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**DEVELOPMENT OF ULTRASOUND-ASSISTED DIGESTION METHODS  
FOR THE DETERMINATION OF TOXIC ELEMENT CONCENTRATIONS  
IN ASH SAMPLES BY ICP-OES**

BY

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Academic Dissertation for the Degree of  
Doctor of Philosophy

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## ABSTRACT

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The present thesis introduces several ultrasound-assisted digestion methods developed for the determination of toxic element concentrations in ash samples by inductively coupled plasma optical emission spectrometry (ICP-OES). Ultrasound-assisted digestion is a quite new technique used for sample pre-treatment purposes, especially in difficult sample matrixes. Elements determined are As, Ba, Co, Cr, Cu, Ni, Pb, Sb, Sr, V, and Zn. Most of the elements determined exist at a trace or ultra trace level in ashes and most are potential risks in the environment or human body even at low concentrations. Most of the selected elements can be determined directly by ICP-OES, but for the determination of Sb the hydride generation technique (HG-ICP-OES) is needed. The accurate analysis of As can be performed with the direct ICP-OES measurement and with the HG device.

Several optimization procedures for digestion methods and ICP-OES measurements were performed. The homogeneity of ultrasound field in the water bath, the robustness of plasma conditions, the optimization of digestion time and the composition of acid mixture were investigated. Interferences of determination procedures were minimized by using matrix matched calibration solutions, optimized volumes of reagents and by performing the measurements under robust plasma conditions. The methods developed were evaluated by statistical tools, reference material and method, recovery tests and multiple linear regression technique. All the methods developed were tested with real ash samples. The suggested analytical procedures were summarised and achieved results were compared with other results published. This thesis is based on four scientific papers: two of them are more focused on the study of ultrasound-assisted digestion (I,II) and the other two are focused on investigations of interferences in the measurements and the determination of hydride forming elements (III,IV).

Keywords: ash, hydride generation, inductively coupled plasma optical emission spectrometry, interference, toxic element, ultrasound-assisted digestion

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## PREFACE

This work was carried out at the Department of Chemistry, University of Jyväskylä during 2005-2011.

I express my deepest gratitude to my supervisor Docent Ari Väisänen for his patient guidance and encouraging attitude during this work. I am very grateful to the Head of the Department, for the opportunity to carry out this work. I also want to thank Professor Jussi Valkonen, Professor Reijo Sillanpää and Docent Rose Matilainen and the rest of the staff of Inorganic and Analytical Chemistry for creating a pleasant and supportive working atmosphere. I am also grateful to Professor Antonio Canals for his guidance and to the rest of his research group for an inspiring working atmosphere.

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Jyväskylä, April, 6<sup>th</sup> 2011

Aki Ilander

## LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following original publications, which are referred to in the text by their Roman numerals.

- I Ilander A., Väisänen A., An ultrasound-assisted digestion method for the determination of toxic element concentrations in ash samples by inductively coupled plasma optical emission spectrometry, *Anal. Chim. Acta* **2007**, 602, 195-201.
- II Ilander A., Väisänen A., The determination of trace element concentrations in fly ash samples using ultrasound-assisted digestion followed with inductively coupled plasma optical emission spectrometry, *Ultrason. Sonochem.* **2009**, 16, 763-768.
- III Ilander A., Väisänen A., Control of matrix interferences by multiple linear regression models in the determination of arsenic and lead concentrations in fly ashes by inductively coupled plasma optical emission spectrometry, *J. Anal. At. Spectrom.* **2010**, 25, 1581-1587.
- IV Ilander A., Väisänen A., The determination of antimony and arsenic concentrations in fly ash by hydride generation inductively coupled plasma optical emission spectrometry, *Anal. Chim. Acta* **2011**, 689, 178-183.

### Author's contribution

In all Papers, the author has had a major role in all the digestion method developments, measurements, analysis of experimental data and writing of the manuscripts.

## ABBREVIATIONS

a	intercept of the y-axis
AAS	atomic absorption spectrometry
b	slope of the regression line
BA	bottom ash
DCP	direct coupled plasma
EIE	easily ionized element
FA	fly ash
FAAS	flame atomic absorption spectrometry
G	value of the Grubb's outlier test
GFAAS	graphite furnace atomic absorption spectrometry
H <sub>0</sub>	null hypothesis
HG	hydride generation
HG-ICP-OES	hydride generation inductively coupled plasma optical emission spectrometry
ICP	inductively coupled plasma
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
LOD	limit of detection
LOQ	limit of quantification
LTE	local thermodynamic equilibrium
MIP	microwave induced plasma
MLR	multiple linear regression
MW	microwave
n	sample size (number of the replicate samples)
NIST	National Institute of Standards and Technology
P	significance level
PTFE	polytetrafluoroethylene
Q	value of the Dixon's outlier test
r	regression correlation coefficient
RF	radio frequency
s	standard deviation of replicate samples
s <sub>a</sub>	standard deviation of the intercept of regression line
s <sub>b</sub>	standard deviation of the slope of regression line
s <sub>d</sub>	standard deviation of the differences between pairs
s <sub>x/y</sub>	residual deviation of the regression line
SRM	standard reference material
t	value of the t-statistic
US	ultrasound
USEPA	United States Environmental Protection Agency
US-TSD	ultrasound two step digestion

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# 1 INTRODUCTION

The focus of the present thesis is in developing methods for determining several toxic elements in ashes by inductively coupled plasma optical emission spectrometry (ICP-OES). This thesis is especially focused on effective ultrasound-assisted digestion methods and the handling of interferences present in ICP-OES measurements. Nowadays microwave accelerated digestion is one of the most widely used methods in sample pre-treatment, but ultrasound-assisted digestion is also becoming a commonly used technique for routine sample pre-treatment.<sup>1-4</sup> The usefulness of ultrasound in sample pre-treatment purposes in the analytical laboratory has been noted by many scientists around the world.<sup>3-5</sup>

One of the most widely used techniques for minor and major element determination in different kinds of solid samples is ICP-OES; other techniques used are inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS). The principles of ICP-OES and hydride generation technique (HG) are well documented in the literature.<sup>6-8</sup> Different kinds of interferences are present in ICP-OES measurements causing both random and systematic errors. In analytical work it is important to ensure that the method used is free from systematic errors; then other errors can be handled as random errors.<sup>9,10</sup> In this study, the evaluation of analytical results is performed using several tools such as standard reference material, limit of detection (LOD), confidence limit of the mean, recovery tests, outlier tests, paired *t*-test and multiple linear regression.<sup>I-IV</sup> The aim of this study is presented in Chapter 2. A literature review on the quality of analytical results, general aspects of sample pre-treatment method, especially microwave accelerated and ultrasound-assisted digestion and interferences of ICP-OES measurements is presented in Chapter 3. Experimental conditions are discussed in Chapter 4. Chapters 5 and 6 summarize results presented in original papers I-IV with comments and conclusions.

## **2 AIM OF THE STUDY**

The aim of this study was to develop methods for the accurate and precise determination of several toxic element concentrations in ashes using ultrasound-assisted digestion followed with inductively coupled plasma optical emission spectrometry (ICP-OES).

The need for methods for analysis of different kinds of ashes has arisen because huge amounts of ashes need reuse or final locations. It is obvious that accurate analyses of toxic elements are crucial in cases of suspected environmental and health risks of ashes. Nowadays ultrasound-assisted digestion for different sample matrices is becoming an alternative pre-treatment method to conventional and microwave digestion methods even in complex sample matrices. More accurate and effective ultrasound-assisted digestion methods are thus needed.

In this study the crucial criteria for the ultrasound digestion method development were accuracy, precision and effectiveness. Effective ultrasound-assisted digestion methods for elements which are toxic and hard to digest in ash samples were also studied. Naturally, analytical results were evaluated for several methods. The element concentrations determined using the ICP-OES technique can be subject to serious interference in a complex sample matrix. Due to this, interfering effects were thoroughly investigated. In this study one important aspect was the practicality of the analysis. It meant that the methods developed could be used for everyday analysis in the laboratory; thus all the methods developed were tested with real ash samples.

## 3 LITERATURE REVIEW

### 3.1 Background of the study

In the last decades, industrial activity has produced massive amounts of different by-products, for instance, bottom and fly ashes. The combustion of agricultural residues, coal, dried sludge, municipal waste, peat and wood has generated large amounts of different kinds of ashes. The worldwide production of coal ash only is estimated to exceed  $550 \times 10^6$  tonnes/year (Mt/year). Over 40 Mt of fly ash is produced in Europe.<sup>11-14</sup> At least 6 Mt of industrial by-products and recycled materials are produced annually in Finland. Some of these by-products are potentially reusable materials for different kinds of construction.<sup>15</sup>

Nowadays the reuse potential of ashes has been noticed worldwide.<sup>11,12,15-18</sup> At the same time, increasing environmental concern about ashes has led to an increasing demand for accurate analysis of ashes.<sup>14</sup> It is well known that accurate determination of toxic elements is crucial in cases of suspected environmental and health risks. According to this, the development of not only accurate but also effective and low cost analysis methods is needed.

#### 3.1.1 Industrial ashes

Metal contamination is a persistent problem in many industrial ashes. Elements such as chromium, cobalt, copper, lead, nickel, vanadium and zinc are potential risks in the environment even at low concentrations.<sup>19-21</sup> Different kinds of ashes generated in combustion processes are important carriers of hazardous substances.<sup>11,16,22,23</sup> Primary constituents of the ashes are oxides of Al ( $\text{Al}_2\text{O}_3$ ), Ca ( $\text{CaO}$ ), Fe ( $\text{Fe}_2\text{O}_3$ ), K ( $\text{K}_2\text{O}$ ), Mg ( $\text{MgO}$ ), Na ( $\text{Na}_2\text{O}$ ), Si ( $\text{SiO}_2$ ) and Ti ( $\text{TiO}_2$ ).<sup>16,24-27</sup> Ashes also contain significant amounts of elements with toxic characters such as As, Ba, Cd, Co, Cr, Cu, Ni, Pb, V, and Zn.<sup>25,28-30</sup> The main problem related to the use of ashes is the direct or indirect harmful effects on the environment and human health.

The fly and bottom ashes from solid waste incineration are typically classified as hazardous residues, but the ash classifying is case-specific.<sup>11,27,31</sup> Classically, wood ashes and ashes derived from the combustion of agricultural wastes were applied to soils to recycle the nutrients. Also ashes generated by burning coal and sewage sludge have been used as soil amendment. Possible applications for municipal solid waste bottom and fly ashes are tested in construction materials (cement and ceramic), geotechnical applications (road pavement and embankments) and agriculture (soil amendment).<sup>12,13,17,18,32-36</sup> Industrial ashes are mostly difficult to analyze, because their composition is unpredictable, highly variable, and heterogeneous.<sup>27,37</sup>

### 3.1.2 Selection of elements determined

The selection of elements determined was based on the toxicity of the element. Most of the elements analyzed exist at trace or ultra trace levels in ashes and most of them are potential risks to the environment or health even at low concentrations.<sup>19,20</sup> The selected elements are As, Ba, Co, Cr, Cu, Ni, Pb, Sb, Sr, V, and Zn. One important element is missing from the list; it is Cd. This is due to its extremely low concentrations in fly ash samples. The sensitivity of an ICP-OES instrument is not sufficient to ensure the quality of accurate measurements of Cd. The determination of low concentrations of Cd is usually performed using an ICP-MS or GFAAS instrument. However, in this thesis all concentrations are determined with an ICP-OES instrument. Table 1 gives limit values for selected elements in soil construction for ashes from coal, peat and wood in Finland.

**Table 1** Three different limit values for selected elements in soil construction for ashes from coal, peat and wood in Finland.<sup>38</sup>

Element	Total concentration mg kg <sup>-1</sup>	Leached concentration <sup>a</sup> mg kg <sup>-1</sup>	Leached concentration <sup>b</sup> mg kg <sup>-1</sup>
As	50	0.5	1.5
Ba	3000	20	60
Co	-	-	-
Cr	400	0.5	3.0
Cu	400	2	6
Ni	-	0.4	1.2
Pb	300	0.5	1.5
Sb	-	0.06	0.18
Sr	-	-	-
V	400	2	3
Zn	2000	4	12

<sup>a</sup> Coated construction, <sup>b</sup> Surfaced construction.<sup>38</sup>

## 3.2 Quality of analytical results

It is important to realize that errors can be present in all analytical results. Typically, errors can be divided into two main types, random and systematic errors.<sup>10,39</sup> It is very important to eliminate the systematic errors and the minimize random errors of the experiment. Briefly, precision depends on random errors and accuracy depends on systematic errors. If random errors are minimized, the results are precise and if systematic errors are not present, the results are accurate.<sup>10,39,40</sup> The quality of analytical results can be studied in many different ways such as calibration, limit of quantification, confidence limit of the mean, recoveries of standard reference materials, recovery tests of added elements and significance tests.<sup>10,40-42</sup> This chapter presents some of means for evaluating analytical results.

