

USE OF MICROWAVE-ASSISTED DIGESTION FOR
DETERMINATION OF ELEMENT CONTENTS IN ENVIRONMENTAL
MATERIALS BY ICP-AES AND FAAS

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ZASTOSOWANIE MINERALIZACJI MIKROFALOWEJ DO OKREŚLENIA
ZAWARTOŚCI ŚLADÓW W PRÓBKACH ŚRODOWISKOWYCH
METODAMI ICP-AES I FAAS

Zaproponowano metody oznaczania: Al, Fe, Ca, Mg, Ba, Cr, Mn, Ni, Cu, Zn, Pb, Cd, V i Sr w próbkach roślinnych, popiołu lotnego i gleby metodami absorpcyjnej spektrometrii atomowej w technice płomieniowej (FAAS) i atomowej spektrometrii emisyjnej ze wzbudzeniem w plazmie indukcyjnie sprzężonej (ICP-AES). Szczególną uwagę zwrócono na przygotowanie próbek, roztwarzanie, będące niezwykle ważnym i istotnym krokiem, w którym próbka narażona jest na zanieczyszczenie. Otrzymane wyniki posłużyły do przeprowadzenia dyskusji na temat roztwarzania i mineralizacji analizowanych materiałów.

Summary

The methods are described for determinations of Al, Fe, Ca, Mg, Ba, Cr, Mn, Ni, Cu, Zn, Pb, Cd, V and Sr in botanical, coal fly ash and soil samples by flame atomic absorption spectrometry (FAAS), and inductively coupled plasma atomic emission spectrometry (ICP-AES). Special attention has been paid to sample preparation, an important stage at which a sample is exposed to contaminants. Results of the analysis of all samples are discussed.

INTRODUCTION

The digestion of samples is a necessary step prior to the determination of trace and minor elements by atomic absorption spectrometry (AAS) [14]. In general, this procedure is very time-consuming and error-prone, most often at the most critical step in the analysis of the sample [6, 23]. The most frequently used methods for the analysis of botanical samples, soil, coal, products and waste forms [13, 17], X-ray absorption fine structure (XAFS) [9] and neutron activation analysis (NAA) [30] were observed. Moreover, recently plasma based instruments have been introduced with the extensive development of both inductively coupled plasma atomic emission spectrometry (ICP-AES) [18, 33] and inductively coupled plasma mass spectrometry (ICP-MS) [15]. The use of the ICP-MS usually required special

conditions for the analysis of slurries, such as the sample introduction by electrothermal vaporizer (ETV), as it was used in the determination of trace elements in coal, fly ash, botanical samples and soil [21]. Ribeiro et al. [36] proposed a method for determination of As, Sb, Hg, Sc and Sn in environmental samples and geological reference materials, such as acidified slurries, by flow injection (FI) coupled with a hydride generation system (HG) and detection by ICP-MS.

The use of the microwave oven for sample dissolution was first reported in 1975 [1]. Kinstong and Jassie [11] presented the principles concerning microwave-assisted digestion in theory and practice. In the last few years, microwave-assisted digestion has become more and more popular [40], partly due to reduction in digestion times. Bettinelli et al. [2, 3] proved that microwave dissolution is a rapid and accurate method for decomposing several types of environmental and biological matrices after microwave-assisted digestion of fly ash reference materials (NIST 1633 and 1633a) in a mixture of *aqua regia* and HF in closed vessels, followed by addition of H_3BO_3 and subsequent ICP-OES analysis. Sensitive trace analytical methods, such as (ICP-MS) [37] or (ICP-AES) [7] usually require a digestion of samples.

Procedures based on digestion by microwave heating have been reported by a number of researchers for geological [31] and biological materials [32, 34] or soils [4, 19]. In the 1980s the use of microwave-assisted digestion dramatically increased and the review by Matusiewicz and Sturgeon [22] reports a wide application of microwave-assisted digestion for the analysis of mineral, environmental and metallurgical samples. A great number of different digestion methods for the samples described above and similar types of environmental materials have been presented and discussed [16, 35, 39]. Examples of mixtures of various oxidants that allow for the effective digestion of organic matrices are $HNO_3/H_2O_2/HF$ [41], $HNO_3/HClO_4$, HNO_3/HCl [25] or $HClO_4/HF$ [27].

An important role in the quality control in environmental analysis is played by certified reference materials (CRM). The quality control procedure is based on the analysis of a CRM with use of a tested analytical method and comparison of the results obtained with the certified values.

The present study has been focused on validation of methods for the determination of the following elements: Al, Fe, Ca, Mg, Ba, Cr, Mn, Ni, Cu, Zn, Pb, Cd, V, and Sr in waste form coal treatment, soil and botanical material using certified reference materials (CRM).

