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An ultrasound-assisted digestion method for the determination of toxic element concentrations in ash samples by inductively coupled plasma optical emission spectrometry

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A method of ultrasound-assisted digestion followed by inductively coupled plasma optical emission spectrometry (ICP-OES) used for the determination of toxic element concentrations (arsenic, barium, cobalt, copper, lead, nickel, strontium, vanadium and zinc) in ash samples was developed. All the measurements were performed in robust plasma conditions which were tested by measuring the Mg II 280.270 nm / Mg I 285.213 nm line intensity ratios. The highest line intensity ratios were observed when a nebulizer gas flow of 0.6 L min^{-1}, auxiliary gas flow of 0.2 L min^{-1} and plasma power of 1400 W were used for radially viewed plasma. The analysis of SRM 1633b showed that the ultrasound-assisted method developed is highly comparable with the microwave digestion method standardized by the United States Environmental Protection Agency (EPA-3052). The ultrasound-assisted digestion with a digestion solution of *aqua regia* and hydro fluoric acid (HF) resulted in recovery rates of over 81 %. One exception is arsenic which resulted in recoveries of about 60 % only; however, it could be digested with good recovery (> 90 %) using a digestion solution of 5 mL of water and 5 mL of *aqua regia*. The major advantage of the ultrasound-assisted digestion over microwave digestion is the high treatment rate (30 samples simultaneously with a sonication time of 18 min).

1. Introduction

Elements such as arsenic, chromium, lead, nickel, and vanadium are potential risks in the environment even in low concentrations [1]. Metal contamination is a persistent problem in many industrial residues. Industrial activity produces all kinds of by-products, for instance, bottom and fly ashes. Fly ashes and aerosol particles generated in combustion processes are important carriers of different kinds of hazardous substances [2-5]. Primary constituents of the ashes are oxides of Si (SiO_2), Al (Al_2O_3), Fe (Fe_2O_3), Ca (CaO), Mg (MgO), Na (Na_2O), K (K_2O), and Ti (TiO_2) [6-8]. Ashes also contain significant amounts of elements with toxic characters such as As, Ba, Cd, Cu, Co, Cr, Ni, Pb, V, and Zn [9-12].

Combustion of coal, wood, agricultural residues, municipal waste, dried sludge and peat has generated large amounts of ashes in recent decades. The total amount of ashes produced is huge. The worldwide production of coal ash only is estimated to exceed 550×10^6 tonnes/year (Mt/year). In the year 2000 the estimated amount of fly ash generated by burning municipal solid waste in the USA, Japan and the European Union was about 25 Mt. In the European Union the amount of ashes generated by the combustion of sewage sludges is expected to soon reach 2 Mt/year [4, 13, 14]. The main problem related with the use of ashes is the direct or indirect harmful effects to the environment and human health. The solid waste incineration fly and bottom ashes are typically classified as hazardous residues, but the ash classifying is case-specific [4, 15].

Classically, wood ashes and ashes derived from combustion of agricultural wastes were applied to soils, because then nutrients can be recycled. 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) [13, 14, 16-20]. Industrial solid wastes are very difficult to analyze, because their composition is unpredictable, highly variable, and heterogeneous [21, 22].

The methods used in the analysis of trace elements in ash samples are based on atomic absorption or emission spectrometry together with a liquid sample introduction system. The main advantages of inductively coupled plasma optical emission spectrometry (ICP-OES) over atomic absorption techniques are multi-element determination and high sample through-put with detection limits low enough for most ash samples [22-24].

Most of the methods of decomposition used in elemental analyses are based on digestion with strong acids (HNO_3, HCl, H_2SO_4, HF) at elevated temperatures, which can lead to the loss of easily volatile elements such as As, Sb, Se and Sn [25-27]. The microwave accelerated digestion has become the most commonly used method for the determination of toxic element concentrations in solid samples by ICP-OES [25, 28, 29]. Another useful sample preparation method for solid samples is ultrasound-assisted digestion [30-32]. In general solid sample digestion is performed by ultrasound water baths or probes. Ultrasound water baths are more often used, because they are cheaper than probes. On the other hand, ultrasound probes often require shorter digestion time than water baths [33]. Possible applications for ultrasound baths and probes are digestion or extraction of solid particulate materials (contaminated soil, coal fly ash, street dust and sediments) [32, 34-36] for elemental analysis. Ultrasound-assisted digestion has also been used in biochemical, biological and pharmaceutical studies [33]. The main benefits of ultrasound-assisted sample pre-treatment over other methods are the speed of digestion, high sample treatment capacity and low reagent usage. Digestion can also be carried out in an ultrasonic water bath using plastic screw-top bottles or polypropylene centrifuge tubes, which means that samples can be centrifuged instead of filtering [32, 37]. Ultrasound-assisted digestion is safer than

