This is an electronic reprint of the original article.
This reprint *may differ* from the original in pagination and typographic detail.

Author(s): Ilander, Aki; Väisänen, Ari

Title: 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

Year: 2010

Version:

Please cite the original version:

Ilander, A. & Väisänen, A. (2010). 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. *Journal of Analytical Atomic Spectrometry*, (25), 1581-1587. doi:10.1039/c004191b

All material supplied via JYX is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

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

Aki Ilander* and Ari Väisänen

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

First published on the web Xth XXXXXXXXX 20XX

A multiple linear regression technique was used to evaluate and correct the matrix interferences in the determination of As and Pb concentrations in fly ashes by inductively coupled plasma optical emission spectrometry. The direct determination of As and Pb in SRM 1633b by ICP-OES failed to obtain the certified concentrations, except in a couple of cases. However, it proved possible to use the multiple linear regression (MLR) technique to correct the determined concentrations to a satisfactory level. This method of correction is based on the multiple regression line obtained from the analysis of 19 synthetic mixtures of matrix and analyte elements (Al, As, Ca, Fe, Pb, and Si) at five levels of concentrations. The matrix interferences in the determination of As were caused by Al, Pb, and Ca whereas the matrix interferences in the determination of Pb were caused by Al and Fe. The most suitable parameters for the determination of As and Pb were a plasma power of 1500 W and a nebulizer flow of 0.5 or 0.6 L min⁻¹. The accuracy of the method was showed with the analysis of SRM 1633b and two fly ash samples with the standard addition method. A recovery rate of 96 % can be reached for Pb at 220.353 nm with three digestion methods (US-TSD, US1 and MW) by using both direct measurement with thoroughly optimized plasma conditions and the MLR method. A recovery rate of 93 % was obtained for As when using the MLR method at 193.696 nm with the digestion method US2, a plasma power of 1500 W, and nebulizer flow of 0.6 L min⁻¹. The corrected and determined concentrations of As and Pb in samples analyzed resulted in a precision of 0.6 to 3.9 %.

Introduction

The combustion of agricultural wastes, coal, municipal waste, peat and wood has generated huge amounts of different kinds of ashes during the previous decades¹. Fly ashes contain significant amounts of elements with a toxic character such as As, Cd, Co, Cr, Pb, Ni, and V^{2,3}. It is well known that those elements are potential risks in the environment even at low concentrations^{3,4}. A significant problem in the use of various kinds of fly ashes is the injurious effect on the environment and human health^{5,6}. Potential applications for fly ashes include construction materials (cement and ceramic), geotechnical structures (road pavement and embankments) and agriculture (soil amendment)^{1,7-9}.

Microwave-accelerated digestion has become the most commonly used sample pre-treatment method for the determination of toxic element concentrations in different kinds of solid samples by ICP-OES¹⁰⁻¹². Microwave-assisted digestion can be performed in open or closed systems. Another practical sample pre-treatment method in the determination of toxic element concentrations in solid samples is ultrasound-assisted digestion. Ultrasound-assisted digestion has been used for elemental analysis of many particulate materials such as contaminated soil, coal fly ash, biological samples and sediment¹³⁻¹⁶.

The methods used in the analysis of toxic elements in fly

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 of the analyte elements in fly ash samples^{17,18}. The main emission lines for the determination of Pb are 217.000 nm, 220.353 nm and 283.306 nm. However, the most sensitive emission line of Pb is 220.353 nm¹⁹. ICP-OES is used less than ICP-MS for the determination of As concentrations. However, As can be determined by ICP-OES. The main emission lines for the determination of As are 188.979 nm and 193.696 nm^{20,21}. 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)^{22,23}. Anyway, several spectral interferences have been found in the determination of As and Pb by ICP-OES²⁴. Direct spectral overlap interference due to Fe was found when Pb was determined in the emission lines 217.000 nm and 283.306 nm^{24,25}. Inter-element interference was found in the determination of Pb in the emission line 220.353 nm from Al and background shift was observed due to Fe^{19,24-27}.

Evaluation and correction of matrix interferences in the ICP-OES measurements can be performed using the multiple linear regression technique²⁸⁻³⁰. This technique is based on the

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

Element	Wavelength nm	r	Atom/Ion I/II	LOD ^a mg kg ⁻¹	Calibration range mg L ⁻¹
<i>Nebulizer flow 0.5 L min⁻¹</i>					
As	193.696	1.0000	I	5.9	0.1 – 10.0
As	188.979	1.0000	I	6.3	0.1 – 10.0
Pb	220.353	0.9999	II	6.4	0.1 – 10.0
Pb	217.000	1.0000	I	5.0	0.1 – 10.0
<i>Nebulizer flow 0.6 L min⁻¹</i>					
As	193.696	1.0000	I	4.7	0.1 – 10.0
As	188.979	0.9999	I	9.9	0.1 – 10.0
Pb	220.353	0.9999	II	4.9	0.1 – 10.0
Pb	217.000	0.9999	I	5.7	0.1 – 10.0

^aLOD = limit of detection when 250 mg sample was digested and filtrate diluted to a volume of 100 mL. Calculated by substituting the intercept and its standard deviations multiplier ($a + 3sa$) into the calibration line $y = bx + a$ ³².

