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

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6 **Abstract**

7 Hydride generation inductively coupled plasma optical emission spectrometry (HG-  
8 ICP-OES) was used in the determination of As and Sb concentrations in fly ash samples.  
9 The effect of sample pre-treatment reagents and measurement parameters used for  
10 hydride generation was evaluated. Due to memory effects observed, the appropriate  
11 read delay time was adjusted to 60 seconds resulting in RSDs 0.6% and 2.3% for As  
12 and Sb, respectively. The most suitable volumes of pre-reduction reagents for 10 mL of  
13 sample were 4 mL of KI/ascorbic acid (5%) and 6 mL of HCl (Conc.). The  
14 determination of Sb was significantly interfered by HF, but the interference could be  
15 eliminated by adding 2 mL of saturated boric acid and heating the samples to 60°C at  
16 least 45 min. The accuracy of the method was studied by analyses of SRM 1633b and  
17 two fly ash samples with the recovery test of added As and Sb. As high a recovery as  
18 96% for SRM 1633b was reached for As using 193.696 nm with two-step ultrasound-  
19 assisted digestion. A recovery rate of 103% was obtained for Sb using 217.582 nm and  
20 the pre-reduction method with the addition of 2 mL of saturated boric acid and heating.  
21 The quantification limits for the determination of As and Sb in the fly ash samples using  
22 two-step ultrasound-assisted digestion followed with HG-ICP-OES were 0.89 and 1.37  
23 mg kg<sup>-1</sup>, respectively.

24 *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].

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

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

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

## 72 **2. Experimental**

### 73 **2.1. Instrumentation**

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

### 92 **2.2. Reagents**

93 All reagents used were of analytical grade and only high purity water of  $18.2 \text{ M}\Omega \text{ cm}$   
94 resistivity produced by a Maxima water purification system supplied by Elga  
95 (Buckinghamshire, UK) was used throughout. Nitric acid (65%) was supplied by

96 Sigma-Aldrich (Steinheim, Germany). Hydrochloric acid (37%) and hydrofluoric acid  
97 (40%) were supplied by VWR (Briare, France). The standard stock solutions of As and  
98 Sb ( $1000 \text{ mg L}^{-1}$ ) for the ICP-OES measurements were supplied by Merck (Darmstadt,  
99 Germany). The working concentration ranges used are shown in Table 1. L(+)-ascorbic  
100 acid (99.7%) and boric acid (99.8%) were supplied by VWR (Fontenay-sous-Bois,  
101 France and Leuven, Belgium). Sodium borohydride (> 98%), potassium iodide (99.5%)  
102 and sodium hydroxide pellets (> 97.5%) were supplied by Merck (Darmstadt, Germany).  
103 Two standard stock solutions were prepared for the interference tests. Standard stock  
104 solutions of Al and Fe ( $10000 \text{ mg L}^{-1}$ ) were prepared by dissolving appropriate amounts  
105 of  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{ H}_2\text{O}$  (> 99.4%) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{ H}_2\text{O}$  (> 99.0%) in 65 mL of 10%  
106  $\text{HNO}_3$  and diluted to a volume of 250 mL with water; both reagents were supplied by  
107 Merck (Darmstadt, Germany). Other standard stock solutions used for interference tests  
108 (Co, Cr, Cu and Ni  $1000 \text{ mg L}^{-1}$ ) were also supplied by Merck (Darmstadt, Germany).  
109 0.5% Sodium borohydride solution as a reducing agent, a mixture of 5% Potassium  
110 iodide and 5% ascorbic acid solution and saturated boric acid solution as a pre-treatment  
111 solution were used throughout.

### 112 **2.3. Samples**

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

### 117 **2.4. Digestion methods**

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

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

- 123 ○ US = Ultrasound, digestion solution of 10 mL (1:1) *aqua regia*, (9 min)
- 124 ○ US-TSD = Ultrasound (two-step): i) digestion solution of 6 mL of HNO<sub>3</sub>, (9 min) ii)  
125 digestion solution of 3 mL HNO<sub>3</sub> and 3 mL HF, (18 min)
- 126 ○ MW = Microwave, digestion solution of 9 mL HNO<sub>3</sub> and 3 mL HF, USEPA method  
127 3052

## 128 ***2.5. Pre-reduction of As and Sb***

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

### 133 ***Method A:***

134 10 mL of SRM or fly ash sample was placed into a 50 mL polypropylene volumetric  
135 flask into which 10 ml of a pre-reduction solution containing 4 mL of KI/ascorbic acid  
136 mixture and 6 mL of hydrochloric acid was added. The mixture was allowed to stand for  
137 at least 30 minutes and then diluted to a volume of 50 mL with water. The sample was  
138 then ready for measurements.