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microwave digestion, because pressure and temperature are substantially lower in ultrasound technique [38].

Interferences during sample introduction in ICP-OES usually occur with samples of high viscosity and complex sample matrix. Most of the matrix effects are caused by the easily ionizable elements (EIEs) [39-41]. Matrix effects in plasma can be reduced by optimizing the processes of atomization and ionization. Accordingly, the EIE interferences can be reduced by using robust plasma conditions and appropriate wavelengths of the analyte elements. The optimization procedure is normally carried out by the determination of the Mg II 280.270 nm / Mg I 285.213 nm line intensity ratio using Mg concentrations of about $1 - 10$ mg L^{-1} with the appropriate matrix element concentrations. Line intensity ratios >8 are regarded as satisfactory [39, 42, 43].

In this study, different types of industrial bottom and fly ashes were analyzed. The aim of this study was to develop an ultrasound-assisted digestion method for the determination of toxic element concentrations in power plant ashes by ICP-OES.

2. Experimental

2.1. Instrumentation

All the measurements were performed with a Perkin-Elmer (Norwalk, CT, USA) model Optima 4300 DV inductively coupled plasma optical emission spectrometer. A Scott type double-pass spray chamber and a cross-flow nebulizer were used throughout. The determination of element concentrations was optimized using different default parameters of the instrument (nebulizer flow $0.5 - 1.1$ L min^{-1}, auxiliary gas flow 0.2 L min^{-1}, plasma gas flow 15 L min^{-1} and plasma power of 1300 or 1400 W). Two wavelengths for each of the elements investigated were tested by both axially and radially viewed plasmas. The

appropriate wavelengths with the correct plasma viewing used in the final determination are shown in Table 1.

2.2. Reagents

All the reagents used were of analytical grade and only high purity water of 18.2 MΩ cm resistivity supplied by Elga (Buckinghamshire, UK) was used throughout. Nitric acid (65 %, p.a.) and hydrochloric acid (36-38 %, p.a.) were supplied by Riedel-de-Haën (Seelze, Germany) and hydrofluoric acid (40 %, p.a.) was supplied by Merck (Darmstadt, Germany). The standard stock solutions (1000 mg L^{-1}) for the ICP-OES measurements were supplied by Merck (Darmstadt, Germany). The working concentration ranges used are shown in Table 1.

2.3. Samples

A coal fly ash standard reference material, SRM 1633b [44], certified by the National Institute of Standards and Technology (NIST), two bottom ash samples collected from municipal solid waste incineration plants and three fly ash samples collected from wood incineration plants were analyzed. All the ash samples were collected in Finland. The ash samples (three fly and two bottom ashes and the reference sample) were each analyzed as six random samples. Only bottom ash samples were sifted with a 2 mm diameter mesh, because other samples were already dust-like. Moisture contents of all the mixture samples were analyzed.

2.4. Ultrasound-assisted digestion procedure

A SRM sample or ash sample of about 250 mg was accurately weighed into a 50 mL plastic screw-top centrifuge tube supplied by Sarstedt (Nümbrecht, Germany) into which 10.5 ml of digestion solution of *aqua regia* (10 mL) and hydrofluoric acid (0.5 mL) was added (mark in future: U1). The tube was closed and placed into a 650 W, 35 kHz, Model Transsonic 820/H ultrasound water bath supplied by ELMA (Singen, Germany). The optimized sonication

procedure lasted 18 minutes, as shown in Figure 1. 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. After digestion the sample solution was filtered (Whatman No. 41, Maidstone, UK) into a 50 mL 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. The sample pre-treatment for arsenic determination was performed with a digestion solution of 5 mL of *aqua regia* and 5 mL of water [37] (Mark in future: U2).