Bold = wavelength selected for the final determination

analysis of synthetic mixtures of the matrix elements and the calculation of a multiple regression line for each element and wavelength analyzed³¹. The expression obtained for the regression line can be tested by correcting the concentrations of matrix elements in both the synthetic mixtures and SRM sample. The significance of the differences between the corrected and the added or certified concentrations can subsequently be tested by significance tests such as the paired *t*-test³². Methods of this kind have successfully been used in the analysis of fertilizers²⁸, geological samples³⁰, and soil samples³³.

The aim of this study was to develop an effective and precise method for the determination of As, and Pb in power plant fly ashes by ICP-OES. The increasing demand for accurate analysis of ashes is caused by increasing environmental concern about of fly ashes. The reuse potential of different kinds of ashes has been noticed worldwide.

Experimental

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 performed with parameters of the instrument (nebulizer flow of 0.5 and 0.6 L min⁻¹, auxiliary gas flow of 0.2 L min⁻¹, plasma gas flow of 15 L min⁻¹ and plasma power of 1400 W and 1500 W). Two wavelengths for both elements investigated were tested in axially viewed plasma. The appropriate wavelengths used in the final determination are shown in Table 1.

Reagents

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

Four standard stock solutions were prepared for the interference tests. Standard stock solutions of Al, Ca, and Fe were prepared by dissolving appropriate amounts of Al(NO₃)₃ · 9 H₂O (p.a.), Ca(NO₃)₂ · 4 H₂O (p.a.), or Fe(NO₃)₃ · 9 H₂O (p.a.) in 50 mL of 2 - 10 % HNO₃ and diluted to a volume of 250 mL with water; all three reagents were supplied by Merck (Darmstadt, Germany). The standard stock solution of Si (1000 mg L⁻¹) was also supplied by Merck (Darmstadt, Germany).

Samples

A coal fly ash standard reference material, SRM 1633b³⁴, certified by the National Institute of Standards and Technology (NIST) and two fly ash samples collected from wood burning plants were analyzed. All the fly ash samples were collected in Finland. Six replicate analyses of each fly ash sample were performed.

Digestion procedures

All four digestion procedures were performed with ultrasound or microwave methods. Those methods were presented with more details in our earlier studies^{15,35}. Three digestion procedures were performed with an ultrasound method (US-TSD, US1, and US2) and one digestion procedure was performed with a microwave method standardized by the USEPA (MW).

- US-TSD = Ultrasound (two-step): i) digestion solution of 6 mL of HNO₃, (9 min) ii) digestion solution of 3 mL HNO₃ and 3 mL HF, (18 min)
- US1 = Ultrasound, digestion solution of 10 mL *aqua regia* and 0.5 mL HF, (18 min)
- US2 = Ultrasound, digestion solution of 10 mL (1:1) *aqua regia*, (9 min)
- MW = Microwave, digestion solution of 9 mL HNO₃ and 3 mL HF, USEPA method 3052

Table 2 Analytical results for two-step (US-TSD) digestion procedures in SRM 1633b (mean of six replicate samples, with the confidence limit of the mean, $P = 0.05$).

Results	As 188.979 nm mg kg ⁻¹	Recovery %	As 193.696 nm mg kg ⁻¹	Recovery %
1400 W: Neb 0.5	140.8 ± 1.9	103.4 ± 1.4	103.7 ± 3.8	76.1 ± 2.8
1400 W: Neb 0.6	148.9 ± 1.2	109.3 ± 0.9	98.5 ± 6.0	72.3 ± 4.5
1500 W: Neb 0.5	139.2 ± 2.8	102.2 ± 2.1	99.3 ± 2.6	72.9 ± 2.0
1500 W: Neb 0.6	146.5 ± 3.0	107.6 ± 2.3	98.0 ± 5.1	72.0 ± 3.8
Certified	136.2 ± 2.6		136.2 ± 2.6	

Results	Pb 217.000 nm mg kg ⁻¹	Recovery %	Pb 220.353 nm mg kg ⁻¹	Recovery %
1400 W: Neb 0.5	260.0 ± 3.9	381.2 ± 5.8	60.8 ± 1.0	89.1 ± 1.5
1400 W: Neb 0.6	273.4 ± 5.0	400.9 ± 7.4	67.9 ± 1.3	99.6 ± 2.0
1500 W: Neb 0.5	260.3 ± 3.5	381.7 ± 5.2	62.4 ± 0.8	91.5 ± 1.2
1500 W: Neb 0.6	286.0 ± 4.9	419.4 ± 7.2	67.0 ± 0.6	98.2 ± 0.9
Certified	68.2 ± 1.1		68.2 ± 1.1	

Results and discussion

5 Calibration

All concentration measurements were carried out using four-point calibration. As and Pb were determined by using two of the most sensitive emission lines to attain the sensitivity required. High values were obtained for the regression correlation coefficients, as shown in Table 1.

