Turk J Chem
35 (2011) , 871 – 880.

doi:10.3906/kim-1104-34

Arsenic and antimony determination in refined and unrefined table salts by means of hydride generation atomic absorption spectrometry–comparison of sample decomposition and determination methods

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Received: 14.04.2011

An evaluation was made of different digestion methods for the determination of arsenic and antimony in table salt samples prior to hydride generation atomic absorption spectrometric analysis. Microwave acid digestion, classical wet digestion, dry ashing, and fusion were applied to the decomposition of salt samples and optimum conditions were investigated. Samples were decomposed by changing heating time, digestion techniques, and the amount and composition of acid, and then the concentrations of arsenic and antimony in an unrefined salt sample were measured. It is concluded that microwave acid digestion decomposes salt samples with a very short heating time and with small amounts of reagents compared with the classical wet digestion methods, which require several hours for the heating step and several milliliters of reagents. The accuracy of the procedure was checked using pond sediment certified reference material. The proposed procedure was applied for the determination of arsenic and antimony in several table salt samples collected in İzmir, Turkey, and the arsenic contents in the samples were found to be below the maximum permissible limits. Microwave digestion in combination with hydride generation atomic absorption spectrometry could be used routinely to monitor these metals in table salt samples.

Key Words: Arsenic, antimony, table salt, hydride generation, atomic absorption spectrometry

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Introduction

Arsenic and antimony are potentially toxic elements. The main sources of these elements in the environment are natural or anthropogenic origin, mining, agricultural facilities, industrialization, and traffic. Atmosphere, surface and ground waters, soil, foods, and plants are affected by the trace elements due to these facilities. The toxicological and physiological behaviors of these elements are strongly dependent on their concentration. They are easily accumulated in organisms and cause deleterious effects in humans when their content goes beyond the allowable limit. Determination of arsenic and antimony content is important to protect the health of people and prevent environmental contamination due of their toxicity.[1] However, direct determinations of these elements are difficult because of their low concentrations in environmental samples. Hydride generation (HG) techniques are widely used for the determination of volatile hydride forming elements in analytical atomic spectrometry to enhance detection power and minimize or eliminate matrix interferences while incurring relatively low additional cost and minimal sophistication.[2] This technique has usually been combined with atomic absorption spectrometry (HG-AAS),[3,4] atomic fluorescence spectrometry (HG-AFS),[5] inductively coupled plasma optical emission spectrometry (HG-ICP-OES),[6] and inductively coupled plasma mass spectrometry (HG-ICP-MS).[7] Among these techniques HG-AAS is one of the most commonly used for the determination of such elements. However, several interferences take place in the determination of arsenic and antimony by HG-AAS.[8] One type of interference occurs at the reaction step, which suppresses the volatile hydride formation. Several cations, particularly transition metals, suppress the formation of the arsine and stibine. The second type of interference may occur during transport of the volatile hydrides to the atomizer. The third type of interference may occur at the atomization step; all the volatile hydrides suppress the absorbance signal of the others.[2,9] Interferences for several cations on the formation of the hydrides of arsenic, antimony,[2,10,11] tin, and germanium[11] were eliminated by masking with EDTA, which avoids or delays reduction of interfering cations to their elements and borides, and thus avoids their interferences. Masking of interferences with other complexing agents like iodide,[12] L-cysteine,[13] 1,10-phenanthroline,[14] and thiourea[15] was also reported.

Salt has an important role as an ingredient of food and a carrier of food additives and/or nutrients. Salt is an essential additive routinely added to the majority of foods for improving taste. Every year, several hundred million tons of salt are produced worldwide. Evaporative crystallization combined with the concentration of seawater by electrodialysis using an ion-exchange membrane is a useful technique for table salt production.[16,17] Since seawater often contains various harmful elements at a trace or ultra-trace level,[18] some of these elements may be present in table salts. Therefore, determination of toxic elements, like arsenic and antimony, in table salt is significant from the viewpoints of quality control and food safety. There is no report in the literature about arsenic and antimony determination in table salts produced in Turkey.