2.5. Microwave digestion procedure

The microwave digestion procedure (mark in future: M1) obtained from the United States Environmental Protection Agency (EPA) (EPA-3052 method) [45] was used as a reference method for ultrasound-assisted digestion procedure. A SRM sample of about 500 mg was accurately weighed into a 100 mL tetrafluormethaxil (TFM) vessel into which 9 mL of HNO_3 and 3 mL of HF were added. After 30 minutes the sample was placed into an ETHOS PLUS microwave digestion system supplied by Milestone (Sorisole, Italy) and heated with a digestion program containing power of 1000 W for 5 min (180 °C) (step 1) and power of 1000 W For 10 min (180 °C) (step 2). Both temperature and pressure were controlled during the microwave digestion procedure. The temperature of 180 ± 1 °C was reached after 5 min of heating. The highest pressure reached during the digestion was about 8 bar. After digestion the sample solution was filtered (Whatman No. 41, Maidstone, UK) into a 100 mL volumetric flask. The residue was washed with 20 mL of water introduced in three portions, and the filtrate diluted to volume with water. The sample solution was transferred into a plastic screw-top bottle for storage. The second microwave digestion procedure (mark in future: M2) was performed with the same digestion program, but with a digestion solution of 10 mL of *aqua regia* and 0.5 mL of HF.

3. Results and discussion

3.1. 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, Cu, Ni, Pb, Sr, V, and Zn). The optimization of each element was performed by taking two of the most sensitive emission lines to attain the sensitivity required. The detection limits of the determination of As, Ba, Co, Cu, Ni, Pb, Sr, V, and Zn in the ash samples were found to be 6.8, 12.4, 0.9, 5.8, 1.6, 3.7, 17.3, 7.7 and 14.6 mg kg^{-1}, respectively. Exceedingly high values were obtained for the regression correlation coefficients, as shown in Table 1.

3.2. Optimization of the ultrasound-assisted digestion procedure

The optimization procedure was performed by determining the concentrations of Ba, Co, Ni, V, and Zn in SRM 1633b. The Five analyte elements selected are known to be hard to dissolve. A mixture of *aqua regia* and hydrofluoric acid was selected as a digestion solution, because ash samples are known to be difficult to digest and they usually contain silicates. The volume of 0.5 mL of HF was found the most suitable for this purpose, because the analyte concentrations determined were not significantly increased by the addition of over 0.5 mL of HF.

Different sonication times (Figure 1.) were tested. Recoveries of analytes at each time level were presented as a mean of three replicate samples. According to the analyte concentrations determined, the sonication time of 18 min was selected, because of four elements investigated resulted in the highest recovery rates, as can be seen in Figure 1. All the element recoveries were over 90 % except for Ba, which resulted in recoveries of about 83%. The ultrasound-assisted digestion resulted in similar concentrations as presented in the literature [9]. The homogeneity of the ultrasound field of the ultrasound water bath was also 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 2.). The ultrasound field homogeneity test was performed repeatedly using the SRM 1633b and a sonication time of 15 min.

3.3. Effect of nebulizer gas flow rate and plasma power on Mg II / Mg I line intensity ratio

It is well known that samples with a complex matrix should be determined under robust plasma conditions. The Mg II 280.270 nm / Mg I 285.213 nm line intensity ratio is a useful parameter in efforts to find the atomization and excitation conditions in plasma [39]. The diagnostics ratio was measured to ensure correct plasma conditions for the method optimization procedure. In accordance with Ivaldi and Tyson [46], the values of the diagnostic ratio were multiplied by 1.85, which makes the results comparable with those obtained using the other instruments. This is due to the different sensitivity of the two Mg lines in an echelle spectrometer. The Mg II 280.270 nm / Mg I 285.213 nm line intensity ratio was determined by the analysis of synthetic mixture of matrix elements containing 10 mg L^{-1} of Mg. The concentrations of the main matrix elements Al, Ca, Fe, K, Mn, Na, P, and Si were 2000, 100, 500, 150, 1, 1750, 10, and 150 mg L^{-1}, respectively.