### 139 ***Method B:***

140 10 mL of SRM or fly ash sample was placed into a 50 mL polypropylene volumetric  
141 flask into which 12 ml of a pre-reduction solution containing 2 mL of saturated boric  
142 acid solution, 4 mL of KI/ascorbic acid mixture and 6 mL of hydrochloric acid was  
143 added. The mixture was placed into a water bath (60°C) and was allowed to stand for at

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

### 146 **3. Results and discussion**

#### 147 ***3.1. Calibration***

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

#### 159 ***3.2. Evaluation of determination parameters***

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



168 with As and Sb concentrations of 200 or 80  $\mu\text{g L}^{-1}$  after which the determination of  
169 samples with 20 fold lower concentrations was immediately performed. Test shows that,  
170 the read delay time should be at least 60 seconds in order to eliminate memory effects,  
171 resulting in RSDs 0.6% and 2.3% of three replicate measurements for As and Sb,  
172 respectively. The memory effect in replicate measurements was significantly higher for  
173 Sb than for As. Three different sample flow rates were tested (1.80, 2.00 and 2.20 mL  
174  $\text{min}^{-1}$ ). Flow rate test resulted in RSDs (0.2-0.7%, 1.1-2.7% and 1.2-2.3%) and (0.1-  
175 0.9%, 1.2-1.9% and 1.4-3.2%) of three replicate measurements for As and Sb at sample  
176 flow rates of 1.80, 2.00 and 2.20 mL  $\text{min}^{-1}$ , respectively. The tests showed that a sample  
177 flow rate of 2.20 mL  $\text{min}^{-1}$  was impractical because quite often the plasma went off  
178 during the measurements. The test shows also that constancy of calibration resulted in  
179 highest with a sample flow rate of 1.80 mL  $\text{min}^{-1}$ . According to tests the highest  
180 repeatability and plasma stability was obtained at a sample flow rate of 1.80 mL  $\text{min}^{-1}$   
181 for the determination of As and Sb. It should be noted; however, that using a sample  
182 flow rate of 1.80 mL  $\text{min}^{-1}$  the maximum intensities found were about 10-20% lower  
183 than using other flow rates (2.00 and 2.20 mL  $\text{min}^{-1}$ ).

### 184 ***3.3. Evaluation of matrix effects in pre-treatment procedures***

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

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

197 The reduction time, the volume of the reduction reagents and the order of introducing  
198 the reduction reagents were also tested. As could be seen in Figure 1b, a 45 minute  
199 reduction time was needed if 2 mL of saturated boric acid was used at 60°C. Other  
200 temperatures were also tested (20 and 85°C) and 60°C was found the most suitable  
201 (Figure 1c). At 20°C a recovery rate of only about 50% (Figure 1d) was obtained for Sb.  
202 85°C was too high resulting in decreased recovery rates from 25 to 40% for both As and  
203 Sb. The effect of hydrochloride acid and KI/ascorbic acid were tested. As could be seen  
204 in Figure 2a, the volume of HCl does not play a significant role in the determination of  
205 As concentrations. On the other hand, HCl has a significant effect on the determination  
206 of Sb concentrations. According to the tests, the volume of KI/Ascorbic acid does not  
207 play as significant role in the determination of Sb as in the determination of As  
208 concentrations (Figure 2b). According to the reagent volume tests (Figures 1 and 2), the  
209 appropriate volumes of KI/ascorbic acid, HCl and saturated boric acid solutions for 10  
210 mL of sample solution were 4, 6 and 2 mL, respectively. Pre-reduction reagent order  
211 tests showed that the order of introducing the reduction reagents did not significantly  
212 affect the determination of As and Sb concentrations in fly ashes.

