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The determination of trace element concentrations in fly ash samples using ultrasound-assisted digestion followed with 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 trace element (chromium, copper, lead, nickel, vanadium and zinc) concentrations in fly ash samples was developed. All the measurements were performed in robust plasma conditions. Ultrasound-assisted digestion procedures using digestion solutions of *aqua regia* and hydrofluoric acid (HF) resulted in recovery rates of over 80 % for all the analyte elements. Ultrasound-assisted two-step digestion with digestion solutions of 6 mL of HNO_3 (Step 1) and 3 mL of HNO_3 + 3 mL of HF (Step 2) resulted in recovery rates of over 92 % for all the analyte elements with one exception, chromium, which had a recovery of about 85 %. The analysis of SRM 1633b showed that the two-step ultrasound-assisted digestion method developed resulted in chromium, copper, nickel and zinc concentrations higher than the microwave digestion method standardized by the United States Environmental Protection Agency (USEPA method 3052). This is the very first time when a digestion method using ultrasound resulted in higher efficiency than microwave (USEPA method 3052) for chromium and nickel in very hard to dissolve samples. The major advantages of the ultrasound-assisted digestion over microwave digestion is the high treatment rate (about 30 samples simultaneously with a sonication time of 18 min) and the possibility to use new sample vessels without a significant increase in costs.

Keywords: emission spectrometry; ultrasound; microwave; fly ash; trace elements

1. Introduction

Industrial and other comparable activity produces many kinds of by-products, for instance, fly ashes. The combustion of agricultural wastes, coal, municipal waste, peat and wood has generated huge amounts of different kinds of ashes during the previous decades [1, 2]. Fly ashes contain significant amounts of elements with a toxic character such as Cd, Cu, Co, Cr, Ni, Pb, V, and Zn [3-5]. Metal contamination is a significant problem in many manufacturing residues, because it is well known that elements such as cadmium, chromium, lead, nickel, and vanadium are potential risks in the environment even at low concentrations [6-8].

The significant problem in the use of various kinds of fly ashes is the injurious effect on the environment and human health. Because of this, fly ashes should be classified in a case-specific way [7, 9]. Potential applications for fly ashes include construction materials (cement and ceramic), geotechnical structures (road pavement and embankments) and agriculture (soil amendment) [10-13]. Industrial solid residues such as fly ashes are very difficult to analyze, because their composition is unpredictable, highly variable, and also extremely heterogeneous [7, 14].

The methods used in the analysis of trace elements in fly ash samples are based on atomic absorption or emission spectrometry together with a liquid sample introduction system. 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 [15-16]. 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) [17-18].

Microwave-accelerated digestion has become the most commonly used sample pre-treatment method for the determination of trace element concentrations in solid samples by ICP-OES

[19-23]. Microwave-assisted digestion can be performed in open or closed digestion systems. The trend nowadays is towards closed systems. The main benefits for the closed systems are the possibilities for controlling both the temperature and pressure and for pre-treating the sample without a significant loss of analyte elements [20, 21]. Another useful sample pre-treatment method for the determination of trace element concentrations in solid samples is ultrasound-assisted digestion [24-28].

In general solid sample digestion is performed by using ultrasonic water baths or probes. Due to a direct contact of the ultrasonic probe with the sample solution, concentrated acids cannot be used in the digestion. This may lead to a serious problem with the dissolution of samples, especially fly ashes, which need concentrated acid mixtures including HF for the total dissolution. Ultrasound-assisted digestion has been used for elemental analysis of many particulate materials such as contaminated soil, coal fly ash, street dust, biological sample and sediment [28-32]. Ultrasonic water baths are used more often, because they are easier to use than probes. On the other hand, ultrasonic probes often require shorter digestion times than water baths [28-30]. 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. When an ultrasonic 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 [27, 33]. Ultrasound-assisted digestion can also be performed more safely than microwave digestion, because pressure and temperature are substantially lower in ultrasound digestion [34].

Several fly ash samples were analyzed in this study. The aim was to develop an effective ultrasound-assisted digestion method for the determination of Cr, Cu, Ni, Pb, V, and Zn in power plant fly ashes by ICP-OES. A new and effective method of digestion is needed due to insoluble compounds of Cr, Cu and Ni in fly ash samples [28].

