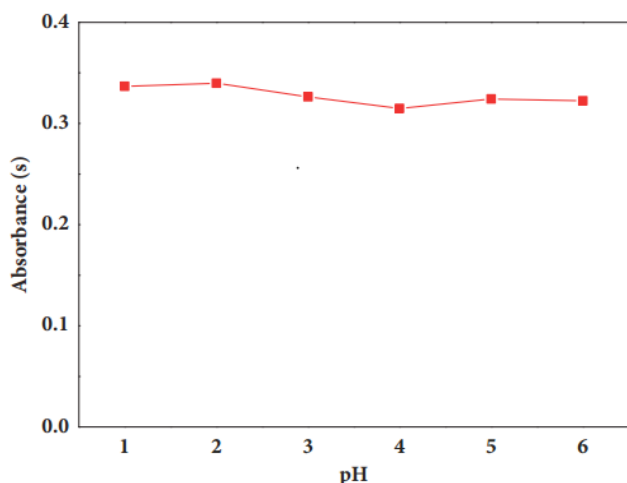

Figure 3. The atomic absorbance of Sb (III) in solutions with the pH value from 2.0 to 6.0

BPHA Concentration

It was also necessary to find the minimal concentration of BPHA. The effect of BPHA concentration on the extraction efficiency of Sb (III) was investigated. The results are illustrated in Figure 4(a) and, as can be seen from it, the absorbance signal of Sb (III) increased with the BPHA concentration from 6×10^{-5} to 8×10^{-5} M and remained constant when the concentration of BPHA is above 8×10^{-5} M. To make the treatment easier, the value of 1×10^{-4} M was chosen for the further study.

Solvent Drop Size

The effect of drop size is shown in Figure 4(b), and it was found that the absorbance of Sb (III) increased with the

increase of the drop size from 2.0 to 6.0 µL. However, the drop size increasing usually resulted in the fall of the microdrop. In general, the stability of the microdrop depends on upward floating force, downward gravity and adhesion forces. In order to enhance the adhesion force of the microdrop, a flared polytetrafluoroethylene tube was attached to the tip of syringe needle. All these things were taken into account, and then 5.0 µL was chosen as the drop size for extraction.

Stirring Rate

It was well known that the stirring rate could affect the extracting speed by changing the mass transfer in the sample solution. The effect of stirring rates on extraction efficiency was studied in the range of 200 to 800 rpm. The results in Figure 4(c) showed that the increasing stirring rate of the sample greatly improved the absorbance of Sb (III). However, the microdrop easily fell off the needle of the microsyringe when the stirring rate was above 600 rpm. Increasing stirring rate could also cause a reduction of [C$_4$min][PF$_6$] microdrop volume, because the dissolution of ionic liquid was enhancing. Thus, 600 rpm was selected as the best stirring rate.

Extraction Time

The extraction efficiency depended on the length of the extraction time until the equilibrium was reached. Although the maximum sensitivity was achieved in equilibrium, complete equivalent was not necessary to obtain accurate analysis. Thus, the effect of extraction time on extraction efficiency had been studied from 2 to 10 min. The results are illustrated in Figure 4(d). There is a sharp increase from 2 to 6 min and a slow increase from 6 to 10 min. As the time went on, microdrop would fall into solutions. In order to avoid it, 6 min was selected as the extraction time which was enough for extracting Sb (III) for determination.

Optimization of Graphite Furnace Atomic Absorption Spectrometry

In order to reduce the chemical interference and the background signal, the work investigated the influence of pyrolysis temperature from 400 °C to 800 °C and atomization temperature from 1800 °C to 2200 °C. The 0.5 µg·L^{-1} Sb(III) standard solutions were dealt with via the pretreatment of SDME and determined by GFAAS. As shown in Figure 5(b), background signals were stronger when the pyrolysis temperature was lower because of the excessive

vaporization of BPHA and ionic liquid at atomization stage, and the strongest signal appeared at 2000 ℃. It was found in Figure 5(a) that the matrix was sufficiently eliminated and maximum absorbance was achieved at the pyrolysis temperature of 600 ℃, however the absorbance decreased with increasing of the pyrolysis temperature due to the loss of Sb at higher temperature. In addition, the time of atomization was 5 s. As the results shown in Figure 5, 2000 ℃ was chosen as the atomization temperature and 600 ℃ as the pyrolysis temperature.