Table 3 The added and the determined concentrations (mg L⁻¹) of the synthetic mixtures of matrix elements with axial viewed plasma, plasma power of 1500 W and nebulizer flow of 0.6 L min⁻¹.

	Added	Found	Found	Added	Found	Found
	As	188.979	193.696	Pb	217.000	220.353
1	0.50	0.771	0.474	0.40	0.332	0.413
2	0.10	0.41	0.064	0.10	0.006	0.114
3	0.40	0.435	0.382	0.10	0.311	0.108
4	0.30	0.574	0.251	0.10	0.057	0.134
5	0.40	0.655	0.321	0.25	0.395	0.242
6	0.10	0.368	0.084	0.25	0.080	0.283
7	0.10	0.134	0.078	0.70	0.960	0.653
8	0.40	0.586	0.360	0.25	0.385	0.271
9	0.10	0.328	0.030	0.40	0.793	0.361
10	0.20	0.447	0.179	0.55	0.490	0.529
11	0.50	0.695	0.413	0.40	0.797	0.372
12	0.50	0.722	0.456	0.40	0.340	0.363
13	0.20	0.213	0.187	0.10	0.362	0.135
14	0.20	0.389	0.160	0.55	0.712	0.559
15	0.30	0.522	0.259	0.55	0.632	0.491
16	0.40	0.408	0.384	0.70	1.003	0.647
17	0.30	0.524	0.286	0.70	0.507	0.659
18	0.30	0.463	0.207	0.25	0.767	0.258
19	0.20	0.422	0.153	0.70	1.060	0.640

Concentration levels of matrix elements in synthetic mixtures:

15 Al = 10-410 mg L⁻¹, Ca = 10-810 mg L⁻¹,
Fe = 5-305 mg L⁻¹, Si = 25-625 mg L⁻¹

Analysis

The SRM 1633b was analyzed to test the validity of the procedure. The concentrations of the two elements (As, and

20 Pb) determined are shown in Table 2. Almost every measurement using different parameters of the determination of As and Pb in SRM 1633b by ICP-OES failed to obtain the certified concentrations, resulting in recoveries from 72 to 420 % (Table 2.). This was the case even if higher plasma power and lower nebulizer flow was used instead of those recommended by the ICP-OES manufacturer. However, the precision of the concentrations determined by ICP-OES was quite similar with the certified concentrations.

Table 4 The results of the paired *t*-tests in evaluation of differences between the added and the determined or corrected concentrations on the multiple regression line calculated from the analytical results of 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 1400 W:				
Nebulizer 0.5 l min ⁻¹	8.789	4.765	3.094	3.163
Nebulizer 0.6 l min ⁻¹	9.193	4.111	4.365	1.046
Axial 1500 W:				
Nebulizer 0.5 l min ⁻¹	8.530	6.116	3.036	2.423
Nebulizer 0.6 l min ⁻¹	8.658	7.002	2.758	1.503
<i>Added / Corrected</i>				
Axial 1400 W:				
Nebulizer 0.5 l min ⁻¹	4.218	10.359	0.857	7.607
Nebulizer 0.6 l min ⁻¹	3.194	1.077	8.592	12.923
Axial 1500 W:				
Nebulizer 0.5 l min ⁻¹	4.804	1.653	7.227	0.481
Nebulizer 0.6 l min ⁻¹	3.584	2.001	2.169	1.590

$t_{\text{critical}(18)} = 2.10$

$t_{\text{critical}(18)}$ = obtained from the *t*-distribution with the 18 degrees of freedom at the confidence level of 95%³².

35 Evaluation of matrix interferences

It is well known that fly ashes are very difficult to analyze, because their composition is unpredictable, highly variable, and also extremely heterogeneous. Evidently the sample matrices of the two fly ash samples and the SRM 1633b were quite different. The interference caused by the elements in the synthetic mixtures on the analyte elements were next

Table 5 Multiple linear regression data from the 19 synthetic mixtures of matrix elements.

