===== **ARTICLES** =====

Simultaneous Determination of 11 Elements in Fly Ash by Inductively Coupled Plasma Orthogonal Acceleration Time-of-Flight Mass Spectrometry After Closed-Vessel Microwave-Assisted Extraction with Ammonium Fluoride[1]

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Abstract—A method for simultaneous multi-element analysis of fly ash samples by inductively coupled plasma orthogonal acceleration time-of-flight mass spectrometry (oaTOF-ICP-MS) after closed-vessel microwave extraction with ammonium fluoride was introduced here. Corrosive and/or toxic acids like HF, HCl or $HClO_4$, as well as HNO_3, which are commonly used during sample preparation of the fly ash samples, are avoided in this method. The spectral effects due to the formation of different Cl, Na, K, Ca, Mg-containing polyatomic species interfering with the determination of a number of elements like As, Se or Ni during the oaTOF-ICP-MS analysis are negligible. Under the optimum experimental extraction conditions evaluated using a fractional factorial design (10 mg of the sample extracted with 5 mL of 140 g/L NH_4F for 10 min at 200°C), analysis of the resulting supernatant with Rh as an internal standard enabled precise and accurate simultaneous determination of 11 elements (Li, Be, Ni, As, Se, Rb, Sb, Cs, W, Tl and U) at trace and ultra-trace levels. The accuracy was assessed by analysing two certified reference materials, namely Fine Fly Ash CTA-FFA-1 and Constituent Elements in Coal Fly Ash Standard Reference Material® 1633b. The precision of the reported method was better than 10%.

Keywords: oaTOF-ICP-MS, trace elements, fly ash, microwave-assisted extraction, fractional factorial design, ammonium fluoride

DOI: 10.1134/S1061934818070092

Fly ash as a by-product of coal combustion is a significant source of potential toxic elements, and its analysis is important for evaluation of the associated and environmental risk as well as for its further use in the industry [1, 2]. From an environmental perspective, trace elements have attracted more attention than the major and minor constituents [3], and many analytical methods like inductively coupled plasma optical emission spectrometry (ICP-OES) [4–17], graphite furnace atomic absorption spectroscopy (GFAAS) [14, 18, 19], hydride generation atomic absorption spectrometry (HGAAS) [14, 19], atomic fluorescence spectrometry (AFS) [20], inductively coupled plasma mass spectrometry (ICP-MS) [3–5, 7, 8, 12, 15, 16, 19, 21–28], instrumental neutron activation analysis (INAA) [6, 19], etc. aim at measuring the elements associated with coal and coal by-products at concentrations down to the trace level.

Inductively coupled plasma mass spectrometry has arisen as one of the preferred methods due to its unique combination of low detection limits, capabilities for rapid multi-element and isotopic determination and wide dynamic range [23]. Despite the significant improvements on solid sample introduction techniques such as laser ablation sampling [29] or slurry sampling electrothermal vaporization [30–34], solution nebulization is still the most preferred method for many ICP-MS applications [35].

Coal fly ash, however, represents a complex and resistant material mainly composed of oxidized compounds of Si, Al, Fe and Ca [36]. Due to this fact, the quantitative liberation of toxicologically important elements is quite difficult and has been for many researchers an analytical challenge for a long time. The methods involved in sample preparation of fly ash samples employed conventional alkali fusion, wet digestion, sequential extraction [7, 8, 12], ultrasound assisted digestion or extraction [10] and microwave digestion and extraction [20, 37]. Employment of the

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alkali fusion which is traditionally used for preparation of coal and coal ash samples [38, 39] results however in a high solid environment of the fused materials. The necessity of vast amounts of concentrated reagents then represents a risk of contamination and may be responsible for matrix interferences [39, 40]. Conventional wet digestion methods are time consuming, susceptible to loss of volatile analytes and contamination, requiring large amount of reagents [36]. Chemical sequential extraction for element fractionation in coal fly ashes [7, 8, 12] has been proved an effective tool to investigate various binding forms of different elements. These methods are however relatively complicated, time-consuming and expensive and so should be only used when appropriate [41]. Ultrasound and microwave-assisted extraction were investigated in an attempt to improve the yield of the extracted metal and reduce the process time, especially with the increasing demand for more environmentally friendly processes [20, 41−43]. Both methods are increasingly finding applications in analytical chemistry and are useful for fast screening of elements in the environment [41]. They cannot however ensure a quantitative extraction of wide range of analytes compare to closed vessel microwave-assisted digestion, being currently the most widely used preparation technique of coal and coal fly ash samples to overcome the main drawbacks of the conventional digestion methods [36]. In contrast to this fact, ultrasound and microwave-assisted extraction (MAE) are among the best green technologies with advantages such as high extraction efficiency and sample throughput, good reproducibility, low consumption of solvents and time, and low carbon dioxide output [44].

In recent years, both the digestion and extraction steps have been carried out using very strong acidic and oxidizing reagents like HNO_3, HCl, H_2O_2 and their mixtures as the best way to achieve satisfactory results [20]; highly toxic HF and explosive $HClO_4$ are usually employed to quantitatively determine trace elements in coal fly ash and coal [36]. The employment of HF may however result in a damage of glass components of the instruments and lead to formation of several volatile fluorides (many analytes such as As, B, Se, Sb, Hg and Cr may volatilize) [24]. The formation of such volatile compounds presents a serious risk of analyte loss after opening the vessel, even if the decomposition of the sample has taken place in a closed system [45, 46]. However, this problematics is much more complex and the final reaction products to be created are strongly dependent on the conditions of the experiment [47, 48]. The addition of H_3BO_3 [24, 36] may solve some drawbacks attributed to the use of HF but increases the salinity of the sample, the cost of analysis and disables the determination of boron in the sample [49].