MATERIALS AND METHODS

A general procedure was followed by digestion of samples using the microwave oven. Samples of ash from power plant from Upper Silesia areas were investigated. Also herb and soil samples were collected in the areas of Upper Silesia: Gliwice and Opole. In the case of herb samples they were also collected in the area of Cairns, Australia.

Coal fly ash – All samples of power ash plant from Upper Silesia district were investigated. Subsamples were homogenized using a mortar and pestle and sieved to pass a 0.2–0.1 mm mesh and air-dried for 24 h to a constant weight before analysis.

Botanical samples – All samples were separated from other plants and placed in polyethylene bags. In the laboratory the samples were washed, initially with tap water and then twice with deionized water. All the samples were dried at 90–102°C for about 6 h to a constant weight. Before mineralization, the samples were cut with polyethylene scissors

or ground to powder in an agate mortar.

Soil sampling – Soil samples were dried at $t < 90^{\circ}\text{C}$ and sieved to pass a 2 mm mesh. Subsamples were homogenized using a mortar and pestle and sieved to pass a 1.6 mm mesh and air-dried for 24 h to a constant weight before analysis.

The microwave systems used for the sample preparation were:

- (1). Milestone microwave system (MLS-1200 MEGA, Sorisole, Italy) with a Teflon vessel (MRD 1000/6/100/110), designed for pressure up to 11×10^6 Pa.
- (2). Microdigest microwave system (Model 3.6, PROLABO, France) with an open system and with 100% power at 250 W.
- (3). Plazmatronika microwave system (Model Standard BM-1S/2, Wroclaw, Poland) with a close system.

Atomic spectroscopic determinations of Cd, Pb and Cu were carried out with a UNICAM 939 SOLAR (Great Britain) spectrometer with pneumatic nebulisation and mono-element lamps with hollow cathode made by Unicam for flame atomic absorption spectrometric analysis (FAAS). Hollow cathode lamps were used throughout the study and D_2 -background correction. In the FAAS determination all elements were based in peak area. Optimum parameters like absorbance maximum and working of apparatus were established separately for each element, based on solutions of known concentration: certified reference material (CRM) and model solutions. The instrumental parameters, found for CRM are listed in Table 1. All analytes were performed also using a 3410+ARL (Applied Research Laboratories) sequential inductively coupled argon plasma atomic emission spectrometer, equipped with a computer DEC pcLPx⁺ 433 sx (Digital). The instrumental operating parameters are given in Table 2. To obtain reliable results an application of certified reference materials (CRM) and model solutions are recommended.

Table 1. Recommended conditions for the spectrometry of trace elements in the CRM using FAAS

Instrumental conditions	Pb	Cd	Cu
Wavelength [nm]	283.3	228.8	324.8
Lamp current – HCL (Hollow Cathode Lamp) [mA]	15	10	10
Slit width [nm]	0.2	0.5	0.5
Gas flow/acetylene [dm^3/min]	1.4	1.1	1.1
Type of flame	oxidizing	oxidizing	oxidizing
Height of burner [mm]	8.0	8.0	8.0

Two samples of certified reference materials were used in the present studies: CTA-FF-1, fine fly ash (certified by the Institute of Nuclear Chemistry and Technology, Warsaw, Poland) and RTH-912, soil (certified by Wageningen Agricultural University, Wageningen, the Netherlands). All were obtained from Promochem (Welwyn Garden City, UK). All materials were stored and handled according to the recommendations of the suppliers.

Table 2. Analytical conditions for ICP-AES

Instrumental parameters		
Incident plasma power	650 W	
Reflected power	< 6W	
Nebulizer pressure	42 psi	
Plasma gas flow rate	7.5 dm ³ /min	
Auxiliary gas flow rate*	0.8 dm ³ /min	
Element parameters		
Element	Wavelength (nm)	Working range (ppm)
Al	396.152	0.25–50
Fe	259.940	0.25–50
Ca	317.993	0.25–50
Mg	279.553	0.015–2.5
Ba	455.427	0.025–5.0
Cr	267.716	0.25–50
Mn	257.610	0.05–10.0
Ni	231.604	0.25–100
Cu	327.396	0.25–100
Cd	226.502	0.25–10
Zn	231.856	0.25–50
Pb	220.353	0.25–100
Co	228.616	0.25–100
Sr	407.771	0.025–5.0

* all of them are functions of plasma power and some of them were automatically controlled; argon utilized was of spectral purity (99.998%)

The consumption rate of liquid sample was about 3 cm³/min, and the observation height is adjustable; it is usually 10 mm.

Microwave oven decomposition

Method I (coal fly ash and soil)

In this method two versions are proposed depending on the microwave oven used. This methodology was validated after analyzing two certified reference materials: CTA-FF-1, fine fly ash and RTH-912, soil. A summary of the digestion procedures with appropriate sample sizes is given in Table 3.

