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The determination of antimony and arsenic concentrations in fly ash by hydride generation inductively coupled plasma optical emission spectrometry (HG-ICP-OES)

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Abstract

Hydride generation inductively coupled plasma optical emission spectrometry (HG-ICP-OES) was used in the determination of As and Sb concentrations in fly ash samples. The effect of sample pre-treatment reagents and measurement parameters used for hydride generation was evaluated. Due to memory effects observed, the appropriate read delay time was adjusted to 60 seconds resulting in RSDs 0.6% and 2.3% for As and Sb, respectively. The most suitable volumes of pre-reduction reagents for 10 mL of sample were 4 mL of KI/ascorbic acid (5%) and 6 mL of HCl (Conc.). The determination of Sb was significantly interfered by HF, but the interference could be eliminated by adding 2 mL of saturated boric acid and heating the samples to 60°C at least 45 min. The accuracy of the method was studied by analyses of SRM 1633b and two fly ash samples with the recovery test of added As and Sb. As high a recovery as 96% for SRM 1633b was reached for As using 193.696 nm with two-step ultrasound-assisted digestion. A recovery rate of 103% was obtained for Sb using 217.582 nm and the pre-reduction method with the addition of 2 mL of saturated boric acid and heating. The quantification limits for the determination of As and Sb in the fly ash samples using two-step ultrasound-assisted digestion followed with HG-ICP-OES were 0.89 and 1.37 mg kg^{-1}, respectively.

Keywords: Antimony; Arsenic; Fly ash; Hydride generation; ICP-OES

1. Introduction

The combustion of agricultural wastes, coal, municipal waste, peat and wood has generated huge amounts of different kinds of ashes during the previous decades [1]. It is well known that fly ashes contain significant amounts of toxic elements such as As, Hg, Pb, Sb, Se, and Sn [2-4]. Those elements are potential risks in the environment even at low concentrations [3,5]. A significant problem in the use of various kinds of fly ashes is the injurious effect on the environment and human health [5,6]. Potential applications for fly ashes include construction materials (cement and ceramic), geotechnical structures (road pavement and embankments) and agriculture (soil amendment) [1,7].

Microwave-accelerated and ultrasound-assisted digestions have become the most commonly used sample pre-treatment methods for the determination of trace element concentrations in different kinds of solid samples by ICP-OES. Those digestion methods have been successfully used for elemental analysis of many particulate materials such as contaminated soil, coal fly ash, biological samples and sediment [8-13]. The methods used in the analysis of trace elements in fly ash samples are based on atomic absorption or emission spectrometry together with a liquid sample introduction system [14,15].

During the last decades, hydride generation atomic spectrometry has become the most used technique for the determination of trace amount of elements that generate volatile species [16-21]. Hydride generation inductively coupled plasma atomic emission spectrometer is a sensitive tool for the determination of elements such as As, Bi, Sb, and Sn [22,23]. This involves a hydride generation device coupled with atomic spectrometry. Usually, there are a few main steps in the system: (1) generation of hydride, (2) collection of hydride, (3) transfer of the hydride, (3) atomization and excitation of the hydride and (5) detection of the signals [17,18,23].

An essential advantage of the hydride generation technique is the separation of analytes from the matrix. This enables reducing or even eliminating interference and increasing the sensitivity at the same time. However, different kinds of interferences are present, such as chemical and spectral interference [16,22,23]. Chemical interferences can be commonly separated to those in liquid phase and gas phase; for example, transition metals can cause chemical interferences in the liquid phase. Several reagents, such as EDTA, thiourea and KI, can be used to reduce chemical interferences, for instance those of transition metals [17,22,23]. Spectral interferences in a hydride generation system, being a consequence of the transport of interfering transition metals to the plasma, are responsible for spectral overlap at some wavelengths [17,22].

Typically As and Sb must be reduced to a lower oxidation state (As (III) and Sb (III)), before the determination of those elements by hydride generation. The most common pre-reduction reagents for As and Sb are KI, L-cysteine, thiourea and a mixture of KI and ascorbic acid [17,24,25]. In the last decades determinations of hydride forming elements by many kinds of apparatus using hydride generation coupled to atomic spectrometry were performed, but the number of papers dealing with the determination of As and Sb in fly ashes is limited.