Effect of Interferences

One of the interferences was other metal ions reacting with chelating agents and the other was co-extraction. In order to validate the selectivity of Sb(III) in microextraction system, different amounts of ions were added to the 1.0 µg·L^{-1} Sb(III) solutions, respectively. After determination, coexisting ions were considered to have interferences when the change of Sb(III) absorption value was more than 5%. The results showed that, the tolerance limit of coexisting ions including Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Cl$^-$, SO$_4^{2-}$, and PO$_4^{3-}$ was 2000 mg·L^{-1}; of coexisting ions including Co^{2+}, Cd^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, and Ag$^+$

was 200 mg·L^{-1}; of coexisting ions including Al^{3+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, and Pb^{2+} was 50 mg.L^{-1}.

Standard Analysis

As shown in the results, the low limit of detection (LOD, 3 SD) was 0.01 ng·mL^{-1}, the relative standard deviation of 0.5 ng·mL^{-1} (n = 6) was 4.2%, and the linear value ranged from 0.02 to 50 ng·mL^{-1}. The regression equation was A = 0.6832C + 0.0034 (A represented the absorbance values and C represented the concentration of Sb(III) whose unit was ng·mL^{-1}). The linear correlation coefficient was 0.9990. A comparison of the main features of the proposed method with other reported methods in the literatures is shown in Table 3. This method is more effective for detecting Sb (III) with lower limit detection and has better precision than majority of the other reported methods.

Samples Analysis

A series of water samples were analyzed by the presented method. The results are shown in Table 4. The recoveries are in the ranges of 98-104% with the different standard of Sb(III) solutions spiked to the water samples. Therefore, it demonstrated a good accuracy of this method.
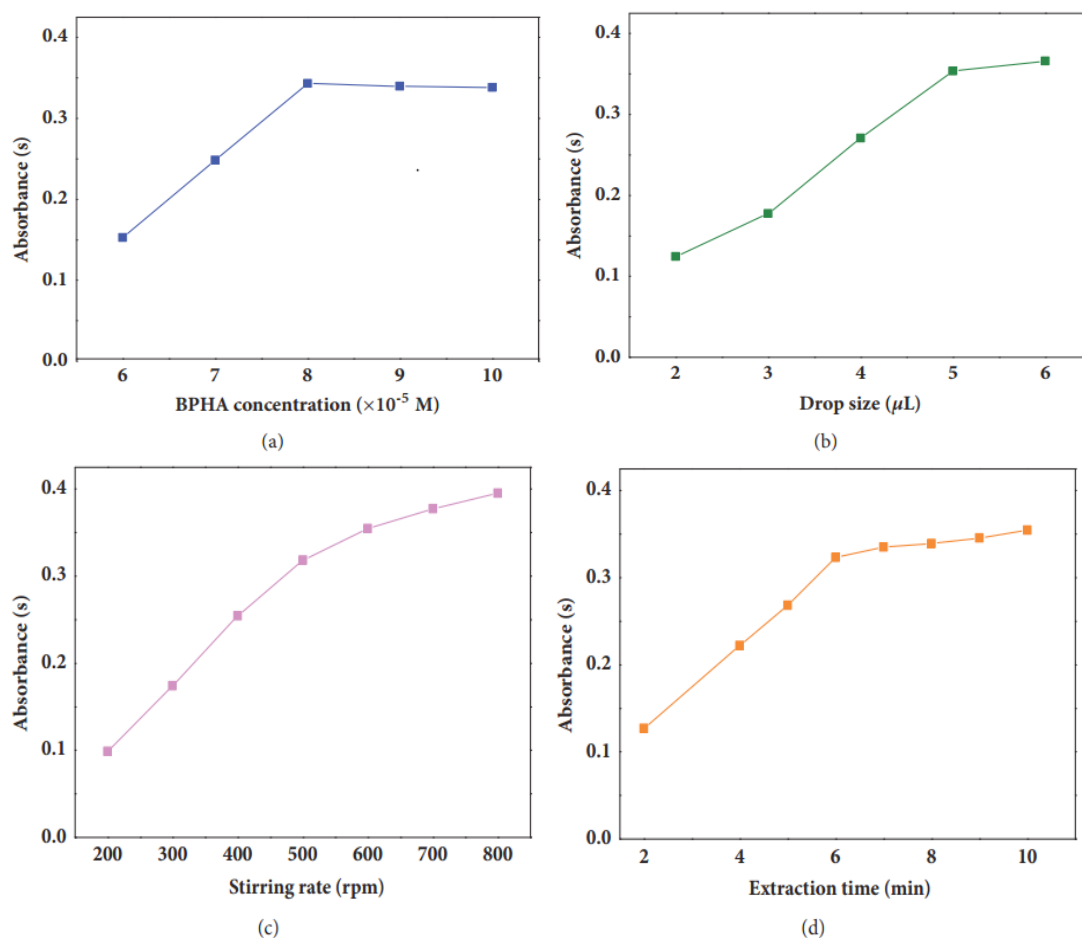