213 The effect of nitric acid on the determined concentrations was also tested. The test  
214 showed that if the HNO<sub>3</sub> concentration in the samples was lower than 10%, it did not  
215 play a significant role in the determination of As and Sb concentrations in fly ashes by  
216 HG-ICP-OES (Figure 2c). Possible interferences caused by matrix elements Al, Co, Cr,  
217 Cu, Fe, and Ni [17] were also tested. The test showed that Al, Co, Cr, Cu, Fe and Ni do

218 not significantly interfere in the determination of As and Sb at concentration levels of  
219 500 mg L<sup>-1</sup> or lower of Al and Fe and 50 mg L<sup>-1</sup> or lower of Co, Cr, Cu or Ni (Table 3).  
220 At those concentrations the relative intensities varied from 97.7 to 101.0% compared to  
221 pure analyte solutions. P. Pohl [17] and P. Pohl *et al.* [32] also found that interference  
222 caused by metals could be eliminated by using masking agents, such as L(+)-ascorbic  
223 acid.

#### 224 **3.4. Recovery test**

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

#### 235 **3.5. Evaluation of wavelengths**

236 The evaluation of wavelengths was performed by determining the concentrations of As  
237 and Sb in SRM 1633b and real fly ash samples. As could be seen in Tables 2, 3, 4 and 5,  
238 there was no significant difference between As wavelengths (188.979 nm and 193.696  
239 nm) or Sb wavelengths (206.638 m and 217.582 nm), so that both wavelengths tested  
240 could be used for the determination of As and Sb concentrations. The highest emission  
241 intensities were obtained at 193.696 nm and 217.582 nm for As and Sb, respectively.  
242

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

### 246 **3.6. Analysis**

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

260 The As and Sb concentrations determined using three different digestion methods for  
261 two fly ash samples are presented in Table 5. The concentrations of As for the real fly  
262 ash samples (FA1 and FA2) by three different digestion methods resulted in  
263 concentrations between 25-50 mg kg<sup>-1</sup>. Significantly different concentrations of Sb  
264 varying from 3 to 25 mg kg<sup>-1</sup> were obtained for real fly ash samples. The lowest  
265 concentrations of Sb for all fly ash samples with boric acid and warming (method B)  
266 were found in the digestion method US, whereas the lowest concentrations of Sb  
267 without boric acid and warming (method A) were obtained in the digestion method US-

268 TSD. The lowest concentrations of As for all fly ash samples were found in the  
269 digestion method MW (both pre-reduction methods). The As and Sb concentration  
270 methods showed the same kind of trend between different digestion methods as in the  
271 case of the SRM samples. The concentrations determined for As and Sb in real fly ash  
272 samples resulted in a precision quite similar as those for the certified material (SRM  
273 1633b).

#### 274 **4. Conclusion**

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

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

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

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

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

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

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

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

**Bold** = suggested wavelength

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

Element	Microwave MW <sup>a</sup>	Ultrasound US <sup>b</sup>	Ultrasound US-TSD <sup>c</sup>	Certified
<i>Method A</i>				
As 188.979 nm	111.2 ± 1.3	124.9 ± 0.9	130.3 ± 1.8	136.2 ± 2.6
<b>As 193.696 nm</b>	111.6 ± 1.3	125.1 ± 0.8	130.6 ± 1.7	
Sb 206.836 nm	<LOQ	2.62 ± 0.11	<LOQ	6*
<b>Sb 217.582 nm</b>	<LOQ	2.65 ± 0.13	<LOQ	
<i>Method B</i>				
As 188.979 nm	111.0 ± 2.4	124.5 ± 0.9	129.8 ± 1.6	136.2 ± 2.6
<b>As 193.696 nm</b>	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*
<b>Sb 217.582 nm</b>	5.84 ± 0.11	3.13 ± 0.10	6.18 ± 0.09	

357 LOQ = limit of quantification ( $< 1.55 \text{ mg kg}^{-1}$ )

358 **Bold** = suggested wavelength

359 Method A= without boric acid and warming

360 Method B= with boric acid and warming

361 \* Non-certified value (SRM 1633b)

362 <sup>a</sup> Microwave, digestion solution of 9 mL HNO<sub>3</sub> and 3 mL HF, USEPA method 3052

363 <sup>b</sup> Ultrasound, digestion solution of 10 mL (1+1) *aqua regia*, 9 min (3 × 3 min),

364 <sup>c</sup> Ultra-sound (two-step): i) digestion solution of 6 mL of HNO<sub>3</sub>, 9 min (3 × 3 min)

365 ii) digestion solution of 3 mL HNO<sub>3</sub> and 3 mL HF, 18 min (6 × 3 min)

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

	<b>As 188.979 nm</b>	<b>As 193.696 nm</b>	<b>Sb 206.836 nm</b>	<b>Sb 217.582 nm</b>
	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