The aim of this study was to develop a sensible and reliable method for the determination of As and Sb in power plant fly ashes by HG-ICP-OES. The increasing demand for an accurate analysis of such ashes is caused by increasing environmental concern. At the same time, the reuse potential of ashes has been noticed worldwide.

2. Experimental

2.1. Instrumentation

All measurements were performed with a Perkin-Elmer (Norwalk, CT, USA) model Optima 4300 DV inductively coupled plasma optical emission spectrometer. The continuous flow hydride generator (FIAS Mercury/Hydride Chemifold Mat No. B0507957) supplied by Perkin-Elmer (Norwalk, CT, USA) was used throughout. The continuous flow hydride generator consisted of readily available components: silicon, PTFE, PVC tubings, adapters, couple of connectors and PTFE membrane. Two mixing T's were used to combine the sample and reductant streams (first T) and to add the stripping argon (second T). After chemical resistant gas/liquid separator with PTFE membrane the gaseous hydrides were transported by the stripping argon flow directly into the base of ICP torch. The 2 mm. i.d. alumina sample injector tube was used. The chemifold apparatus was directly connected into injector tube and uses the ICPs flow rate pump. More detailed information for hydride generator components and apparatus designs were presented in report authored by C. P. Bosnak and L. Davidowski [25]. The element concentrations were determined with the following parameters of the instrument [25]: nebulizer flow of 0.5 L min^{-1}, auxiliary gas flow of 0.2 L min^{-1}, plasma gas flow of 17.0 L min^{-1} and plasma power of 1450 W. Two wavelengths for both elements were tested in axially viewed plasma. The wavelengths used are shown in Table 1.

2.2. Reagents

All reagents used were of analytical grade and only high purity water of 18.2 MΩ cm resistivity produced by a Maxima water purification system supplied by Elga (Buckinghamshire, UK) was used throughout. Nitric acid (65%) was supplied by

Sigma-Aldrich (Steinheim, Germany). Hydrochloric acid (37%) and hydrofluoric acid (40%) were supplied by VWR (Briare, France). The standard stock solutions of As and Sb (1000 mg L^{-1}) for the ICP-OES measurements were supplied by Merck (Darmstadt, Germany). The working concentration ranges used are shown in Table 1. L(+)-ascorbic acid (99.7%) and boric acid (99.8%) were supplied by VWR (Fontenay-sous-Bois, France and Leuven, Belgium). Sodium borohydride (> 98%), potassium iodide (99.5%) and sodium hydroxide pellets (> 97.5%) were supplied by Merck (Darmstadt, Germany). Two standard stock solutions were prepared for the interference tests. Standard stock solutions of Al and Fe (10000 mg L^{-1}) were prepared by dissolving appropriate amounts of $Al(NO_3)_3 \cdot 9\ H_2O$ (> 99.4%) and $Fe(NO_3)_3 \cdot 9\ H_2O$ (> 99.0%) in 65 mL of 10% HNO_3 and diluted to a volume of 250 mL with water; both reagents were supplied by Merck (Darmstadt, Germany). Other standard stock solutions used for interference tests (Co, Cr, Cu and Ni 1000 mg L^{-1}) were also supplied by Merck (Darmstadt, Germany). 0.5% Sodium borohydride solution as a reducing agent, a mixture of 5% Potassium iodide and 5% ascorbic acid solution and saturated boric acid solution as a pre-treatment solution were used throughout.

2.3. Samples

A coal fly ash standard reference material, SRM 1633b [27], certified by the National Institute of Standards and Technology (NIST), and two fly ash samples collected from Finnish wood burning plants were analyzed. Six replicate analyses of each fly ash sample were performed.

2.4. Digestion methods

All three digestion procedures were performed with ultrasound or microwave methods. Those methods were presented with more details in our earlier studies [28,29]. Two

digestion procedures were performed with an ultrasound method (US or US-TSD) and one digestion procedure was performed with a microwave method standardized by the USEPA (MW).