Procedure I: nitric – perchloric – hydrochloric acids and hydrogen peroxide – open system

500 mg of samples (coal fly ash and soil), 10.0 cm³ of 68% nitric acid, 4.0 cm³ of 38% hydrochloric acid, and 6.0 cm³ of 30% hydrogen peroxide were placed in the borosilicate bottles of microwave oven. A set microwave program was run: 1 min at 80%; 8 min at 40%; 10 min at 30%; 2 min at 0% (rest), and 1 min at 65% (program 1). At the second stage, after passing the time, bottles were cooled for 1 h and next 6.0 cm³ of 68% nitric acid was added and digestion continued under new parameters: 50% and 20 min. The samples with residues

Table 3. Operating conditions for microwave oven dissolution

Sample	Weight [mg]	Acid [cm ³]			Steps in program Time [min] Power [W]
		HNO ₃	H ₂ O ₂	HCl	
Fly ash, soil	500	10.0 6.0	6.0	4.0	Program I – stage 1 1 min, 80 W; 8 min, 40 W; 10 min, 30 W; 2 min, 0 W; 1 min, 65 W Program I – stage 2 20 min, 50 W
Fly ash	100	3.0 10.0	– 6.0	9.0 4.0	Program II 1 min, 65 W; 7 min, 40 W; 10 min, 35 W, 30 s, 70 W; 5 min, 40 W; 5 min, 30 W, 2 min, 0 W, 1 min, 20 W
Fly ash	500	I:20.0 II: 5.0 I: 10.0 II: 6.0 3.0	– – 6.0 – –	– – 4.0 – 9.0	Program III* 2 min, 70 W; 1 min, 0 W; 15 min, 50 W; 20 min, 30 W; 2 min, 60 W; 50 s, 0 W; 5 min, 60 W
Soil	100	1.0	–	3.0	Program IV – stage 1 ^b 3:20 min, 250 W; 3:20, 400 W; 3:20 min, 650 W; 3:20 min, 250 W Program IV – stage 2 30 s, 250 W, 30 s, 0 W, 3 min, 250 W; 3 min, 400 W; 3 min, 600 W, 20 min, 0 W
Coal fly ash	100	10			Program V 20 min, 150 W
Botanical materials	300	24.0 5.0 + 5.0 5.0	4.0 5.0 ^c –	– – ^d – ^e	Program IA 1 min, 70%; 2 min, 0 %, 4 min, 50%; 1 min, 0%; 8 min, 30%; 1 min, 0%; 2 min, 60% Program IIA 5 min, 50%; 2 min, 0%; 10 min, 30%; 10 min, 40%; 5 min, 30%; 5 min, 25%; 1 min, 80%; 10 min, 0%

* + 15 cm³ of H₂SO₄, ^b + 2.0 cm³ of HF, ^c H₂O_{dem}, ^d + 5.0 cm³ of H₂SO₄, ^e + 1.0 cm³ of HClO₄

were filtrated; the residues washed with water and the filtrates diluted to volume 100 cm³ with deionized water. In addition, 100 mg of samples (coal fly ash), 3.0 cm³ of 68% nitric acid, and 9.0 cm³ of 38% hydrochloric acid were placed in the borosilicate bottles of microwave oven. The heating program consisted of eight-stage power and time setting: 65%, 1 min; 40%, 7 min; 35%, 10 min; 70%, 30 s; 40%, 5 min; 30%, 5 min; 0%, 2 min, and 20%, 1 min (program II). The samples with residues were filtrated; the residues washed with water and the filtrates diluted to volume 100 cm³ with deionized water. At a second series of experiments, samples were digested with 10.0 cm³ of 68% nitric acid, 6.0 cm³ of 30% hydrogen peroxide and 4.0 cm³ of 38% hydrochloric acid in the Microdigest microwave oven according to the same parameters described above.

500 mg of samples (coal fly ash) were digested with 20.0 cm³ of 68% nitric acid in the Microdigest microwave oven with the following program: 70%, 2 min; 0%, 1 min; 50%, 15 min; 30%, 20 min; 60%, 2 min; 0%, 50 s; and 60%, 5 min (program III). At the second stage, after passing the time, bottles were cooled for 1 h and next, 5.0 cm³ of 68% nitric acid and 15.0 cm³ of 98% sulfuric acid were added and digestion continued under the same parameters. After completion of the heating cycle, the rack was removed from the oven and the bottles were cooled in a water-bath for about 40 min. The samples with residues were filtrated; the residues washed with water and the filtrates diluted to volume 100 cm³ with deionized water. The digestion of coal fly ash samples was performed with 10.0 cm³ of 68% nitric acid, and 4.0 cm³ of 38% hydrochloric acid, and 6.0 cm³ of 30% hydrogen peroxide under the same parameters (program III – stage 1). At the second stage, after passing the time, bottles were cooled for 1 h and next, 6.0 cm³ of 68% nitric acid was added and digestion continued under the same parameters (program III – stage 2). After digestion, the solutions were transferred quantitatively to the 100 cm³ measuring flask, filtrated and filled with distilled water to the mark.