### 3.2.1 Calibration

The calibration procedure of chemical analysis is based on several known standard samples. The number of calibration samples is typically at least three or four, and possibly more calibration samples are used in a quantitative calibration.<sup>10,41</sup> A plot for a linear calibration standard takes the algebraic form  $y = bx + a$ , where  $b$  is the slope of the line and  $a$  is its intercept on the y-axis.<sup>10,41,43</sup> A quantitative analysis of an unknown sample is based on the comparison of concentrations determined against a calibration curve.<sup>10,42</sup> Nowadays the determination of element concentrations are mainly performed by instrumental techniques such as atomic absorption or emission spectrometry.<sup>10,40,44</sup> In these techniques the calibration standards are measured under the same instrument conditions and sample matrix as the unknown samples. It is important to include the value for a blank sample in the calibration curve.<sup>10,43</sup>

The calibration curve can be evaluated by calculating the correlation coefficient  $r$ .  $r$  is calculated at calibration points  $(x_1, y_1), (x_2, y_2), \dots, (x_n, y_n)$ , where  $n$  is the number of the calibration points. The equation for  $r$  is widely presented in the literature.<sup>10,41,45</sup> The correlation coefficient can vary between -1 and 1.<sup>10,41</sup> The value  $r = \pm 1$  means that all experimental points are exactly on the linear line. The slope  $b$  and intercept  $a$  of the calibration line can be found by the method of least squares under three important assumptions: (1) All the errors are present in the y direction, (2) the variation in the y direction errors must be the same for all values of x, (3) errors are normally distributed.<sup>41</sup> Then slope  $b$  and intercept  $a$  are calculated from the equations<sup>41,42,43,45</sup>

$$b = \frac{\sum_i \{(x_i - \bar{x})(y_i - \bar{y})\}}{\sum_i (x_i - \bar{x})^2} \quad , \quad (1)$$

$$a = \bar{y} - b\bar{x} \quad . \quad (2)$$

The errors in the calibration line can be estimated by using statistical calculations. Random errors of the intercept ( $s_a$ ) and slope ( $s_b$ ) of the calibration line must be calculated. At first, the residual deviation of the regression line  $s_{y/x}$  is estimated with the equation<sup>10,41,42</sup>

$$s_{y/x} = \left[ \frac{\sum_i (y_i - \hat{y}_i)^2}{n-2} \right]^{\frac{1}{2}}, \quad (3)$$

where  $y_i$  is the measured signal value, the corresponding  $\hat{y}_i$  is the fitted value on the calibration line and  $n-2$  is the number of degrees of freedom in the data. When  $s_{y/x}$  is calculated, the standard deviation of the calibration line intercept ( $s_a$ ) and slope ( $s_b$ ) can be estimated from the following equations<sup>10,41-44,46</sup>

$$s_a = s_{y/x} \left[ \frac{\sum_i x_i^2}{n \sum_i (x_i - \bar{x})^2} \right]^{\frac{1}{2}}, \quad (4)$$

$$s_b = \frac{s_{y/x}}{\left[ \sum_i (x - \bar{x})^2 \right]^{\frac{1}{2}}}. \quad (5)$$

The confidence limits for intercept  $a$  and slope  $b$  are then  $a \pm ts_a$  and  $b \pm ts_b$ , respectively, where  $t$  has  $(n-2)$  degrees of freedom.<sup>10,41</sup> Values of  $t$  with different degrees of freedom and confidences are presented in statistical textbooks.<sup>10,40,42</sup>

### 3.2.2 Limits of detection and quantification

The limit of detection (LOD) and the limit of quantification (LOQ) have an important role for the evaluation of the quality of the measurement.<sup>9,46,47</sup> Shortly, the limit of detection means the lowest concentration or amount of the analyte that can be reliably distinguished from blank or that can be detected with a reasonable statistical certainty, whereas the limit of quantification means the lowest concentration or amount of analyte that can be quantitatively determined with an acceptable level of precision.<sup>10,46-48</sup> The LOD and LOQ values can be obtained by substituting  $(a + 3 s_a)$  or  $(a + 10 s_a)$  into the calibration line  $y = bx + a$ , respectively.<sup>10,41,43,48-50</sup>

### 3.2.3 Replicate samples and confidence limits of the mean

The analytical measurements should be performed by the analysis of an appropriate number of replicate samples ( $n$ ) to ensure the quality of the results.<sup>40,47,48,51,52</sup> Typically the number of the replicate samples of mean varies from three to six.<sup>48,52,53</sup> If the sample means are normally distributed, then 95% of values lie within  $\pm 2$  standard deviations ( $s$ ) of the mean and 99.7% of the values lie within  $\pm 3$  standard deviations ( $s$ ) of the mean.<sup>10,40,54,55</sup> The element concentrations determined are usually presented as mean values with standard deviations or confidence limits of mean at the level of 95%.<sup>40-42,56,57</sup> In small sample series ( $n < 30$ ) the confidence limit of the mean can be calculated with the following equation<sup>40-42</sup>

$$\mu = \bar{x} \pm t \left( \frac{s}{\sqrt{n}} \right) . \quad (6)$$

The value of  $t$  depends on the number of degrees of freedom ( $n - 1$ ) and the degree of confidence (95-99%). Values of  $t$  with different degrees of freedom and confidences are presented in statistical textbooks.<sup>10,40,42</sup>

### 3.2.4 Standard reference materials and recovery tests

Standard reference materials play a significant role in the quality control of elemental analysis from different kinds of solid samples. If appropriate reference materials are available they are a powerful tool in the assessment and control of the accuracy of the analytical method applied. The recovery rates of the elements studied in standard reference materials are widely used.<sup>48,53,58-64</sup> The standard reference samples closest to the real samples are typically used in the determination of the selected elements because of the similarity of sample matrices.<sup>9,61,65</sup>

A recovery test of an added concentration (spiked samples) can be used for the evaluation of the accuracy of the method.<sup>48,53,66,67</sup> A recovery test is typically performed using a minimum of 6 replicate samples unfortified and fortified with the analyte at different concentrations.<sup>48,53,66,67</sup> The recovery rate is determined by dividing the difference between the fortified and unfortified concentration with the spiked concentration. Recovery or addition of concentration studies should be performed for different types of matrices, several examples of each matrix type and at different levels of analyte concentration for each matrix type.<sup>9,48,53,66-68</sup>

### 3.2.5 Significance tests

One of the essential properties of an analytical method is that the method must be free from systematic errors.<sup>10,40,69</sup> The use of significance tests is an easy technique for evaluating many kinds of experimental results and they are widely used.<sup>10,40,42,49,67,69-71</sup> The general idea of significance tests is to test the truth of a hypothesis known as a null hypothesis ( $H_0$ ). The null hypothesis is that there is no significant difference between the determined and known results. If the  $H_0$  is true, the differences between the results can be attributed to random errors.<sup>10,40,42</sup> There are many kinds of significance tests for the evaluation of the quality of analytical data<sup>10,42,67,69,70</sup>, but only the some tests such as  $t$ -tests and outlier-tests are presented in this thesis.

It is possible that one or two experimental values differ substantially from other values; those values are called outliers.<sup>10,42</sup> There are simple statistical tests to evaluate whether or not values are outliers. Possible outliers can be detected by Dixon's or Grubbs' test at the significance level of 5%.<sup>10,42,70</sup> It should be noted that before rejecting values it is sensible to explore 1) are results normally distributed? 2) are enough replicate samples measured (at least 4)? 3) is the rejection of a value necessary?<sup>10,40</sup>

Dixon's test is a useful method to investigate the data for outliers. The test can be performed by using different values of data in the following equation<sup>10,40</sup>

$$Q = \frac{|suspect - nearest|}{(largest - smallest)} \quad (7)$$

Grubbs' test is another method to find outliers in the data set. The test can be performed with the follow equation<sup>42</sup>

$$G = \frac{|x_s - \bar{x}|}{s} \quad (8)$$

where  $x_s$  is the suspected value and  $s$  is the standard deviation of values including the suspected outlier.<sup>42</sup> If a calculated  $Q$  or  $G$  value exceeds the critical values, the suspected value is found to be an outlier and it should be rejected. The critical  $Q$  and  $G$  values are found in statistical books and manuals.<sup>10,40,42</sup>

The accuracy of the method can be evaluated by comparing the means of two samples or two methods with the  $t$ -test, such as the mean of a standard method vs. the mean of a developed method.<sup>10,39,42,71</sup> The null hypothesis is true if there is no significant difference between the data sets tested. The  $t$ -test is usually performed at the confidence level of 95%.<sup>10,42,71</sup> If the precision of the methods



used do not differ significantly, the standard deviations of the methods can be pooled. Pooled standard deviations can be calculated from the equation<sup>10,40,67</sup>

$$s = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}} \quad , \quad (9)$$

where the  $(n_1 + n_2 - 2)$  is the degrees of freedom and  $s_1$  and  $s_2$  are the standard deviations of the methods. After that a  $t$ -test of the two means  $t_{\text{statistic}}$  can be calculated using the equation<sup>10,67</sup>

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{s \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \quad . \quad (10)$$

At times test samples can contain substantially different amounts of analyte; then the above  $t$ -test is not appropriate and the evaluation of the results should be performed by the paired  $t$ -test.<sup>10,40,42,71</sup> In that test the analytical data are studied as pairs and the difference of each pair  $d$  is estimated. The  $t$  value is calculated with the equation<sup>10,67,69,71</sup>

$$t = \frac{x_d \sqrt{n}}{s_d} \quad , \quad (11)$$

where  $x_d$  is the mean of differences between pairs,  $n$  is the number of pairs and  $s_d$  is the standard deviation of the differences between the pairs. The degrees of freedom is defined by the number of the pairs  $(n - 1)$ .<sup>10,40,67</sup> It should be noted that the differences between pairs should have both negative and positive values, otherwise systematic errors are obtained. If a calculated  $t$  value exceeds a critical value, the null hypothesis should be rejected. It means that there is a significant difference between two means or pairs studied at the confidence level of 95% and the method probably includes a systematic error.<sup>10,40</sup> The critical  $t$  values are presented in statistical textbooks.<sup>10,42,67</sup>

### 3.3 General aspects of solid sample pre-treatment

The pre-treatment of solid samples such as soil, sediment and ash contains several steps; those usually are drying, homogenization and appropriate handling and storage.<sup>72-74</sup> Sample digestion is one of the most common procedures in analytical chemistry, because most quantitative analytical techniques such as AAS and ICP require that samples should be introduced in a liquid form.<sup>74-76</sup> The digestion of the sample matrix plays a significant role in almost all analytical processes. To be effective, sample digestion methods must efficiently decompose the sample matrix so that the analytes of interest are completely released and soluble and are in a form compatible with the

analytical method used. Successful sample digestion is therefore a crucial prerequisite to accurate and precise analysis for solid samples.<sup>2,75,77,78</sup>

Wet digestion is a method of converting the components of matrix into a simple chemical form. It is typically performed by supplying energy and using chemical reagents.<sup>74,75</sup> Energy can be introduced into samples in many different ways such as hotplate, conventional oven, microwave or ultrasound.<sup>4,74,75,79</sup> Most wet digestion methods involve the use of some combination of acids such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl and HF with or without a strong oxidizing agent H<sub>2</sub>O<sub>2</sub>.<sup>2,74,75,78</sup> Contamination of the samples or losses of analytes are the most significant systematic errors that can occur during pre-treatment steps such as sampling, storage and digestion of samples. Sources of contamination include materials from tools and vessels, reagents and laboratory air.<sup>72-74,80-82</sup> Loss of elements is typically caused by volatilization, chemical reaction with vessels or tools and adsorption. Synthetic polymeric materials can be recommended for storage of samples; using such materials can achieve minimal contamination and loss of analytes.<sup>72,74,82</sup>

This chapter gives a short overview of microwave accelerated and ultrasound-assisted digestion. Other sample pre-treatment methods such as dry ashing, PTFE bomb digestion and reflux method are not discussed in this thesis.