Element / parameters	Multiple linear regression expression	R
<i>As 188.979 nm</i>		
1400 W: Neb 0.5	+ [0.93069As] - [0.0001844Ca]	0.969
1400 W: Neb 0.6	+ [0.88128As] - [0.0001659Ca]	0.979
1500 W: Neb 0.5	+ [0.97257As] - [0.0001298Ca]	0.988
1500 W: Neb 0.6	+ [0.89014As] - [0.0002204Ca]	0.975
<i>As 193.696 nm</i>		
1400 W: Neb 0.5	+ [0.9679As] - [0.05222Pb] + [0.0000832Al]	0.995
1400 W: Neb 0.6	+ [0.9432As] + [0.0000983Al] + [0.0000415Ca]	0.996
1500 W: Neb 0.5	+ [1.01As] + [0.0001083Al]	0.998
1500 W: Neb 0.6	+ [1.02As] + [0.0001443Al]	0.999
<i>Pb 217.000 nm</i>		
1400 W: Neb 0.5	+ 0.1288 + [0.9053Pb] - [0.00121Al] + [0.000243Ca] - [0.000589Fe]	0.979
1400 W: Neb 0.6	+ [0.8969Pb] - [0.001473Al] + [0.000347Ca] - [0.000878Fe]	0.985
1500 W: Neb 0.5	+ [0.9544Pb] - [0.001383Al] + [0.000325Ca] - [0.000478Fe]	0.989
1500 W: Neb 0.6	+ 0.11927 + [0.90366Pb] - [0.0009468Al] + [0.0002948Ca] - [0.0009239Fe]	0.983
<i>Pb 220.353 nm</i>		
1400 W: Neb 0.5	+ [1.084Pb] + [0.0001044Al] - [0.0000752Fe]	0.999
1400 W: Neb 0.6	+ [1.0985Pb] + [0.0001088Al]	0.997
1500 W: Neb 0.5	- 0.05528 + [1.15Pb] + [0.0001169Al]	0.999
1500 W: Neb 0.6	- 0.052085 + [1.14Pb] + [0.0001046Al] - [0.00010182Fe]	0.999

evaluated by the multiple linear regression (MLR) method.

The interference caused by the matrix elements Al, Ca, Fe, and Si in the determination of As and Pb were studied in 19 synthetic mixtures (Table 3) of matrix elements at five concentrations. The concentrations were selected to include one level lower and one higher than those determined in SRM 1633b and the real fly ash samples. The synthetic mixtures of matrix elements were produced such that the matrix element concentrations did not correlate with each other. The interference effects were evaluated at wavelengths and parameters (plasma power and nebulizer flow) which had produced statistically unacceptable analyte concentrations (Table 4). The calculations were carried out by selecting the added element concentrations and measured analyte concentrations as independent variables and the added analyte concentrations as a dependent variable. The calculations were performed using SigmaStat statistical software (Jandel scientific). The multiple linear regression parameters calculated for As and Pb are shown in Table 5. Only statistically significant ($P < 0.05$) correction parameters were taken into consideration.

As can be seen in Table 5, Al, Ca, and Fe were the most significant interfering elements in the sample matrix. Those elements may significantly affect analyte element concentrations because they usually occur at high concentrations in the sample matrix. According to the multiple linear regression data, the determination of As (both wavelengths) using different measurement parameters yielded too high concentrations. Two exceptions were As at 193.696 nm with plasma power of 1500 W and nebulizer flow of 0.5 L min⁻¹ and 0.6 L min⁻¹, which resulted in too low concentrations. Interference in the determination of As at 188.979 nm was caused by Ca concentration in the matrix. Interference in the determination of As at 193.696 nm was mainly caused by Al (Table 5). When plasma power of

1400 W was used the measurement of As was interfered also by Ca and Pb. According to the MLR data the determination of Pb at 217.000 nm resulted in too high concentrations, whereas the determination of Pb at 220.353 nm resulted in too low concentrations. Interference in the determination of Pb at 220.353 nm was caused by Al, and Fe. The determination of Pb at 217.000 nm was enormously interfered by Al, Ca, and Fe (Table 5). Due to this accurate determination of Pb at 217.000 nm cannot be performed.

According to M.G.A.Korn *et al.*¹⁹, R.K. Winge *et al.*²⁴, P.W.J.M Boumans²⁵, A. Asway *et al.*²⁷ and Iv. Boevski *et al.*³⁶, several spectral interferences have been found in the determination of As and Pb by ICP-OES. The most commonly detected interfering elements are Al and Fe for the determination of Pb concentrations. Spectral overlap interference due to Fe and background interference due to Al and Fe were found in the determination of Pb in the emission line 217.000 nm^{19,36}. Inter-element interference from Al and background shift due to Fe have been found when Pb was determined in the emission line 220.353 nm^{19,36}. According to A. Asway *et al.*²⁷, the determination of As at emission lines 188.979 nm and 193.696 nm was interfered by Fe, but that interference could be corrected by a widely used background correction technique.

Evaluation of wavelengths and determination parameters

The correction was evaluated using wavelengths and measured parameters which produced statistically acceptable analyte concentrations (Table 4). According to the paired *t*-tests, the correction of the As at 188.979 nm was not satisfactory because none of the tested parameters produced statistically acceptable analyte concentrations. However, it should be noted that the corrected mean concentration of As (188.979 nm) approached the added mean concentration. As can be seen in Table 4, the correction of the As at 193.696 nm performed very well, because three of the tested

Fig. 1 Recovery rates of standard addition method in the determination of As with a plasma power 1500 W and nebulizer flow 0.5 L min⁻¹. Precision of the method resulted in 1-4 %.

parameters produced statistically acceptable analyte concentrations. The correction of the Pb at 217.000 nm did not perform well, because only one of the parameters tested produced statistically acceptable analyte concentrations, whereas the correction of the Pb at 220.353 nm performed very well when plasma power of 1500 W was used. As can be seen in Table 5, the correlation coefficients of As (193.696 nm) and Pb (220.353 nm) were higher than those for other wavelengths.