The parallel samples were digested also with 3.0 cm³ of 68 % nitric acid and 9.0 cm³ of 38% hydrochloric acid with the same parameters (program III) and the procedure described above.

Procedure II: nitric – hydrochloric – hydrofluoric – boric acids – close system

100 mg of samples (soil), 1.0 cm³ of 68% nitric acid, and 3.0 cm³ of 38% hydrochloric acid, and 2.0 cm³ of 40% hydrofluoric acid were placed in the polytetrafluoroethylene (PTFE) vessel microwave oven (SiF₄ removal). The heating program, consisted of five-stage power and time setting: 250 W, 3 min, 20 s; 400 W, 3 min, 20 s; 650 W, 3 min, 20 s; 250 W, 3 min; and 0 W, 20 min (1 stage of the program IV). After completion of the heating cycle, the rack was removed from the oven and the vessels were cooled in a water-bath for about 60 min. Next, all samples evaporated with 10.0 cm H₃BO₃ (BF₃ removal) were digested according to the following program: 250 W, 30 s; 0 W, 30 s; 250 W, 3 min; 400 W, 3 min; 600 W, 3 min; and 0 W, 20 min (2 stage of the program IV). After completion of the heating cycle, the rack was removed from the oven and the vessels were cooled in a water-bath for about 40 min. Next, all samples were diluted to volume 50 cm³ with deionized water.

Samples of coal fly ash (500 mg) were digested with 10.0 cm³ of 68% nitric acid in the Plazmatronika microwave system, with the following program: 150 W, 20 min (program V) [28].

Procedure III: nitric – hydrochloric – hydrofluoric – sulfuric acids and hydrogen peroxide – conventional digestion method

500 mg of samples (soil) were heated in a platinum crucible on a hot plate at 200°C for 30 min, in the presence of 5.0 cm³ deionized water, 3.0 cm³ of 68% nitric acid, and 9.0 cm³ of 38% hydrochloric acid, and evaporated on the heating plate almost to dryness. When cool, 5.0 cm³ H₂O₂ (30%) was added and they were digested on the heating plate almost to dryness (15 min). After cooling, 2.0 cm³ H₂O₂ was added to expel nitrogen oxides. The solutions with residue were filtered through soft paper (N 388 Φ). Next, the deposits were washed and dried in the quartz furnace. They were then heated to a controlled temperature of 400°C for 1 h. Next, H₂SO₄ (1:1 v/v) was added to HF (0.3:2 v/v) and digested on the heating plate, 2.0 cm³ HNO₃ was added and heated to expel SO₃. Then, 20.0 cm³ HCl (1:1 v/v) was added and digested on the heating plate for 30 min. After digestion, solutions were transferred quantitatively to the 100 cm³ polyethylene measuring flask and filled with distilled water to the mark.

For other samples of such coal fly ash, digestion was carried out in a platinum crucible on a hot plate at 200°C for 30 min, in the presence of 0.6 cm³ sulfuric acid and 2.0 cm³ of 40% hydrofluoric acid, and evaporated on the heating plate almost to dryness. After cooling, 10.0 cm³ of 68% nitric acid was added and digested on the heating plate almost to dryness (to remove SO₃). Next, all solutions were transferred quantitatively to the 100 cm³ polyethylene measuring flask and filled with distilled water to the mark.

Method II (botanical samples)

Procedure I: nitric acid – hydrogen peroxide – open system

300 mg of samples (medicinal herbs), 5.0 cm³ of 68% nitric acid, and 1.0 cm³ of 30% hydrogen peroxide were placed in the borosilicate bottles of microwave oven. A set microwave program was run: 1 min at 70%; 2 min at 0%; 4 min at 50%; 1 min 0%; 8 min 30%; 1 min 0% and 2 min 60% (I stage of the program IA) [43]. At the second stage, after passing the time, bottles were cooled for 40 min and next 8.0 cm³ of 30% hydrogen peroxide was added and mineralization continued with the same parameters. To compare the microwave dissolution method HNO₃ was tested (program IA).

All samples (300 mg) were mineralized with 24.0 cm³ of 68% nitric acid, and 4.0 cm³ of 30% hydrogen peroxide in the Plazmotronika microwave oven with the following program: 50%, 5 min; 0%, 2 min; 30%, 10 min; 40%, 10 min; 30%, 5 min; 25%, 5 min; 80%, 1 min, and 0%, 10 min (program IIA).

Procedure II: nitric acid – sulfuric acid – deionized water – open system

300 mg of samples were mineralized with HNO₃ – H₂SO₄ – H₂O_{dei} (1 + 1 + 1 v/v) mixture – stage I (program IIA). Next, 5.0 cm³ of 68% HNO₃ was added (stage 2) and samples were mineralized in the Plazmatronika microwave system under the same parameter program IIA described above. To compare the microwave dissolution method HNO₃ – HClO₄ (5 + 1) mixture was tested (program IIA).