Figure 4. (a) The atomic absorbance of Sb(III) in solutions with the concentration of BPHA from 6×10^{-5} M to 10×10^{-5} M. (b) The atomic absorbance of Sb(III) in solutions with the drop size from 2.0 to 6.0 µL. (c) The atomic absorbance of Sb(III) in solutions with the stirring rate from 200 to 800 rpm. (d) The atomic absorbance of Sb (III) in solutions with the extraction time from 2 to 10 min.
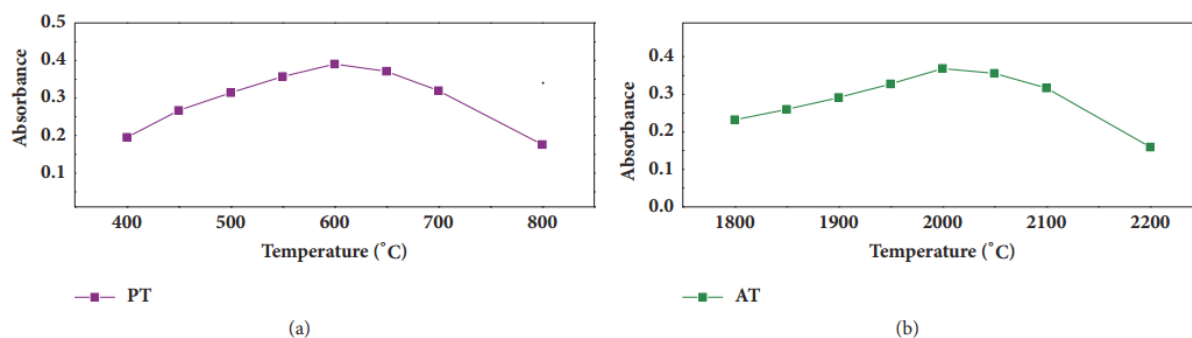
Figure 5. (a) The absorbance of Sb (III) with the pyrolysis temperature (PT) from 400 ℃ to 800 ℃. (b) The absorbance of Sb (III) with the atomization temperature (AT) from 1800 ℃ to 2200 ℃.

Table III. Comparison of the proposed method with other methods for determination of antimony (III).

Method	Linear ranges (ng.mL^{-1})	Limits of detection (ng.mL^{-1})	Enrichment factor	Relative standard deviation (%)	References
SDME-GFAAS	0.02-50	0.01	112	4.2	(Xiaoshan et al., 2018)
DLLME-ETAAS[a]	0.05-5	0.05	115	4.5	(Rivas et al., 2009)
CPE-ETAAS[b]	-	1.82	45	2.6	(Fan, 2005)
VASEME-ETAAS[c]	0.4-8	0.09	53	5.4	(Efekhari et al., 2015)
HFSLME-TAFFAAS[d]	5-200	0.8	160	7.8	(Zeng et al., 2011)

[a]Dispersive liquid-liquid microextraction-electrothermal atomic absorption spectrometry, [b]Cloud point extraction-electrothermal atomic absorption spectrometry, [c]Vortex-assisted surfactant-enhanced emulsification microextraction-electrothermal atomic absorption spectrometry, [d]Hollow fiber supported liquid membrane extraction-thermo spray flame furnace atomic absorption spectrometry

Table IV. Determination of Sb (III) in water samples

Samples	Added (µg.L^{-1})	Found (µg.L^{-1})	Recovery (%)
Bottle mineral water	0.0	< limits of detection	-
	0.1	0.102 ± 0.01	102±1
	0.4	0.401 ± 0.008	100±2
River water	0.0	< limits of detection	-
	0.1	0.104 ± 0.015	104±2
	0.4	0.407 ± 0.012	102±3
Tap water	0.0	< limits of detection	-
	0.1	0.098 ± 0.011	98±1
	0.4	0.398 ± 0.009	99±2