- US = Ultrasound, digestion solution of 10 mL (1:1) *aqua regia*, (9 min)
- US-TSD = Ultrasound (two-step): i) digestion solution of 6 mL of HNO_3, (9 min) ii) digestion solution of 3 mL HNO_3 and 3 mL HF, (18 min)
- MW = Microwave, digestion solution of 9 mL HNO_3 and 3 mL HF, USEPA method 3052

2.5. Pre-reduction of As and Sb

When As and Sb concentrations are determined with HG-ICP-OES, a pre-reduction of the elements into the oxidation state III is necessary. A mixture of KI (5%) and ascorbic acid (5%) was used as a reducing agent for As and Sb. Two different pre-reduction procedures A and B were performed for As and Sb as follows:

Method A:

10 mL of SRM or fly ash sample was placed into a 50 mL polypropylene volumetric flask into which 10 ml of a pre-reduction solution containing 4 mL of KI/ascorbic acid mixture and 6 mL of hydrochloric acid was added. The mixture was allowed to stand for at least 30 minutes and then diluted to a volume of 50 mL with water. The sample was then ready for measurements.

Method B:

10 mL of SRM or fly ash sample was placed into a 50 mL polypropylene volumetric flask into which 12 ml of a pre-reduction solution containing 2 mL of saturated boric acid solution, 4 mL of KI/ascorbic acid mixture and 6 mL of hydrochloric acid was added. The mixture was placed into a water bath (60°C) and was allowed to stand for at

least 45 minutes after which the flask was diluted to a volume of 50 mL with water. The sample was then ready for measurements.

3. Results and discussion

3.1. Calibration

All concentration measurements were carried out using four-point calibration. Multi-element calibration standards were used for both elements. The sample matrix of calibration standards was matched similar as samples. As and Sb were determined by using two of the most sensitive emission lines to attain the sensitivity required. The quantification limits for the determination of As and Sb (pre- reduction method B) in the fly ash samples using an US-TSD as a digestion method (pre-treatment method B) were found to be 0.89 and 1.37 mg kg^{-1}, respectively. It should be noted that the best quantification limits for the determination of As and Sb in the fly ash samples using US as a digestion method (pre-treatment method A) were found to be 0.16 and 0.45 mg kg^{-1}, respectively. Extremely high values were obtained for the regression correlation coefficients, as shown in Table 1.

3.2. Evaluation of determination parameters

Some of the instrument parameters used was taken from the field application report supplied by Perkin Elmer [25] such as plasma power, plasma gas flow, nebulizer flow and auxiliary gas flow. The determination parameters optimized were washing and read delay time as well as the sample flow rate. Axially viewed plasma was used throughout. To maintain the plasma in a stable condition it was found useful to introduce water for at least 20s between every sample. According to the literature [15,30,31] memory effects can be handled by using appropriate washing solution and with long enough rinsing time between each sample. Memory effects were tested by introducing samples

with As and Sb concentrations of 200 or 80 µg L^{-1} after which the determination of samples with 20 fold lower concentrations was immediately performed. Test shows that, the read delay time should be at least 60 seconds in order to eliminate memory effects, resulting in RSDs 0.6% and 2.3% of three replicate measurements for As and Sb, respectively. The memory effect in replicate measurements was significantly higher for Sb than for As. Three different sample flow rates were tested (1.80, 2.00 and 2.20 mL min^{-1}). Flow rate test resulted in RSDs (0.2-0.7%, 1.1-2.7% and 1.2-2.3%) and (0.1-0.9%, 1.2-1.9% and 1.4-3.2%) of three replicate measurements for As and Sb at sample flow rates of 1.80, 2.00 and 2.20 mL min^{-1}, respectively. The tests showed that a sample flow rate of 2.20 mL min^{-1} was impractical because quite often the plasma went off during the measurements. The test shows also that constancy of calibration resulted in highest with a sample flow rate of 1.80 mL min^{-1}. According to tests the highest repeatability and plasma stability was obtained at a sample flow rate of 1.80 mL min^{-1} for the determination of As and Sb. It should be noted; however, that using a sample flow rate of 1.80 mL min^{-1} the maximum intensities found were about 10-20% lower than using other flow rates (2.00 and 2.20 mL min^{-1}).

3.3. Evaluation of matrix effects in pre-treatment procedures

The evaluation of pre-treatment conditions and matrix effects were performed by determining the concentrations of elements in SRM 1633b with different volumes of pre-reduction solutions. The effect of hydrofluoric acid was thoroughly tested. As could be seen in Figure 1a, tests showed that HF does not play a significant role in the determination of As concentrations in fly ashes by HG-ICP-OES when the HF concentration remains below 2%. According to the tests, HF has a significant effect on the determination of Sb concentrations (Figure 1a). The recoveries of Sb at both wavelengths were dramatically lower when HF was present even at low concentrations.