The reliability of metal determination in complex matrices mainly depends on the dissolution process used. Sample digestion techniques, such as microwave, and conventional wet acid digestion for total metals determination have been widely used for the dissolution of samples.[19,20] Such digestion techniques require the use of concentrated acids and high temperatures, and often-high pressures, to affect the total dissolution of elements from solid samples.[21,22] The classical wet and dry ashing and fusion digestion procedures are generally slow and time consuming and require high amounts of reagents. Microwave digestion has been described in the literature as a successful sample pretreatment in analytical chemistry and has been preferred because it is more suitable with respect to both time and recovery than classical wet and dry digestion procedures.[23]

The purpose of the present study was to investigate the determination of arsenic and antimony in refined and unrefined table salt samples in order to improve salt quality. The performances of digestion procedures, namely, wet ashing, dry ashing, and fusion and microwave digestion were compared in this study. Arsenic and antimony determination utilizing HG-AAS with the continuous flow and batch method was done and compared. The accuracy of the procedures was confirmed using certified reference material. The selected method was applied to various table salt samples produced in Turkey.

Experimental

Reagents

All chemicals used in this work were of analytical reagent grade and were used without further purification. Distilled-deionized water was used throughout. As(III) stock standard solution (1000 mg L^{-1}) was prepared by dissolving As_2O_3 (Merck) in concentrated HCl (Merck) and diluting with distilled water. Sb(III) stock standard solution (1000 mg L^{-1}) was prepared by dissolving $KSbO.C_4H_4O_6$ (Merck) in distilled water. Eight percent KI solution was prepared from KI (Merck), and 0.6% and 4% $NaBH_4$ solutions were prepared by dissolving $NaBH_4$ (Merck) pellets in 0.15 mol L^{-1} and 0.01 mol L^{-1} NaOH, respectively. EDTA (0.01 mol L^{-1}) (Merck) was used for masking interferences in arsenic and antimony determination. The glassware used for the analyses was cleaned with detergent and water, and left in a 10% nitric acid bath for 24 h afterwards; all the glassware was thoroughly rinsed with deionized water before use.

The certified material NIES No.2 pond sediment was obtained from the National Institute for Environmental Studies (Tsukuba, Japan). The unrefined salt sample was collected from Çamaltı Saltpan at the shore of İzmir Bay. Commercially available table salt samples were purchased from a market in İzmir, Turkey.

Apparatus

A GBC 904 PBT model atomic absorption spectrometer with GBC HG-3000 continuous-flow hydride generation system was used for arsenic and antimony determination. A Vestel model 550 W microwave oven and a Parr Instrument Company No: 4782, 45 mL microwave acid digestion bomb with PTFE sample decomposition and PFA external cups were used.

Digestion procedures

Four types of digestion procedures were applied to the table salt sample: dry and wet ashing, and fusion and microwave digestion. In order to calculate precision, 3 replicate measurements were performed for all digestion. The procedures are described below.

Dry ashing

One gram of sample was placed into a high form porcelain crucible. The furnace temperature was slowly increased from room temperature to 450 °C over 1 h. The samples were heated for about 6 h until a white

residue was obtained. The residue was dissolved with 1-2 mL of concentrated nitric acid and filtered through blue band filter paper. The sample was diluted to 10 mL with distilled water. A blank was also prepared in the same way.

Wet ashing

Preliminary studies have shown that mixtures of HNO_3 – H_2O_2 are better than either HNO_3 or HCl or binary mixtures of HNO_3 and HCl or H_2SO_4 in terms of complete dissolution in a short time for wet digestion. Therefore, the mixture of HNO_3 – H_2O_2 was used in this wet digestion procedure. One gram of sample was placed into a glass beaker, followed by the addition of 12 mL of 2:1 HNO_3 – H_2O_2. This mixture was heated on a hot plate until near dryness and then the residue was dissolved in distilled water. The digest was transferred to a 10 mL volumetric flask and diluted to the mark with distilled water. A blank was also prepared in the same way.

Fusion

One gram of Na_2CO_3 was placed in a platinum crucible and then 0.8-1.0 g of the salt sample was added. The sample was covered with 4.0 g of Na_2CO_3. The fusion was continued in an electrical furnace for 60 min at 900 °C. The content was dissolved with HNO_3 and evaporated to dryness. Then the remainder was dissolved with distilled water, filtrated, and diluted to 10 mL.