According to Tables 4 and 5, the most suitable wavelengths and determination parameters are As (193.696 nm) and Pb (220.353 nm), plasma power of 1500 W and nebulizer flow of 0.5 L min⁻¹ or 0.6 L min⁻¹. The concentrations of As and Pb determined using plasma power of 1500 W and nebulizer flow of 0.5 L min⁻¹ should be corrected using multiple linear regression; when plasma power of 1500 W and nebulizer flow of 0.6 L min⁻¹ was used, only the As concentrations needed correction.

According to M.G.A.Korn *et al.*¹⁹, R.K. Winge *et al.*²⁴, and Iv. Boevski *et al.*³⁶, the most suitable emission line for the determination of Pb is 220.353 nm. According to A. Asfaw *et al.*²⁷, typically used emission lines for the determination of As were all exposed to different types of spectral interference, but the most practical emission line for the determination of As was 193.696 nm because the correction of that emission line can be easily done.

Standard addition method

The standard addition method was used to confirm the analysis of real fly ash samples in which the main matrix element concentrations differed from the SRM 1633b. The standard addition method was performed in samples FA1 and FA2 using digestion methods US-TSD and US2 with a plasma power of 1500 W and nebulizer flow of 0.5 L min⁻¹ and 0.6 L min⁻¹. The concentrations of Ca were of about 5 to 15-fold higher in real fly ash samples than in the SRM sample, which may cause serious matrix interferences in ICP-OES. The standard addition method was performed at two levels of

Fig. 2 Recovery rates of standard addition method in the determination of Pb with a plasma power 1500 W and nebulizer flow 0.5 L min⁻¹. Precision of the method resulted in 1-3 %.

concentrations (50 % and 200 % addition) (Fig. 1 and Fig. 2). The standard addition method resulted in recovery rates from 75 % to 103 % (determined), whereas standard addition with MLR method resulted in recovery rates from 90 % to 106 % (corrected). As can be seen in Fig. 1 and Fig. 2, the MLR correction was performed successfully in the determination of As and Pb in fly ash samples.

MLR correction

The MLR data of the matrix elements were used to correct the determined As, and Pb concentrations of SRM 1633b and two fly ash samples. The directly determined, corrected and certified concentrations of SRM 1633b with the recoveries are shown in Table 6.

The MLR correction of the Pb concentrations (with plasma power of 1500 W and nebulizer flow of 0.5 L min⁻¹) of the SRM was applied with great success in the digestion methods US-TSD and MW, resulting in recovery rates from 96.0 % to 97.6 %. On the other hand, the determination of the concentrations (with plasma power of 1500 W and nebulizer flow of 0.6 L min⁻¹) of the SRM for Pb was also quite successful in the digestion method US-TSD, US1 and MW, resulting in recovery rates from 96.9 % to 98.3 % (Table 6). The corrected concentrations of the SRM for Pb by the digestion method US2 was not successful, because the determined concentrations were lower than the quantification limit.

The corrected concentration of the SRM for As was not successful because all results remained too low. The most suitable corrected concentrations of the SRM for As was obtained using the digestion method US2. The corrected As recoveries varied from 83.5 % to 92.9 % in the SRM sample. However, it should be noted that the corrected mean concentration of As approached the certified value. The correction for the determined As concentrations of SRM 1633b was significantly higher in digestion methods US-TSD and US1 than digestion methods US2 and MW because their significant matrix element concentrations results were in even

Table 6 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 at synthetic mixtures of matrix elements (mean of six replicate samples, with the confidence limit of the mean, $P = 0.05$).