In the ICP-MS analysis of coal and coal ashes, several elements like Si, P, S, K, Ca, Fe and Cl originating from the sample matrix or acids used in sample dissolution are problematic as they serve as precursors for the formation of polyatomic ions [15, 16, 24, 26, 36, 50] whose determination is challenging, especially with commonly used low-resolution quadrupole mass spectrometers [7, 21, 26, 27, 37]. The collision/reaction cell ICP-MS is an effective correction technique to minimize the interferences on the analyte of interest for conventional quadrupole ICP-MS [7, 21, 26, 27]. While a decrease of the multi-element capabilities could be observed for older quadrupole ICP-MS systems, this problem has been dealt with in modern quadrupole ICP-MS instruments. Samples with a complex matrix can be dealt with a sector-field ICP-MS which can handle polyatomic interferences originating from major elements thanks to the high mass resolution of the spectrometer. The price for the higher resolution is however the loss of sensitivity. On the other hand, the multi-element capability is kept. Nevertheless, the high cost of the instrumentation may make these methods less accessible to routine laboratories.

Inductively coupled plasma time-of-flight mass spectrometers are more reachable for routine analytical practice when compared with the high resolution ICP-MS instrumentation. These instruments' advantage is the simultaneous mass determination and high speed without any compromise in mass range, sensitivity or precision [51]. The higher resolution of the oaTOF mass analyzer compare to quadrupole ICP-MS could be an advantage while determining several analytes such as Sc in the presence of large quantities of Si [52]. However, it is not adequate to completely deal with the interference signals caused by polyatomic species observed during the analysis of samples with a complex matrix [53−55]. Several approaches such as the mathematical correction equations [53, 55] without [53] or with the use of microwave digestion [55] or methods employing matrix modification [54, 56] were successfully used during the analysis of different sample matrices in order to manage the spectral effects during the TOF-ICP-MS analysis.

Several works can be found describing the analysis of fly ash using quadrupole ICP-MS [7, 21, 26, 27, 37] which feature collision and/or reaction cells or mathematical corrections for attenuating the interferences and high resolution ICP-MS instruments [15, 23]. However, no method is currently available for this purpose using the TOF-ICP-MS. Modified sample preparation process is introduced in this work using ammonium fluoride for extraction of several elements from coal fly ashes prior to TOF-ICP-MS analysis. In combination with a closed vessel MAE, with the flexibility of vessel options, choices of sample size, temperature, amounts of solvent, and number of samples [57], simple, rapid, interference-free and high-throughput method was developed. Using the described method, the use of some other reagents like mineral acids, being usually necessary for complete

sample digestion is not needed which is in agreement with green chemistry trends [58].

EXPERIMENTAL

Instrumentation. The detailed description of the Optimass8000 oaTOF-ICP-MS instrument used throughout this study (GBC Scientific Equipment Pty. Ltd., Australia) is given in ref. [51]. The details of the typical operating and instrument conditions can be found in refs. [53–56]. The resolution (full width at half maximum intensity) of 1800 and sensitivity of 15 000 counts/s per µg/L (mass integrated peak) was achieved for $^{139}La^+$ under these conditions. The same parameters were 2100 and 17 000 counts/s per µg/L for $^{238}U^+$.

The microwave-assisted extraction of samples was carried out in Speedwave™ MWS-3$^+$ (Berghof, Germany) microwave system with the maximum total output of the microwave generator 1450 W. The sample throughput of the MWS-3$^+$ system was increased by using the Multitube System (MT) employed with the DAC-100S digestion vessels [49]. This arrangement allows simultaneous extraction/digestion of three samples in one DAC-100S PTFE vessel by placing three MT perfluoroalkoxy polymer (PFA) tubes into each of the vessels.

The Avanta P double beam atomic absorption spectrometer (GBC Scientific Equipment Pty. Ltd., Australia) was used in the emission mode for determination of Na and K and in the absorption mode for determination of Ca, Fe, Si and Mg. The operating and instrument conditions are in detail summarized in refs. [49, 56].

The determination of C was performed by an independent accredited analytical laboratory using the Eltra CW-800M analyzer (Eltra GmbH, Germany).

Reagents and standards. The UltraClear (SG, Germany) pure water system was used to purify water to 0.05 µS/cm, which was further employed for preparation of all solutions. Nitric acid (65%, w/w) of Selectipur quality (Lach-Ner, Neratovice, Czech Republic) was further purified by sub-boiled distillation. Stock solution containing 1 g/L Rh obtained from SCP Science (Canada) was used to prepare internal standard solution. Multi-element stock solution "A" comprising of 10 mg/L of Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, Ge, Hf, Hg, Li, Mn, Mo, Ni, Pb, Pd, Pt, Rb, Re, Ru, Sb, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W and Zr was prepared from single element standards of 1 g/L obtained from SCP Science or Analytika Ltd. (Czech Republic). Stock solution "B" containing 100 mg/L of Ce, La, Nd, Pr, U ("B1") and 20 mg/L of Dy, Eu, Er, Gd, Ho, Lu, Sc, Sm, Tb, Tm, Y, and Yb ("B2") was prepared using a multi-element solution purchased from Analytika Ltd. and 10 g/L of U. Ammonium fluoride was of pro-analysis grade (p.a.) and obtained from Sigma-Aldrich (USA). The

stock solutions of Ca, Fe, K, Mg, and Na (1 g/L) were purchased from Analytika Ltd..