### 3.3.1 Microwave accelerated digestion

The use of microwaves as an energy source in wet digestion procedures was developed several decades ago.<sup>75</sup> At first, most of the designs used open vessels at atmospheric pressure.<sup>1,2,75</sup> The main advantage of microwave digestion compared with conventional wet digestion and dry ashing is the speed of digestion.<sup>72,74</sup> The typical time to complete wet digestion by conventional digestion method is about 1-2 hours, whereas open vessel digestion using microwaves can be completed in 5-15 minutes.<sup>1,75,83</sup> Microwave accelerated digestion has become the most common sample pre-treatment method for the determination of trace element concentrations in solid samples by ICP-OES.<sup>1,2,75,77,78,84</sup>

Microwaves are electromagnetic energy with frequencies in the range of 300 to 300000 MHz. A frequency of 2450 MHz is generally used in microwave digestion; the same frequency is also used in home microwave devices.<sup>74,75,83</sup> Microwave energy consists of an electric field and a magnetic field, but the electric field is important for the heating process in microwave accelerated digestion.<sup>74,75</sup> Ionic conduction and dipole rotation are the two fundamental mechanisms for transferring energy from the electric field to the substance being heated. Ionic conduction is the migration of ions in an applied electromagnetic field and dipole rotation is an interaction in which polar molecules try to align themselves with the rapidly changing electric field of the microwave.<sup>1,74,75,83</sup>

Microwaves interact with materials by reflection, transmission or absorption of the energy.<sup>74,75</sup> Metals are reflective materials and they are typically used for the construction of the microwave cavity. Vessel materials used to contain the sample and acid should be transparent to microwave energy. If vessels absorb microwave energy, the situation may be dangerous.<sup>74</sup> Teflon is the material most used to construct vessels, because it is transparent to microwaves, resistant to acids and has a good thermal stability.<sup>1,74,75</sup> Other good materials for use in a microwave environment are quartz, glass and polystyrene. Acids are absorptive materials and effective digestion solutions and therefore commonly used in microwave accelerated digestion.<sup>74,75</sup>

Microwave accelerated digestion can be performed in open or closed digestion systems. The trend nowadays is towards closed systems.<sup>2,77</sup> Open vessel work involves the risk of environmental contamination as well as mechanical or volatile loss of the analytes.<sup>74,75,78</sup> The use of open vessels also limits the maximum sample temperature to the boiling point of the acid.<sup>75</sup> On the other hand open vessel digestion is much safer than closed vessel digestion, because it takes place at atmospheric pressure.<sup>2,74,75</sup> Closed vessel systems for acid digestion have some advantages: 1. Higher temperatures of digestion can be used; 2. Loss of volatile elements during digestion is eliminated or reduced; 3. Less acids are required; 4. Potentially hazardous fumes produced are contained within the vessel; 5. Airborne contamination is eliminated or substantially reduced.<sup>1,2,74,75,77</sup> The digestion procedures for microwave accelerated methods last typically 10-60 minutes and the program can be divided into several steps.<sup>1,2,78</sup> Generally 6-24 samples can be treated simultaneously; the sample treatment capacity depends on the microwave device used.<sup>75,85</sup>

Microwave accelerated digestion has been used and well documented for the elemental analysis of many particulate materials.<sup>2,77,78,86,87</sup> Such methods for coal, coal fly ash, sediment, and soil samples are presented in Table 2. Microwave technology is being applied not only in analytical chemistry but also in organic synthesis and inorganic reactions in the preparation of catalysts.<sup>75,78</sup>

**Table 2** Microwave accelerated digestion methods for solid SRM samples.

Matrix	Elements	Digestion	Recovery rates	Ref.
Coal fly ash SRM 1633b	Cd,Co,Cr,Cu,Mn, Ni,Pb,Zn	HNO <sub>3</sub> +HF+H <sub>2</sub> O <sub>2</sub> + H <sub>3</sub> PO <sub>4</sub> , 73 min	91-107%	[84]
Coal fly ash SRM 1633b	As,Co,Cr,Cu,Fe,Mn, Ni,Pb,Sb,Se,V,Zn	HNO <sub>3</sub> +HF+H <sub>2</sub> O <sub>2</sub> + H <sub>3</sub> PO <sub>4</sub> , 45.5 min	75-103%	[88]
Coal fly ash SRM 1633b	As,Co,Cr,Cu,Fe,Mn, Ni,Pb,Sb,V,Zn	HNO <sub>3</sub> +HCl+HF, 42 min	94-140%	[89]
Coal fly ash SRM 1633b	As,Co,Cr,Cu,Ni, Pb,V,Zn	HNO <sub>3</sub> +H <sub>2</sub> O <sub>2</sub> +HF, 73 min	91-109%	[90]
Coal fly ash SRM 1633a	Cd,Cr,Ni,Cu,Pb,Zn	HNO <sub>3</sub> +HF+HClO <sub>4</sub> , 33 min	90-153%	[91]
Coal SRM 1632c	Al, Ca,Co, Cr,Cu, Fe, Mg,Mn,Ni,Pb,Zn	HNO <sub>3</sub> +H <sub>2</sub> O <sub>2</sub> , 73 min	92-108%	[92]
Coal SRM 1632c	As,Ba,Be,Co,Cr,Cu, Mn,Ni,Pb,Sb,Se,V,Zn	HNO <sub>3</sub> 60 min	89-111%	[93]
Sediment MESS-1	Cu,Cd,Ni,Pb	HNO <sub>3</sub> +HF+H <sub>2</sub> O <sub>2</sub> , 30 min	88-113%	[94]
Soil LGC6138	Cr,Cu,Ni,Pb,V,Zn	HNO <sub>3</sub> 36 min	96-135%	[95]
Soil CRM141R	Cd,Co,Cr,Cu,Mn, Pb,Zn	HNO <sub>3</sub> +HCl,	82-101%	[96]

### 3.3.2 Ultrasound-assisted digestion

Another sample pre-treatment method for the determination of trace element concentrations in solid samples is ultrasound-assisted digestion.<sup>4,5,79,97-100</sup> The use of ultrasound as a heat source is not as common as the use of microwaves in digestion procedures.<sup>1,2,4,5,86</sup> However, the use of ultrasound in biological, geological and medical applications is well known.<sup>79,101</sup>

Ultrasound consists of pressure waves at frequencies between 20 kHz and 1 MHz; those waves can be transmitted through any substance such as solids, liquids or gases.<sup>74,79,100,102,103</sup> Basic laboratory systems operate at frequencies between 20 and 80 kHz. The process in which bubbles form, grow and undergo implosive collapse is known as cavitation. Ultrasound cavitation can release large amounts of energy and it can produce both mechanical and chemical effects. Rapid compression of gases and vapors within bubbles produces extremely high temperatures (5000 °C) and pressure (1000-2000 atm.) creating localized "hot spots".<sup>79,102</sup> If cavitation occurs in a liquid near to a solid surface

those “hot spots” impact very strongly on the solid surface and can result in serious damage to the impact area.<sup>74,102</sup>

Solid sample digestion can in generally be performed by using ultrasound water baths or probes (an ordinary probe, a cup-horn system or a flow cell system).<sup>5,79,100,102</sup> Both techniques have some advantages and disadvantages.<sup>5,79</sup> Baths are used more often because they are cheaper and easier to use than probes. Using a bath for digestion means that no special reaction vessels are required, as all glass and plastic vessels or centrifuge tubes can be placed directly into the bath.<sup>5,79,104</sup> The use of baths offers the possibility of a high sample treatment capacity.<sup>5,79,105</sup> On the other hand, ultrasound probes often require shorter digestion times than water baths because of significantly higher maximum power.<sup>5,79,106</sup> Unlike baths, the power input of probes can be readily controlled so that the precise power of the system can be regulated. In the use of a probe there is a problem about accurate temperature control unless precautions are taken. Due to a direct contact of the ultrasound probe with the sample solution cavitation (corrosive) problems of the probe system may be present. In the use of baths, the position of the reaction vessel could significantly affect in results, because of possible inhomogeneity of ultrasound power in different locations of the bath.<sup>79</sup>

The main benefits of ultrasound-assisted (water bath) sample pre-treatment over other methods are the speed of digestion, a high sample treatment capacity (at least a capacity of 36 samples/30 minutes has been documented) and low reagent usage.<sup>5,107</sup> When an ultrasound water bath is used, the digestion can be performed in plastic screw-top bottles or polypropylene centrifuge tubes, which means that samples can be centrifuged instead of filtering.<sup>105,108,109</sup> Ultrasound-assisted digestion can also be performed more safely than closed vessel microwave digestion, because pressure and temperature are substantially lower in the former.<sup>109</sup> It should be noted that some researchers use combined ultrasound and microwave techniques for digestion.<sup>103</sup> Ultrasound-assisted digestion has been used for elemental analysis of many particulate materials such as geological samples, sediment, sewage sludge and soil.<sup>5,97-99,107,109,110</sup> Ultrasound-assisted digestion methods for particulate samples are presented in Table 3.

**Table 3** Ultrasound-assisted digestion methods for environmental SRM samples.

Matrix	Elements	Digestion	Recovery rates	Ref.
Coal fly ash, SRM 1633b	Co,Cr,Cu,Fe,Mn, Ni,Ti,V,Zn	Bath: <i>Aqua regia</i> +HF, 30 min	87-109%	[107]
Coal fly ash, SRM 1633b	Cd,Cr,Mn,Ni,Pb	Cup-horn Sonoreactor: HNO <sub>3</sub> +HF, 5-15 min	96-105%	[5]
Vehicle exhaust particulates, CRM-8	Cu,Ni,Pb,Zn	Bath: HNO <sub>3</sub> +HClO <sub>4</sub> +HF, 25 min	96-101%	[104]
Urban particu- late material, SRM 1648	As,Cd,Co,Cr, Cu,Fe,Mg,Mn, Ni,Pb,V,Zn	Bath: HNO <sub>3</sub> +HCl +HF, 60 min	23-130%	[99]
Soil BCR141R	Cd,Cr,Ni,Pb	Bath: HNO <sub>3</sub> +HCl, 40 min	96-99%	[111]
Sediment SRM 1646a	As,Co,Cr,Cu, Fe,Mg,Mn,Ni, Pb,Sn,V,Zn	Probe: HNO <sub>3</sub> +HCl, 1-59 min	18-146%	[112]
Sediment PACS-1	Cd,Cr,Cu,Fe, Ni,Pb,V,Zn	Bath: HNO <sub>3</sub> +HF+ H <sub>2</sub> O <sub>2</sub> , 30 min	70-110%	[97]
Sewage sludge BCR146R	Cd,Cr,Co,Cu, Mn,Ni,Pb,Zn	Probe: HNO <sub>3</sub> +HCl, 20 min	72-98%	[98]
Plant samples GBW07605	Mg,Mn,Zn	Probe: HCl, 3 min	88-98%	[113]

Many laboratories have recognized the potential of ultrasound energy in sample pre-treatment.<sup>5,74,114</sup> Ultrasound energy can be applied for simple, quick, safe and effective digestion of different kinds of matrices.<sup>4,5,115-119</sup> It is predicted that ultrasound digestion will become a common technique for routine sample pre-treatment.<sup>4,74</sup>

### 3.4 Interferences in ICP-OES

ICP-OES is a widely used method for the determination of element concentrations in solid samples.<sup>120-123</sup> Like other determination methods (e.g. FAAS and GFAAS), ICP-OES is subject to different kinds of interference. It is important to reduce or eliminate interferences caused by the sample matrix to ensure accurate determination of element concentrations.<sup>6,120,124,125</sup>

Interferences are certainly a challenge in ICP-OES and a number of papers deal with that subject area.<sup>126-133</sup> Interferences can be divided into several modes.<sup>7,8,121,124,125,134,135</sup> One way is to divide them into four types: matrix, chemical, ionization and spectral interferences.<sup>124,125,135</sup> Chemical interferences

are quite low due to the high operation temperature of the plasma and the comparatively long residence time for the sample in the plasma.<sup>124,135</sup> Therefore only the other three modes of interference are discussed in this thesis.

### 3.4.1 Spectral interferences

Spectral interferences are commonly observed in ICP-OES measurements due to the intense element emission lines in the high temperature environment of the plasma.<sup>7,124</sup> Spectral interferences can be divided into several categories: simple background shift, sloping background shift, direct overlap, and complex background shift.<sup>121,124,125</sup> All those interferences are extensively described and well documented.<sup>7,120,121,124,125</sup> Corrections for those interferences can be made, for example, with the following methods: optimized background correction point or points (simple and sloping background shift), inter-element correction (direct spectral overlap) and multiple linear regression techniques (complex background shift).<sup>7,120,121,124,136</sup>

Detailed information about the interferences in different elements, their wavelengths and correction methods can be found in the literature e.g. Boumans P.W.J.M.<sup>7</sup>, Winge R.K. *et al.*<sup>137</sup> and Daskalova N. *et al.*<sup>138</sup> Examples of the correction of different kinds of spectral interference are presented in Table 4.