CONCLUSIONS

The optimization method, combined with single drop microextraction using BPHA-[C_4mim][PF_6] system for separation of impurities, detected by GFAAS has been described to determine trace Sb (III) in water samples. After a series of analysis of optimization conditions, an excellent accuracy, precision and lower limit detection were obtained by this method. The relative standard deviation of the 0.5 µg·L^{-1} Sb (III) was 4.2% (n = 6). The detection limit (signal-to-noise ratio of 3) and the enrichment coefficient of Sb (III) were 0.01 µg·L^{-1} and 112, respectively. What is more, the introduction of BPHA-[C_4mim][PF_6] system was not only eco-friendly comparing with traditional organic solution but also

efficient for extraction. After the rapid extraction by SDME with the system of BPHA-[C_4mim][PF_6], the samples could be injected and detected directly. Thus, this method is simple, effective, and environment-friendly way to determine the trace concentration of Sb (III) in water samples.

REFERENCES

1. Al-Ashban, R.M.; Aslam, M.; Shah, A.H. (2004). A toxic traditional eye cosmetic study in Saudi Arabia. *Kohl (Surma), Public Health*, 118(4), 292-298.

2. Dupont, J.; Consorti, C.; Suarez, P.; de Souza, R. (2004). Preparation of 1-butyl-3-methyl imidazolium-based room temperature ionic liquids. *Organic Syntheses,*

Collective, 10, 184. DOI: 10.1002/0471264180. os079.28.

3. Efekhari, M.; Chamsaz, M.; Arbab-Zavar, H.; Efekhari, A. (2015). Vortex-assisted surfactant-enhanced emulsification microextraction based on solidification of floating organic drop followed by electrothermal atomic absorption spectrometry for speciation of antimony(III,V). *Environmental Modeling and Assessment*, 187:4129. DOI: 10.1007/s10661-014-4129-3.

4. Fan, Z. (2005). Speciation analysis of antimony(III) and antimony(V) by flame atomic absorption spectrometry after separation/pre-concentration with cloud point extraction. *Microchimica Acta*, 152(1-2), 29-33.

5. Georges, Audi, Bersillon, O.; Blachot, J.; Wapstra, A. H. (2003). The NUBASE evaluation of nuclear and decay properties. *Nuclear Physics*, 729 (1), 3-12.

6. Ghiasvand, A.R.; Shadabi, S.; Mohagheghzadeh, E.; Hashemi, P. (2005). Homogeneous liquid-liquid extraction method for the selective separation and pre-concentration of ultra trace molybdenum, *Talanta*, 66(4), 912-916.

7. Grund, Sabina C.; Hanusch, Kunibert, Breunig, Hans J.; Wolf, Hans Uwe. (2006). Antimony and antimony compounds in Ullmann's encyclopedia of industrial chemistry. WileyVCH, Weinheim. DOI: abs/10.1002/14356007. a03_055.pub2.

8. Gurkan, R. and Eser, M. (2016). Application of ultrasonic-assisted cloud point extraction/flame atomic absorption spectrometry (UA-CPE/FAAS) for pre-concentration and determination of low levels of antimony in some beverage samples. *Journal of the Iranian Chemical Society*, 13(9), 1579-1591.

9. Li, P.; Chen, Y.-J.; Hu, X.; Lian, H.-Z. (2015). Magnetic solid phase extraction for the determination of traceantimony species in water by inductively coupled plasma mass spectrometry. *Talanta*, 134, 292-297.

10. Lopez-Garcıa, I.; Rengevicova, S.; Munoz-Sandoval, M.J.; Hernandez-Cordoba, M. (2017). Speciation of very low amounts of antimony in waters using magnetic core-modifed silver nanoparticles and electrothermal atomic absorption spectrometry. *Talanta*, 162, 309-315.

11. Makris, K.C. (2013). Association of drinking-water source and use characteristics with urinary antimony concentrations. *Journal of Exposure Science and Environmental Epidemiology*, 23, 120-127.

12. Margul, E.; Sague, M.; Queralt, I.; Hidalgo, M. (2013). Liquid phase microextraction strategies combined with total refection X-ray spectrometry for the determination of low amounts of inorganic antimony species in waters. *Analytica Chimica Acta*, 786, 8-15.