Quality assurance and quality control. The commercially supplied reference materials Constituent Elements in Coal Fly Ash Standard Reference Material® 1633b (National Institute of Standards & Technology, USA) and certified reference material Fine Fly Ash CTA-FFA-1 (Institute of Nuclear Chemistry and Technology, Warsaw, Poland) intended primarily for use in calibration and verification of apparatus and methods, respectively, for determining components in fly ashes were analyzed.

Microwave-assisted extraction. The certified reference material (CRM) Fine Fly Ash CTA-FFA-1 was employed for optimization of the MAE procedure. The portion around 250 mg of this sample was at first ground in the vibration mill Wig-L-Bug 30 (Crescent Dental Mfg. Co.) for reassurance of the sample homogeneity. Then, 10 mg of the CTA-FFA-1 were weighed into the MT-tubes and NH_4F was added at constant volume 5 mL with different concentration of NH_4F being 60, 100 and 140 g/L, respectively, which equals to the absolute amount of 300, 500 and 700 mg of NH_4F in the MT-tubes. These MT-tubes were placed into the outer digestion vessel, where 20 mL of the appropriate concentration of NH_4F were added. The level of NH_4F was higher in the outer vessel than in the PFA tubes. The evaporation of the solution from the PFA tubes was thus prevented by compensation of the vapour pressures [49].

The extractions were performed at the temperature of 160, 180 or 200°C held for 5, 10 or 15 min (with a ramp set at 5 min at 50% power of the MWS-3$^+$). The resulting solutions were diluted to 10 mL with deionised water. Before analysis all solutions were filtered through a 0.45 µm Nylon syringe filters (Whatman Autovial).

Sample analysis. Quantification of the concentration of the trace element by oaTOF-ICP-MS was done by constructing calibration curves by linear regression. The differences in the calibration slopes of fly ash extracts and aqueous standards were insignificant at significance level 0.05, and as will be discussed later, thus the employment of simple calibration standards was possible. Calibration solutions: blank, 1, 2, 5, 10, 20 and 50 µg/L of Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, Ge, Hf, Hg, Li, Mn, Mo, Ni, Pb, Pd, Pt, Rb, Re, Ru, Sb, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W and Zr and 0.1, 0.2, 0.5, 1, 2 and 5 µg/L Ce, La, Nd, Pr, U and 0.02, 0.04, 0.1, 0.4 and 1 µg/L of Dy, Eu, Er, Gd, Ho, Lu, Sc, Sm, Tb, Tm, Y, and Yb were prepared by dilution of multielement stock solutions "A" (500 µg/L) and "B" (50 + 10 µg/L) in 50 mL volumetric flasks on a daily basis. Any possible instrumental drift and non-spectral effects were compensated by addition of 1.0 µg/L of Rh to all samples and solutions. Regression coefficients greater than 0.999 were obtained regularly. Five second data acquisition

Table 1. Variables and levels investigated using the fractional factorial experimental design

Variable	Code	−1	0	+1
Amount of NH_4F, mg	A	300	500	700
Extraction temperature, °C	B	160	180	200
Extraction time, min	C	5	10	15

time, ten replicates and peak area mode were used for the measurement. The solutions were analyzed along with a blank containing the same amount of ammonium fluoride and prepared in the same way as the samples. Before the analysis, the samples were diluted with deionized water in 1 : 4 ratio.

The analysis by flame atomic absorption/emission spectrometry for the determination of Na, K, Ca, Fe, Si and Mg was performed as described previously [49, 56].

Experimental design and statistical data treatment. Three-level 3^{k-p} fractional factorial design (where k is the number of factors investigated, and p describes the size of the fraction of the full factorial used), with three factors (3^{3-1}) and with three replicates ($n = 3$), was used to find the optimal conditions for the extraction and evaluate the significance of the factors (variables), as well as the interactions between them [59, 60]. The fractional factorial experimental design 3^{3-1} ($n = 3$) was used because of the reduced number of experiments (27 against 81 experiments using the full design) but also because no loss of significant information occurs. The studied factors were: mass of the extraction agent (A), extraction temperature (B) and extraction time (C). All factors were evaluated at three levels, low (denoted as −1), middle (denoted as 0) and high (denoted as +1). Table 1 summarizes the levels for the experimental design.

The responses for each experiment were calculated as the average mean of concentrations obtained for Li, Be, Ni, As, Se, Rb, Sb, Cs, W, Tl and U in CTA-FFA-1 Fine Fly Ash. The yield of the extraction data (%) for the Li, Ni, As, Rb, Sb, Cs, W, U, i.e. elements whose concentration was certified and resulted in a quantitative extraction, are summarized in Table 2. The Statistica 12 computer program (StatSoft, Inc., USA) and QC Expert™ 2.5, TriloByte Statistical Software (Pardubice, Czech Republic) were used for data processing.

RESULTS AND DISCUSSION

Selection of extraction agent. We reported previously [49, 61] that ammonium fluoride is able to impact effectively both silicate and alumina matrix. If ammonium fluoride or ammonium hydrogen fluoride are the reagents, different reaction products are created for many analytes (in the form of oxides, hydrox-ides, salts, etc.) and compare to the reaction with HF [62]. For ammonium fluorides, both in the anhydrous state or in the aqueous solution, the formation of ammonium fluorometallates or oxofluorometallates was reported [62]. The resulting products are more thermally stable, in contrast to those obtained with HF [49, 62], NH_4F is also significantly less toxic than HF, which is a requirement for the replacement of HF and the utilization of the fluoride-containing species. When the experimental conditions employing a closed vessel microwave-assisted extraction with the use of NH_4F as an extractant are used, Si and B can be quantitatively determined in various environmental samples [49]. Quantitative extraction of larger number of analytes with the use of only NH_4F would be favourable from this point of view. Relating to the ICP-MS analysis, all the above mentioned facts may be important in several aspects. Increasing number of reaction agents may influence the formation of different polyatomic species arising from ions of both the reagents and from the matrix components released to the analyzed solution by this agent. In addition, the higher number of reagents increases the risk of contamination. Due to this fact NH_4F was investigated for extraction of different analytes prior to ICP-MS measurement.