Microwave digestion

The microwave digestion procedure was applied to the table salt samples. One gram of sample was digested with 3 mL of HNO_3 and 1 mL of H_2O_2 in the microwave oven and diluted to 10 mL with distilled water. The dissolution program consisted of 3 steps: 40% power for 8 min, 60% power for 8 min, and 80% power for 2 min. A blank was also prepared in the same way.

Analysis of the standard reference material

In order to verify the accuracy of the digestion procedures, certified reference material NIES No.2 pond sediment was also decomposed using the same procedures and analyzed for arsenic and antimony.

Measurement procedure

Batch type hydride generation system

Whenever EDTA masking of the metal ion interferences was necessary, a batch type hydride generation system with a 20 mL reaction vessel made in our laboratory[9] was used for arsenic and antimony determination with the GBC 904 PBT apparatus. Concentrations of arsenic and antimony in the digested samples were quantified by the batch type HG-AAS according to the analytical procedure reported previously.[9,24] Detailed instrumental operating parameters and working conditions for arsenic and antimony determination are summarized in Table 1.

Table 1. Instrumental operating parameters for HG-AAS in arsenic and antimony determination.

Element	Arsenic	Antimony
System type	Flame	Flame
Lamp current (mA)	8.0	10.0
Wavelength (nm)	193.7	217.6
Slit width	1.0	0.2
Slit height	Normal	Normal
Instrument mode	Absorbance BC on	Absorbance BC on
Sampling mode	Automated sampling	Automated sampling
Flame type	Air-Acetylene	Air-Acetylene
Acetylene flowrate (L min^{-1})	1.59	2.10
Air flowrate (L min^{-1})	10.6	13.50
Read time (s)*	30	30
Measurement mode	Peak Area	Peak Area
Carrier gas	Nitrogen	Nitrogen
N_2 flow rate (mL min^{-1})	50	50
HCl (mol L^{-1})*	2.0	2.0
$NaBH_4$ (%)*	0.6	0.6
HCl flow rate (mL min^{-1})	2.0	2.0
$NaBH_4$ flow rate (mL min^{-1})	2.0	2.0
Sample flow rate (mL min^{-1})	8.0	8.0

* In the batch method: 0.1 mol L^{-1} HCl, 4% $NaBH_4$ and 45 s read time were used. Carrier gas (N_2) flowrate was 150 mL min^{-1}.

As(V) does not give any signal, and therefore was reduced to As(III) before measurements. In order to mask the interferents and reduce As(V) to As(III) before the measurements, the sample solutions were prepared to contained 8.0% (m/v) KI and kept for 15 min for reduction. The sample solutions contained 4.0×10^{-3} mol L^{-1} EDTA whenever mentioned.

Continuous flow hydride generation system

A 3-channel peristaltic pump was used: for the sample, HCl, and $NaBH_4$ solutions. Sample and standard solutions contained 2.0 mol L^{-1} HCl, which was mixed with 10.2 mol L^{-1} HCl and 0.6% $NaBH_4$. The resulting mixture was transferred into the gas-liquid separator from where the gaseous hydrides were transported to the quartz tube atomizer of the AAS. Instrumental operating parameters and working conditions for continuous flow HG-AAS in arsenic and antimony determination are shown in Table 1.

Results and discussion

Optimization of batch type HG-AAS parameters

The following chemical and physical parameters were optimized to achieve the best analytical performance of the HG-AAS system for the reliable quantification of As and Sb in table salt samples. To obtain a stable and robust analytical signal, the quartz tube atomizer and the lamp were allowed to warm up for at least 15 min before starting a measurement sequence. Additionally, the responses of the HG-AAS system to a 10 μg L^{-1} As(III) and Sb(III) standard solutions were measured from time to time during long runs in order to control the changes in the signal response.

Nitrogen gas flow rate

Carrier gas flow rate is an important parameter, because it controls the speed of the HG and transports the volatile hydrides to the quartz tube atomizer. Nitrogen flow was used to transfer generated hydride from the reaction cell to the atomizer. Standard solutions of 10 μg L^{-1} As(III) and Sb(III) were prepared and then their absorbances were read at different nitrogen flow rates. As shown in Figure 1, when the gas flow rate was increased from 50 to 150 mL min^{-1} the signal intensities for the As(III) and Sb(III) standard solutions significantly increased. Further increases in the nitrogen gas flow to 250 mL min^{-1} decreased signal intensities. Consequently, a gas flow rate of 150 mL min^{-1} was used for all subsequent investigations.