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 spectrometry. A Scott type double-pass spray chamber and a cross-flow nebulizer were used throughout. The determination of element concentrations was performed with optimized default parameters of the instrument (nebulizer flow 0.6 L min^{-1}, auxiliary gas flow 0.2 L min^{-1}, plasma gas flow 15 L min^{-1} and plasma power of 1400 W) [28]. Two wavelengths for each of the elements investigated were tested in radially viewed plasma. The appropriate wavelengths 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 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.

2.3. Samples

A coal fly ash standard reference material, SRM 1633b [35], certified by the National Institute of Standards and Technology (NIST) and four 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.

2.4. Microwave digestion procedure (MW)

The microwave digestion procedure obtained from the United States Environmental Protection Agency (USEPA method 3052) [36] was used as a reference method for the ultrasound-assisted digestion procedure. The same microwave digestion procedure has been used in our earlier study [28].

2.5. Ultrasound-assisted digestion procedure (US)

An SRM sample or fly 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 12 mL of digestion solution of HNO_3 (9 mL) and HF (3 mL) was added. The tube was closed and placed into a 650 W, 35 kHz, Model Transsonic 820/H ultrasonic water bath (60 °C) supplied by ELMA (Singen, Germany). The sonication procedure was divided into six equal steps (3 min) with the sample tube shaken by hand between each step. The shaking was used to prevent sedimentation. After digestion the sample solution was filtered (Whatman No. 42, Maidstone, UK) into a 100 mL plastic volumetric flask. The residue was washed with 15 mL of water introduced in four portions, and the filtrate diluted to volume with water. The sample solution was transferred into a plastic screw-top bottle for storage. The other ultrasound-assisted digestion procedure was performed with the same digestion program, but with a digestion solution of 3 mL of *aqua regia* and 3 mL of HF.

2.6. Two-step ultrasound-assisted digestion procedure (US-TSD)

An SRM sample or fly 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 an appropriate volume of digestion solution was added. The tube was closed and placed into a 650 W, 35 kHz, Model Transsonic 820/H ultrasonic water bath supplied by ELMA (Singen, Germany). The sonication procedure was divided into equal digestion steps (3 min) with the

sample tube shaken by hand between each digestion steps. After digestion step 1 the sample solution was centrifuged (Heraeus Instruments Megafuge 1.0, 2500 rpm in 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. After the second step the sample solution was filtered (Whatman No. 42, Maidstone, UK) into the same 100 mL plastic volumetric flask with the first step solution. The residue was washed with 15 mL of water introduced in four portions, and the filtrate diluted to volume with water. The sample solution was transferred into a plastic screw-top bottle for storage.

The optimized two-step ultrasound-assisted digestion procedure included digestion solutions and sonication times with temperatures as follows:

(1) Step 1: The sample was digested with the solution of 6 mL of HNO_3 for 9 min (3×3 min) sonication in 60 °C.

(2) Step 2: The residue from the step 1 was digested with the solution of 3 mL of HNO_3 + 3 mL of HF for 18 min (6×3 min) sonication in 60 °C.

3. Results and discussion

3.1. Optimization of the ultrasound-assisted digestion

The optimization of the ultrasound procedure was performed by determining the concentrations of elements in SRM 1633b. According to our earlier studies [28] the most suitable sonication time for this purpose is 18 min. The homogeneity of the ultrasound field of the ultrasonic water bath was shown in our earlier studies [28]. The digestion solution of 9 mL of HNO_3 and 3 mL of HF was adapted from the USEPA method 3052 [36]. In that case a comparison between the ultrasound and microwave techniques was logical. Several mixtures of HNO_3, *aqua regia*, H_2O_2 and HF as a digestion solution were tested. According to the

tests, the accurate determination of analyte elements can not be performed without the use of digestion solutions containing HF. According to the tests, the digestion solutions of 9 mL of HNO_3 and 3 mL of HF as well as 3 mL of *aqua regia* and 3 mL of HF were found as the most suitable digestion solutions.