Element / Results	Determined mg kg^{-1}	Recovery %	Corrected mg kg^{-1}	Recovery %
<i>As 193.696 nm</i>				
Method: US-TSD				
1500 W : Neb 0.5	99.3 ± 2.6	72.9 ± 2.0	115.3 ± 2.6	84.7 ± 2.0
1500 W : Neb 0.6	98.0 ± 5.0	72.0 ± 3.8	120.0 ± 5.1	88.1 ± 3.8
Method: US1				
1500 W : Neb 0.5	103.0 ± 2.4	75.6 ± 1.8	115.2 ± 2.2	84.6 ± 1.6
1500 W : Neb 0.6	96.5 ± 4.2	70.9 ± 3.1	113.7 ± 4.7	83.5 ± 3.5
Method: US2				
1500 W : Neb 0.5	123.7 ± 2.4	90.8 ± 1.8	125.7 ± 2.5	92.3 ± 1.7
1500 W : Neb 0.6	122.7 ± 2.1	90.1 ± 1.5	126.5 ± 2.1	92.9 ± 1.6
Method: MW				
1500 W : Neb 0.5	119.6 ± 1.4	87.8 ± 1.1	121.7 ± 1.4	89.4 ± 1.0
1500 W : Neb 0.6	116.3 ± 1.6	85.4 ± 1.2	120.1 ± 1.6	88.2 ± 1.2
Certified	136.2 ± 2.6		136.2 ± 2.6	
<i>Pb 220.353 nm</i>				
Method: US-TSD				
1500 W : Neb 0.5	62.4 ± 0.8	91.4 ± 1.1	66.5 ± 0.7	97.6 ± 1.0
1500 W : Neb 0.6	67.0 ± 0.6	98.3 ± 0.8	63.9 ± 0.4	93.6 ± 0.6
Method: US1				
1500 W : Neb 0.5	64.4 ± 1.1	94.4 ± 1.6	75.4 ± 1.0	110.5 ± 1.5
1500 W : Neb 0.6	66.5 ± 1.4	97.6 ± 2.1	72.5 ± 1.5	106.3 ± 2.1
Method: US2				
1500 W : Neb 0.5	< LOQ	< 15 %	< LOQ	< 15 %
1500 W : Neb 0.6	< LOQ	< 15 %	< LOQ	< 15 %
Method: MW				
1500 W : Neb 0.5	65.3 ± 0.5	95.7 ± 0.8	65.5 ± 0.7	96.0 ± 0.9
1500 W : Neb 0.6	66.1 ± 1.2	96.9 ± 1.8	62.9 ± 1.4	92.3 ± 2.1
Certified	68.2 ± 1.1		68.2 ± 1.1	

US-TSD = Ultrasound (two-step): i) digestion solution of 6 mL of HNO_3 , 9 min (3×3 min)

ii) digestion solution of 3 mL HNO_3 and 3 mL HF, 18 min (6×3 min)

US1 = Ultrasound, digestion solution of 10 mL *aqua regia* and 0.5 mL HF, 18 min (6×3 min)

US2 = Ultrasound, digestion solution of 10 mL (1+1) *aqua regia*, 9 min (3×3 min)

MW = Microwave, digestion solution of 9 mL HNO_3 and 3 mL HF, USEPA method 3052

15-fold higher. This is quite surprising because ultrasound method yielded significantly higher Al concentrations than microwave method with a mixture of 9 ml of HNO_3 and 3 ml of HF as the digestion solution. The corrected concentrations of As and Pb in the SRM 1633b showed the same trend in precision as in the certified concentrations.

The determined and corrected concentrations for four different digestion methods of two fly ash samples are presented in Table 7. The corrected concentrations of As for all real fly ash samples (FA1 and FA2) by four different digestion methods were quite similar, almost every concentration being between 27 - 37 mg kg^{-1} . The corrected concentrations of Pb for real fly ash samples were between 118 and 170 mg kg^{-1} . The results were highly dependent on the digestion method used. The lowest concentrations of Pb for all fly ash samples were obtained in the digestion method US2 with other digestion methods producing quite similar concentrations, as in the case of the SRM samples. The corrected concentrations of As and Pb depended on the matrix

element concentrations in the fly ash samples with the same kind of trend in corrections as in the analysis of the SRM 1633b with only a few exceptions. The corrected and determined concentrations of As and Pb in real fly ash samples analyzed resulted in similar precision as those of the certified material (SRM 1633b). It should be noted that slightly low concentrations of As in SRM 1633b may be due to loss of As during the digestion step. As can be seen in Fig. 1, the standard addition method with MLR correction resulted in recovery rates from 93.6 % to 106.1 % for As in a case of real fly ash samples.

Conclusions

Almost every direct determination of As and Pb concentrations in the SRM 1633b samples by using ICP-OES resulted in values that were too low. But then the analysis of Pb concentrations in SRM samples was successfully performed by using the multiple linear regression technique,

Table 7 The determined and corrected concentrations in four different digestion methods of two fly ash samples based on the multiple regression line calculated from the analytical results at synthetic mixtures of matrix elements (mean of six replicate samples, with the confidence limit of the mean, $P = 0.05$).