HCl concentration

An acidic medium was required for the formation of hydrides. The effects of hydrochloric acid concentration within the range 0.05-0.5 mol L^{-1} on the atomic absorption signal of As(III) and Sb(III) are shown in Figure 2. The highest absorbance was obtained in 0.1 mol L^{-1} HCl for As(III) and Sb(III). In subsequent experiments, As(III) and Sb(III) measurements were made in 0.1 mol L^{-1} HCl medium.

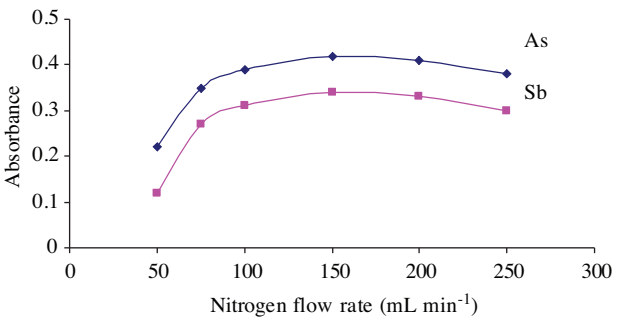

Figure 1. Effect of nitrogen flow rate on the absorption of 10 μg L^{-1} As(III) and Sb(III) standard solutions.

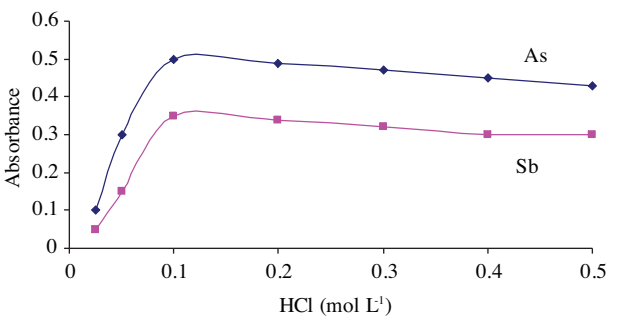

Figure 2. Effect of HCl concentration on arsenic and antimony absorption in the batch type hydride generation technique (the concentrations of As(III) and Sb(III) were fixed at 10 μg L^{-1}).

$NaBH_4$ concentration

$NaBH_4$ concentration significantly influences the HG efficiency. Optimization of $NaBH_4$ concentration was carried out between 0.25% and 5.0%. From Figure 3, the signal intensity increased up to a concentration of 4.0% $NaBH_4$ and then remained at the same value. Therefore, 4% (m/v) was chosen for further studies.

Pre-reduction with KI/ascorbic acid

KI + ascorbic acid in HCl medium has been successfully used for prereduction of As(V) and Sb(V) for total As and Sb determinations by HG-AAS. Various concentrations of KI (1.0%-16.0%) stabilized by addition of ascorbic acid (5%, w/v) were tested for their potential to quantitatively reduce As(V) to As(III) and Sb(V) to Sb(III). As shown in Figure 4, KI concentration of 8.0% (m/v) is sufficient for the quantitative prereduction and was used for subsequent experiments.

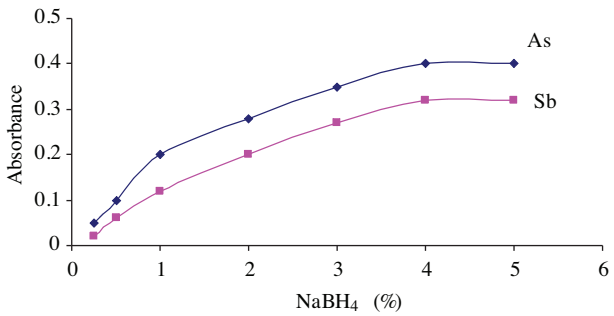

Figure 3. Effect of $NaBH_4$ concentration on arsenic and antimony absorption in the batch type hydride generation technique (the concentrations of As(III) and Sb(III) were fixed at 10 μg L^{-1}).