Optimization of the experimental conditions for microwave extraction. Three parameters were examined on the extraction results and efficiency, respectively, for individual analytes, which include the mass of the extraction agent, temperature and extraction time (Table 1). The effects and significance of the variables in the extraction process were evaluated using Pareto's charts, including a vertical line that corresponds to the 95% limit which indicates the statistical significance. Pareto's charts were constructed for total of 11 elements for which accurate concentration was evaluated via the two certified reference materials of fly-ashes as will be discussed later. Figure 1 shows that the factors influencing the extraction efficiency are strongly dependent on the type of the element. For the extraction of Li, Be, Se, Rb, Sb, Cs, Tl and U the mass of the extractant has a positive effect on the extraction efficiency. While for Li the analytical response increases linearly with the increasing amount of the extractant, it changes quadratically with the amount of extractant for the other above mentioned elements. What can be further seen from the Fig. 1 is that the extraction temperature significantly influences the extraction efficiency of Li, Rb, Cs, As, W and U. While for As and Cs the analytical response is improved linearly by increasing the extraction temperature, for Li, Rb, and U the effect is opposite and the extraction efficiency drops quadratically with increasing temperature. The time of the extraction has positively influenced the extraction of Li, Be, Ni, As, Se, W, and U. Important interactions between the mass of the extractant and temperature were observed

Table 2. Design and experimental results for the extraction of selected elements from CRM Fine Fly Ash CTA-FFA-1

No.	n	Mass of NH$_4$F, mg	Temp., °C	Time, min	Recovery, %[a]							
					Li	Ni	As	Rb	Sb	Cs	W	U
11	2	300	180	15	88.4	82.4	74.1	72.5	56.1	77.2	85.2	1.9
18	2	700	200	15	108.8	82.4	84.5	98.7	103.3	79.5	103.0	87.7
24	3	500	200	5	103.1	85.1	69.2	91.3	85.3	85.3	78.7	73.7
8	1	700	180	5	108.0	75.1	77.1	98.6	106.1	80.2	89.4	85.8
16	2	700	160	10	103.6	75.1	69.5	100.9	77.8	75.6	85.3	78.3
13	2	500	160	15	107.0	77.0	75.6	87.8	75.1	79.1	83.7	77.0
1	1	300	160	5	99.5	71.5	73.4	79.9	57.6	69.0	77.4	58.2
26	3	700	180	5	93.6	69.9	78.1	102.6	110.4	83.7	91.7	89.8
23	3	500	180	10	104.5	83.5	78.5	92.4	95.4	81.0	96.0	83.5
3	1	300	200	10	101.9	80.0	91.0	82.0	56.3	77.8	87.7	60.8
17	2	700	180	5	96.1	80.0	65.1	100.7	93.6	81.6	74.9	76.4
15	2	500	200	5	105.7	83.0	76.3	95.9	94.4	81.9	81.4	84.3
10	2	300	160	5	95.6	76.3	71.4	77.0	58.5	69.4	74.2	61.4
19	3	300	160	5	92.8	79.3	72.2	75.2	54.8	58.7	73.7	62.3
9	1	700	200	15	109.5	78.1	76.4	100.0	108.2	82.7	88.7	88.0
27	3	700	200	15	107.0	77.2	78.1	103.6	119.1	83.0	91.8	90.0
2	1	300	180	15	64.0	80.7	52.3	52.8	27.4	73.6	83.0	1.4
12	2	300	200	10	101.7	94.3	94.5	84.7	68.5	78.8	82.9	75.1
20	3	300	180	15	74.7	80.3	58.4	62.0	23.2	72.0	83.8	19.7
4	1	500	160	15	99.4	81.5	70.0	95.4	75.6	79.8	82.5	73.6
5	1	500	180	10	98.9	86.5	74.8	91.9	106.7	80.1	88.6	79.3
25	3	700	160	10	106.4	80.0	70.7	97.3	109.2	75.9	84.7	81.4
14	2	500	180	10	96.2	99.4	91.5	97.9	93.5	98.6	108.2	98.2
7	1	700	160	10	109.4	84.5	54.9	98.8	84.8	74.6	66.0	82.0
21	3	300	200	10	98.9	83.9	94.4	81.0	55.0	76.3	85.4	42.7
6	1	500	200	5	92.1	76.1	73.3	98.0	98.9	76.2	78.5	76.3
22	3	500	160	15	107.5	76.8	81.0	97.6	101.8	82.1	87.4	102.2

[a]Recovery = $100\% \times c_1/c_2$, where c_1 is the concentration found in CRM Fine Fly Ash CTA-FFA-1 by the proposed method and c_2 is the concentration certified by the producer of CRM.

for the extraction of Li, Se, Rb, U, Sb, W and Tl. The interactions observed influence in all cases the analytical results positively.