Blanks were always run in the same way. A total of two samples (CRM) were spaced on the microwave oven carousel and the digestion program was set as reported in Table 3. In the present work, for direct analysis of ions by FAAS the peak area method for the measurement of signals was used, as recommended [5, 26], to obtain the best precision.

RESULTS AND DISCUSSION

Optimum parameters for digestion and mineralization (acid volumes and their ratio) should be matched to the individual organic and inorganic material analyzed. On the other hand, time and power of microwave energy applied and the number of heating periods depend on the number of samples placed in the oven and should be established experimentally. Two samples of certified reference materials were used in the present studies.

Analytical results for botanical samples

The slight acid matrixes in liquid solution after dissolution guarantee to avoid problems during an analysis of the samples by FAAS or ICP-AES. For mineralization of plant samples, mixtures of the following reagents were used: HCl, HNO₃, HClO₄, H₂SO₄ and H₂O₂. However, despite such a wide spectrum of oxidizing agents, the choice of a relatively universal oxidant was quite difficult. In view of Pb trace determination, the application of sulfuric acid would be undesirable (co-precipitation of Pb with CaSO₄). Samples digestion for the determination of lead was carried out using nitric acid, instead of H₂SO₄. This acid was used for lead because of the reported interference of sulfate on the atomic absorption signal of lead [8]. In the case of samples digestion only with HNO₃, visual observation of the colored solutions showed that the dissolution was not complete and significantly higher for Cr, Mn, Fe and Ba. This method does not ensure a quantitative dissolution process for the analytes level. Previous investigations showed a high effectiveness of mosses and herbs mineralization in the open systems using HNO₃ + H₂O₂ [26]. In the present work this mixture was tested in mineralization carried out in low-pressure vessels and prolonging the microwave dissolution time. All the samples of medicinal herbs were digested (HNO₃ + H₂O₂) to clear solutions. However, for samples containing large amount of silicate, the slight white precipitate was allowed to settle before the analysis. In another experiment HNO₃ + HClO₄ (program IIA) mixture was tested. A mixture described above was used instead of hydrogen peroxide. However, the results of the analysis of herbs done according to the conditions (mixture) recommended by Karadjova et al. [12] were satisfactory (Table 4); a significant improvement of precision and repeatability were achieved. A visual observation of digestion showed that those oxidant mixtures containing H₂O₂ or HClO₄ produced colorless solutions without any organic solid residues.

Therefore, the microwave dissolution programmers: program IA and program IIA (HNO₃ + H₂O₂), were tested (Table 4). The relative standard deviation (RSD) for the elements determined by ICP-AES was generally much lower than 5%, except for Cr. This assured the homogeneity of the samples after digestion. As can be seen (Table 4), the results for Cu, Cd and Pb using program IIA determined by FAAS and ICP-AES are in agreement with data [29]. It should be emphasized that both series of results (FAAS and ICP-AES) are in agreement ($r = 0.99698$). This shows that matrix does not influence the analyte determinations and therefore the calibration graph method may be used in this case. Based on the experiments the optimum conditions for the determination of investigated ions in the analyzed samples were established. The contents of particular ions in examined samples are collected in Tables 4 and 5. Investigations carried out in the area of Gliwice, Opole, and Cairns (Australia) revealed that medicinal herbs are useful as good bioindicators for environmental pollution by heavy metals. These samples were chosen because of their abundance on the examined area in the industrial zone as well as in the clean, unpolluted area, which enabled comparison of metal contents in these regions.

Table 4. The results of analysis of *Urticae folium* FP V by microwave mineralization – ICP-AES (ppm), n = 6

Element	Found *	Found**	F***	F _{0.05}	t _{exp.}	t _{0.05}
Cu [%]	3.80 ± 0.12	3.63 ± 0.09	1.78	9.01	0.017	3.18
Mg [%]	0.49 ± 0.02	0.47 ± 0.02	1.00	9.01	0.08	3.18
Fe [%]	0.02 ± 2.22	0.02 ± 3.42	2.58	9.01	0.20	3.18
Sr	119 ± 4.56	109 ± 4.11	1.22	9.01	0.02	3.18
Mn	84.2 ± 1.43	80.0 ± 1.12	1.63	9.01	0.26	3.18
Ba	28.5 ± 0.47	29.7 ± 0.31	2.44	9.01	0.15	3.18
Cu	2.49 ± 0.98	2.54 ± 0.72	1.08	9.01	0.03	3.18
Pb	0.98 ± 0.05	0.88 ± 0.09	3.24	9.01	0.19	3.18
Cd	0.09 ± 0.01	0.08 ± 0.02	2.04	9.01	0.17	3.18