3.2. Evaluation of the two-step ultrasound-assisted digestion

Two-step digestion procedures were performed by determining the concentrations of Cr, Cu, Ni, Pb, V, and Zn in SRM 1633b. The procedure was composed of two different digestion steps. The first step was performed with a digestion solution of 10 mL of 0.1 M HNO_3 or 6 mL of HNO_3. The purpose of the first step was to dissolve easily digestible materials and to make the second step easier. The second step was performed with a digestion solution of 3 mL of HNO_3 + 3 mL of HF or 3 mL of *aqua regia* + 3 mL of HF.

Two-step digestion methods with the same digestion solution but with two different digestion procedures, US-TSD1 and US-TSD2, were tested. The procedures differed in that the sample solutions of the two steps were filtered into the same volumetric flask in procedure US-TSD1 and into different volumetric flasks in US-TSD2. Significant differences were not found for Cu, Ni, Pb, V and Zn between the methods US-TSD1 and US-TSD2. According to the t-tests, the concentrations of chromium were significantly higher in method US-TSD1 than method US-TSD2. This is quite interesting because methods US-TSD1 and US-TSD2 differed with the filtrates of two steps only. The method US-TSD2 contains two different flasks which should make the matrix of the second step easier for ICP-OES. This is due to lower concentrations of EIEs, especially calcium and magnesium. It is well known that the EIEs may lead to serious matrix effects with ICP-OES [17, 18]; however, in this case the analysis can be performed without significant such effects. It should be noted that the measurement was performed with thoroughly optimized plasma conditions [28]. Two-step digestion procedures (US-TSD1 and US-TSD2) with a digestion solution of 3 ml of *aqua regia* and 3

ml of HF resulted in significantly higher concentrations than the US digestion procedure for Cu, Pb and Zn. Two-step digestion procedures (US-TSD1 and US-TSD2) with a digestion solution of 6 mL of HNO_3 and 3 mL of HNO_3 + 3 mL of HF resulted in significantly higher concentrations than the US digestion procedure for Cr, Cu, Ni and V. According to the t-tests, the ultrasound-assisted digestion with two steps using digestion solutions of 6 ml of HNO_3 (Step 1) and 3 mL of HNO_3 + 3 mL of HF (Step 2) and filtrating into the same volumetric flask is the most suitable for the analysis of trace elements in fly ash samples.

3.3. Calibration

All the concentration measurements were carried out using a four-point calibration. Multi-element calibration standards were used for all elements (Cu, Cr, Ni, Pb, V, and Zn). Calibration standards were made for each of the digestion methods. The optimization for each element was performed by taking two of the most sensitive emission lines to attain the sensitivity required. The quantification limits for the determination of Cr, Cu, Ni, Pb, V, and Zn in the fly ash samples using an US-TSD as a digestion method were found to be 17.1, 13.6, 10.7, 31.8, 16.1 and 21.6 mg kg^{-1}, respectively. Exceedingly high values were obtained for the regression correlation coefficients, as shown in Table 1. It should be noted that lower LODs can be reached by using lower concentrations of HF [28].

3.4. 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 sample FA1 using a digestion method US-TSD with the digestion solution of 9 mL of HNO_3 + 3 mL of HF. The concentrations of calcium were of about tenfold higher in real fly ash samples than in the SRM sample, which may cause serious matrix interferences in ICP-OES even if the measurement is performed under robust

plasma conditions. The main matrix elements Al, Ca, Fe, K, Mg, S and Si resulted in concentrations of 98, 83, 158, 39, 10, 31 and 329 mg L^{-1} in the filtrates of digested samples, respectively. The standard addition method was performed with two levels of concentrations (50% and 200% addition) (Table 2). The standard addition method resulted in recovery rates between 92 -100 %, with one exception, lead, which could not be accurately determined. The reason for the slightly low lead recovery was probably the difficult sample matrix and also the low concentrations. The lead recovery rates were of about 78% and 96% at standard additions of 50% and 200%, respectively.