The results of the 3^{3-1} design are presented in Table 2, from which corresponding response surfaces were constructed, as illustrated in Fig. 2. Each plot shows the effects of two variables within their studied ranges and visualizes the tendency of each factor to influence the extraction efficiency of investigated element. In order to ensure the most robust conditions for the utilization of the method to as many analytes as possible, experimental conditions were finally selected as follows: 700 mg of the extractant, 200°C extraction temperature held for 10 min.

Quantitative extraction was achieved for all of the elements mentioned above (Fig. 2) under these extraction conditions.

Evaluation of matrix effects. Concentration of matrix elements in analyzed samples significantly influences the occurrence of both spectral and non-spectral matrix effects during the oaTOF-ICP-MS multielement analysis [53−56]. The quantitative values of apparent element concentration as measured on the Optimass 8000 in the presence of 0−1000 mg/L of the elements (C, Ca, Cl, K, Mg, Na, P, and S) suspected to generate polyatomic ions interfering with the determination of important elements such as As, Co, Cr, Cu, Ga, Mn, Ni, Se, Ti, V or Zn, etc. were previously published [53, 55]. Table 3 summarizes the concentration data of important matrix elements deter-
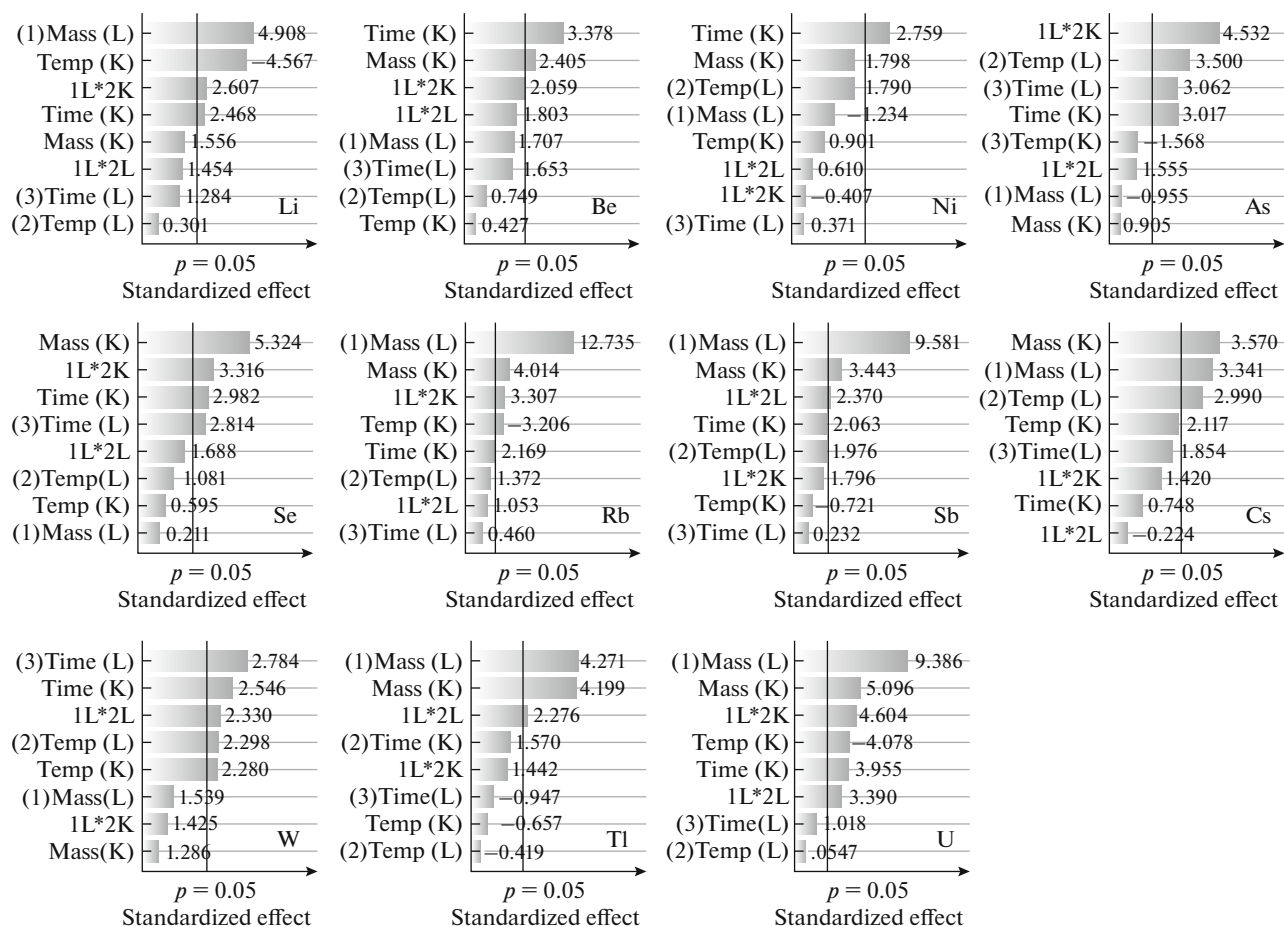
Fig. 1. Pareto charts of the standardized effects in the fractional factorial design 3^{3-1} for the study of variables: (1) amount of NH_4F, (2) extraction temperature, (3) time, and their interactions on the extraction of selected elements. The L and K letters indicate the linear and quadratic effect of the factor, respectively.

mined in the extract of CTA-FFA-1 and NIST SRM 1633b as well as the concentrations declared by the producers. It is obvious from the data that the concentration of major elements like Ca and Mg resulted in very low concentration values which can be attributed to the formation of insoluble fluorides. The complete dissolution of Si from the materials was indicated by the obtained values, which were in accordance to the certified values. Relating the concentration of Na, the quantitative extraction was achieved only for the NIST SRM 1633b. For CTA-FFA-1 whose Na concentration was one order higher than for NIST SRM 1633b, the recoveries were of about 32%. Similarly, the recoveries of K in CTA-FFA-1 and NIST SRM 1633b were only 60 and 61%, respectively. Although KF and NaF are easily soluble in the water, different reaction products may be created with ammonium fluoride like oxofluorometallates, etc. for which different solubility will be observed.