369 \* concentration interval of interfering element =  $0-50\text{mg L}^{-1}$

370 \*\* concentration interval of interfering element =  $0-500\text{mg L}^{-1}$

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		
<i>Addition 50 %</i>		
As 188.979 nm	102.9 ± 2.2	97.5 ± 2.3
<b>As 193.696 nm</b>	<b>102.8 ± 2.1</b>	<b>96.5 ± 2.3</b>
Sb 206.836 nm	96.8 ± 3.2	98.6 ± 2.4
<b>Sb 217.582 nm</b>	<b>98.8 ± 2.9</b>	<b>97.8 ± 2.6</b>
<i>Addition 200 %</i>		
As 188.979 nm	100.2 ± 1.8	93.4 ± 2.3
<b>As 193.696 nm</b>	<b>100.3 ± 1.6</b>	<b>93.8 ± 2.2</b>
Sb 206.836 nm	97.6 ± 2.4	96.0 ± 2.9
<b>Sb 217.582 nm</b>	<b>97.4 ± 2.2</b>	<b>96.5 ± 3.0</b>
FA2		
<i>Addition 50 %</i>		
As 188.979 nm	101.5 ± 2.8	104.8 ± 4.0
<b>As 193.696 nm</b>	<b>102.4 ± 2.7</b>	<b>105.6 ± 4.0</b>
Sb 206.836 nm	103.0 ± 1.8	104.8 ± 3.7
<b>Sb 217.582 nm</b>	<b>102.4 ± 1.6</b>	<b>104.8 ± 3.6</b>
<i>Addition 200 %</i>		
As 188.979 nm	104.8 ± 2.3	101.7 ± 1.9
<b>As 193.696 nm</b>	<b>104.6 ± 2.2</b>	<b>101.6 ± 1.8</b>
Sb 206.836 nm	104.0 ± 1.3	103.5 ± 1.6
<b>Sb 217.582 nm</b>	<b>103.5 ± 1.2</b>	<b>103.6 ± 1.4</b>

374 **Bold** = suggested wavelength

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

Element	Microwave MW <sup>a</sup>	Ultrasound US <sup>b</sup>	Ultrasound US-TSD <sup>c</sup>
<i>Method A</i>			
FA1			
As 188.979 nm	24.7 ± 1.1	40.0 ± 0.7	43.3 ± 1.4
<b>As 193.696 nm</b>	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
<b>Sb 217.582 nm</b>	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
<b>As 193.696 nm</b>	23.6 ± 1.2	44.0 ± 0.6	45.7 ± 1.3
Sb 206.836 nm	<LOQ	2.62 ± 0.11	<LOQ
<b>Sb 217.582 nm</b>	<LOQ	2.63 ± 0.10	<LOQ
<i>Method B</i>			
FA1			
As 188.979 nm	26.6 ± 1.0	41.8 ± 0.6	42.7 ± 1.3
<b>As 193.696 nm</b>	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
<b>Sb 217.582 nm</b>	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
<b>As 193.696 nm</b>	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
<b>Sb 217.582 nm</b>	5.85 ± 0.28	3.20 ± 0.08	6.05 ± 0.13

378 LOQ = limit of quantification ( $< 1.55 \text{ mg kg}^{-1}$ )

379 **Bold** = suggested wavelength

380 Method A= without boric acid and warming

381 Method B= with boric acid and warming

382 <sup>a</sup> Microwave, digestion solution of 9 mL HNO<sub>3</sub> and 3 mL HF, USEPA method 3052

383 <sup>b</sup> Ultrasound, digestion solution of 10 mL (1+1) *aqua regia*, 9 min (3 × 3 min)

384 <sup>c</sup> Ultrasound (two-step): i) digestion solution of 6 mL of HNO<sub>3</sub>, 9 min (3 × 3 min)

385 ii) digestion solution of 3 mL HNO<sub>3</sub> and 3 mL HF, 18 min (6 × 3 min)