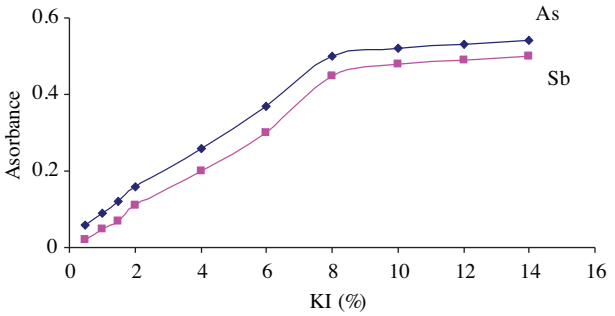

Figure 4. Effect of different concentrations of KI/ascorbic acid on the reduction efficiency (the concentrations of As(III) and Sb(III) were fixed at 10 μg L^{-1}).

Analytical characteristics of the procedure

Linear calibration graphs were obtained using the continuous flow and batch method for arsenic and antimony. Limits of detection (LOD) were calculated by dividing 3 times the standard deviation of the absorbance signal of 10 reagent blanks by the slope of the calibration line obtained using optimal experimental conditions for arsenic and antimony. The precision of the method (RSD) was also calculated (Table 2).

Table 2. Analytical characteristics of the batch and continuous flow hydride generation method for arsenic and antimony determination.

Measurement method	Element	R^2	LOD (μg L^{-1})	RSD[a] (%)
Continuous flow-HG-AAS	As	0.9998	0.5	2.8
	Sb	0.9994	0.5	3.4
Batch type-HG-AAS	As	0.9995	1.2	3.7
	Sb	0.9993	1.5	4.2

[a]Relative standard deviation for 10 μg L^{-1} As, Sb (n = 8).

Minimization of interferences

The use of masking agents in HG is one of the most important methods for control of liquid-phase interferences due to transition metals. The masking agents, like EDTA, complex the interfering ions and prevent their reduction by $NaBH_4$. However, since the EDTA complexation reaction takes places at pH usually more than 5, its applicable in the batch type hydride generation method, where soon after $NaBH_4$ injection pH increased to above 5.5, is successful. In the continuous flow hydride generation system much higher acidities are used and the masking reaction with EDTA is not effective.[2,11] It is known that several metal ions in sample solution may suppress hydride generation reaction; therefore, recoveries of As(III) and Sb(III) added to the sample solutions were studied using the batch and continuous flow systems, and the results were compared. The results are shown in Table 3. According to these results, batch type HG-AAS gave acceptable recoveries for the determination of arsenic and antimony in the unrefined salt sample.

Table 3. Determination of As and Sb in unrefined salt sample with batch and continuous flow system HG-AAS (The microwave digestion procedure was applied to unrefined salt sample).

Element	As			Sb		
	Added (μg L^{-1})	Found[a] (μg L^{-1})	Recovery (%)	Added (μg L^{-1})	Found[a] (μg L^{-1})	Recovery (%)
Batch type-HG-AAS	–	BLD[b]	–	–	BLD[b]	–
	2.0	1.97 ± 0.37	99	2.0	1.95 ± 0.42	98
	4.0	3.94 ± 0.41	98	4.0	3.91 ± 0.29	98
Continuous flow-HG-AAS	–	BLD[b]	–	–	BLD[b]	–
	2.0	1.92 ± 0.14	96	2.0	1.88 ± 0.17	94
	4.0	3.78 ± 0.21	95	4.0	3.79 ± 0.24	95

[a]Mean ± standard deviation, n = 3.

[b]BLD: Below the limit of detection

Accuracy studies

Performances of each sample digestion procedure (dry and wet ashing, and fusion and microwave digestion) prior to the determination of arsenic and antimony using HG-AAS were compared in this study. The methods were applied to the determination of arsenic and antimony in standard reference material (NIES No.2 pond sediment) in order to check the accuracy. The results are shown in Table 4. There was a good harmony between the certified values and our values for arsenic and antimony. As can be seen in Table 4, quantitative recoveries for As and Sb were obtained whichever of the 4 digestion methods was used. However, the microwave digestion procedure was preferred since this procedure is more suitable with respect to both time and recovery than the other digestion procedures.