**Table 4** Examples of correction methods for different kinds of spectral interferences.

Determined element	Interfering element	Type of interference	Correction Method	Ref.
As 193.696 nm	Fe	Background shift	BGC <sup>a</sup>	[133]
Pb 220.3 nm	Al 220.4 nm, Fe	Direct overlap, Background shift	IEC <sup>b</sup>	[132]
Cr 267.716 nm	Pt 267.715 nm	Direct overlap	IEC <sup>b</sup>	[125]
Sn 189.989 nm	As, Ag, Bi	Complex background shift	MLR <sup>c</sup>	[139]

<sup>a</sup>BGC = Background correction, <sup>b</sup>IEC = Inter-element correction, <sup>c</sup>MLR=Multiple linear regression

### 3.4.2 Matrix interferences

In this thesis, matrix interferences mean interferences that arise in the sample introduction in the ICP-OES. Interferences can arise in the different steps of the sample introduction system; those are aerosol formation, transport and filtration.<sup>134,140</sup> The efficiency of the sample introduction system is controlled by the surface tension and viscosity of samples.<sup>124,128,134,141</sup> Differences in the physical properties of the sample and calibration samples lead to variations in the aerosol droplet size and aerosol transportation. Results can be erroneously high or low, depending on how the efficiency of the sample introduction system is affected.<sup>8,124,128,134</sup>

There are two powerful methods to reduce or eliminate the effect of aerosol transportation interferences: use of internal standards or matrix matching.<sup>123,124,127,128,134,135,140,142</sup> Internal standards are used by adding the same concentration of the selected element to all standard, blank, and sample solutions. During the measurement the intensity of the internal standard signal is used to correct mathematically for intensity differences between standards and real samples. Internal standardization is commonly used, if difficult matrix interference is present.<sup>125,127,131,134,141,143-145</sup> The selection of internal standards is of crucial importance, because the method will be effective only if the behaviour of the internal standard is similar to that of the analytes measured. Potential internal standards are e.g. Be, Dy, Gd, La, Lu, Sc, Sm and Y.<sup>134,143-146</sup>

Matrix matching is an efficient and reliable method for the minimization of matrix interferences. In this method, matrices of the blank and the standards are carefully matched to be the same as the real sample matrix, the typically matched characteristics being the acid concentration and some significant element concentration.<sup>124,128,134,146,147</sup> It should be noted that the matching could be difficult if the matrix composition is poorly defined.<sup>125,128,134</sup> Elements such as Al, Ca, Fe, Ni, and V can cause significant interference to several elements.<sup>7,137,138</sup> For instance, the determination of As (193.696 nm) and Pb (220.353 nm) is subject to significant interference if 1000 mg L<sup>-1</sup> of Al is present.<sup>137</sup>

### 3.4.3 Ionization interferences

Ionization interferences typically occurs when easily ionized elements (EIE) such as Ca, K, Mg and Na are present.<sup>134,140,143,148,149</sup> The effect of EIEs in the plasma technique is quite complex. First, the EIEs in the samples can decrease, increase or not affect the analyte's signal. Second, there is no single explanation of the way those interferences are generated.<sup>8,134,140,143</sup> There are many things affecting EIE interference, such as the concentration and nature of the interfering element, the characteristics of the emission line, the plasma operation conditions and the plasma observation zone.<sup>131,134,140,150,151</sup> More information about the causes and influence of EIE interference can be found in the literature, for example Todoli J-L. *et al.*<sup>134</sup> At least two methods can be used for the evaluation, reduction or elimination of the effect of EIEs. Those methods are matrix matching and a study of the ionic-to-atomic line intensity ratio.<sup>127,131,140,146,148,149,151</sup>

### 3.4.4 Robust conditions of the plasma

Differences in the plasma conditions can be observed by a study of plasma thermal capability. That study can tell how close the plasma is to a local thermodynamic equilibrium (LTE).<sup>128,149,152,153</sup> The LTE conditions can be evaluated by calculating the ionic-to-atomic line intensity ratio. The intensity ratio MgII(280.270 nm)/MgI(285.213 nm) is commonly used.<sup>128,131,140,148,150-</sup>



<sup>152,154,155</sup> Some other line pairs can also be used for the same purpose, such as CrII(267.716 nm)/CrI(357.868 nm) and NiII(231.604)/NiI(232.138 nm).<sup>148,149,152,153</sup> When this line intensity ratio is higher than 8, the plasma is said to work under robust conditions. The plasma robustness in ICP-OES measurements indicates conditions where the plasma is able to keep the variation of an analyte signal to a minimum when the matrix composition changes.<sup>128,152</sup> Robust conditions are typically connected to a few circumstances such as a high power of the radio frequency (RF) generator, a low nebulizer gas flow rate and a large diameter of the injector.<sup>152</sup> According to the literature,<sup>148-150,152-154</sup> robust conditions are usually obtained when the RF power is between 1200-1500 W and the nebulizer gas flow rate is between 0.4-0.7 L min<sup>-1</sup>. Literature<sup>149,150</sup> comments indicate that when working with a radial view it is easier to attain robust conditions than working with an axial view in ICP-OES.

Robust conditions of the plasma are typically used to minimize or eliminate matrix interferences caused by acids, EIEs and other elements in the matrix.<sup>128,131,134,140,148,152,153</sup> The effect of the EIEs depends on the working conditions; typically the EIE effects are highest when working under non robust plasma conditions. A general conclusion for the evaluation of the EIE effect by Mg ratio is that it decreases in the presence of EIEs.<sup>134,155</sup>

### 3.4.5 Interferences in hydride generation ICP-OES

Hydride generation (HG) techniques connected to different kinds of excitation sources (i.e. ICP, MIP and DCP) in the emission spectrometry are widely used.<sup>156-160</sup> The determination of elements such as As, Bi, Ge, Sb, Se, Sn and Te for hydride generation technique are commonly used.<sup>156-160</sup> NaBH<sub>4</sub> is typically used for the formation of hydrides.<sup>156-164</sup> An essential advantage of the hydride generation technique is that it separates the elements of interest from the sample matrix. This way interferences are reduced or even eliminated. The benefits are improved sensitivity and limit of detection in emission spectrometry techniques.<sup>158,159,163,165,166</sup>

However, significant chemical and spectral interferences can occur when the HG technique is used. Interferences could arise in both liquid and gas phases.<sup>158,163,165,166</sup> Liquid phase interferences can be divided into two groups, compound and matrix interferences. Compound interference can appear when the oxidation state or chemical background of the analyte in the sample differs from that of the standards. Matrix interference can occur when sample matrix affects the hydride formation. Transition metals and some acids such as HNO<sub>3</sub> and HF are the main sources of matrix interference.<sup>156,158,165-167</sup> Interferences in the gas phase can also be divided into two groups, transport and atomization interferences. Transport interferences are caused by a delay and/or loss of the analyte hydride between the hydride forming generator and plasma. Typically, atomization interferences are not a significant problem in ICP-OES due to the high atomization and excitation temperature of the plasma and the

comparatively long residence time of the sample in the plasma.<sup>124,135,158,166</sup> Spectral interferences can be caused by a transport of interfering transition elements such as Co, Cu and Ni into the plasma.<sup>163,165,166</sup>

There is no simple method to minimize or eliminate interferences in HG technique, especially in the case of simultaneous determination of hydride-forming elements.<sup>158,163,166</sup> Interferences can be minimized by an optimization of several operation parameters, sample acidification, NaBH<sub>4</sub> concentration, flow rates of the reagents, concentration of hydride-forming elements and RF power.<sup>159,163,168,169</sup> Interferences of metals in the liquid phase can be effectively reduced or erased by complexing, masking or removing agents such as ascorbic acid, chelex-100, histidine, L-cysteine, potassium iodide, tartaric acid and thiourea.<sup>158,163,165,166,168,169</sup> Spectral interferences in the hydride generation technique can be handled with the same methods as in normal emission spectrometry<sup>158,165</sup>, such as those was presented in section 3.4.1. Matrix matching and internal standards could also be used in the determination of hydride-forming elements. Several examples with recoveries in SRMs, the instruments used and some hydride-forming elements determined in different matrices are presented in Table 5.

**Table 5** Recovery rates of hydride-forming elements in SRMs using different instruments with an HG device.

Element	Sample	Instrument	Recovery Rates	Ref.
As,Sb	SRM 1633a Coal fly ash	CF-HG-MSP-OES <sup>a</sup>	94-99%	[169]
As,Sb	SRM 1633a Coal fly ash	ECHG-MSP-OES <sup>b</sup>	96-97%	[170]
As,Sb,Se	SRM 2710 Montana soil	USN-HG-MIP-OES <sup>c</sup>	96-98%	[62]
As,Sb,Se,Sn	PAC-1, Marine sediment	SS-HG-MIP-OES <sup>d</sup>	93-112%	[159]
As,Se	SRM 2782 Industrial sludge	HG-ICP-OES <sup>e</sup>	101-109%	[171]
As,Se	SRM 1566a Oyster tissue	DHGN-ICP-OES <sup>f</sup>	108-109%	[172]
As	BCR 278R Mussel tissue	HG-ICP-OES <sup>e</sup>	100%	[173]

<sup>a</sup>CF-HG-MSP-OES = continuous flow hydride generation microstrip plasma optical emission spectrometry

<sup>b</sup>ECHG-MSP-OES = electrochemical hydride generation microstrip plasma optical emission spectrometry

<sup>c</sup>USN-CVG-MIP-OES = ultrasonic nebulizer hydride generation microwave induced plasma optical emission spectrometry

<sup>d</sup>SS-HG-MIP-OES = slurry sampling hydride generation microwave induced plasma optical emission spectrometry

<sup>e</sup>HG-ICP-OES = hydride generation inductively coupled plasma optical emission spectrometry

<sup>f</sup>DHGN-ICP-OES = direct hydride generation nebulizer inductively coupled plasma optical emission spectrometry

## 4 EXPERIMENTAL

All the experiments were carried out in the laboratory of Inorganic and Analytical Chemistry at the Department of Chemistry, University of Jyväskylä during 2005-2010. A summary of the experiments is presented below; more detailed information is given in the papers I-IV.

### 4.1 Instrumentation

All the measurements were performed with a Perkin-Elmer (Norwalk, CT, USA) model Optima 4300 DV inductively coupled plasma optical emission spectrometer (papers I-IV). A Scott type double-pass spray chamber and a cross-flow nebulizer were used throughout in papers I-III and the continuous flow hydride generator supplied by Perkin-Elmer (Norwalk, CT, USA) was used in paper IV. The element concentrations were determined with instrument parameters presented in Table 6.

**Table 6** Instrument parameters used in papers (I-IV).

Paper	Plasma (view)	RF power (W)	Plasma gas flow (Ar L min <sup>-1</sup> )	Aux. gas flow (Ar L min <sup>-1</sup> )	Neb. gas flow ( Ar L min <sup>-1</sup> )
I	Radial	1400	15.0	0.2	0.6
II	Radial	1400	15.0	0.2	0.6
III	Axial	1400 or 1500	15.0	0.2	0.5 or 0.6
IV	Axial	1450	17.0	0.2	0.5

The ultrasound-assisted digestion was carried out in an ELMA Model Transsonic 820/H ultrasound water bath with an operating power of 650 W and frequency of 35 kHz (papers I-IV).

The microwave accelerated digestion was done in a MILESTONE Model Ethos Plus microwave digestion system with an operating power of 1000 W and frequency of 2450 MHz (papers I-IV).

## 4.2 Reagents and samples

All the reagents used were of analytical grade and only high purity water of 18.2 M $\Omega$  cm resistivity produced by a Maxima water purification system supplied by Elga was used. All the concentrated acids used were of analytical grade and the standard stock solutions (1000 mg L<sup>-1</sup>) for the measurements were supplied by Merck. The standard stock solutions (10000 mg L<sup>-1</sup>) for the interference tests were prepared (papers III and IV). More detailed information about the reagents is given in the papers.

One fly ash (papers I-IV) SRM 1633b<sup>174</sup> (Trace elements in coal fly ash) standardized by NIST (National Institute of Standards and Technology) was used for analyses. Two bottom ash (paper I) and eleven fly ash samples (papers I-IV) were also analyzed. All fly ash (FA) samples were collected from wood burning plants and both bottom ash (BA) samples were collected from municipal solid waste incineration plants in Finland.

## 4.3 Digestion of ash samples

### 4.3.1 Microwave accelerated digestion methods

The microwave accelerated digestion method from the United States Environmental Protection Agency (USEPA 3052 method)<sup>175</sup> was used as a reference method. The second microwave method used was based on this method but a different digestion solution was used.

1. An SRM sample of about 500 mg was accurately weighed into a 100 mL tetrafluormethaxil vessel into which 9 mL of conc. HNO<sub>3</sub> and 3 mL of conc. HF were added. After 30 minutes the sample was placed into a microwave digestion system and heated with a digestion program containing a power of 1000 W for 5 min, during which a temperature of 180 °C was reached (step 1) and a power of 1000 W for 10 min at 180 °C (step 2) (papers I-IV).
2. The microwave accelerated digestion method was performed with the same digestion program, but with a digestion solution of 10 mL of *aqua regia* and 0.5 mL of conc. HF (paper I).

After both microwave digestion procedures the sample solution was filtered (Whatman No. 41) into a 100 mL plastic volumetric flask. The residue was washed with 20 mL of water introduced in three portions, and the filtrate was diluted to volume with water. The sample solution was transferred into a plastic screw-top bottle for storage (papers I-IV).