Element / Results	As 193.696 nm Determined mg kg^{-1}	Corrected mg kg^{-1}	Pb 220.353 nm Determined mg kg^{-1}	Corrected mg kg^{-1}
<i>FA1</i>				
Method: US-TSD				
1500 W : Neb 0.5	31.5 ± 0.9	34.5 ± 1.4	150.9 ± 3.5	154.8 ± 3.6
1500 W : Neb 0.6	31.8 ± 1.6	36.3 ± 1.3	156.1 ± 3.9	157.2 ± 3.9
Method: US1				
1500 W : Neb 0.5	29.2 ± 2.1	34.6 ± 1.9	137.4 ± 1.1	152.9 ± 1.3
1500 W : Neb 0.6	27.3 ± 1.7	35.0 ± 1.8	136.9 ± 1.8	149.6 ± 2.1
Method: US2				
1500 W : Neb 0.5	30.5 ± 1.4	34.1 ± 1.4	109.7 ± 0.7	118.9 ± 0.8
1500 W : Neb 0.6	31.3 ± 1.1	36.4 ± 1.1	110.8 ± 0.7	118.6 ± 0.7
Method: MW				
1500 W : Neb 0.5	39.6 ± 0.7	40.4 ± 0.7	123.1 ± 2.4	131.4 ± 2.8
1500 W : Neb 0.6	41.1 ± 1.9	42.7 ± 1.9	124.6 ± 2.2	132.4 ± 2.5
<i>FA2</i>				
Method: US-TSD				
1500 W : Neb 0.5	19.6 ± 1.9	24.9 ± 1.9	155.1 ± 3.5	162.9 ± 3.9
1500 W : Neb 0.6	20.4 ± 2.2	27.8 ± 2.3	150.9 ± 2.7	149.3 ± 3.6
Method: US1				
1500 W : Neb 0.5	22.6 ± 1.8	27.5 ± 1.5	139.9 ± 2.8	155.1 ± 2.8
1500 W : Neb 0.6	20.3 ± 1.6	26.9 ± 1.0	135.1 ± 3.0	140.3 ± 3.1
Method: US2				
1500 W : Neb 0.5	27.6 ± 1.4	30.3 ± 1.4	113.4 ± 0.7	122.4 ± 0.9
1500 W : Neb 0.6	26.2 ± 0.9	30.1 ± 0.9	116.1 ± 1.2	120.3 ± 1.4
Method: MW				
1500 W : Neb 0.5	30.1 ± 0.9	31.9 ± 0.9	155.3 ± 0.9	169.4 ± 1.0
1500 W : Neb 0.6	29.9 ± 1.1	32.5 ± 1.1	156.4 ± 2.6	164.4 ± 2.8

US-TSD = Ultrasound (two-step): i) digestion solution of 6 mL of HNO_3 , 9 min (3×3 min)

ii) digestion solution of 3 mL HNO_3 and 3 mL HF, 18 min (6×3 min)

US1 = Ultrasound, digestion solution of 10 mL *aqua regia* and 0.5 mL HF, 18 min (6×3 min)

US2 = Ultrasound, digestion solution of 10 mL (1+1) *aqua regia*, 9 min (3×3 min)

MW = Microwave, digestion solution of 9 mL HNO_3 and 3 mL HF, USEPA method 3052

whereas the corrected concentrations of the SRM for As were still too low. However, it should be noted that the corrected mean concentration of As approached the certified value resulting in a recovery of 92.9 %.

The results proved that it is possible to use the multiple linear regression technique to evaluate matrix interferences in the determination of As, and Pb in the fly ash samples by ICP-OES. Only 19 synthetic mixtures of matrix elements were required to obtain reliable results. The matrix interferences in the determination of As were caused by Al, Pb, and Ca whereas the matrix interferences in the determination of Pb were caused by Al and Fe. Similar interferences on the determination of As and Pb have been presented^{19,24,27}; however, without the interference caused by Ca. In the case of the fly ash samples from wood combustion, the As and Pb concentrations were dramatically interfered by Ca at wavelengths 188.979 nm and 217.000 nm, respectively. The analysis showed that the sample matrix can strongly interfere

with the determination of As and Pb causing significant changes in the determined element concentrations.

The most suitable wavelengths for the determination of As and Pb were 193.696 nm and 220.353 nm, respectively. This is concordant with the observations presented in the literature^{24,27,36}. The most suitable instrument parameters for the determination of As and Pb were plasma power of 1500 W and nebulizer flow of 0.5 L min^{-1} or 0.6 L min^{-1} . The determination of As and Pb using plasma power of 1500 W and nebulizer flow of 0.5 L min^{-1} resulted in concentrations that must be corrected using multiple linear regression. The determination of As and Pb with plasma power of 1500 W and nebulizer flow of 0.6 L min^{-1} resulted in concentrations where only As had to be corrected by the MLR technique. It is well known that the accurate determination of toxic elements such as As and Pb are crucial in cases of suspected environmental and health risks.

Notes and references

Department of Chemistry, University of Jyväskylä, P.O. Box 35, FIN-40014 Jyväskylä, Finland. Fax: +358 14 260 2501; Tel: +358 14 260 2613; E-mail: aki.ilander@ju.fi

70 36 Iv. Boevski, N. Daskalova, I Havezov, Spectrochim. Acta, Part B, 2000, **55**, 1643.