The values of the diagnostic ratio (Figure 2) showed the efficiency of a plasma power of 1400 W. All the nebulizer gas flows for both the plasma viewings tested produced higher diagnostic ratios with 1400 W than 1300 W power. The values of the Mg II 280.270 nm / Mg I 285.213 nm line intensity ratio varied from 0.4 to 13.4 when nebulizer gas flow varied between 0.5-1.1 L min^{-1}. According to the values, robust plasma conditions can be obtained with a nebulizer gas flow of 0.6 L min^{-1} and a plasma power of 1400 W for radially viewed plasma only. The measurement of digested ash samples with an axially viewed plasma can not be performed under robust plasma conditions.

3.4. Analysis

The coal fly ash standard reference material, SRM 1633b, and two bottom and three fly ash samples collected from different incineration plants were analyzed. Nine elements, As, Ba, Co, Cu, Ni, Pb, Sr, V and Zn, were selected because of their toxic character and their presence in incineration ashes. The concentrations (mean ± confidence level of the mean) of the nine elements in SRM 1633b digested by ultrasound or microwave methods and determined by ICP-OES are shown in Table 3. As can be seen, method U2 resulted in the best method for arsenic determination (recovery > 90 %), but it was not a useful method for other elements of interest (recoveries from Co 10 % to V 27 %).

A Comparison of digestion techniques (ultrasound vs. microwave) was made using methods M2 and U1, because those methods used the same digestion solution but different digestion techniques. As can be seen in Table 3, the ultrasound-assisted digestion U1 was slightly better than microwave method M2. The element recoveries were 2 -15 % higher for method U1 than method M2 with one exception, arsenic, having similar recoveries in both methods. In a comparison of element recoveries between EPA-3052 digestion method and ultrasound method the studied methods were M1 and U1. As can be seen in Table 3, the barium, strontium and zinc concentrations were higher in the ultrasound method U1 than the microwave method M1. The U1 method resulted in Ba, Sr and Zn recoveries significantly better than the method M1. In general, the ultrasound-assisted digestion method with 10 mL *aqua regia* and 0.5 mL hydrofluoric acid as the digestion solution and the standard method (microwave, EPA-3052) resulted in almost equal element concentrations.

The analysis of ash samples (BA and FA) collected from the incineration plants showed the same trends in element concentrations as the analysis of the SRM sample (Tables 4 and 5). The concentrations of Co resulted in lower than the calibration standards but, however the quantification limits determined were reached. This was in a case of couple of samples only.

In the case of high concentrations of copper the determination was performed with the diluted samples. The determination of Ba and Sr concentrations by using M1 as a digestion method did not yield satisfactory results. The determination of As, Co, Cu, Pb, V and Zn using methods M1 and U1 resulted in almost equal concentrations. The dissolution of Ni was successful with microwave method M1 but not with ultrasound-assisted method U1. The concentrations of Cu, Pb and Zn in bottom ash samples were significantly higher than in the fly ash samples (2 - 20 times higher); on the other hand, the concentrations of Sr and V in the fly ash samples were significantly higher than in the bottom ash samples (3 - 7 times higher). According to this, recycling bottom and fly ashes in soil amendments is not recommended, because the Ba, Cu, Pb and Zn concentrations were significantly higher than the allowed maxima in the soil. Maximum concentrations of Ba, Cu, Pb, and Zn in Finnish soil are 600, 400, 300 and 700 mg kg^{-1}, respectively. The Ba, Cu, Pb and Zn concentrations determined were 200 - 1400 mg kg^{-1}, 90 - 5000 mg kg^{-1}, 30 - 2000 mg kg^{-1}, 380 - 3100 mg kg^{-1}, respectively. As can be seen in Tables 3 and 4, element concentrations in incineration ashes are very challenging to analyze, because the composition of ashes is unpredictable, highly variable, and heterogeneous, especially in solid waste incineration ashes (Table 5). According to this, the evaluation of recycling of ash is very difficult.