Due to this, saturated boric acid solution was tested for the elimination of this interference. The HF was successfully eliminated by adding 2 mL of saturated boric acid into a pre-reduction solution and heating the sample solution to 60°C at least 45 min (Table 2 and Figure 1b).

The reduction time, the volume of the reduction reagents and the order of introducing the reduction reagents were also tested. As could be seen in Figure 1b, a 45 minute reduction time was needed if 2 mL of saturated boric acid was used at 60°C. Other temperatures were also tested (20 and 85°C) and 60°C was found the most suitable (Figure 1c). At 20°C a recovery rate of only about 50% (Figure 1d) was obtained for Sb. 85°C was too high resulting in decreased recovery rates from 25 to 40% for both As and Sb. The effect of hydrochloride acid and KI/ascorbic acid were tested. As could be seen in Figure 2a, the volume of HCl does not play a significant role in the determination of As concentrations. On the other hand, HCl has a significant effect on the determination of Sb concentrations. According to the tests, the volume of KI/Ascorbic acid does not play as significant role in the determination of Sb as in the determination of As concentrations (Figure 2b). According to the reagent volume tests (Figures 1 and 2), the appropriate volumes of KI/ascorbic acid, HCl and saturated boric acid solutions for 10 mL of sample solution were 4, 6 and 2 mL, respectively. Pre-reduction reagent order tests showed that the order of introducing the reduction reagents did not significantly affect the determination of As and Sb concentrations in fly ashes.

The effect of nitric acid on the determined concentrations was also tested. The test showed that if the HNO_3 concentration in the samples was lower than 10%, it did not play a significant role in the determination of As and Sb concentrations in fly ashes by HG-ICP-OES (Figure 2c). Possible interferences caused by matrix elements Al Co, Cr, Cu, Fe, and Ni [17] were also tested. The test showed that Al, Co, Cr, Cu, Fe and Ni do

not significantly interfere in the determination of As and Sb at concentration levels of 500 mg L^{-1} or lower of Al and Fe and 50 mg L^{-1} or lower of Co, Cr, Cu or Ni (Table 3). At those concentrations the relative intensities varied from 97.7 to 101.0% compared to pure analyte solutions. P. Pohl [17] and P. Pohl *et al*. [32] also found that interference caused by metals could be eliminated by using masking agents, such as L(+)-ascorbic acid.

3.4. Recovery test

The recovery test was used to confirm the analysis of real fly ash samples (FA1 and FA2) in which the main matrix element concentrations differed from SRM 1633b. The recovery test of added As and Sb was performed at two levels of concentrations (50% and 200% addition) (Table 4). Addition of As and Sb concentrations was performed after digestion in sample solution. The recovery test for both pre-reduction methods (A and B) with all digestion methods (US, US-TSD and MW) and both real fly ash samples (FA1 and FA2) resulted in recovery rates from 93% to 106%. The recovery test with the digestion method US-TSD followed with pre-reduction method B, using a mixture of KI/ascorbic acid, HCl and saturated boric acid as the reducing agent, resulted in recovery rates from 97% to 105% (Table 4).

3.5. Evaluation of wavelengths

The evaluation of wavelengths was performed by determining the concentrations of As and Sb in SRM 1633b and real fly ash samples. As could be seen in Tables 2, 3, 4 and 5, there was no significant difference between As wavelengths (188.979 nm and 193.696 nm) or Sb wavelengths (206.638 m and 217.582 nm), so that both wavelengths tested could be used for the determination of As and Sb concentrations. The highest emission intensities were obtained at 193.696 nm and 217.582 nm for As and Sb, respectively.

These wavelengths had also better LOD and LOQ values than others. Therefore 193.696 nm and 217.582 nm, respectively, are suggested for the determination of As and Sb in fly ash samples by HG-ICP-OES.