#### 4.3.2 Ultrasound-assisted digestion methods

1. An ash sample of about 250 mg was accurately weighed into a 50 mL plastic screw-top centrifuge tube into which 10.5 mL of a digestion solution of *aqua regia* (10 mL) and conc. HF (0.5 mL) was added. The tube was closed and placed into an ultrasonic water bath. The sonication procedure was divided into six equal steps (3 min) with the sample bottle shaken by hand between each step. The shaking was used to prevent sedimentation (papers I and III).
2. The second ultrasound-assisted digestion method was performed with a digestion solution of 5 mL of *aqua regia* and 5 mL of water. An ash sample of about 250 mg was accurately weighed into a 50 mL plastic screw-top centrifuge tube into which the digestion solution was added. The sonication procedure was divided into three equal steps (3 min) with the sample bottle shaken between each step (papers I, III and IV).
3. The third ultrasound-assisted digestion method was performed with a digestion solution of 9 mL of conc. HNO<sub>3</sub> and 3 mL of conc. HF. An ash sample of about 250 mg was accurately weighed into a 50 mL plastic screw-top centrifuge tube into which the digestion solution was added. The sonication procedure was divided into six equal steps (3 min) with the sample bottle shaken between each step. (paper II).
4. The fourth ultrasound-assisted digestion method was performed with a digestion solution of 3 mL of *aqua regia* and 3 mL of conc. HF. An ash sample of about 250 mg was accurately weighed into a 50 mL plastic screw-top centrifuge tube into which the digestion solution was added. The sonication procedure was divided into six equal steps (3 min) with the sample bottle shaken between each step. (paper II).
5. The fifth ultrasound-assisted digestion method was performed with a digestion solution of 9 mL of conc. HNO<sub>3</sub> and 3 mL of conc. HF. An ash sample of about 250 mg was accurately weighed into a 50 mL plastic screw-top centrifuge tube into which the digestion solution was added. The tube was closed and placed into an ultrasonic water bath. After digestion step 1 the sample solution was centrifuged (2500 rpm for 10 min) and the solution was pipetted into a 100 mL plastic volumetric flask. The acid mixture for the second step was added and the last part of the digestion procedure was performed (papers II-IV).

The optimized two-step ultrasound-assisted digestion procedure included solutions and sonication times with temperatures as follows (papers II-IV):

- (1) Step 1: The sample was digested with a solution of 6 mL of conc.  $\text{HNO}_3$  for 9 min ( $3 \times 3$  min) sonication at 60 °C.
- (2) Step 2: The residue from step 1 was digested with a solution of 3 mL of conc.  $\text{HNO}_3$  + 3 mL of conc. HF for 18 min ( $6 \times 3$  min) sonication at 60 °C.

After all ultrasound digestion procedures the sample solution was filtered (Whatman No. 41) into a 50 or 100 mL plastic volumetric flask. The residue was washed with 15 mL of water introduced in 3 portions, and the filtrate diluted to volume with water. The sample solution was transferred into a plastic screw-top bottle for storage (papers I-IV).

## 5 RESULTS AND DISCUSSION

Several new methods of ultrasound-assisted digestion followed by inductively coupled plasma optical emission spectrometry (ICP-OES) used for the determination of antimony, arsenic, barium, chromium, cobalt, copper, lead, nickel, strontium, vanadium and zinc concentrations in ash samples were developed. The instrument parameters were first optimized.<sup>I</sup> Second, the ultrasound field was tested.<sup>I</sup> Third, several optimized ultrasound-assisted digestion methods were developed.<sup>II</sup> Fourth, an interference study of arsenic and lead was performed.<sup>III</sup> Fifth, two hydride forming elements were accurately determined by HG-ICP-OES.<sup>IV</sup> After that a summary of methods was developed and a comparison of analytical results produced with published results was presented.<sup>I-IV</sup>

### 5.1 Calibration

All the concentration measurements were carried out using a four-point calibration. Multi element calibration standards were used for all elements (As, Ba, Co, Cr, Cu, Ni, Pb, Sb, Sr, V, and Zn).<sup>I-IV</sup> The sample matrix (acids and other reagents) of calibration standards for all measurements was matched to be similar to the samples. All elements were determined by using two of the most sensitive emission lines to attain the sensitivity required.

The regression correlation coefficient  $r$ , the limit of detection (LOD) and limit of quantification (LOQ) were calculated. The wavelengths, the calibration range and the calibration data for the elements are presented in Table 7. Several LOD and LOQ values for some element in Table 7 were occurred different determination methods.<sup>I-IV</sup> As can be seen, high values were obtained for regression correlation coefficients. The LOQ values of some elements such as As, Co, and Sb, are very good while some values, those for Ba, Sr, and Zn, could be



better. Excellent LOQ values for As and Sb were obtained using the hydride generation technique and appropriate measurement parameters and the optimization of the reagents used.

**Table 7** Calibration data for the determination of elements by ICP-OES (papers I-IV).

Element	Wavelengths (nm)	r	LOD (mg kg <sup>-1</sup> )	LOQ (mg kg <sup>-1</sup> )	Calibration ranges (mg L <sup>-1</sup> )
As	188.979	0.9999	2.6 <sup>I</sup> ,9.9 <sup>III</sup>	8.6 <sup>I</sup> ,33.0 <sup>III</sup>	0.1-10.0
	193.696	0.9999	2.1 <sup>I</sup> ,4.7 <sup>III</sup>	6.8 <sup>I</sup> ,15.7 <sup>III</sup>	0.1-10.0
As*	188.979	1.0000	0.12 <sup>IVa</sup> ,0.39 <sup>IVb</sup>	0.40 <sup>IVa</sup> ,1.29 <sup>IVb</sup>	0.002-0.200
	193.696	1.0000	0.05 <sup>IVa</sup> ,0.27 <sup>IVb</sup>	0.16 <sup>IVa</sup> ,0.89 <sup>IVb</sup>	0.002-0.200
Ba	230.425	0.9999	4.2 <sup>I</sup>	14.1 <sup>I</sup>	0.2-20.0
	233.527	0.9999	3.7 <sup>I</sup>	12.4 <sup>I</sup>	0.2-20.0
Co	228.616	1.0000	0.3 <sup>I</sup>	0.9 <sup>I</sup>	0.1-10.0
	238.892	0.9999	1.3 <sup>I</sup>	4.3 <sup>I</sup>	0.1-10.0
Cr	267.716	0.9999	5.1 <sup>II</sup>	17.1 <sup>II</sup>	0.1-10.0
	357.869	0.9999	3.1 <sup>II</sup>	11.1 <sup>II</sup>	0.1-10.0
Cu	324.752	0.9999	1.9 <sup>I</sup> ,5.4 <sup>II</sup>	6.3 <sup>I</sup> ,18.1 <sup>II</sup>	0.1-10.0
	327.393	0.9999	1.7 <sup>I</sup> ,4.1 <sup>II</sup>	5.8 <sup>I</sup> ,13.6 <sup>II</sup>	0.1-10.0
Ni	231.604	0.9999	0.5 <sup>I</sup> ,3.2 <sup>II</sup>	1.6 <sup>I</sup> ,10.7 <sup>II</sup>	0.1-10.0
	232.003	0.9999	2.8 <sup>I</sup> ,7.0 <sup>II</sup>	9.3 <sup>I</sup> ,23.3 <sup>II</sup>	0.1-10.0
Pb	217.000	0.9999	2.8 <sup>I</sup> ,5.0 <sup>II</sup> ,5.7 <sup>III</sup>	9.2 <sup>I</sup> ,16.7 <sup>II</sup> ,19.0 <sup>III</sup>	0.1-10.0
	220.353	0.9999	1.1 <sup>I</sup> ,6.4 <sup>II</sup> ,4.9 <sup>III</sup>	3.7 <sup>I</sup> ,21.3 <sup>II</sup> ,16.3 <sup>III</sup>	0.1-10.0
Sb*	206.836	0.9999	0.19 <sup>IVa</sup> ,0.46 <sup>IVb</sup>	0.62 <sup>IVa</sup> ,1.55 <sup>IVb</sup>	0.002-0.200
	217.582	0.9999	0.14 <sup>IVa</sup> ,0.41 <sup>IVb</sup>	0.45 <sup>IVa</sup> ,1.37 <sup>IVb</sup>	0.002-0.200
Sr	232.235	0.9998	3.7 <sup>I</sup>	12.2 <sup>I</sup>	0.2-20.0
	460.733	0.9999	5.2 <sup>I</sup>	17.3 <sup>I</sup>	0.2-20.0
V	290.880	0.9999	2.3 <sup>I</sup> ,4.8 <sup>II</sup>	7.7 <sup>I</sup> ,16.1 <sup>II</sup>	0.1-10.0
	309.310	0.9999	3.6 <sup>I</sup> ,4.6 <sup>II</sup>	12.1 <sup>I</sup> ,15.5 <sup>II</sup>	0.1-10.0
Zn	206.200	0.9998	4.4 <sup>I</sup> ,6.4 <sup>II</sup>	14.6 <sup>I</sup> ,21.2 <sup>II</sup>	0.2-20.0
	213.857	0.9999	5.9 <sup>I</sup> ,6.5 <sup>II</sup>	19.6 <sup>I</sup> ,21.6 <sup>II</sup>	0.2-20.0

LOD = Calculated by substituting the intercept and its standard deviations multiplier ( $a + 3s_a$ ) into the calibration line  $y = bx + a$ .

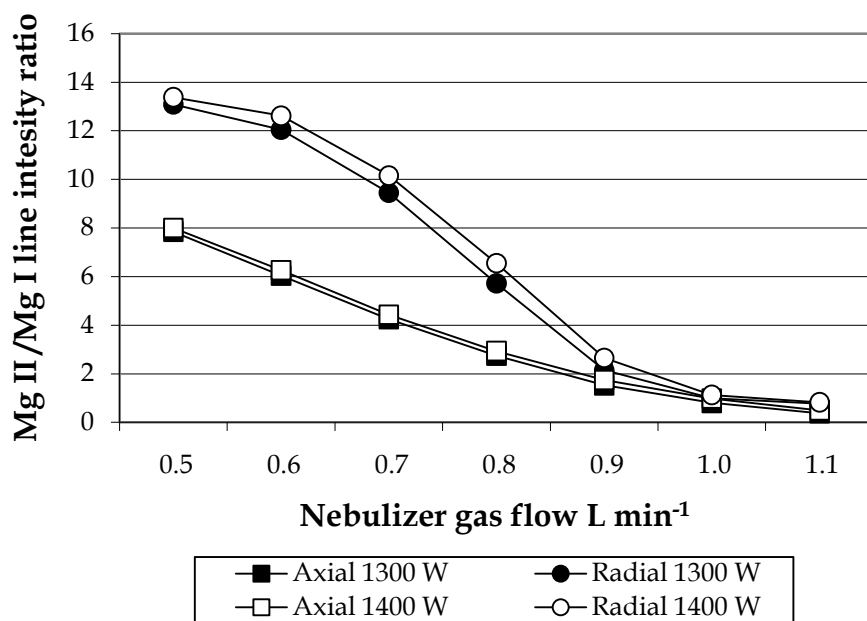
LOQ = Calculated by substituting the intercept and its standard deviations multiplier ( $a + 10s_a$ ) into the calibration line  $y = bx + a$ .

\*determined by HG-ICP-OES, <sup>a</sup>without boric acid, <sup>b</sup> with boric acid

## 5.2 Robust conditions of the plasma

In this work, the LTE conditions of plasma were evaluated by calculating the MgII(280.270 nm)/MgI(285.213 nm) line intensity ratio. The ratio was determined by the analysis of synthetic mixture of matrix elements (Al, Ca, Fe,

K, Mn, Na, P, and Si)<sup>I</sup> containing 10 mg L<sup>-1</sup> of Mg. The values of the ionic to atomic line intensity ratio are presented in Figure 1.



**Figure 1** Values of Mg II /Mg I line intensity ratio for a synthetic mixture of the matrix elements containing 10 mg L<sup>-1</sup> of Mg at different nebulizer gas flow rates and RF power. Precision of measurement values resulted in 1-3 %.

As can be seen in Figure 1, the values of the line intensity ratio demonstrated the efficiency of a RF power of 1400 W and the radial view. All the nebulizer gas flows for both the plasma viewings tested produced slightly higher line intensity ratios with 1400 W than with 1300 W RF power (Figure 1). The line intensity ratio in radially viewed plasma was about two times higher than that in axially viewed plasma when the nebulizer gas flow was varied from 0.5 to 0.8 L min<sup>-1</sup>. According to the intensity ratio, robust plasma conditions (ratio >8) could be obtained when the nebulizer gas flow varied from 0.5 to 0.7 L min<sup>-1</sup> with RF power of 1300 W and 1400 W for radially viewed plasma. As can be seen in Figure 1, robust plasma conditions cannot be obtained for axially viewed plasma with one exception of a nebulizer gas flow of 0.5 L min<sup>-1</sup> where an intensity ratio of 8 was barely reached with both RF powers.