4. Conclusion

The analysis of arsenic, barium, cobalt, copper, nickel, lead, strontium, vanadium, and zinc concentrations in ash samples was successfully performed. The effectiveness of the ultrasound-assisted digestion and ICP-OES measurements using robust plasma conditions was demonstrated. It should be noted that incineration ashes are very difficult to digest. The optimization of the ICP-OES nebulizer gas flow and plasma power was based on the Mg II 280.270 nm/Mg I 285.213 nm line intensity ratio. Even under robust plasma conditions,

especially in axially but also radially viewed plasmas may be subject to considerable interference. According to the intensity ratios determined, the robust plasma conditions can be obtained with a nebulizer gas flow of 0.6 L min^{-1} and a plasma power of 1400 W for radially viewed plasma only.

The main advantages of the ultrasound-assisted digestion over other methods are the speed of digestion and high sample treatment capacity. The fact that 30 samples can be treated simultaneously in 18 minutes is significant when this method is compared with the conventional methods of digestion. Ultrasound-assisted digestion can also be performed more safely than microwave digestion, because pressure and temperature are substantially lower in ultrasound digestion. Consequently the loss of elements by volatilization, such as, As, Se, and Hg is not significant.

Element concentrations in incineration ashes are very challenging to analyze, because the composition of ashes is unpredictable, highly variable, and heterogeneous, therefore the evaluation of recycling of ashes is very difficult. We plan to investigate the use of the ultrasound-assisted digestion method in the determination of chromium in complex sample matrix by ICP-OES.

Acknowledgements

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Table 1 Optimization of the wavelengths and calibration data of the determination of samples by ICP-OES.

Element	Wavelength nm	Atom/Ion I/II	r	LOD (mg kg^{-1})[a]	LOQ (mg kg^{-1})[b]	Recovery (%)[c]	Calibration ranges (mg L^{-1})
As	**193.696 Radial**	**I**	**0.9999**	**2.1**	**6.8**	**92.6 ± 2.8**	0.1 - 10.0
	188.979 Radial	I	0.9999	2.6	8.6	94.3 ± 2.3	
Ba	**233.527 Radial**	**II**	**0.9999**	**3.7**	**12.4**	**100.8 ± 6.6**	0.2 - 20.0
	230.425 Radial	II	0.9999	4.2	14.1	88.6 ± 0.8	
Co	**228.616 Radial**	**II**	**1.0000**	**0.3**	**0.9**	**88.5 ± 0.6**	0.1 - 10.0
	238.892 Radial	II	0.9999	1.3	4.3	0 ± 0	
Cu	**327.393 Radial**	**I**	**0.9999**	**1.7**	**5.8**	**95.5 ± 2.7**	0.1 - 10.0
	324.752 Radial	I	0.9999	1.9	6.3	95.0 ± 2.4	
Ni	**231.604 Radial**	**II**	**1.0000**	**0.5**	**1.6**	**91.0 ± 1.4**	0.1 - 10.0
	232.003 Radial	I	0.9999	2.8	9.3	92.0 ± 0.5	
Pb	**220.353 Radial**	**II**	**0.9999**	**1.1**	**3.7**	**96.8 ± 2.8**	0.1 - 10.0
	217.000 Radial	I	0.9999	2.8	9.2	58.1 ± 21.4	
Sr	**460.733 Radial**	**I**	**0.9999**	**5.2**	**17.3**	**99.7 ± 4.8**	0.2 - 20.0
	232.235 Radial	II	0.9998	3.7	12.2	89.0 ± 0.3	
V	**290.880 Radial**	**II**	**0.9999**	**2.3**	**7.7**	**105.8 ± 0.1**	0.1 - 10.0
	309.310 Radial	II	0.9999	3.6	12.1	0 ± 0	
Zn	**213.857 Radial**	**I**	**0.9999**	**4.4**	**14.6**	**98.4 ± 6.0**	0.2 - 20.0
	206.200 Radial	II	0.9998	5.9	19.6	95.5 ± 7.3	

[a] LOD = limit of detection when 250 mg sample was digested and filtrate dilute to a volume of 50 mL. Calculated by substituting the intercept and its standard deviations multiplier ($a + 3s_a$) into the calibration line $y = bx + a$ [47].

[b] LOQ = limit of detection when 250 mg sample was digested and filtrate dilute to a volume of 50 mL. Calculated by substituting the intercept and its standard deviations multiplier ($a + 10s_a$) into the calibration line $y = bx + a$ [47].