The presence of major matrix elements whose quantitative extraction is not achieved will significantly less influence the determination of problematic elements in contrast to procedures where total sample decomposition is used. Relating the concentration of Ca, Mg, Na and K whose concentration in supernatants is lower than 25 mg/L these values will not significantly interfere during the oaTOF-ICP-MS analysis [53, 55]. Similarly, the interference from polyatomic ions containing P or S is not expected to be significant as the concentration of the analytes in original samples is about one order lower in contrast to the above mentioned elements. According to the certificates the concentration of P and S in NIST SRM 1633b is 2.3 g/kg and 2.075 ± 0.011 g/kg, respectively and 725 ± 74 mg/kg for P in CTA-FFA-1.

As the ammonium fluoride matrix can have a considerable effect on the progress of the analysis and the quality of the obtained results a calibration curve using aqueous standard samples and one containing ammonium fluoride in the same concentrations as used for sample preparation was constructed for all elements determination. Table 4 shows the comparison of the slope values of matrix matched calibration with the slopes of aqueous calibration. The presented slopes of
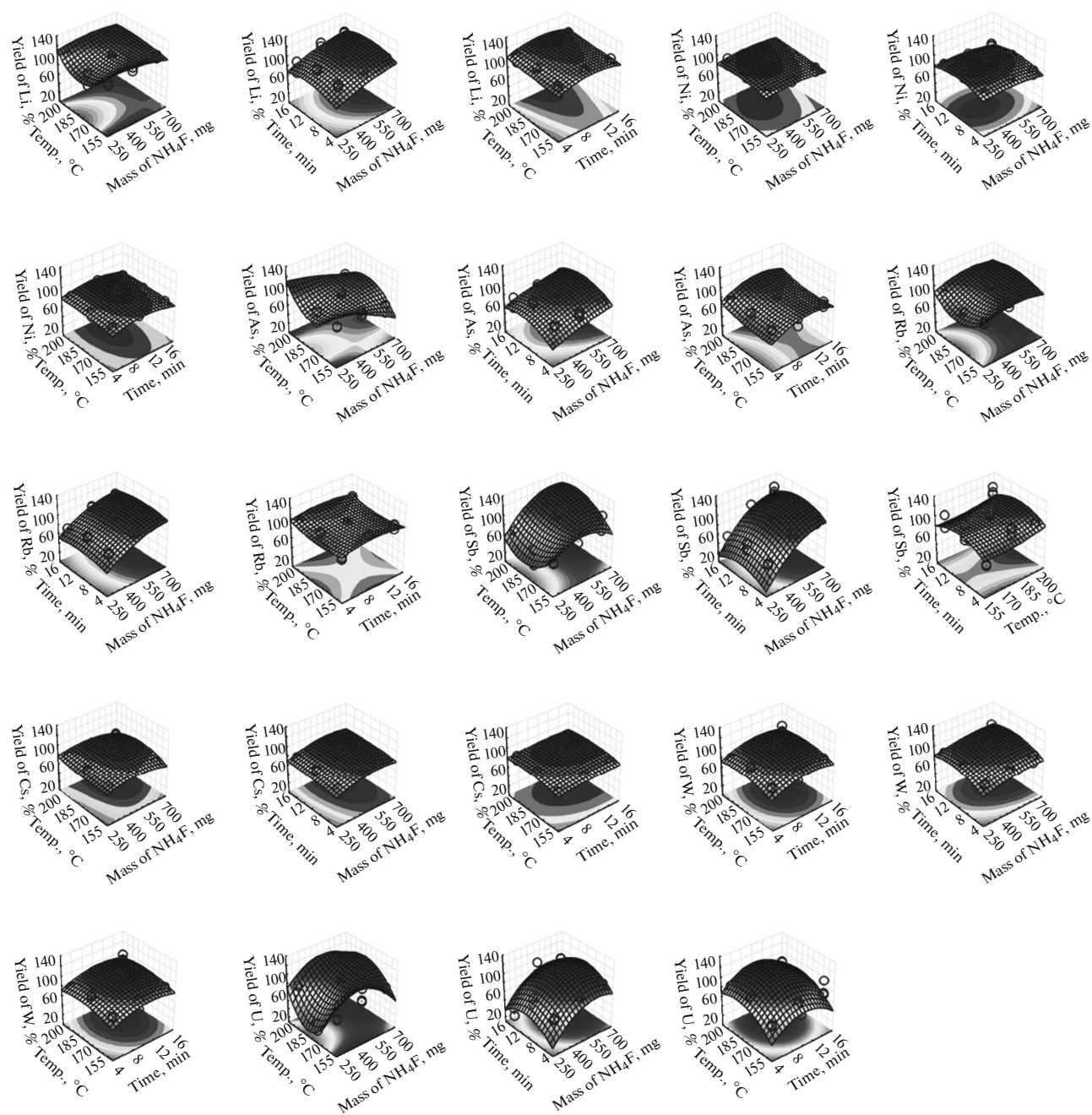
Fig. 2. Response surface plots from 3^{3-1} design for the recovery yield (%) of selected elements in the NH_4F extract as a function of NH_4F amount, extraction temperature and time. Recovery yields (%) were evaluated as the ratio: (the value obtained from an analytical process via a calibration graph/the reference value) × 100.