### 5.3 Evaluation of digestion methods

First, the homogeneity of the ultrasonic field was tested. According to the Grubbs and Dixons outlier tests, significant differences in element concentrations were not observed between the samples digested at different locations in the ultrasound water bath (Table 8), with one exception for test 1, vanadium. The ultrasound field homogeneity test was performed repeatedly using the SRM 1633b and a sonication time of 15 min. The test shows that at

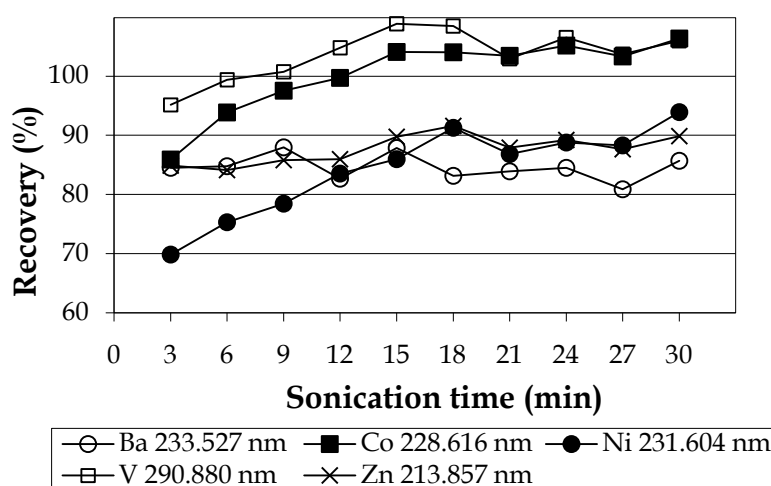
least six samples can be digested at the same time in a homogeneous ultrasonic field.

Second, several acid compositions and different sonication times were tested. The most appropriate acid composition is presented in Table 9. Recoveries (mean of three replicate samples) of five analytes using different sonication times are presented in Figure 2. According to the analyte concentrations determined, the sonication time of 18 min was selected, because it resulted in the highest recovery rates for the four elements investigated.

**Table 8** Ultrasound field homogeneity test (six locations).

<i>Outlier test</i> <i>Critical value</i> ( <i>P</i> =0.05)	<i>Dixon</i>		0.621		<i>Grubbs</i>		1.887	
	value	result	value	result	value	result	value	result
	<i>Test 1</i>		<i>Test 2</i>		<i>Test 1</i>		<i>Test 2</i>	
As	0.333	+	0.263	+	1.525	+	1.498	+
Ba	0.205	+	0.601	+	1.324	+	1.799	+
Co	0.405	+	0.553	+	1.566	+	1.860	+
Cu	0.432	+	0.333	+	1.680	+	1.635	+
Ni	0.551	+	0.413	+	1.825	+	1.682	+
Pb	0.258	+	0.320	+	1.468	+	1.404	+
Sr	0.437	+	0.477	+	1.614	+	1.681	+
V	0.867	-	0.167	+	2.017	-	1.054	+
Zn	0.143	+	0.401	+	1.414	+	1.710	+

(+) = no outlier, (-) = one outlier



**Figure 2** Effect of sonication time on element recoveries (mean of three samples) of ultrasound-assisted digestion in SRM 1633b. Precision of the recovery rates resulted in 2 - 4 %.

The concentrations determined for the elements in SRM 1633b digested by different methods are shown in Table 9. As can be seen, digestion method U2 was found to be most suitable for arsenic determination (recovery > 90 %), but it was

not a useful digestion method for other elements of interest (recoveries varied from 10% for Co to 27% for V). According to Table 9, HF was needed for the digestion of elements in ash with one exception, arsenic, which resulted in the highest recovery without HF. As can be seen in Table 9, the Ba, Sr and Zn concentrations were significantly higher in the ultrasound method U1 than in the microwave method M1.

In general, the ultrasound-assisted digestion method U1 and the standard microwave method (USEPA method 3052)<sup>175</sup> resulted in almost equal element concentrations; there were some exceptions such as Ba and Sr. Regardless of the quite satisfactory results, improvement in the digestion was needed for some elements such as Cu, Ni and Zn.

**Table 9** Element concentrations (mg kg<sup>-1</sup>) determined for three different digestion procedures in SRM 1633b (mean of six replicate samples, with the confidence limit of the mean, P = 0.05).

Element	Microwave M1 <sup>a</sup>	Ultrasound U1 <sup>b</sup>	Ultrasound U2 <sup>c</sup>	Certified
As	115 ± 5	81 ± 10	123 ± 3	136.2 ± 2.6
Ba	113 ± 12	577 ± 11	165 ± 4	709 ± 27
Co	54 ± 1	52 ± 1	5 ± 1	50*
Cu	94 ± 2	94 ± 2	22 ± 1	112.8 ± 2.6
Ni	110 ± 1	102 ± 3	12 ± 1	120.6 ± 1.8
Pb	63 ± 4	58 ± 4	18 ± 1	68.2 ± 1.1
Sr	47 ± 5	869 ± 11	264 ± 3	1041 ± 14
V	336 ± 2	300 ± 6	81 ± 1	295.7 ± 3.6
Zn	163 ± 2	185 ± 3	34 ± 2	210*

\* Non certified value (SRM 1633b)

<sup>a</sup> M1 = Microwave, digestion solution of 9 mL of conc. HNO<sub>3</sub> +3 mL of conc. HF, USEPA 3052 method<sup>175</sup>

<sup>b</sup> U1 = Ultrasound, digestion solution of 10 mL *aqua regia* + 0.5 mL conc. HF, 18 min (6 × 3 min)

<sup>c</sup> U2 = Ultrasound, digestion solution of 5 mL *aqua regia* + 5 mL water, 9 min (3 × 3 min)

## 5.4 Improvement of the digestion method for several elements

Six elements, Cr, Cu, Ni, Pb, V and Zn, were studied because of their toxic character and a general need for improvement in their digestion. Several mixtures of *aqua regia*, HF, HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> as a digestion solution were tested.<sup>11</sup> Those tests showed that digestion solutions of 9 mL of conc. HNO<sub>3</sub> and 3 mL of conc. HF, as well as 3 mL of *aqua regia* and 3 mL of conc. HF, were found to be most suitable. Next, two step digestion procedures were tested. The idea for a two step digestion method was adapted from sequential extraction procedures.

Ultrasound two step digestion (US-TSD) procedures were performed by determining the concentrations in SRM 1633b. The purpose of the first step was to dissolve easily digestible materials and remove at least some of the elements such as Ca and Mg which possibly precipitate with HF. Tests showed that digestion solutions of 9 mL of conc. HNO<sub>3</sub> and 3 mL of conc. HF were found most suitable.<sup>11</sup> After the first step with a digestion solution of 6 mL of conc. HNO<sub>3</sub> the second step was performed with a digestion solution of 3 mL of conc. HNO<sub>3</sub> + 3 mL of conc. HF. The digestion time for the US-TSD method resulted in a total of 27 min (9+18 min). The concentrations of the elements obtained by different digestion methods are shown in Table 10.

**Table 10** Element concentrations determined (mg kg<sup>-1</sup>) for three different digestion procedures in SRM 1633b (mean of six replicate samples, with the confidence limit of the mean,  $P = 0.05$ ).

Element	Microwave MW <sup>a</sup>	Ultrasound US <sup>b</sup>	Ultrasound US-TSD <sup>c</sup>	Certified
Cr	167 ± 2	151 ± 3	169 ± 1	198.2 ± 4.7
Cu	94 ± 2	99 ± 1	104 ± 3	112.8 ± 2.6
Ni	110 ± 1	106 ± 2	112 ± 2	120.6 ± 1.8
Pb	65 ± 2	64 ± 4	100 ± 14	68.2 ± 1.1
V	286 ± 4	284 ± 2	292 ± 3	295.7 ± 3.6
Zn	163 ± 2	204 ± 4	207 ± 4	210*

\*Non-certified value (SRM 1633b)

<sup>a</sup> MW = Microwave, digestion solution of 9 mL conc. HNO<sub>3</sub> + 3 mL conc. HF, USEPA method 3052<sup>175</sup>

<sup>b</sup> US = Ultrasound, digestion solution of 9 mL conc. HNO<sub>3</sub> + 3 mL conc. HF, 18 min (6 × 3 min)

<sup>c</sup> US-TSD = Ultrasound (two-step): i) digestion solution of 6 mL of conc. HNO<sub>3</sub>, 9 min (3 × 3 min) ii) digestion solution of 3 mL conc. HNO<sub>3</sub> + 3 mL conc. HF, 18 min (6 × 3 min)

A comparison of digestion techniques with the same digestion solution was made using methods MW and US. According to the *t*-tests ( $P = 0.05$ ), Cu and Zn concentrations were significantly higher using the US than in the MW method. On the other hand, the MW method resulted in significantly higher concentrations for Cr and Ni than the US method. Significant differences between US and MW methods were not found for Pb and V (Table 10).

As can be seen in Table 10, the highest accuracy was reached with the ultrasound-assisted two-step digestion (US-TSD) for all investigated elements with one exception, Pb, which gave concentrations significantly higher than the certified ones. The US-TSD resulted in recoveries of 92%, 93%, 146%, 99% and 99% for Cu, Ni, Pb, V and Zn, respectively. The determination of Cr yielded a recovery rate of 85% using the MW and US-TSD methods. It should be noted that some of the chromium compounds are difficult to digest even with the use of conc. HF under high temperatures and pressures.<sup>2</sup> Confidence limits of the mean for all elements and digestion methods were quite similar with one

exception in the US-TSD method, Pb, for which the confidence limit was several times higher than for others.

A significant improvement for the digestion of the elements studied was obtained (Table 10). Only Pb was a problem in the US-TSD method, because the certified value was significantly exceeded. The high recovery (146%) of Pb was probably due to matrix interferences in the measurement and, thus, more investigation of determination of Pb is needed.

## 5.5 Interferences in the ICP-OES measurements

The As and Pb results were not satisfactory in different digestion methods such as US2<sup>I</sup> and US-TSD<sup>II</sup>. Therefore a multiple linear regression (MLR) technique was used to evaluate and correct the matrix interferences in the determination of As and Pb concentrations in fly ashes.

In this case, the interferences caused by the matrix elements Al, Ca, Fe, and Si<sup>7,137</sup> in the determination of As and Pb were studied. More detailed information about the MLR method was presented in paper III. The interference effects were evaluated at wavelengths and instrument parameters which had produced statistically unacceptable analyte concentrations using the paired *t*-test (Table 11). The test showed that the most suitable parameters for the determination of As and Pb were a RF power of 1500 W and a nebulizer gas flow of 0.5 or 0.6 L min<sup>-1</sup>.

**Table 11** The results of the paired *t*-tests in the evaluation of differences between the added and determined or corrected concentrations on the multiple regression line calculated from the analytical results of 19 synthetic mixtures of the analyte elements.

Parameters / Element	As 188.979 nm	As 193.696 nm	Pb 217.000 nm	Pb 220.353 nm
<i>Added / Determined</i>				
Axial, 1500 W:				
Neb. gas flow: 0.5 L min <sup>-1</sup>	8.530	6.116	3.036	2.423
Neb. gas flow: 0.6 L min <sup>-1</sup>	8.658	7.002	2.758	<b>1.503</b>
<i>Added / Corrected</i>				
Axial, 1500 W:				
Neb. gas flow: 0.5 L min <sup>-1</sup>	4.804	<b>1.653</b>	7.227	<b>0.481</b>
Neb. gas flow: 0.6 L min <sup>-1</sup>	3.584	<b>2.001</b>	2.169	<b>1.590</b>
$t_{\text{critical}(18)} = \mathbf{2.10}$				

$t_{\text{critical}(18)}$  = obtained from the *t*-distribution with the 18 degrees of freedom at the confidence level of 95%

As can be seen in Table 11, the most suitable wavelengths are 193.696 nm for As and 220.353 nm for Pb. According to Table 11, an MLR correction for both elements was needed, when the As and Pb concentrations were determined

using a RF power of 1500 W and a nebulizer gas flow of 0.5 L min<sup>-1</sup>, but the determination of As and Pb with a RF power of 1500 W and a nebulizer gas flow of 0.6 L min<sup>-1</sup> resulted in concentrations where only As had to be corrected by the MLR technique.

The MLR parameters calculated for As 193.696 nm and Pb 220.353 nm are shown in Table 12. The calculations were performed by SigmaStat and only statistically significant ( $P < 0.05$ ) correction parameters were taken into consideration.

**Table 12** Multiple linear regression data from the 19 synthetic mixtures of matrix elements.

Element / parameters	Multiple linear regression expression	R
<i>As 193.696 nm</i>		
Axial, 1500 W:		
Neb. gas flow: 0.5 L min <sup>-1</sup>	+ [1.01As] + [0.0001083Al]	0.998
Neb. gas flow: 0.6 L min <sup>-1</sup>	+ [1.02As] + [0.0001443Al]	0.999
<i>Pb 220.353 nm</i>		
Axial, 1500 W:		
Neb. gas flow: 0.5 L min <sup>-1</sup>	- 0.05528 + [1.15Pb] + [0.0001169Al]	0.999
Neb. gas flow: 0.6 L min <sup>-1</sup>	- 0.052085 + [1.14Pb] + [0.0001046Al] - [0.00010182Fe]	0.999

According to Table 12, the matrix interferences in the determination of As at 193.696 nm were caused by Al, whereas the matrix interferences in the determination of Pb at 220.353 nm were caused by Al and Fe by using a RF power of 1500 W and a nebulizer gas flow of 0.5 or 0.6 L min<sup>-1</sup>. According to the MLR data<sup>III</sup>, the As at 188.979 nm and Pb at 217.000 nm concentrations were interfered by Ca and Al, Ca and Fe, respectively. Due to this an accurate determination of As at 188.979 nm and Pb at 217.000 nm cannot be performed. The results of paper III showed that the sample matrix can strongly interfere with the determination of As and Pb concentrations in fly ash samples.