3.5. Analysis

It is well known that samples with a complex matrix should be analyzed under robust plasma conditions [17, 18]. According to our earlier studies [28], robust plasma conditions for fly ash materials 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 fly ash samples with an axially viewed plasma can not be performed under robust plasma conditions [28]. The coal fly ash standard reference material, SRM 1633b, and four fly ash samples collected from different wood burning plants were analyzed. Six elements, Cu, Cr, Ni, Pb, V and Zn, were selected because of their toxic character and these elements are also known to be hard to dissolve. The concentrations (mean ± confidence level of the mean) of the six elements in SRM 1633b digested by ultrasound or microwave methods and determined by ICP-OES are shown in Table 3. Differences with various digestion methods were studied by using the t-test ($P = 0.05$). According to the tests, the significant differences were obtained between the methods tested.

A comparison of digestion techniques (ultrasound vs. microwave) with the same digestion solution was made using methods MW and US with digestion solutions of 9 mL of HNO_3 and 3 mL of HF (Figure 1). According to the t-tests, Cu and Zn concentrations resulted in

significantly higher using the ultrasound method than in the microwave method. Significant differences between ultrasound and microwave methods were not found for Pb and V; however, the microwave method resulted in significantly higher concentrations for Cr and Ni (Table 3).

According to the t-tests, the Cr concentrations were significantly higher in the microwave method than the ultrasound method for all the digestion solutions (except two-step digestion). Cu, Pb, Ni and V were found in similar concentrations for both ultrasound and microwave methods, whereas Zn resulted in concentrations significantly higher using the ultrasound.

As can be seen in Table 3, concentrations of Cu, Pb and Zn were significantly higher in the ultrasound method (US) with a digestion solution of 9 mL of HNO_3 and 3 mL of HF, than in the ultrasound method (US) with a digestion solution of 3 mL of *aqua regia* and 3 mL of HF. The concentration of Cr and Ni were significantly higher using the ultrasound method US (3 mL of *aqua regia* and 3 mL of HF) than in the ultrasound method US (9 mL of HNO_3 and 3 mL of HF).

The ultrasound-assisted two-step digestion (US-TSD) using the digestion solutions of 6 mL of HNO_3 (Step 1) and 3 mL of HNO_3 + 3 mL of HF (Step 2) resulted in higher or significantly higher concentrations than the other methods for all the elements investigated (Table 3). The highest accuracy was reached with US-TSD for all elements with one exception, lead, which resulted in concentrations significantly higher than the certified ones (Figure 1). The precision of analytical results produced by the US-TSD method is also highly comparable with the microwave method.

In general, the ultrasound-assisted digestion methods and microwave method (USEPA method 3052) resulted in almost equal element concentrations in SRM 1633b. The trace element concentrations determined differed by 1 - 21 % between the methods used (without Pb of method US-TSD).

The certified concentrations of Pb were reproduced in a case of SRM, but the analysis of real fly ash samples was subject to significant interference. Reason for the high concentrations of Pb by US-TSD method could not be resolved. This is probably due to a two step digestion with a digestion solution containing HF. The accurate determination of Pb can be performed with microwave and ultrasound methods without dividing it into steps.

The ultrasound-assisted digestion US with a digestion solution of HNO_3 and HF resulted in recovery rates of over 87 % for SRM 1633b, except that the recovery of Cr was about 80 %. Ultrasound-assisted digestion US with a digestion solution of *aqua regia* and HF resulted in recovery rates of over 80 % for all the elements of interest. The standard microwave digestion method USEPA 3052 with a digestion solution of HNO_3 and HF resulted in recovery rates of over 77 %. The highest accuracy was observed for US-TSD with digestion solutions of 6 mL of HNO_3 (Step 1) and 3 mL of HNO_3 + 3 mL of HF (Step 2) resulting in recoveries of 92%, 93%, 146%, 99% and 99% for Cu, Ni, Pb, V and Zn, respectively. The determination Cr was performed with the recovery rate of 85% by using the MW and US-TSD methods. It is well known that some of the chromium compounds are difficult to digest even with the use of HF under high temperatures and pressures [20] although recovery of about 91% has been reached by using the microwave digestion followed with ICP-OES [38]. The recovery rates from 91% to 107% have been observed for Cu, Ni, V and Zn using the microwave digestion method for SRM 1633b [38]. According to this, the element concentrations determined in this study are comparable with those presented in the literature [38].