3.6. Analysis

The coal fly ash standard reference material, SRM 1633b, and two fly ash samples collected from different wood burning incineration plants were analyzed. As and Sb were selected as analyte elements because of their toxic character and their presence in incineration ashes. The concentrations (mean ± confidence level of the mean) of the two elements in SRM 1633b digested by ultrasound or microwave methods and determined by HG-ICP-OES are shown in Table 2. As could be seen, the determination of As was performed with recovery rates between 81-96%, whereas Sb recoveries were 51-103%. The highest As recovery of 96% was obtained with the digestion method US-TSD followed with HG-ICP-OES (method B); this is higher than that determined by M. A. Vieira et al. [33] in SRM 1633b by HGAAS. The highest Sb recovery, 103%, was obtained with the digestion method US-TSD. It should be noted that in SRM 1633b the Sb concentration is not certified although it is given. Using the recovery test in Table 4, As and Sb were also successfully determined in FA1 and FA2.

The As and Sb concentrations determined using three different digestion methods for two fly ash samples are presented in Table 5. The concentrations of As for the real fly ash samples (FA1 and FA2) by three different digestion methods resulted in concentrations between 25-50 mg kg^{-1}. Significantly different concentrations of Sb varying from 3 to 25 mg kg^{-1} were obtained for real fly ash samples. The lowest concentrations of Sb for all fly ash samples with boric acid and warming (method B) were found in the digestion method US, whereas the lowest concentrations of Sb without boric acid and warming (method A) were obtained in the digestion method US-

TSD. The lowest concentrations of As for all fly ash samples were found in the digestion method MW (both pre-reduction methods). The As and Sb concentration methods showed the same kind of trend between different digestion methods as in the case of the SRM samples. The concentrations determined for As and Sb in real fly ash samples resulted in a precision quite similar as those for the certified material (SRM 1633b).

4. Conclusion

The determination of As and Sb element concentrations in fly ash samples was successfully performed using the hydride generation inductively coupled plasma optical emission spectrometry (HG-ICP-OES). The most suitable method for the determination of As and Sb was the digestion method US-TSD and a pre-reduction procedure with a mixture of 4 mL of KI/ascorbic acid, 6 mL of HCl and 2 mL of saturated boric acid as a reducing agent (method B), followed by the HG-ICP-OES measurement at 193.696 nm and 217.582 nm. The quantification limits for the determination of As and Sb in the fly ash samples using two-step ultrasound-assisted digestion followed with HG-ICP-OES resulted in 0.89 and 1.37 mg kg^{-1}, respectively.

The recovery rates of As and Sb were as high as 96% and 103%, respectively. The concentrations determined for As and Sb in fly ash samples (RSDs 1.9-5.8%) resulted in a quite similar precision as those of the SRM 1633b (RSDs 1.2-2.1%). The As recovery in all digestion methods was similar to or higher than those obtained by M. A. Vieira et al. for SRM 1633b by HGAAS [33].

The major interference in the determination of Sb was caused by HF; therefore boric acid with warming was needed in the determination of Sb. The accuracy of the method was demonstrated with the analysis of SRM 1633b and two fly ash samples with the recovery test of added As and Sb. The recovery test for both pre-reduction methods with

all digestion methods for both real fly ash samples was successfully performed. It is well known that the accurate determination of toxic elements such as As and Sb is crucial in cases of suspected environmental and health risks.

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346 Table 1 Calibration data of the determination of samples by HG-ICP-OES.

Element	Wavelength (nm)	r	Atom/Ion (I/II)	LOD[a] (mg kg^{-1})	LOQ[b] (mg kg^{-1})	Calibration range (µg L^{-1})
As	188.979	1.0000	I	0.39	1.29	2 - 200
As	**193.696**	1.0000	I	0.27	0.89	2 - 200
Sb	206.836	0.9999	I	0.46	1.55	2 - 200
Sb	**217.582**	0.9999	I	0.41	1.37	2 - 200

347 [a] LOD = limit of detection when 250 mg sample was digested and filtrate diluted to a volume of 100 mL and sample
348 further diluted 10mL/50mL (US-TSD, method B). Calculated by substituting the intercept and its standard deviations
349 multiplier ($a + 3s_a$) into the calibration line $y = bx + a$ [26].

350 [b] LOQ = limit of quantification when 250 mg sample was digested and filtrate diluted to a volume of 100 mL and
351 sample further diluted 10mL/50mL (US-TSD, method B). Calculated by substituting the intercept and its standard
352 deviations multiplier ($a + 10s_a$) into the calibration line $y = bx + a$ [26].