* Mean ± s.d. (standard deviation): HNO₃ + H₂O₂ program IA,

** Mean ± s.d.: HNO₃ + H₂O₂ program IIA,

F*** – experimental value of the Fisher's test at significance level 0.05,

F_{0.05} – critical value of the Fisher's test at significance level 0.05,

t_{0.05} – critical value of the Student's test at significance level 0.05

Table 5. Average concentration of Pb Cd and Cu in samples of medicinal herbs by FAAS (n = 6); all concentrations given in ppm

Sample/location	Pb	Cd	Cu
Folium <i>Urticae dioica</i> – express way	11.1	0.58	30.6
Folium <i>Urticae dioica</i> – clean area	3.68	1.61	9.87
Folium <i>Urticae dioica</i> – allotment	3.72	1.48	15.3
Folium <i>Urticae dioica</i> – urban way	17.3	2.01	32.7
Folium <i>Menthae piperitae</i> – clean area (Australia)	0.08	0.78	11.7
Folium <i>Menthae piperitae</i> – urban road (Australia)	2.81	1.04	6.82
Folium <i>Menthae piperitae</i> – clean area (Australia)	1.13	0.14	4.89
Folium <i>Ocimum basilicum</i> – urban road (Australia)	1.28	1.70	15.1
Folium <i>Ocimum basilicum</i> – clean area (Australia)	0.73	0.09	8.09

Analytical results for coal fly ash samples

To find the optimal conditions for the microwave digestion procedure of environmental samples fine fly ash (CTA-FF-1) was used. Three different microwave digestions were tested (program I, II and III) as certified reference material. The program I using HNO₃ + HCl + H₂O₂ (10 + 4 + 6) mixture – stage 1; HNO₃ – stage 2 [41] and HCl + HNO₃ (9 + 3) mixture [24] gave low results for Al, Fe, Mg, Mn, Sr, Cr, Co, Ni and Cu (program I). However, poor accuracy of the results for the elements in the sample suggests that the procedure presented above is not acceptable. The reason for the poor recovery of trace

elements in fly ash might be the fact that the digestion was not complete when this method was used. Next, the tested effects of prolonging the microwave digestion time and effects of microwave power were increased (program II). However, the results of the analysis of CRM fly ash, performed according to conditions in program II were satisfactory only for Fe and Mn a significant reduction of precision and repeatability was achieved using proposed new parameters – program III – more power and longer time digestion. Good agreement of results with the certified reference materials was obtained using microwave digestion with acid mixture: $\text{HNO}_3 + \text{HCl}$ (3 + 9). It should be emphasized that the analysis of fly ash certified material (CTA-FFA-1) was successful; the element recoveries were highly satisfactory (Table 6).

For the comparison purposes these materials were digested using a mixture of $\text{HNO}_3 + \text{H}_2\text{SO}_4$ (2 + 10) in stage 1 and $\text{H}_2\text{O}_{\text{dem}}$ in stage 2 using the Microdigest microwave open systems with the operation conditions as in program III. The digestion was incomplete.

Table 6. The results of analysis of CTA-FFA-1 Fine Fly Ash by ICP–AES (ppm), $n = 6$

Element	Found*	Certified	Recovery (%)
Al [%]	14.1 ± 0.22	14.87 ± 0.39	94.8
Fe [%]	5.01 ± 0.46	4.89 ± 0.14	102
Mg [%]	1.58 ± 0.30	n.a.	–
Mn	1099 ± 78.5	1066 ± 41	103
Sr	252 ± 18.1	250 ± 13	100
Cr	156.0 ± 2.41	156 ± 8	100
Co	38.1 ± 6.11	39.8 ± 1.7	95.8
Ni	102 ± 6.71	99.0 ± 5.8	103
Cu	157 ± 12.6	158 ± 9	99.4

* mean ± s.d. ($n = 6$); $\alpha = 0.05$, n.a. – not available, not certified value

From the results obtained for certified reference materials sample it can be concluded that:

- The use of HNO_3 and HCl mixture generally gave better recoveries according to conditions of program III than those of program I or II in the microwave digestion. In the case of using another medium, the results obtained for Al, Fe, Mg, Mn, Sr, Cr, Co, Ni, V and Cu were observed to be too low. The most probable source of error is the loss of elements in a form of adsorbing or volatile compounds.
- Precision of the results after microwave digestion ($\text{HNO}_3 + \text{HCl}$) was at the level of a few percent (usually < 5.5%).

In contrast to the previously considered digestion methods using open system, at the heating cycle, fly ash certified samples according to the parameters recommended by Plazmatronika [28] were not in agreement with certified values. The results of digestion – according to program III can be recommended as a suitable procedure to digest coal fly ash for successful determination of major and trace elements. In conclusion, $\text{HNO}_3 + \text{HCl}$ mixture can be considered as a uniform digestion medium for environmental materials under the digestion conditions reported (open system).