The determination of element concentrations in fly ash samples from wood burning showed the same trend in precision as in the analysis of the SRM 1633b (Table 4). As can be seen, element concentrations in wood burning fly ashes are challenging to analyze because the composition of the fly ashes is unpredictable, highly variable, and heterogeneous.

4. Conclusion

The analysis of chromium, copper, nickel, lead, vanadium, and zinc concentrations in fly ash samples was successfully performed. Element concentrations in incineration fly ashes are challenging to analyze, because the composition of fly ashes is unpredictable, highly variable, and heterogeneous. It was found that certain elements of fly ashes are very difficult to digest. The effectiveness of the ultrasound-assisted digestion and ICP-OES measurement using robust plasma conditions was demonstrated. Even under robust plasma conditions, especially in axially, but also in radially viewed plasmas, considerable matrix interferences may take place.

The two-step digestion procedure US-TSD was successful in the determination of chromium, copper, nickel, vanadium and zinc concentrations by ICP-OES. The digestion of fly ash samples can be improved by the two-step digestion procedure. The analysis of SRM 1633b showed that the ultrasound-assisted digestion methods developed are comparable with the microwave digestion method (USEPA method 3052) in the determination of trace element concentrations in fly ash samples by ICP-OES. In general the ultrasound-assisted digestion methods have a higher tendency for dissolving zinc, whereas microwave is more efficient for chromium. In this work, however, higher concentrations of chromium were observed for two-step ultrasound-assisted digestion than the microwave digestion using a mixture of HNO_3 and HF as a digestion solution. The determination of Cu, Ni and Zn was significantly improved by US-TSD method when compared to earlier US methods [28]. The recovery rates of Cu, Ni and Zn has been increased from 83%, 85% and 88% to 92%, 93% and 99%, respectively. The accurate determination of lead failed using the US-TSD method but, however, could be performed with microwave and US methods.

The main advantages of the ultrasound-assisted digestion over other methods are the speed of digestion and a 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. The speed of digestion is high even if the two-step procedure is used. The two-step digestion is preferred for samples with sample matrix problems, especially samples with high EIE concentrations. The two-step digestion offers a possibility to filtrate and analyze two different digestion solutions. Ultrasound-assisted digestion can also be performed more safely than microwave digestion because pressure and temperature are substantially lower in ultrasound digestion. The digestion vessel (a centrifuge tube) offers 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.

Acknowledgements

References

[1] U-M. Mroueh, M. Wahlström, Resour. Conserv. Recycl. 35 (2002) 117-129.

[2] L. Reijnders, Resour. Conserv. Recycl. 43 (2005) 313-336.

[3] O. Hjelmar, J. Hazard. Mater. 47 (1996) 345-368.

[4] Z. Mester, M. Angelone, C. Brunori, C. Cremisini, H. Muntau, R. Morabito, Anal. Chim. Acta 395 (1999) 157-163.

[5] J. Marrero, G. Polla, R.J. Rebagliati, R. Plá, D. Gómes, P Smichowski, Spectrochim. Acta Part B 62 (2007) 101-108.

[6] 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.

[7] T. Sabbas, A.Polettini, S.R. Pomi, T. Astrup, O. Hjelmar, P. Mostbauer, G. Cappai, G. Magel, S. Salhofera, C. Speiser, S. Heuss-Assbichler, R. Klein, P. Lechner, Waste Manage. 23 (2003) 61-88.

[8] M. Paul, M. Seferinoglu, G.A. Aycik, Å Sandtröm, M.L. Smith, J. Paul, Int. J. Miner. Process. 79 (2006) 27-41.

[9] S.V. Vassilev, C.G. Vasileva, Fuel 86 (2007) 1490-1512.

[10] R. Kumar, S. Kumar, S.P. Mehrotra, Resour. Conserv. Recycl. 52 (2007) 157 - 179.

[11] N.P. Rajamane, J. A. Peter, P. S. Ambily, Cem. Concr. Compos. 29 (2007) 218-223.

[12] L. Reijnders, Build. Environ. 42 (2007) 1036-1042.

[13] S. Türkel, J. Hazard. Mater. 147 (2007) 1015-1019.