The directly determined, corrected and certified concentrations of As and Sb in SRM 1633b with the recoveries are shown in Table 13. As can be seen, the MLR correction of the Pb concentrations (RF power of 1500 W, neb. gas flow of 0.5 L min<sup>-1</sup>) in the digestion method US-TSD was performed successfully resulting in a recovery rate of 97.6 %. The direct determination of Pb concentrations (RF power of 1500 W, neb. gas flow of 0.6 L min<sup>-1</sup>) in the digestion method US-TSD was also performed successfully resulting in a recovery rate of 98.3 % (Table 13). The confidence limit of the mean for both parameters in the digestion method US-TSD was found to be about 1%, which is very good compared with the previous Pb result in Table 10.

The corrected concentration of the SRM for As was not successful because all results were still too low. The most appropriate corrected concentrations of As was obtained using the digestion method US2 (RF power of 1500 W, neb. gas flow of 0.6 L min<sup>-1</sup>); the corrected As recovery resulted in 92.9% in the SRM sample (Table 13). The confidence limit of the mean for the same instrument parameters in the corrected SRM sample resulted in 1.6%. However, it should be noted that the corrected mean concentration of As approached the certified value. The analysis of the Pb concentration in the SRM sample was successfully performed by direct determination or using the multiple linear regression technique (Table 13), whereas the analysis of As still needs improvement.

**Table 13** The determined and corrected concentrations in four different digestion methods of the SRM 1633b based on the multiple regression line calculated from the analytical results of synthetic mixtures of matrix elements (mean of six replicate samples, with the confidence limit of the mean,  $P = 0.05$ ).

Element /Parameters	Determined mg kg <sup>-1</sup>	Recovery %	Corrected mg kg <sup>-1</sup>	Recovery %
<i>As 193.696 nm</i>				
Axial, 1500 W, US-TSD <sup>a</sup> :				
Neb. gas flow: 0.5 L min <sup>-1</sup>	99.3 ± 2.6	72.9 ± 2.0	115.3 ± 2.6	84.7 ± 2.0
Neb. gas flow: 0.6 L min <sup>-1</sup>	98.0 ± 5.0	72.0 ± 3.8	120.0 ± 5.1	88.1 ± 3.8
Axial, 1500 W, US2 <sup>b</sup> :				
Neb. gas flow: 0.5 L min <sup>-1</sup>	123.7 ± 2.4	90.8 ± 1.8	125.7 ± 2.5	92.3 ± 1.7
Neb. gas flow: 0.6 L min <sup>-1</sup>	122.7 ± 2.1	90.1 ± 1.5	126.5 ± 2.1	92.9 ± 1.6
Certified	136.2 ± 2.6		136.2 ± 2.6	
<i>Pb 220.353 nm</i>				
Axial, 1500 W, US-TSD <sup>a</sup> :				
Neb. gas flow: 0.5 L min <sup>-1</sup>	62.4 ± 0.8	91.4 ± 1.1	66.5 ± 0.7	97.6 ± 1.0
Neb. gas flow: 0.6 L min <sup>-1</sup>	67.0 ± 0.6	98.3 ± 0.8	63.9 ± 0.4	93.6 ± 0.6
Axial, 1500 W, US2 <sup>b</sup> :				
Neb. gas flow: 0.5 L min <sup>-1</sup>	< LOQ	< 15 %	< LOQ	< 15 %
Neb. gas flow: 0.6 L min <sup>-1</sup>	< LOQ	< 15 %	< LOQ	< 15 %
Certified	68.2 ± 1.1		68.2 ± 1.1	

LOQ = limit of quantification

<sup>a</sup>US-TSD = Ultrasound (two-step): i) digestion solution of 6 mL of conc. HNO<sub>3</sub>, 9 min (3 × 3 min) ii) digestion solution of 3 mL conc. HNO<sub>3</sub> + 3 mL conc. HF, 18 min (6 × 3 min)

<sup>b</sup>US2 = Ultrasound, digestion solution of 5 mL *aqua regia* + 5 mL water, 9 min (3 × 3 min)

## 5.6 Hydride generation technique

Hydride generation inductively coupled plasma atomic emission spectrometer is a sensitive tool for the determination of elements such as As, Bi, Sb, and Sn; therefore the HG technique makes it possible to determine Sb and try to improve the determination of As concentrations in fly ash samples. Different

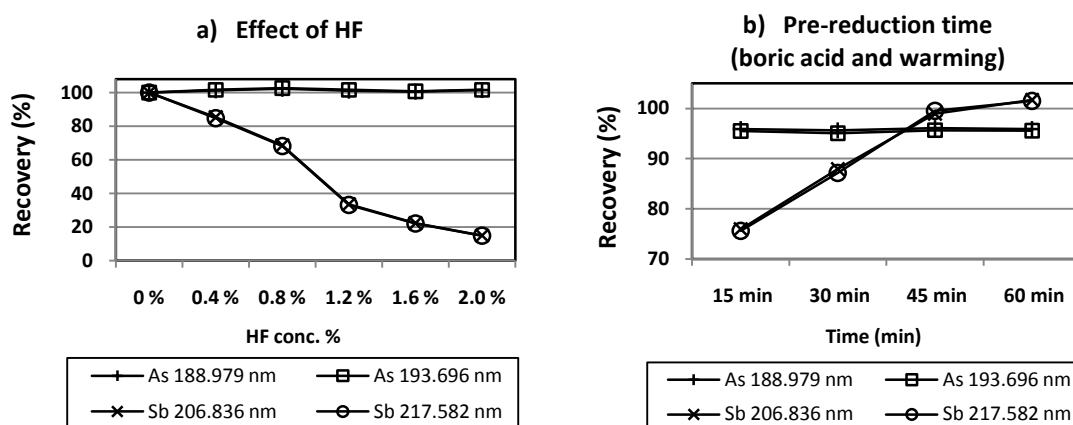


parameters were tested such as the memory effect, the influence of pre-reduction reagents and acids.<sup>IV</sup> At first, elimination of memory effect was studied. The test showed that memory effect was significantly higher for Sb than for As. The read delay time should be at least 60 seconds in order to eliminate the memory effects.

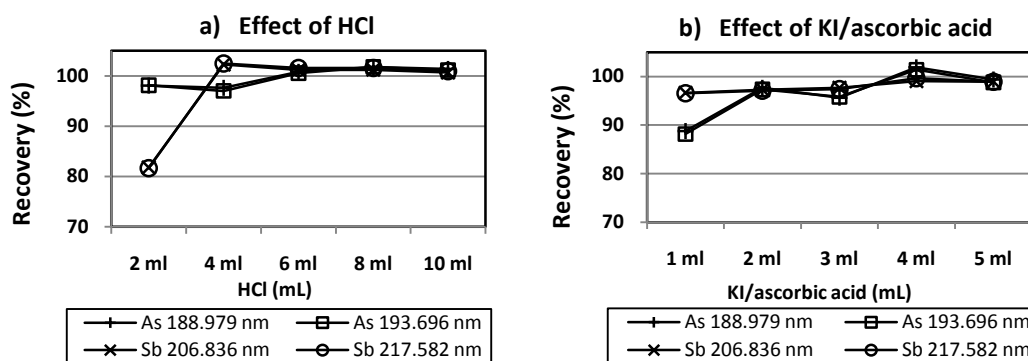
Then the effect of different acids, of the volume of pre-reduction reagents and of the pre-reduction time was tested (Figures 3 and 4). As could be seen in Figure 3, tests showed that HF has a significant effect on the determination of Sb concentrations (Figure 3a) and at least 45 minutes of pre-reduction time was needed (Figure 3b). Tests also showed that if the HNO<sub>3</sub> concentration in the samples was lower than 10%, it did not significantly affect the determination of As and Sb concentrations.<sup>IV</sup>

Two different pre-reduction procedures, method A and method B, were performed for As and Sb. Unlike method A, method B contained boric acid and the pre-reduction was performed at 60°C. Boric acid was used to eliminate the effect of hydrogen fluoride. Possible interferences caused by matrix elements Al, Co, Cr, Cu, Fe, and Ni were also tested. The test showed that in this case those elements do not interfere in the determination of As and Sb concentrations in the fly ash samples.<sup>IV</sup>

According to the reagent volume tests, the appropriate volumes of 5% KI/ascorbic acid mixture, conc. HCl and sat. H<sub>3</sub>BO<sub>3</sub> solutions for 10 mL of sample solution were 4, 6 and 2 mL, respectively (Figure 4 and paper IV). It should be noted that if only As concentrations in fly ash are determined, there is no need to use boric acid.



**Figure 3** Test of pre-treatment conditions in the determination of As and Sb in SRM 1633b or a synthetic sample using a mixture of 4 ml of 5% KI/ascorbic acid and 6 mL of conc. HCl as pre-reduction reagent. a) Synthetic sample containing 100  $\mu\text{g L}^{-1}$  of As and Sb, 9.0% of HNO<sub>3</sub> with a pre-treatment time of 60 min, b) SRM sample, digestion method US-TSD, sat. H<sub>3</sub>BO<sub>3</sub> 2 mL at a temperature of 60°C. In test of b) 1.2% of HF and 9.0% of HNO<sub>3</sub> were derived from digestion method US-TSD.



**Figure 4** 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 5% KI/ascorbic acid, b) 6 mL of conc. HCl. The pre-treatment time of 60 min and temperature of  $20^\circ\text{C}$  were used throughout.

As could be seen in Table 14, there is no significant difference between method A and B for the determination of As, unlike the determination of Sb concentrations. The highest As recovery of 96% was obtained with the digestion method US-TSD (pre-reduction methods A or B). The highest Sb recovery, 103%, was obtained with the digestion method US-TSD with pre-reduction method B. The confidence limits of the mean for the As and Sb measurements in the digestion method US-TSD were about 1.5%, which were very good considering the concentration level at which determination was performed. As can be seen in Table 14, the determination of As and Sb concentrations in the SRM samples by HG-ICP-OES was successful.

**Table 14** Element concentrations determined ( $\text{mg kg}^{-1}$ ) in SRM 1633b using three different digestion procedures (mean of six replicate samples, with the confidence limit of the mean,  $P = 0.05$ ).

Element/parameters	Microwave MW <sup>a</sup>	Ultrasound US <sup>b</sup>	Ultrasound US-TSD <sup>c</sup>	Certified
<i>Method A</i>				
As 193.696 nm	$111.6 \pm 1.3$	$125.1 \pm 0.8$	$130.6 \pm 1.7$	$136.2 \pm 2.6$
Sb 217.582 nm	<LOQ	$2.65 \pm 0.13$	<LOQ	6*
<i>Method B</i>				
As 193.696 nm	$111.3 \pm 2.3$	$124.8 \pm 0.7$	$130.2 \pm 1.6$	$136.2 \pm 2.6$
Sb 217.582 nm	$5.84 \pm 0.11$	$3.13 \pm 0.10$	$6.18 \pm 0.09$	6*

LOQ = limit of quantification, \* Non-certified value (SRM 1633b),

*Method A* = without boric acid and warming, *Method B* = with boric acid and warming

<sup>a</sup> MW = Microwave, digestion solution of 9 mL of conc.  $\text{HNO}_3$  + 3 mL of conc. HF, USEPA method 3052<sup>175</sup>

<sup>b</sup> US = Ultrasound, digestion solution of 5 mL *aqua regia* + 5 mL water, 9 min ( $3 \times 3$  min),

<sup>c</sup> US-TSD = Ultrasound (two-step): i) digestion solution of 6 mL of conc.  $\text{HNO}_3$ , 9 min ( $3 \times 3$  min) ii) digestion solution of 3 mL of conc.  $\text{HNO}_3$  + 3 mL of conc. HF, 18 min ( $6 \times 3$  min)

## 5.7 Quality of analytical results

In this thesis, the analytical results were evaluated using various techniques presented in Table 15.

**Table 15** Evaluation of the quality of analytical results.

Evaluation technique	Paper I	Paper II	Paper III	Paper IV
Correlation coefficient	+	+	+	+
Several wavelengths	+	+	+	+
LOD and LOQ	+	+	+	+
Replicate samples	+	+	+	+
Confidence limit of the mean	+	+	+	+
SRM sample	+	+	+	+
Comparison of standard method	+	+	+	+
Outlier test	+	*	*	*
<i>t</i> -test	-	+	-	-
Paired <i>t</i> -test	-	-	+	-
Recovery test of added element	-	+	+	+
Multiple linear regression	-	-	+	-

(+) = used, (-) = not used, (\*) = not needed

As can be seen in papers I-IV, efforts were made to confirm the quality of analytical results by using several quality control tools. This was necessary to attain the objective of this investigation; the determination of selected elements with high accuracy and precision.