353 **Bold =** suggested wavelength

Table 2 Element concentrations determined (mg kg^{-1}) in SRM 1633b using three different digestion procedures (mean of six replicate samples, with the confidence limit of the mean, $P = 0.05$).

Element	Microwave MW[a]	Ultrasound US[b]	Ultrasound US-TSD[c]	Certified
Method A				
As 188.979 nm	111.2 ± 1.3	124.9 ± 0.9	130.3 ± 1.8	136.2 ± 2.6
As 193.696 nm	111.6 ± 1.3	125.1 ± 0.8	130.6 ± 1.7	
Sb 206.836 nm	<LOQ	2.62 ± 0.11	<LOQ	6*
Sb 217.582 nm	<LOQ	2.65 ± 0.13	<LOQ	
Method B				
As 188.979 nm	111.0 ± 2.4	124.5 ± 0.9	129.8 ± 1.6	136.2 ± 2.6
As 193.696 nm	111.3 ± 2.3	124.8 ± 0.7	130.2 ± 1.6	
Sb 206.836 nm	5.81 ± 0.12	3.11 ± 0.14	6.16 ± 0.10	6*
Sb 217.582 nm	5.84 ± 0.11	3.13 ± 0.10	6.18 ± 0.09	

LOQ = limit of quantification (< 1.55 mg kg^{-1})
Bold = suggested wavelength
Method A= without boric acid and warming
Method B= with boric acid and warming
* Non-certified value (SRM 1633b)
[a] Microwave, digestion solution of 9 mL HNO_3 and 3 mL HF, USEPA method 3052
[b] Ultrasound, digestion solution of 10 mL (1+1) *aqua regia*, 9 min (3 × 3 min),
[c] Ultra-sound (two-step): i) digestion solution of 6 mL of HNO_3 , 9 min (3 × 3 min)
ii) digestion solution of 3 mL HNO_3 and 3 mL HF, 18 min (6 × 3 min)

Table 3 Influence of metals on the determination of synthetic As and Sb samples (50 µg L^{-1}) by HG-ICP-OES. Relative intensity (%) tolerance of As and Sb measurements with interfering element for pre-treatment method A.

	As 188.979 nm	**As 193.696 nm**	**Sb 206.836 nm**	**Sb 217.582 nm**
	Intensity (%)	Intensity (%)	Intensity (%)	Intensity (%)
Al (III)**	99.6-100.0	98.8-100.0	98.9-100.0	99.1-100.1
Co (II)*	99.6-100.9	99.6-101.0	99.0-101.0	99.5-100.7
Cr (III)*	100.0-100.6	100.0-100.9	100.0-100.5	100.0-100.6
Cu (II)*	98.9-100.8	99.1-100.4	97.8-100.0	97.9-100.0
Fe (III)**	99.1-100.1	99.5-100.9	99.2-100.2	99.2-100.1
Ni (II)*	99.1-100.0	99.0-100.0	97.7-100.0	97.8-100.0

* concentration interval of interfering element = 0-50mg L^{-1}
** concentration interval of interfering element = 0-500mg L^{-1}

371 Table 4 Recoveries of added As and Sb for pre-reduction method B with digestion
372 methods US-TSD and MW (mean of four replicate samples, with the confidence limit of
373 the mean, $P = 0.05$).

Element	Method US-TSD Recovery (%)	Method MW Recovery (%)
FA1		
Addition 50 %		
As 188.979 nm	102.9 ± 2.2	97.5 ± 2.3
As 193.696 nm	**102.8 ± 2.1**	**96.5 ± 2.3**
Sb 206.836 nm	96.8 ± 3.2	98.6 ± 2.4
Sb 217.582 nm	**98.8 ± 2.9**	**97.8 ± 2.6**
Addition 200 %		
As 188.979 nm	100.2 ± 1.8	93.4 ± 2.3
As 193.696 nm	**100.3 ± 1.6**	**93.8 ± 2.2**
Sb 206.836 nm	97.6 ± 2.4	96.0 ± 2.9
Sb 217.582 nm	**97.4 ± 2.2**	**96.5 ± 3.0**
FA2		
Addition 50 %		
As 188.979 nm	101.5 ± 2.8	104.8 ± 4.0
As 193.696 nm	**102.4 ± 2.7**	**105.6 ± 4.0**
Sb 206.836 nm	103.0 ± 1.8	104.8 ± 3.7
Sb 217.582 nm	**102.4 ± 1.6**	**104.8 ± 3.6**
Addition 200 %		
As 188.979 nm	104.8 ± 2.3	101.7 ± 1.9
As 193.696 nm	**104.6 ± 2.2**	**101.6 ± 1.8**
Sb 206.836 nm	104.0 ± 1.3	103.5 ± 1.6
Sb 217.582 nm	**103.5 ± 1.2**	**103.6 ± 1.4**