[14] M. Hoenig, Trends Anal. Chem. 17 (1998) 272-276.

[15] J. Nölte, ICP Emission Spectrometry, A Practical Guide, Wiley-VCH, Weinheim, 2003.

[16] J. Becker, Trends Anal. Chem. 24 (2005) 243-254.

[17] J-L. Todoli, J-M. Mermet, Spectrochim. Acta Part B 54 (1999) 895-929.

[18] N. Daskalova, Iv. Boevski, Spectrochim. Acta, Part B 54 (1999) 1099-1122.

[19] H. M. Kingston, L. B. Jassie, Introduction to Microwave Sample Preparation: Theory and Practice, American Chemical Society, Washington D.C., 1988.

[20] K. Lamble, S. Hill, Analyst 123 (1998) 103R-133R.

[21] A. Agazzi, C. Pirola, Microchem. J. 67 (2000) 337-341.

[22] J.A. Nóbrega, L.C. Trevizan, G.C.L. Araújo, A.R.A. Nogueira. Spectrochim. Acta Part B 57 (2002) 1855-1876.

[23] A. Iwashita, T. Nakajima, H. Takanashi, A. Ohki, Y. Fujita, T. Yamashita, Fuel 85 (2006) 257-263.

[24] T. J. Mason, Sonochemistry: The Uses of Ultrasound in Chemistry, The Royal Society of Chemistry, Cambridge, 1990.

[25] C. Brunori, I. Ipolyi, L. Macaluso, R. Morabito, Anal. Chim. Acta 516 (2004) 101-107.

[26] D. Hristozov, C.E. Domini, V. Kmetov, V. Stefanova, D. Georgieva, A. Canals, Anal. Chim. Acta 516 (2004) 187-196.

[27] A. Väisänen, A. Kiljunen, Intern. J. Environ. Anal. Chem. 85 (2005) 1037-1049.

[28] A. Ilander, A. Väisänen, Anal. Chim. Acta. 602 (2007) 195-201.

[29] A. Elik, Talanta 66 (2005) 882-888.

[30] T.G. Kazi, M.K. Jamali, A. Siddiqui, G.H. Kazi, M.B. Arain, H.I. Afridi, Chemosphere 63 (2006) 411-420.

[31] H. Matusiewicz, M. Slachcinski, Microchem. J. 86 (2007) 102-111.

[32] F. Priego-Capote, M.D. Luque de Castro, J. Biochem. Biophys. Methods 70 (2007) 299-310.

[33] A. Väisänen, R. Suontamo, J. Silvonen, J. Rintala, Anal. Bioanal. Chem. 373 (2002) 93-97.

[34] I lavilla, P. Vilas, J. Milos, C. Bendicho, Anal. Chim. Acta 577 (2006) 119-125.

[35] T.E. Gills, Certificate of Analysis, Standard Reference Material 1633b, National Institute of Standards and Technology, Gaithersburg, 1993.

[36] U.S. Environmental Protection Agency, EPA-Method 3052, Microwave assisted acid digestion of siliceous and organically based matrices. U.S. Government printing office, Washington DC, 1996.

[37] J.N. Miller, J.C. Miller, Statistics and Chemometrics for Analytical Chemistry, 4th edition, Pearson Education Limited, Dorchester, 2000.

[38] A. Iwashita, T. Nakajima, H. Takanashi, A. Ohki, Y. Fujita, T. Yamashita, Talanta 71 (2007) 251-257.

Table 1 Calibration data of the determination of samples by ICP-OES using a four-point calibration.

Element	Wavelength nm	r	LOD $(mg\ kg^{-1})^a$	LOQ $(mg\ kg^{-1})^b$	Calibration ranges $(mg\ L^{-1})$
Cr	267.716	0.9999	5.1	17.1	0.1 - 10
Cu	327.393	1.0000	4.1	13.6	0.1 - 10
Ni	231.604	0.9999	3.2	10.7	0.1 - 10
Pb	220.353	0.9999	9.5	31.8	0.1 - 10
V	290.880	1.0000	4.8	16.1	0.1 - 10
Zn	213.857	1.0000	6.5	21.6	0.2 - 20

[a] LOD = 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 $(a + 3s_a)$ into the calibration line $y = bx + a$ [37].