One significant quality control technique was missing, the use of internal standards. In this study the use of an internal standard is almost impossible because the composition of ashes is unpredictable, highly variable, and heterogeneous. The ashes can include a large variety of elements, especially in the case of municipal solid waste ashes.

## 5.8 Suggested determination procedures for elements selected

In Table 16 are presented the suggested procedures (digestion method, instruments and parameters) for the determination of element concentrations in ash samples. The suggestions are based on papers I-IV.

**Table 16** Suggested procedures for the determination of elements studied in ash samples by using ultrasound-assisted digestion methods.

Element	Wavelength Axial/Radial	Digestion Procedure	Ref.
<i>ICP-OES; Plasma 15.0, Aux. 0.2, Neb. 0.6, RF power 1400 W</i>			
As	193.696 nm Radial	US2	[I]
Ba	233.527 nm Radial	US1	[I]
Co	228.616 nm Radial	US1	[I]
Cr	267.716 nm Radial	US-TSD	[II]
Cu	327.393 nm Radial	US-TSD	[II]
Ni	231.604 nm Radial	US-TSD	[II]
Pb	220.353 nm Radial	US <sup>b</sup>	[II]
Sr	460.733 nm Radial	US1	[I]
V	290.880 nm Radial	US-TSD	[II]
Zn	213.857 nm Radial	US-TSD	[II]
<i>ICP-OES; MLR correction, Plasma 15.0, Aux. 0.2, Neb. 0.5, RF power 1500 W</i>			
As	193.696 nm Axial	US2	[III]
Pb	220.353 nm Axial	US-TSD	[III]
<i>ICP-OES; Plasma 15.0, Aux. 0.2, Neb. 0.6, RF power 1500 W</i>			
Pb	220.353 nm Axial	US-TSD	[III]
<i>HG-ICP-OES; Plasma 17.0, Aux. 0.2, Neb. 0.5, RF power 1450 W</i>			
As	193.696 nm Axial	US-TSD	[IV]
Sb	217.582 nm Axial	US-TSD	[IV]

## 5.9 Comparisons of SRM results

The SRM 1633b results obtained in this investigation were compared with the SRM 1633b element concentrations determined by several authors. The published recoveries of determined elements in SRM 1633b by using microwave or ultrasound digestion are presented in Table 17. As could be seen, Cu and Cr recoveries are slightly lower by using ultrasound-assisted digestion than with microwave accelerated digestion. Generally, recoveries of ultrasound and microwave digestion are quite similar for the elements presented in Table 17. Confidence limits of the mean of selected elements for microwave digestion methods<sup>84,88-90</sup> range from 1 to 13% and those for ultrasound digestion methods<sup>5,107,I-IV</sup> range from 1 to 22%, but the confidence limits of the mean for our suggested procedures in Table 16<sup>I-IV</sup> varied only from 1 to 6%. It should be noted that times for microwave digestion methods (MW) vary from 42 to 73 minutes whereas times for ultrasound digestion methods (US) vary from 15 to 30 minutes.

**Table 17** Recoveries of elements determined in SRM 1633b by using microwave or ultrasound digestion.

Ref.	MW [84]	MW [88]	MW [89]	MW [90]	US [5]	US [107]	US [I-IV]
As	-	88%	103%	97%	-	-	96%
Co	107%	95%	112%	109%	-	104%	104%
Cr	93%	99%	94%	91%	103%	87%	85%
Cu	100%	92%	100%	107%	-	90%	92%
Ni	99%	101%	94%	95%	96%	98%	93%
Pb	94%	101%	96%	92%	97%	-	98%
Sb	-	81%	128%	-	-	-	103%
V	-	-	97%	93%	-	99%	99%
Zn	99%	87%	94%	91%	-	90%	99%

MW = microwave accelerated digestion, US = ultrasound-assisted digestion

A comparison of US digestion methods using the SRM 1633b sample can be made between our papers I-IV and those by De La Calle *et al.*<sup>5</sup>, and Pontes *et al.*<sup>107</sup>. Our paper II was published at first, then 5 months later Ref.<sup>5</sup> was published and 9 months later Ref.<sup>107</sup> was published.

As could be seen in Table 17, our recoveries and those of Ref.<sup>107</sup> are similar with two exceptions, Ni and Zn. The confidence limits of the mean are also similar in those papers. Only one significant difference between those papers is found in the LOQ values. Pontes *et al.*<sup>107</sup> is obtained from 1.5 to 7 times lower LOQ values for some elements (Cu, Ni, V, and Zn).

Recoveries of Ref.<sup>5</sup> are very good (Table 17), especially the recovery of Cr. A closer review of this paper shows that the confidence limits of mean are quite wide, those vary from 12 to 22 %. Our recoveries were sometimes lower such as for Cr, but the confidence limits of the mean vary only from 1 to 3 %, if Pb concentration is determined using procedures of paper III. According to Table 17 our ultrasound-assisted digestion methods compared well with the other methods published.

## 5.10 Results of real ash samples

The element concentrations obtained with the most suitable digestion methods and instrument parameters are presented in Tables 18 and 19 (papers I-IV). The reuse potential of ash can be evaluated by comparing these element concentrations with the limit values for soil construction.<sup>38</sup>

**Table 18** Determined concentrations (mg kg<sup>-1</sup>) with confidence limits of the mean ( $P = 0.05$ ) for real ash samples in papers I and II and limit values for selected elements.

Element	BA2 <sup>I</sup>	FA2 <sup>I</sup>	FA3 <sup>I</sup>	FA3 <sup>II</sup>	FA4 <sup>II</sup>	Limit
	U1	U1	U1	US-TSD	US-TSD	Value <sup>a</sup>
<i>ICP-OES; Plasma 15.0, Aux. 0.2, Neb. 0.6, RF Power 1400 W</i>						
As 193.696 nm	< LOQ	< LOQ	< LOQ	-	-	50
Ba 233.527 nm	670 ± 150	1300 ± 200	840 ± 70	-	-	3000
Cr 267.716 nm	-	-	-	127 ± 5	33 ± 9	400
Cu 327.393 nm	5000 ± 5000	108 ± 4	450 ± 30	326 ± 5	105 ± 4	400
Ni 231.604 nm	80 ± 30	54 ± 2	61 ± 2	128 ± 4	13 ± 4	-
Pb 220.353 nm	800 ± 200	62 ± 5	160 ± 5	104 ± 12*	74 ± 10*	300
Sr 460.733 nm	170 ± 30	610 ± 50	410 ± 10	-	-	-
V 290.880 nm	40 ± 3	119 ± 4	183 ± 4	28 ± 1	24 ± 1	400
Zn 213.857 nm	2600 ± 700	690 ± 30	732 ± 12	421 ± 15	770 ± 4	2000

<sup>a</sup> Limit values (total concentration) for selected elements in soil construction for coal, peat and wood ashes from Finland<sup>38</sup>, BA = bottom ash, FA = fly ash

U1 = Ultrasound, digestion solution of 10 mL *aqua regia* + 0.5 mL conc. HF, 18 min (6 × 3 min)

US-TSD = Ultrasound (two-step): i) digestion solution of 6 mL of conc. HNO<sub>3</sub>, 9 min (3 × 3 min) ii) digestion solution of 3 mL conc. HNO<sub>3</sub> + 3 mL conc. HF, 18 min (6 × 3 min)

\* US<sup>b</sup> with digestion solution of 9 mL conc. HNO<sub>3</sub> + 3 mL conc. HF, 18 min (6 × 3 min) in paper II was used, because of the determination problem for Pb<sup>II</sup> using the US-TSD method

As can be seen in Table 18, the element concentrations in BA2<sup>I</sup> and FA3<sup>I</sup> samples found with the digestion method U1 include at least one value exceeding the limit value. It means that direct reuse in soil construction is not possible for those ashes. According to Table 18, element concentrations in sample FA2<sup>I</sup> determined with the digestion method U1, and in samples FA3<sup>II</sup> and FA4<sup>II</sup> found with the digestion method US-TSD do not exceed limit values. It means that the found element concentrations allow the reuse in soil construction. It should be noted that many aspects have to be investigated such as leach tests and concentration of other elements and compounds, before those ash materials can be reused in soil construction.

According to Table 19, the As and Pb concentrations do not exceed the limit values, except one As concentration in sample FA2<sup>IV</sup> with the digestion method US-TSD, for which the confidence limit of mean exceeds the limit value of As. That forbids a direct reuse of sample FA2<sup>IV</sup> in soil construction.

**Table 19** Determined concentrations ( $\text{mg kg}^{-1}$ ) with confidence limits of the mean ( $P = 0.05$ ) for real ash samples in papers III and IV and limit values for selected elements.

Element	FA1 <sup>III</sup>	FA2 <sup>III</sup>	FA1 <sup>IV</sup>	FA2 <sup>IV</sup>	Limit
	US-TSD	US-TSD	US-TSD	US-TSD	Value <sup>a</sup>
<i>ICP-OES; MLR correction, Plasma 15.0, Aux. 0.2, Neb. 0.5, RF Power 1500 W</i>					
As 193.696 nm	34.5 ± 1.4	24.9 ± 1.9	-	-	50
Pb 220.353 nm	154.8 ± 3.6	162.9 ± 3.9	-	-	300
<i>ICP-OES; Plasma 15.0, Aux. 0.2, Neb. 0.6, Power 1500 W</i>					
Pb 220.353 nm	156.1 ± 3.9	150.9 ± 2.7	-	-	300
<i>HG-ICP-OES; Plasma 17.0, Aux. 0.2, Neb. 0.5, RF Power 1450 W (method B)</i>					
As 193.696 nm	-	-	42.8 ± 1.2	49.3 ± 2.9	50
Sb 217.582 nm	-	-	24.7 ± 0.8	6.05 ± 0.13	-

<sup>a</sup> Limit values (total concentration) for selected elements in soil construction for coal, peat and wood ashes from Finland<sup>38</sup>, FA = fly ash

US-TSD = Ultrasound (two-step): i) digestion solution of 6 mL of conc.  $\text{HNO}_3$ , 9 min (3 × 3 min) ii) digestion solution of 3 mL conc.  $\text{HNO}_3$  + 3 mL conc. HF, 18 min (6 × 3 min)

## 6 CONCLUSIONS

This thesis introduces several new ultrasound-assisted digestion methods for the determination of toxic element concentrations in different kinds of ash samples by ICP-OES. The efficacy of ultrasound-assisted digestion methods followed with ICP-OES was proved with the analysis of SRM 1633b (Coal Fly Ash) standardized by the NIST. Ultrasound-assisted digestion methods using different digestion solutions were also compared with the microwave digestion method standardized by the USEPA (USEPA 3052 method). The ultrasound-assisted digestion is a new technique for use for sample pre-treatment purposes, compared with typical digestion methods.

The results also showed that the ultrasound-assisted digestion technique is useful even in the case of difficult sample matrices. The advantages of ultrasound-assisted digestion using a water bath over other methods are the speed of digestion and a high sample treatment capacity. Ultrasound-assisted digestion can also be performed more safely than microwave digestion with closed sample vessels, because pressure and temperature are substantially lower in ultrasound digestion. The digestion vessels (centrifuge tubes) offer the possibility to use a centrifuge in the separation of fractions and the possibility to use new sample vessels without a significant increase in costs.

The evaluation of robust plasma conditions was based on the MgII(280.270 nm)/MgI(285.213 nm) line intensity ratio. Robust plasma conditions for ash samples can be obtained with a nebulizer gas flow not more than 0.7 L min<sup>-1</sup> and a RF power of at least 1300 W for radially viewed plasma. Robust plasma conditions for axially viewed plasma in ash samples can be obtained using a low nebulizer gas flow (0.5 L min<sup>-1</sup>); even then robust plasma conditions were barely reached. It should be noted that even under robust plasma conditions, especially in axially but also in radially viewed plasmas, considerable matrix interferences may take place.



The results proved that it is possible to use the multiple linear regression technique to evaluate and correct for matrix interferences in the determination of As and Pb in the fly ash samples by ICP-OES. The matrix interference in the determination of As was caused by Al, whereas in the determination of Pb the interference was caused by Al and Fe when using the most suitable RF power and nebulizer gas flow.

The HG-ICP-OES makes it possible to determine hydride forming elements even at significantly lower concentrations compared with a direct ICP-OES measurement. The results showed that the major interference in the determination of Sb was caused by HF; therefore  $H_3BO_3$  with warming was needed in the determination of Sb by the HG-ICP-OES technique.

The recoveries and confidence limits of the mean in ultrasound-assisted and microwave accelerated digestion of the SRM 1633b sample were quite similar for the elements studied. The accuracy, precision and effectiveness of the ultrasound-assisted digestion, especially those of ultrasound two step digestion and ICP-OES or HG-ICP-OES measurements, were demonstrated. All the developed methods were validated for real ash samples. In this study, one important criterion of the methods developed was practicality and the possibility to use in day-to-day analyses in the laboratory. Several ideas related to ultrasound-assisted digestion arose during this work, creating further possibilities for research in the near future.

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