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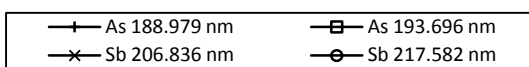
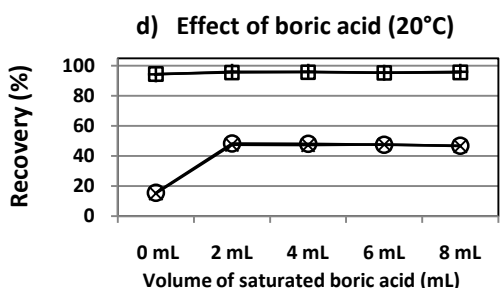
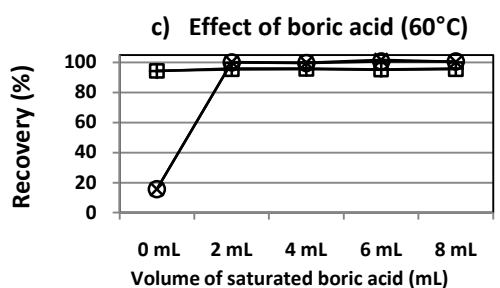
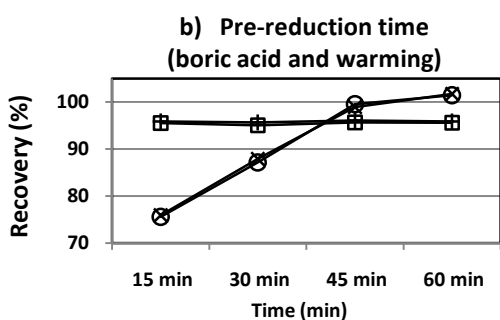
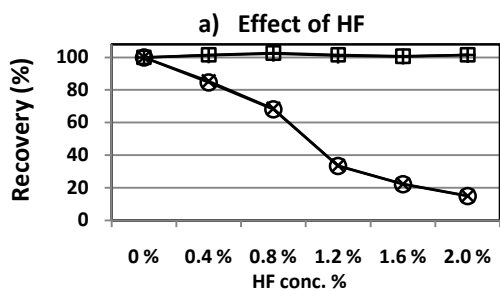
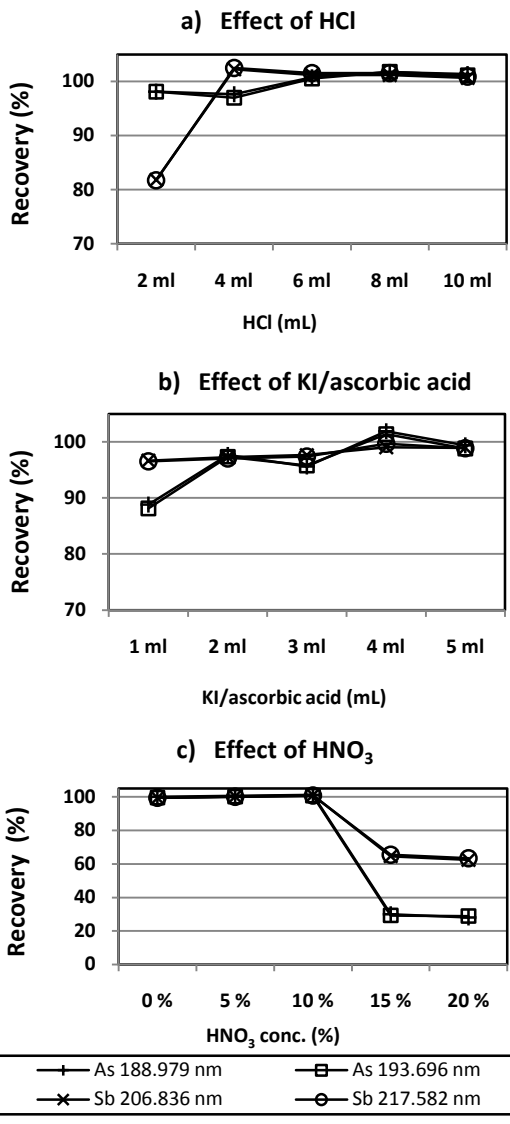


Figure 1 Test of pre-treatment conditions in the determination of As and Sb in SRM 1633b or synthetic sample using a mixture of 4 ml of KI/ascorbic acid and 6 mL of HCl as a pre-reduction reagents. a) Synthetic sample containing  $100 \mu\text{g L}^{-1}$  of As and Sb, 9.0% of  $\text{HNO}_3$  and pre-treatment time of 60 min, b) SRM sample, digestion method US-TSD, saturated boric acid 2 mL and temperature of  $60^\circ\text{C}$ , 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  $\text{HNO}_3$  (9.0%) was derived from digestion method US-TSD.



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Figure 2 Test of pre-treatment conditions in the determination of As and Sb in synthetic samples containing 200  $\mu\text{g L}^{-1}$  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.