- 1 L. Reijnders, *Resour. Conserv. Recycl.*, 2005, **43**, 313.
- 2 O. Hjelmar, *J. Hazard. Mater.*, 1996, **47**, 345.
- 3 M. Izquierdo, X. Querol, J. Davidovits, D. Antenucci, H. Nugteren, C. Fernández-Pereira, *J. Hazard. Mater.*, 2009, **166**, 561.
- 10 4 L. Ebdon, L. Pitts, R. Cornelis, H. Crews, O.F.X. Donald, Ph. Quevauviller, *Trace Element Speciation for Environment, Food and Health*, RSC. MPG Books Ltd, Bodmin, Cornwall, UK, 2001.
- 5 T. Sabbas, A. Poletti, S. R. Pomi, T. Astrup, O. Hjelmar, P. Mostbauer, G. Cappai, G. Magel, S. Salhofer, C. Speiser, S. Heuss-Assbichler, R. Klein, P. Lechner, *Waste Manage.*, 2003, **23**, 61.
- 15 6 S. V. Vassilev, C. G. Vasileva, *Fuel*, 2007, **86**, 1490.
- 7 R. Kumar, S. Kumar, S.P. Mehrotra, *Resour. Conserv. Recycl.*, 2007, **52**, 157.
- 8 R. Rajamma, R. J. Ball, L. A. C. Tarelho, G. C. Allen, J. A. Labrincha, V. M. Ferreira, *J. Hazard. Mater.*, 2009, **172**, 1049.
- 20 9 L. Reijnders, *Build. Environ.*, 2007, **42**, 1036.
- 10 H. M. Kingston, L. B. Jassie, *Introduction to Microwave Sample Preparation: Theory and Practice*, American Chemical Society, Washington D.C., 1988.
- 25 11 K. Lambie, S. Hill, *Analyst*, 1998, **123**, 103R.
- 12 K. Srogi, *Analytical Letters*, 2007, **40**, 199.
- 13 T. J. Mason, *Sonochemistry: The Uses of Ultrasound in Chemistry*, The Royal Society of Chemistry, Cambridge, 1990.
- 14 D. Hristozov, C.E. Domini, V. Kmetov, V. Stefanova, D. Georgieva, A. Canals, *Anal. Chim. Acta*, 2004, **516**, 187.
- 30 15 A. Ilander, A. Väisänen, *Anal. Chim. Acta*, 2007, **602**, 195.
- 16 F. Priego-Capote, M.D. Luque de Castro, *J. Biochem. Biophys. Methods*, 2007, **70**, 299.
- 17 J. Nölte, *ICP Emission Spectrometry, A Practical Guide*, Wiley-VCH, Weinheim, 2003.
- 35 18 A. Iwashita, T. Nakajima, H. Takanashi, A. Ohki, Y. Fujita, T. Yamashita, *Talanta*, 2007, **71**, 251.
- 19 M. G. A. Korn, J.B. de Andrade, D. S. de Jesus, V. A. Lemos, M. L. S. F. Bandeira, W. N. L. dos Santos, M. A. Bezerra, F. A. C. Amorim, A. S. Suoza, S. L. C. Ferreira, *Talanta*, 2006, **69**, 16.
- 40 20 PerkinElmer, *Optima Simultaneous Spectrometers, Wavelength Tables*, PerkinElmer inc. Connecticut, USA, 2001.
- 21 D. Q. Hung, O. Nekrasova, R. G. Compton, *Talanta*, 2004, **64**, 269.
- 22 J-L. Todoli, J-M. Mermet, *Spectrochim. Acta, Part B*, 1999, **54**, 895.
- 45 23 N. Daskalova, Iv. Boevski, *Spectrochim. Acta, Part B*, 1999, **54**, 1099.
- 24 R. K Winge, V. A. Fassel, V. J. Peterson, M. A. Floyd, *Inductively Coupled Plasma-Atomic Emission Spectroscopy: An Atlas of Spectral Information*, Elsevier, Amsterdam, 1985.
- 25 P. W. J. M. Boumans, *Inductively Coupled Plasma Emission Spectroscopy, Part I, Methodology, Instrumentation, and performance*, Chemical Analysis Vol. 90., Wiley & Sons, New York, 1987.
- 50 26 M. Stepan, P. Musil, E. Poussel, J. M. Mermet, *Spectrochim. Acta, Part B* 2001, **56**, 443.
- 27 A. Asfaw, G. Wibetoe, *Spectrochim. Acta, Part B* 2009, **64**, 363.
- 28 R. Matilainen, J. Tummanvuori, *J. AOAC Int.*, 1996, **79**, 22.
- 29 T. Piippanen, J. Rautiainen, J. Tummanvuori, *Anal. Chim. Acta*, 1997, **349**, 327.
- 30 A. Väisänen, R. Matilainen, J. Tummanvuori, *Fresenius' J. Anal. Chem.*, 2000, **367**, 755.
- 60 31 E. Fox, K. Shotton and C. Ulrich, *SigmaStat statistical software – User's manual. version 2.0*, Jandel Corporation, 1995.
- 32 J. N. Miller, J. C. Miller, *Statistics and Chemometrics for Analytical Chemistry*, 4th edition, Pearson Education Limited, Dorchester, 2000.
- 65 33 A. Väisänen, A. Ilander, *Anal. Chim. Acta*, 2006, **570**, 93.
- 34 T.E. Gills, *Certificate of Analysis, Standard Reference Material 1633b*, National Institute of Standards and Technology, Gaithersburg, 1993.
- 35 A. Ilander, A. Väisänen, *Ultrasonics Sonochemistry*, 2009, **16**, 763.