13. Marsden, P.D.; Jones, P.D.; Chang, C.P.; Bray, R.S. (Eds.). (2002). Clinical manifestations, diagnosis and treatment of Leishmaniasis, Elsevier. *Amasterdan*, 198, 193.

14. Mitani, C. and Anthemidis, A.N. (2013). On-line liquid phase microextraction based on drop-in plug sequential injection lab-at valve platform for metal determination. *Analytica Chimica Acta*, 771, 50-55.

15. Nadiki, H.H.; Taher, M.A.; Ashkenani, H. (2013). Ionic liquid ultrasound assisted dispersive liquid-liquid/micro-volume back extraction procedure for pre-concentration and determination of ultra trace amounts of thallium in water and biological samples. *International Journal of Environmental Analytical Chemistry*, 93(6), 623-636.

16. Pourya Biparva and Amir Abbas Matin. (2012). Chapter 4 microextraction techniques as as ample preparation step for metal analysis, atomic absorption spectroscopy, 61–88.

17. Rivas, R.E.; Lopez-Garcıa, I.; Hernandez-Cordoba, M. (2009). Speciation of very low amounts of arsenic and antimony in waters using dispersive liquid-liquid microextraction and electrothermal atomic absorption spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 64(4), 329-333.

18. Samadi-Maybodi, A. and Rezaei, V. (2012). A cloud point extraction for spectrophotometric determination of ultra trace antimony without chelating agent in environmental and biological samples. *Microchimica Acta*, 178(3-4), 399-404.

19. Shotyk, W.; Krachler, M.; Chen, B. (2005). Antimony global environmental contaminant. *Journal of Environmental Monitoring*, 7(12), 1135-1136.

20. Smichowski, P. (2008). Antimony in the environment as a global pollutant: a review on analytical methodologies for its determination in atmospheric aerosols. *Talanta*, 75(1), 2–14.

21. Sundar, S.; Chakravarty, J. (2010). Antimony toxicity. *International Journal of Environmental Research and Public Health*, 7 (12), 4267–4277. DOI: 10.3390/ijerph7124267.

22. Wen, X.; Deng, Q.; Guo, J. (2011). Ionic liquid-based single drop microextraction of ultra-trace copper in food and water samples before spectrophotometric determination. *Spectrochimica Acta*, Part A: *Molecular and Biomolecular Spectroscopy*, 79(5), 1941-1945.

23. Wieser, M.E. (2006). Atomic weights of the elements (IUPAC technical report). *Pure and Applied Chemistry*, 78(11), 2051-2066. DOI: 10.1351/pac200678112051.

24. Wilson, N.J.; Craw, D.; Hunter, K. (2004). Antimony distribution and environmental mobility at an historic

antimony smelter site, New Zealand. *Environmental Pollution*, 129(2), 257-266.

25. WHO. (2003). *Ammonia in drinking-water. Background document for preparation of WHO guidelines for drinking-water quality*, WHO, Geneva.

26. Xiaoshan H.; Mingxin G.; Zhuliangzi Lu.; Yiping Hang. (2018). Determination of trace antimony(III) in water samples with single drop microextraction using BPHA-[C₄mim][PF₆] system followed by graphite furnace atomic absorption spectrometry. *International Journal of Analytical Chemistry*. DOI: org/10.1155/2018/8045324.

27. Yousefi, S.R.; Shemirani, F.; Jamali, M.R. (2010). Determination of antimony(III) and total antimony in aqueous samples by electrothermal atomic absorption spectrometry after dispersive liquid-liquid microextraction (DLLME). *Analytical Letters*, 43(16), 2563-2571.

28. Zeng, C.; Yang, F.; Zhou, N. (2011). Hollow fiber supported liquid membrane extraction coupled with thermo spray flame furnace atomic absorption spectrometry for the speciation of Sb(III) and Sb(V) in environmental and biological samples. *Microchemical Journal*, 98(2), 307-311.

29. Zhang, L.; Morita, Y.; Sakuragawa, A. and Isozaki, A. (2007). Inorganic speciation of As(III, V), Se(IV, VI) and Sb(III, V) in natural water with GFAAS using solid phase extraction technology. *Talanta*, 72(2), 723-729.

30. Zhang, Y.; Mei, M.; Ouyang, T. and Huang, X. (2016). Preparation of a new polymeric ionic liquid-based sorbent for stir cake sorptive extraction of trace antimony in environmental water samples. *Talanta*, 161, 377-383.