Analysis of table salts

The Codex Alimentarius has established the maximum permissible concentration of metals in food grade salt.[25] According to this standard, food grade salt should not contain contaminants in amounts and in such form that

may be harmful to the health of the consumer. In particular the maximum limit of arsenic shall not exceed 0.5 μg g^{-1}. In the present study, concentrations of As and Sb were determined by obtaining calibration graphs using the batch type HG-AAS in 4 table salt samples after microwave digestion. The results are listed in Table 5. Arsenic levels were below the maximum limits given by Codex Alimentarius. Although there is no limit value for antimony in the Codex Alimentarius, concentrations of antimony in the salts were very low, in the range 12.2 to 26.4 ng g^{-1}.

Table 4. Comparison of digestion and measurement procedures for arsenic and antimony determination of standard reference material (NIES No.2 pond sediment, the certified value for arsenic is 12.0 $\pm$ 2 μg g^{-1} and reference value for antimony is 2.0 μg g^{-1}, n = 3).

Digestion method	Continuous flow-HG-AAS				Batch type-HG-AAS			
	As(III) (μg g^{-1})	Recovery (%)	Sb(III) (μg g^{-1})	Recovery (%)	As(III) (μg g^{-1})	Recovery (%)	Sb(III) (μg g^{-1})	Recovery (%)
Dry ashing	11.2 $\pm$ 0.25	93	1.89 $\pm$ 0.17	95	11.4 $\pm$ 0.47	95	1.92 $\pm$ 0.34	96
Wet ashing	11.4 $\pm$ 0.22	95	1.87 $\pm$ 0.16	94	11.6 $\pm$ 0.45	97	1.93 $\pm$ 0.31	97
Fusion	11.2 $\pm$ 0.27	93	1.88 $\pm$ 0.14	94	11.8 $\pm$ 0.42	98	1.91 $\pm$ 0.38	96
Microwave	11.5 $\pm$ 0.18	96	1.93 $\pm$ 0.19	97	11.9 $\pm$ 0.39	99	1.96 $\pm$ 0.32	98

Table 5. Determination of arsenic and antimony in various refined table salt samples consumed in Turkey (n = 3).

Sample	As(III) (ng g^{-1})	Sb(III) (ng g^{-1})
1	18.2 $\pm$ 0.8	12.2 $\pm$ 0.7
2	24.5 $\pm$ 0.9	15.2 $\pm$ 0.9
3	32.6 $\pm$ 1.2	22.8 $\pm$ 1.1
4	15.4 $\pm$ 0.6	26.4 $\pm$ 1.2
5	25.6 $\pm$ 0.5	18.7 $\pm$ 0.8
6	31.4 $\pm$ 1.1	22.6 $\pm$ 1.2
7	20.3 $\pm$ 0.7	21.8 $\pm$ 0.6
8	28.7 $\pm$ 0.9	16.4 $\pm$ 0.5

Recently, the heavy metal contents of refined and unrefined table salts from Turkey, Egypt, and Greece have been studied.[26] Copper, nickel, cobalt, manganese, lead, and cadmium levels were given but arsenic and antimony levels have not so far been reported in the table salts consumed in Turkey.

Conclusion

This study reports, for the first time, determination of arsenic and antimony in table salt samples produced in Turkey. From the results, it is seen that arsenic and antimony determination of the table salt samples could be successfully done by using HG-AAS, after microwave digestion, fusion, and wet and dry ashing procedures. The wet and dry ashing and fusion procedures are more time-consuming and complicated than the microwave

digestion procedure without any advantages in terms of digestion efficiency. The use of microwave digestion in table salt samples is simpler, effective, faster, and provides less contamination for sample preparation. Arsenic and antimony in the unrefined salt samples were determined using batch and continuous flow hydride generation techniques. The results show that the batch technique gave acceptable recoveries. In the salt samples collected from the market in Turkey, although all the arsenic and antimony concentrations measured were low, there were significant differences in the levels of arsenic and antimony among the table salt brands. It may be concluded that table salt samples do not impose any significant health hazard to consumers due to the presence of these toxic metals.

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