the calibration lines are expressed as relative sensitivities. Relative intensity was analytical response defined by counts per second (cps) of the peak area of individual analytical signal calculated and averaged from the ten measurements at each concentration and divided by the response of the internal standard element Rh. The paired *t*-test (at significance level 0.05) revealed

that the slope values of matrix matched calibration and that of aqueous calibration are not significantly different as its *p*-value was 0.185. The presence of ammonium fluoride thus does not influence the sensitivity and is not responsible for inducing non-spectral effects during the oaTOF-ICP-MS analysis. Thus, for quantification a direct aqueous calibration method

Table 3. Summary of results for the analysis of CTA-FFA-1 and NIST SRM 1633b

Element	CTA-FFA-1				NIST SRM 1633b			
	concentration[a, b], mg/kg		R^c, %	RSD[d], %	concentration[a, b], mg/kg		R^c, %	RSD[d], %
	declared	found			declared	found		
Trace elements								
$^{7}Li^{+}$	128 ± 22	133 ± 4	104	1.6	e	187 ± 24	99[f]	6.3
$^{9}Be^{+}$	27	28 ± 3	104	5.3	e	13 ± 2	104[f]	7.0
$^{60}Ni^{+}$	99 ± 6	95 ± 15	96	8.2	121 ± 2	122 ± 4	101	1.7
$^{75}As^{+}$	54 ± 3	51 ± 3	95	2.9	136 ± 3	134 ± 1	98	2.3
$^{78}Se^{+}$	4.6	4.7 ± 0.7	102	6.9	10.2 ± 0.2	10 ± 2	98	7.9
$^{85}Rb^{+}$	185 ± 5	184 ± 11	99	3.0	140	143 ± 4	102	1.5
$^{121}Sb^{+}$	18 ± 3	17 ± 2	95	4.9	6	6.2 ± 0.6	103	4.5
$^{133}Cs^{+}$	48 ± 2	46 ± 2	95	2.5	11	10.0 ± 0.9	91	4.7
$^{182}W^{+}$	11 ± 1	11.1 ± 0.7	101	2.9	5.6	5.6 ± 0.2	100	2.2
$^{205}Tl^{+}$	e	7.3 ± 0.2	104[f]	0.2	5.9	5.5 ± 0.2	93	6.3
$^{238}U^{+}$	15.1 ± 0.8	14 ± 2	93	5.1	8.8 ± 0.4	8.4 ± 0.2	95	5.8
Major elements								
Na	21.9 ± 0.8	7.1 ± 0.8	32	5.6	2.01 ± 0.03	2.1 ± 0.2	104	3.8
K	22.0	13.1 ± 0.8	60	3.1	19.5 ± 0.3	11.8 ± 0.8	61	3.4
Ca	22.9	<0.033	g	g	15.1 ± 0.6	<0.033	g	g
Mg	15.5	2.3 ± 0.2	15	4.3	4.82 ± 0.08	1.4 ± 0.1	30	4.9
Fe	50 ± 1	5.6 ± 0.3	12	3.1	78 ± 2	29 ± 4	38	6.0
Si	225 ± 9	216 ± 4	96	1.0	230.2 ± 0.8	230 ± 18	100	3.9
C	e	1.2 ± 0.2[h]	g	6.5	e	2.7 ± 0.5[h]	g	9.3

[a]Mean ± 2SD ($n = 3$).

[b]Values were evaluated with the use of calibration with matrix-free standards ($n = 5$) and Rh as internal standard element.

[c]Recovery (%) expressed as the ratio: (observed value obtained from an analytical process via a calibration graph/ the reference value) × 100.

[d]Relative standard deviation (%) of three independent analyses.

[e]Not available.

[f]Analytical recovery, R (%), evaluated for samples spiked with 5 µg/L for listed elements.

[g]Not determined.

[h]The determination of C was performed in original samples by the Eltra CW-800M analyzer.

using Rh as internal standard element, which is less time consuming than standard additions or the matrix matched method thus may be used.

Trueness and precision. Coal Fly Ash NIST SRM 1633b and Fine Fly Ash CTA-FFA-1 certified reference materials were analyzed in order to prove the trueness and precision. As seen from Table 3, good agreement between the results obtained using an aqueous calibration for quantification was achieved for 11 elements by the proposed microwave-extraction method and the declared values. The accuracy for elements whose concentration was not certified was assessed using a second approach. This involved the calculation of analytical recoveries, which were determined for samples of extracts in three replicates using standard additions as shown in Table 3. For all ele-

ments, the obtained recoveries were between 91 and 106%, which confirms that the accuracy of the method is within 10%. Using the described procedure an accurate results were obtained also for the elements like As, Se or Ni for which the use of collision/reaction cell [7, 21, 26] or mathematical corrections [37] are needed when using quadrupole ICP-MS.