374 **Bold =** suggested wavelength

Table 5 Element concentrations determined (mg kg^{-1}) for two fly ash samples (FA1 and FA2) collected from Finland (mean of six replicate samples, with the confidence limit of the mean, $P = 0.05$).

Element	Microwave MW[a]	Ultrasound US[b]	Ultrasound US-TSD[c]
Method A			
FA1			
As 188.979 nm	24.7 ± 1.1	40.0 ± 0.7	43.3 ± 1.4
As 193.696 nm	24.8 ± 1.0	39.9 ± 0.7	43.2 ± 1.3
Sb 206.836 nm	2.32 ± 0.16	15.8 ± 0.4	2.64 ± 0.32
Sb 217.582 nm	2.44 ± 0.15	16.4 ± 0.5	2.72 ± 0.30
FA2			
As 188.979 nm	23.4 ± 1.3	44.2 ± 0.7	45.6 ± 1.4
As 193.696 nm	23.6 ± 1.2	44.0 ± 0.6	45.7 ± 1.3
Sb 206.836 nm	<LOQ	2.62 ± 0.11	<LOQ
Sb 217.582 nm	<LOQ	2.63 ± 0.10	<LOQ
Method B			
FA1			
As 188.979 nm	26.6 ± 1.0	41.8 ± 0.6	42.7 ± 1.3
As 193.696 nm	26.8 ± 1.0	41.8 ± 0.5	42.8 ± 1.2
Sb 206.836 nm	24.8 ± 0.9	19.1 ± 0.5	24.4 ± 0.8
Sb 217.582 nm	25.1 ± 0.9	19.7 ± 0.4	24.7 ± 0.8
FA2			
As 188.979 nm	25.6 ± 1.2	44.2 ± 0.5	49.6 ± 3.0
As 193.696 nm	25.7 ± 1.0	44.3 ± 0.4	49.3 ± 2.9
Sb 206.836 nm	5.78 ± 0.34	3.19 ± 0.10	6.03 ± 0.14
Sb 217.582 nm	5.85 ± 0.28	3.20 ± 0.08	6.05 ± 0.13

LOQ = limit of quantification (< 1.55 mg kg^{-1})
Bold = suggested wavelength
Method A= without boric acid and warming
Method B= with boric acid and warming
[a] Microwave, digestion solution of 9 mL HNO_3 and 3 mL HF, USEPA method 3052
[b] Ultrasound, digestion solution of 10 mL (1+1) *aqua regia*, 9 min (3× 3 min)
[c] Ultrasound (two-step): i) digestion solution of 6 mL of HNO_3 , 9 min (3 × 3 min)
ii) digestion solution of 3 mL HNO_3 and 3 mL HF, 18 min (6 × 3 min)