Summing up, calibrations of the apparatus and selection of measurement conditions were done on the basis of certified reference materials (CRM) i.e. fine fly ash. The results summarized in Table 6 show that digestion of fly ash certified materials was successful and recovery of ions from material was quantitative. Based on the experiments, the optimum conditions for the determinations of CRM CTA-FF-1 in the analyzed samples were established. The results of analyzed ions in examined sample are gathered in Table 7.

Analytical results for soil samples

To find the optimal conditions for the microwave digestion procedure of soil samples, reference material – Soil (RTH-912), which was digested using two parallel mineralizations, was used.

Table 7. The results of analysis of coal fly ash by microwave oven dissolution – ICP-AES (ppm),
n = 6

Element	Mean \pm s.d.	RSD
Al [%]	13.3 \pm 2.26	4.72
Ca [%]	5.27 \pm 0.50	2.48
Fe [%]	6.16 \pm 0.59	2.66
Mg [%]	1.02 \pm 0.18	5.03
Zn	1820 \pm 110	1.70
Sr	2030 \pm 559	7.69
Mn	760 \pm 56.7	2.08
V	491 \pm 64.9	3.70
Cu	379 \pm 16.5	1.17
Ni	340 \pm 25.1	2.06
Cr	186 \pm 21.0	3.22
Co	77.1 \pm 15.2	5.60
Cd	17.1 \pm 2.01	4.58

RSD – relative standard deviation, s.d. – standard deviation

1. Microwave oven:

- (i) *open system* – various acid mixtures ($\text{HNO}_3 + \text{HCl} + \text{H}_2\text{O}_2$ – stage 1 in program I and HNO_3 – stage 2 in program I; $\text{HNO}_3 + \text{HCl}$; $\text{HNO}_3 + \text{H}_2\text{SO}_4$) were tested to determine the best dissolution procedure, a mixture of $\text{HNO}_3 + \text{HCl} + \text{H}_2\text{O}_2 / \text{HNO}_3$ proved to be the most satisfactory. With this mixture different heating programs to verify the difference in the recoveries were tested for all materials analyzed. Only conditions in program I (conditions described in the experimental part of this work) gave the best results (Table 8). The element recoveries were highly satisfactory, except for Fe and Al. Maximum power of 215% ensures a quantitative mineralization of ions using the mixture described above. Good accordance of the results proves that the worked out procedure was sufficient for this purpose.

- (ii) *close system* – digestion with $\text{HNO}_3 + \text{HCl} + \text{HF}$ (SiF_4 removal) – program IV – stage 1. Next, samples were treated with 10.0 cm^3 of 99% boric acid and samples were digested according to conditions program IV (stage 2). Using 2.0 cm^3 HF and 2.0 cm^3 HCl and 1.0 cm^3 HNO_3 , as suggested in Milestone application notes [20], resulted in somewhat higher values for all elements (Table 8). These results show that the present digestion procedure – microwave digestion using a mixture of HCl and HF and HNO_3 – is suitable for digestion of soil for successful determination of all elements – visually observed – complete dissolution. Boric acid solution was added after dissolution to neutralize free HF in the solution by formic tetrafluoroboric acid. Without this step FAAS and ICP-AES can not be used to analyze the solution since it will attack the quartz torch of the instrument. Obviously, comparison with a summary of the comparison data showed that the mean concentration of each element studied was within the 95% confidence interval (Table 8), except for Fe and Al.
2. *Wet digestion* on the hot plate in the platinum vessels (conventional digestion method). Digestion with $\text{HNO}_3 + \text{HCl} + \text{H}_2\text{O}_{\text{aq}}, \text{H}_2\text{O}_2, \text{H}_2\text{SO}_4, \text{HF}$. RM was used for control of accuracy, and dissolution was complete. The values for RTH-912 are shown in Table 9. The mean heavy metal concentrations found for the reference materials were the same as the certified values.

Finally, it is suggested that the microwave oven (open and close) system is a good alternative to the conventional wet digestion method (no loss of metals during the digestion

Table 8. The results of analysis of RTH-912 Soil by microwave oven dissolution – ICP-AES (ppm), $n = 6$

Element	Found	Certified	Recovery [%]
Fe [%]	2.80 ± 0.34 (3.40)	3.66 ± 0.20	76.2
Ca [%]	6.90 ± 0.28 (2.89)	6.92 ± 0.29	99.1
Al [%]	0.41 ± 0.08 (1.23)	0.57 ± 0.035	71.9
Mg	5711 ± 8.02 (3.51)	5701 ± 15.12	100.1
Mn	722 ± 0.30 (1.15)	792 ± 29.20	91.2
Zn	338 ± 59.44 (4.28)	410 ± 16.70	82.4
Cu	119 ± 19.40 (4.56)	127 ± 3.99	93.6
Pb	77.0 ± 9.26 (3.56)	73.4 ± 6.86	104.8
Ni	49.5 ± 5.12 (2.89)	55.9 ± 3.90	88.4
Ba	293 ± 11.15 (1.78)	293 ± 11.15	100
Cr	110 ± 3.11 (2.16)	112 ± 7.10	98.2
Sr	73.0 ± 1.02 (2.01)	74.0 ± 2.22	98.6
Co	13.6 ± 1.70 (3.46)	13.7 ± 0.75	99.3
Cd**	1.25 ± 0.11 (0.09)	1.26 ± 0.20	99.2