[c] Optimization recoveries were calculated by 50 % and 200 % element concentration addition.

Bold = Selected wavelength in the final determination

Table 2 Ultrasound field homogeneity test (six locations).

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

+ = no outlier
- = one outlier

Table 3 Determined element concentrations (mg kg^{-1}) of four different digestion procedures (M1, M2, U1 and U2) in SRM 1633b (mean of six replicate samples, with the confidence limit of the mean, P = 0.05).

| Element | Microwave | Ultrasound | | | Certified |
	M1[a]	M2[b]	U1[c]	U2[d]	
As	115 ± 5	83 ± 8	81 ± 10	123 ± 3	136,2 ± 2,6
Ba	113 ± 12	542 ± 32	577 ± 11	165 ± 4	709 ± 27
Co	54 ± 1	48 ± 3	52 ± 1	5 ± 1	50*
Cu	94 ± 2	82 ± 4	94 ± 2	22 ± 1	112,8 ± 2,6
Ni	110 ± 1	93 ± 3	102 ± 3	12 ± 1	120,6 ± 1,8
Pb	63 ± 4	48 ± 2	58 ± 4	18 ± 1	68,2 ± 1,1
Sr	47 ± 5	851 ± 31	869 ± 11	264 ± 3	1041 ± 14
V	336 ± 2	293 ± 12	300 ± 6	81 ± 1	295,7 ± 3,6
Zn	163 ± 2	179 ± 4	185 ± 3	34 ± 2	210*

* Non certified value (SRM 1633b)

[a] Microwave, acid: 9 mL HNO$_3$ + 3 mL HF, EPA-3052 method

[b] Microwave, acid: 10 ml Aqua regia + 0.5 mL HF, 5min (0 →180 °C) + 10 min (hold 180 °C)

[c] Ultrasound, acid: : 10 ml Aqua regia + 0.5 mL HF, 18 min (6 × 3 min)

[d] Ultrasound, acid: : 10 ml (1:1) Aqua regia, 9 min (3 × 3 min)

Table 4 Determined element concentrations (mg kg^{-1}) of three fly ashes (FA 1 – FA 3) from Finland (mean of six replicate samples, with the confidence limit of the mean, P = 0.05).

Element	Microwave		Ultrasound-assisted	
	M1[a]	M2[b]	U1[c]	U2[d]
FA 1				
As	< LOQ	< LOQ	< LOQ	< LOQ
Ba	202 ± 8	521 ± 11	480 ± 90	390 ± 20
Co	11 ± 1	10 ± 1	11 ± 1	6 ± 2
Cu	331 ± 7	291 ± 4	320 ± 20	210 ± 7
Ni	143 ± 4	108 ± 1	120 ± 3	55 ± 7
Pb	30 ± 3	42 ± 2	71 ± 5	40 ± 2
Sr	221 ± 8	762 ± 6	700 ± 100	580 ± 20
V	22 ± 1	32 ± 1	32 ± 4	21 ± 1
Zn	432 ± 9	376 ± 8	400 ± 20	271 ± 9
FA 2				
As	11 ± 6	< LOQ	< LOQ	< LOQ
Ba	700 ± 60	1287 ± 12	1300 ± 200	1220 ± 80
Co	14 ± 1	11 ± 1	14 ± 1	5 ± 1
Cu	114 ± 8	90 ± 2	108 ± 4	76 ± 6
Ni	64 ± 2	48 ± 1	54 ± 2	17 ± 1
Pb	45 ± 2	41 ± 2	62 ± 5	49 ± 1
Sr	300 ± 20	603 ± 6	610 ± 50	613 ± 11
V	120 ± 1	104 ± 2	119 ± 4	103 ± 3
Zn	729 ± 14	619 ± 6	690 ± 30	440 ± 10
FA 3				
As	15 ± 5	< LOQ	< LOQ	9 ± 2
Ba	570 ± 50	910 ± 30	840 ± 70	650 ± 30
Co	33 ± 1	25 ± 1	30 ± 2	13 ± 1
Cu	481 ± 9	400 ± 10	450 ± 30	270 ± 10
Ni	71 ± 2	53 ± 2	61 ± 2	26 ± 1
Pb	159 ± 4	129 ± 3	160 ± 5	120 ± 3
Sr	218 ± 6	400 ± 10	410 ± 10	326 ± 11
V	188 ± 4	183 ± 4	183 ± 4	141 ± 5
Zn	810 ± 20	670 ± 20	732 ± 12	363 ± 11