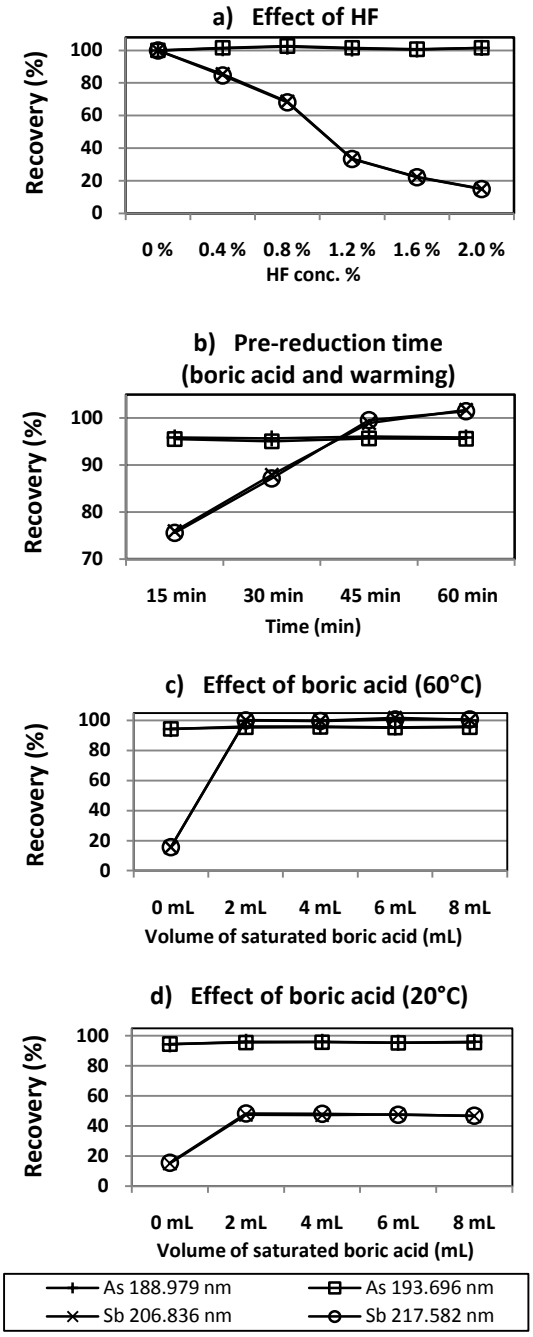

Figure 1 Test of pre-treatment conditions in the determination of As and Sb in SRM 1633b or synthetic sample using a mixture of 4 ml of KI/ascorbic acid and 6 mL of HCl as a pre-reduction reagents. a) Synthetic sample containing 100 µg L^{-1} of As and Sb, 9.0% of HNO_3 and pre-treatment time of 60 min, b) SRM sample, digestion method US-TSD, saturated boric acid 2 mL and temperature of 60°C, c) and d) SRM sample, digestion method US-TSD and pre-treatment time of 60 min. In cases of b), c) and d) conc. of HF (1.2%) and HNO_3 (9.0%) was derived from digestion method US-TSD.

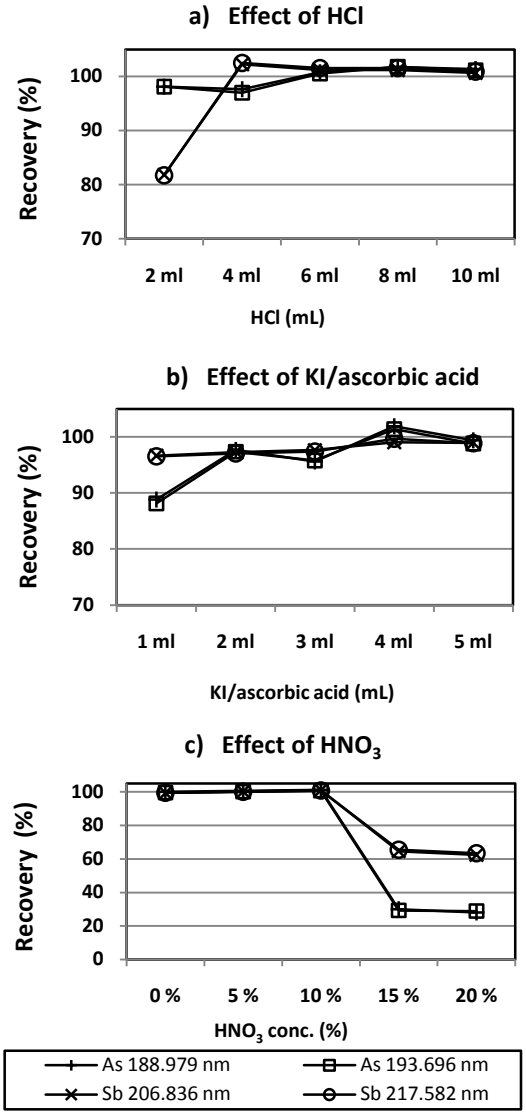

Figure 2 Test of pre-treatment conditions in the determination of As and Sb in synthetic samples containing 200 µg L^{-1} of As and Sb. a) 4 mL of KI/ascorbic acid, b) 6 mL of HCl, c) 4 mL of KI/ascorbic acid and 6 mL of HCl. The pre-treatment time of 60 min and temperature of 20 °C was used throughout.