[b] LOQ = limit of quantification 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 $(a + 10s_a)$ into the calibration line $y = bx + a$ [37].

Table 2 Recovery rates of standard addition method (mean of four replicate samples, with the confidence limit of the mean, $P = 0.05$).

Element	Wavelength nm	Recovery Addition 50 %	Recovery Addition 200 %
Cr	267.716	92.3 ± 3.3	96.9 ± 1.9
Cu	327.393	97.8 ± 2.4	99.7 ± 1.8
Ni	231.604	95.8 ± 4.2	96.6 ± 1.8
Pb	220.353	78.4 ± 5.8	95.9 ± 6.6
V	290.880	95.5 ± 2.2	97.9 ± 2.6
Zn	213.857	91.0 ± 1.7	96.4 ± 2.4

Table 3 Element concentrations determined (mg kg^{-1}) for four different digestion procedures in SRM 1633b (mean of six replicate samples, with the confidence limit of the mean, $P = 0.05$).

Element	Microwave MW[a]	Ultrasound US[b]	Ultrasound US[c]	Ultrasound US-TSD[d]	Certified
Cr	167 ± 2	151 ± 3	160 ± 5	169 ± 1	198.2 ± 4.7
Cu	94 ± 2	99 ± 1	93 ± 2	104 ± 3	112.8 ± 2.6
Ni	110 ± 1	106 ± 2	111 ± 3	112 ± 2	120.6 ± 1.8
Pb	65 ± 2	64 ± 4	55 ± 5	100 ± 14	68.2 ± 1.1
V	286 ± 4	284 ± 2	280 ± 6	292 ± 3	295.7 ± 3.6
Zn	163 ± 2	204 ± 4	188 ± 8	207 ± 4	210*

[*] Non-certified value (SRM 1633b)

[a] Microwave, digestion solution of 9 mL HNO$_3$ and 3 mL HF, USEPA method 3052

[b] Ultrasound, digestion solution of 9 mL HNO$_3$ and 3 mL HF, 18 min (6×3 min)

[c] Ultrasound, digestion solution of 3 mL *aqua regia* and 3 mL HF, 18 min (6×3 min)

[d] 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)

Table 4 Element concentrations determined (mg kg^{-1}) for four fly ash samples (FA1 – FA4) collected from Finland (mean of six replicate samples, with the confidence limit of the mean, P = 0.05).

Element	Microwave	Ultrasound	Ultrasound	Ultrasound
	MW[a]	US[b]	US[c]	US-TSD[d]
FA1				
Cr	109 ± 3	107 ± 2	106 ± 4	122 ± 7
Cu	452 ± 6	460 ± 12	450 ± 30	483 ± 8
Ni	68 ± 1	64 ± 2	62 ± 4	72 ± 6
Pb	177 ± 4	160 ± 30	140 ± 20	372 ± 6
V	155 ± 3	160 ± 2	149 ± 5	168 ± 3
Zn	753 ± 5	794 ± 7	780 ± 60	740 ± 20
FA2				
Cr	83 ± 4	64 ± 1	73 ± 2	82 ± 3
Cu	120 ± 30	111 ± 10	120 ± 12	111 ± 5
Ni	62 ± 2	53 ± 1	57 ± 2	55 ± 2
Pb	59 ± 4	71 ± 7	40 ± 9	319 ± 9
V	100 ± 2	99 ± 2	96 ± 3	106 ± 3
Zn	690 ± 20	700 ± 30	730 ± 40	662 ± 11
FA3				
Cr	43 ± 3	92 ± 9	107 ± 8	127 ± 5
Cu	309 ± 3	297 ± 9	295 ± 9	326 ± 5
Ni	136 ± 3	121 ± 4	126 ± 3	128 ± 4
Pb	55 ± 7	104 ± 12	50 ± 20	460 ± 20
V	19 ± 1	18 ± 1	16 ± 1	28 ± 1
Zn	420 ± 50	410 ± 20	388 ± 13	421 ± 15
FA4				
Cr	< LOQ	< LOQ	< LOQ	33 ± 9
Cu	99 ± 3	104 ± 10	104 ± 5	105 ± 4
Ni	16 ± 1	17 ± 2	16 ± 4	13 ± 4
Pb	38 ± 4	74 ± 10	33 ± 9	540 ± 20
V	< LOQ	< LOQ	< LOQ	24 ± 1
Zn	722 ± 14	770 ± 40	790 ± 70	770 ± 4