LOQ = limit of quantification

[a] Microwave, acid: 9 mL HNO_3 + 3 mL HF, EPA-3052 method

[b] Microwave, acid: 10 ml Aqua regia + 0.5 mL HF, 5min (0 →180 °C) + 10 min (hold 180 °C)

[c] Ultrasound, acid: : 10 ml Aqua regia + 0.5 mL HF, 18 min (6 × 3 min)

[d] Ultrasound, acid: : 10 ml (1:1) Aqua regia, 9 min (3 × 3 min)

Table 5 Determined element concentrations (mg kg^{-1}) of two bottom ashes (BA 1, BA 2) from Finland (mean of six replicate samples, with the confidence limit of the mean, P = 0.05).

Element	Microwave		Ultrasound-assisted	
	M1[a]	M2[b]	U1[c]	U2[d]
BA 1				
As	23 ± 5	< LOQ	< LOQ	10 ± 4
Ba	240 ± 20	760 ± 40	670 ± 60	270 ± 10
Co	17 ± 1	30 ± 30	16 ± 2	7 ± 1
Cu	1300 ± 700	1100 ± 400	1100 ± 700	700 ± 500
Ni	23 ± 11	18 ± 4	24 ± 8	30 ± 30
Pb	45 ± 8	50 ± 10	55 ± 1	42 ± 9
Sr	95 ± 7	270 ± 20	230 ± 9	300 ± 400
V	26 ± 1	29 ± 3	24 ± 2	11 ± 1
Zn	660 ± 50	580 ± 50	640 ± 120	286 ± 12
BA 2				
As	< LOQ	< LOQ	< LOQ	< LOQ
Ba	400 ± 40	1400 ± 130	670 ± 150	850 ± 140
Co	50 ± 40	50 ± 60	26 ± 5	12 ± 6
Cu	3000 ± 1500	3300 ± 1500	5000 ± 5000	3000 ± 3000
Ni	130 ± 30	100 ± 30	80 ± 30	70 ± 20
Pb	2000 ± 2000	900 ± 300	800 ± 200	1200 ± 400
Sr	117 ± 11	248 ± 6	170 ± 30	190 ± 11
V	39 ± 4	45 ± 5	40 ± 3	50 ± 50
Zn	3100 ± 900	2900 ± 600	2600 ± 700	2500 ± 400

LOQ = limit of quantification

[a] Microwave, acid: 9 mL HNO$_3$ + 3 mL HF, EPA-3052 method

[b] Microwave, acid: 10 ml Aqua regia + 0.5 mL HF, 5min (0 →180 °C) + 10 min (hold 180 °C)

[c] Ultrasound, acid: : 10 ml Aqua regia + 0.5 mL HF, 18 min (6 × 3 min)