* mean \pm s.d. (RSD), $n = 6$, $\alpha = 0.05$, ** determined by FAAS

process). The results are collected in Table 9. The values of results (Table 9) for particular elements were compared by test F and the means of t -test [10] for 95% confidence level ($n = 6$), showing for each element that the use of microwave digestion and conventional digestion procedure are reliable and the results of the analysis of soils were satisfactory ($F < F_{0.05}$). Furthermore, no matrix interferences occurred during the atomization step. The obtained result analyses of soils are presented in Table 10. These results are in good accordance with those published [38]. Thus, for determining analytes by FAAS and ICP-AES, microwave digestion seems to be an efficient method to destroy organic matter.

Table 9. Comparison of results for differential digestion methods (soil): mixture A ($\text{HNO}_3 + \text{HCl} + \text{H}_2\text{O}_2/\text{HNO}_3$)

Element	Comparison of methods					
	Method I (conventional digestion) and Method II (Milestone)		Method I (conventional digestion) and Method III (mixture A)		Method II (Milestone) and Method III (mixture A)	
	F	t	F	t	F	t
Al	2.36 < 9.01	0.11 < 4.30	5.65 < 9.01	1.07 < 4.30	1.08 < 9.01	0.15 < 4.30
Fe	1.04 < 9.01	0.31 < 4.30	1.41 < 9.01	0.47 < 4.30	0.83 < 9.01	0.49 < 4.30
Mg	–	–	3.84 < 9.01	0.49 < 4.30	–	–
Ca	1.68 < 9.01	0.10 < 4.30	–	–	–	–
Mn	1.12 < 9.01	0.07 < 4.30	4.66 < 9.01	2.03 < 4.30	4.14 < 9.01	2.01 < 4.30
Ba	1.50 < 9.01	0.04 < 4.30	–	–	–	–
Zn	1.31 < 9.01	0.36 < 4.30	1.28 < 9.01	0.37 < 4.30	1.68 < 9.01	0.36 < 4.30
Cu	2.01 < 9.01	0.04 < 4.30	2.01 < 9.01	0.05 < 4.30	2.04 < 9.01	0.04 < 4.30
Cr	1.81 < 9.01	0.13 < 4.30	1.81 < 9.01	1.22 < 4.30	1.90 < 9.01	0.40 < 4.30
Sr	1.12 < 9.01	0.11 < 4.30	–	–	–	–
Pb	1.12 < 9.01	0.64 < 4.30	1.40 < 9.01	0.58 < 4.30	1.57 < 9.01	0.08 < 4.30
Ni	2.39 < 9.01	2.32 < 4.30	1.90 < 9.01	0.83 < 4.30	1.32 < 9.01	0.21 < 4.30
Co	8.92 < 9.01	0.86 < 4.30	1.90 < 9.01	0.20 < 4.30	6.06 < 9.01	0.36 < 4.30

F – experimental value of the Fisher's test at significance level 0.05; t – experimental value of the Student's test at significance level 0.05

CONCLUSION

In conclusion, the role of CRM in trace element analysis is crucial, providing the means to establish calibration accuracy, as well as verifying correct operation of the complete analytical system, for the specific CRM matrix. For a technique such as FAAS, the knowledge and capability of the analyte in the selection of appropriate CRM is important as well. There is no other way to provide such verification.

The microwave oven digestion method using mixed acids proved to be a reliable and rapid method for decomposing several types of botanical and environmental matrices prior

Table 10. Average concentration of analyte in samples of soil determined with application of RM by ICP-AES and FAAS (n = 6); all concentrations given in ppm

Soil/locations	Pb*	Cd*	Cu*	Sr	Mn	Ba	Cr	Ni	Co	Zn
Allotment	51.9	1.37	23.5	39.1	108	52.9	32.5	12.5	3.35	191
Urban road	64.1	1.11	30.7	-	-	-	-	-	-	-
Clean area	4.11	0.97	9.21	-	-	-	-	-	-	-

* determined by FAAS

to elemental analysis with atomic FAAS and ICP-AES methods. These methods applying the open vessel are particularly useful for botanical materials whose mineralization was completed. Obviously the procedures evaluated in this work are suitable dissolution techniques for coal fly ash and soil. The data of this study make it possible to conclude that microwave mineralization with close system and open system can be recommended for the spectrometry methods of a wide range of medico-biological and environmental objects.

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