LOQ = limit of quantification

[a] Microwave, digestion solution of 9 mL HNO_3 and 3 mL HF, USEPA method 3052

[b] Ultrasound, digestion solution of 9 mL HNO_3 and 3 mL HF, 18 min (6×3 min)

[c] Ultrasound, digestion solution of 3 mL *aqua regia* and 3 mL HF, 18 min (6×3 min)

[d] Ultrasound (two-step): i) digestion solution of 6 mL of HNO_3 , 9 min (3×3 min)
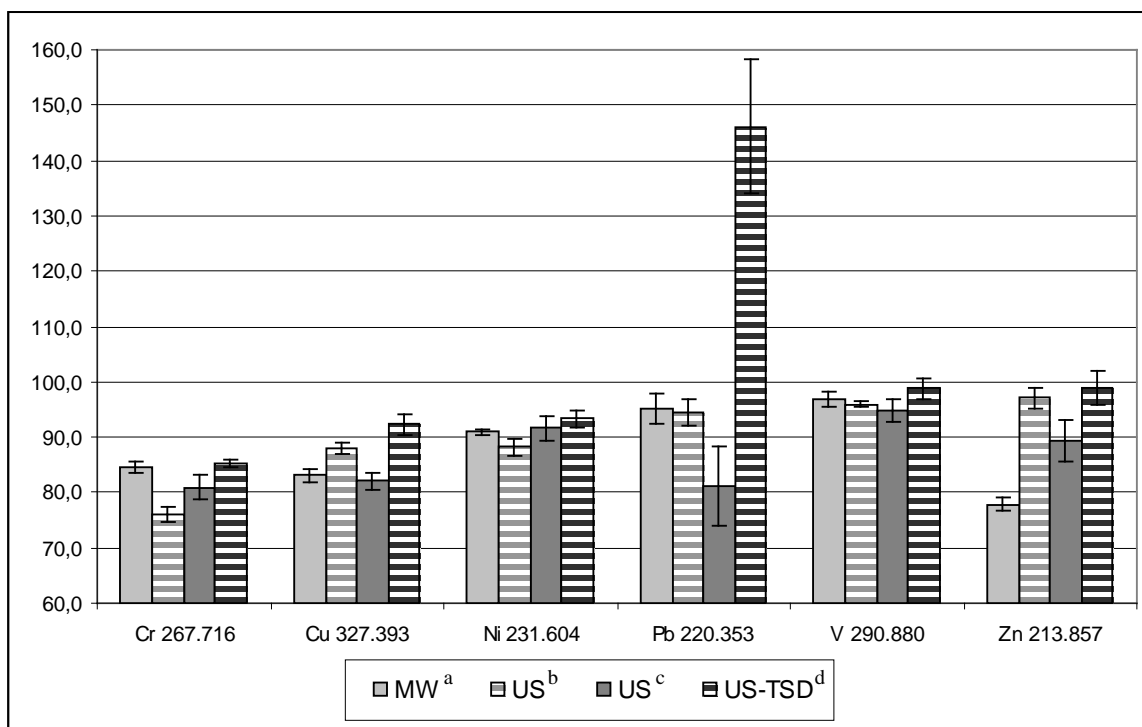ii) digestion solution of 3 mL HNO_3 and 3 mL HF, 18 min (6×3 min)

Figure 1 Determined recovery rates of four different digestion procedures in SRM 1633b (mean of six replicate samples, with the confidence limit of the mean, $P = 0.05$).

[a] Microwave, digestion solution of 9 mL HNO_3 and 3 mL HF, USEPA method 3052

[b] Ultrasound, digestion solution of 9 mL HNO_3 and 3 mL HF, 18 min (6×3 min)

[c] Ultrasound, digestion solution of 3 mL *aqua regia* and 3 mL HF, 18 min (6×3 min)

[d] 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)