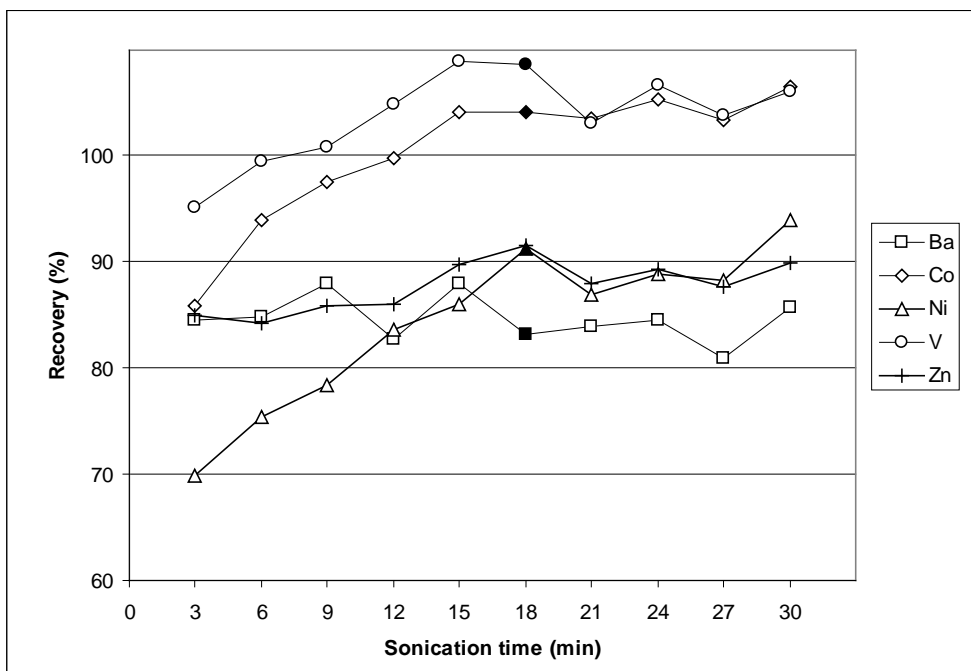[d] Ultrasound, acid: : 10 ml (1:1) Aqua regia, 9 min (3 × 3 min)

Figure 1 Effect of sonication time on element recoveries (mean of three replicate samples) of ultrasound-assisted digestion in SRM 1633b. Precision of the recovery rates resulted 2 - 4 %. Selected sonication time was 18 min.
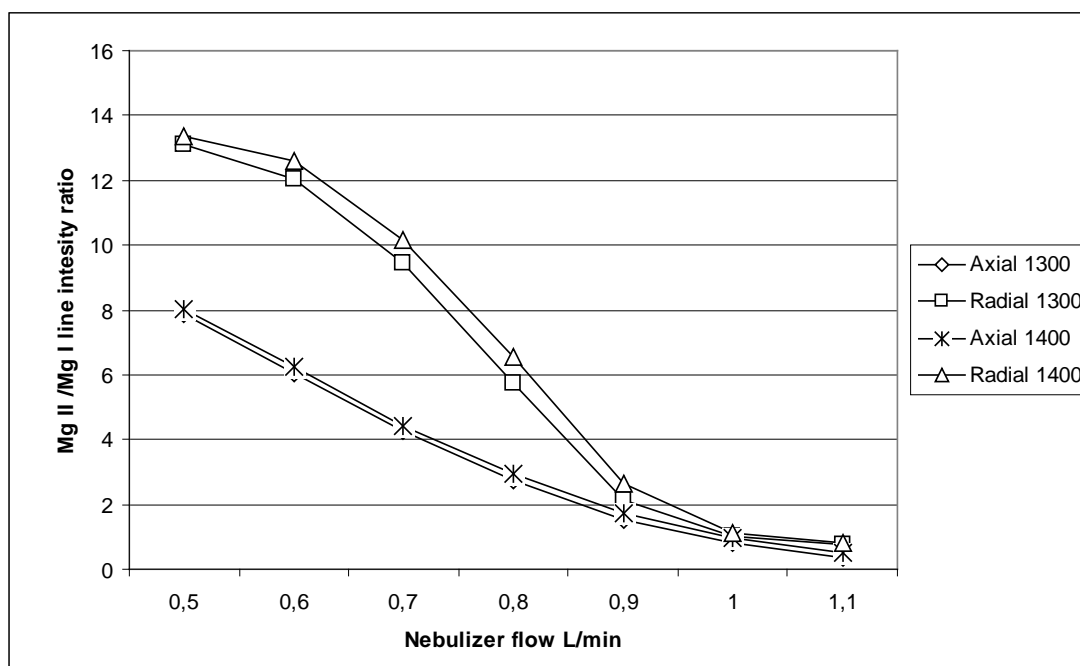
Figure 2 Values of Mg II 280.270 nm / Mg I 285.213 nm line intensity ratio for synthetic mixture of the matrix elements containing 10 mg L^{-1} of Mg by different nebulizer gas flow rates with plasma power of 1300 W using axial (●) and radial (■) plasma viewing and 1400 W using axial (○) and radial (□) plasma viewing. Error of measurement values were 1 - 3 %.