However, the determination of some of the trace elements like Cd, Pb, Ba, Cr, Hg, etc. which can be considered as potentially toxic [63], could not be accurately done by the presented method. Low recovery yields of trace elements may be attributed to the formation of insoluble fluorides or co-precipitation with the fluoride. The insoluble fluoride precipitates formed during NH_4F extraction of fly-ash samples may incorporate trace elements differentially into the

Table 4. Comparison of linear calibrations method using a least square regression for matrix-free standards and those containing ammonium fluoride for selected elements determination by oaTOF-ICP-MS method and appropriate LODs and LOQs values

Element	Relative sensitivity[a]		Instrument LOD, ng/L		Method LOD and LOQ, µg/kg	
	aqueous[b]	NH_4F^c	aqueous[b]	NH_4F^c	LOD	LOQ
$^7Li^+$	0.1112	0.1298	65	37	37	123
$^9Be^+$	0.0437	0.0424	87	98	98	327
$^{60}Ni^+$	0.1054	0.1207	73	314	314	1047
$^{75}As^+$	0.0609	0.0564	67	150	150	500
$^{78}Se^+$	0.0106	0.0083	726	476	476	1587
$^{85}Rb^+$	0.4249	0.4663	9.0	209	209	697
$^{121}Sb^+$	0.2226	0.1958	3.4	31	31	103
$^{133}Cs^+$	0.9086	0.9141	1.3	2.1	2.1	7.0
$^{182}W^+$	0.436	0.4367	2.7	17	17	57
$^{205}Tl^+$	1.2432	1.1742	0.37	1.6	1.6	5.3
$^{238}U^+$	2.2848	2.1722	0.04	0.09	0.09	0.3

[a]Relative sensitivities are simply the computed slopes of the calibration lines where relative intensity was the analytical response defined by counts per second (cps) of the peak area of individual analytical signal calculated and averaged from the ten measurements at each concentration and divided by the response of the internal standard element Rh.

[b]Calibration with matrix-free standards ($n = 5$).

[c]Each calibration solution ($n = 5$) contains the same amount of NH_4F as the sample.

structures of the precipitated major element fluorides, which therefore act as carriers for trace elements [35]. In addition, some analytes like Pb, Zn, Cd or Cu exist in carbonate phase [12] of fly ash that influences their leaching behavior.

Intra-day comparison was used to evaluate the precision of the method. It is expressed as relative standard deviation (RSD) of analyses of a sample, which was independently prepared and analyzed three times during one day. The value used for the computation was obtained as a mean of an analysis having ten replicates. Table 3 shows that the values of the intra-day RSD were typically lower than 10%. Thus, the precision of the method was acceptable. This also confirms the sufficient homogeneity of the material, as these values of RSD were obtained for the sample masses of 10 mg. The observations that the use of such small sample mass does not affect the trueness or the precision of the analysis of coal and coal ash are in accordance to those reported previously by Lachas et al. [3].

Limits of detection and quantification. Table 4 shows the limits of detection (LOD) and quantification (LOQ) for each isotope, which were calculated, respectively, as a 3 times and 10 times the standard deviation of the blank response at the given m/z position, divided by the slope of the calibration graph. The values are evaluated as the instrument LOD and method LOD and LOQ. The time of the integration was set to 5 s and blanks and standards were determined in ten replicates. In order to evaluate the instrument LOD, we analyzed the blanks containing deionized water alone or with ammonium fluoride and in all cases internal standard to reflect how the mere presence of NH_4F influences the detection capability. The problems with contamination were of a little importance except for Ni, Rb, or Sb, as shown in Table 4. This was ensured by using NH_4F of sufficient purity.

Sample throughput. The analysis of each sample comprised of sample introduction, ten replicate measurements and rinsing. Under the conditions summarized in experimental section, the simultaneous analysis of all elements took approximately three minutes for each sample, which means that ca 20 samples could be analyzed in an hour. Using the full capacity of the 8-position carousel of the MWS-3+ microwave oven and the PFA multitube system [49], three MT PFA tubes were placed into a standard DAC-100S PTFE vessel, thus three samples were extracted simultaneously in one DAC-100S digestion vessel and therefore it was possible to extract up to 24 samples in one microwave run. The total time needed for the microwave procedure is 30 min (including extraction and cooling down of the reaction vessel) for 24 samples. The sample preparation, i.e. weighing, pipetting of the extractant, diluting etc., takes approximately 90 min for 24 samples. With this setup, it is possible to prepare and analyze a minimum of 96 samples in an 8 h working day, which equals to 12 samples/h.

CONCLUSIONS

The presented method using ammonium fluoride for extraction of the elements from fly ash samples offers an efficient and simple way to accurately quantify 11 elements in this difficult matrix by oaTOF-ICP-MS method. The main benefit of the proposed approach is that the matrix interference is insignificant. Thus, simple calibration method can be performed for precise and accurate determination of elements even such as As, Se or Ni, which are more problematic if ICP-MS instruments with inadequate resolving power are used. Another advantage of this procedure is its speed and simplicity. The determination of all elements is done simultaneously; individual analytes do not require specific setting, which may be another benefit. As the purpose of this proposed method is to eliminate different polyatomic ions causing spectral interferences, the procedure is expected to be beneficial both for quadrupole and for TOF-ICP-MS. The method is avoiding handling of the very corrosive and toxic HF. The relatively low price of NH_4F compared to HF, absence of significant waste generation and speed of MAE are other benefits. The method thus contributes to the green chemistry. However, the quality of the used ammonium fluoride limits the LODs. Additionally, some elements of potential interest like Ba, Cd, Hg, Pb, etc. could not be determined accurately using the presented approach due to problems with inclusion and/or co-precipitation in the precipitated matrix. Further, relating the analysis of solutions with high fluoride content, special attention should be paid to the care of ICP-MS cones. Rather than using nickel cones, using more chemically resistant Pt-cones is recommended, as they can usually be used longer before they need cleaning. Nevertheless, despite the above mentioned drawbacks of oaTOF-ICP-MS instrumentation, this procedure is currently the sole solution to reduce the interferences to a manageable level. On the other hand, it is expected that the quantification of elements like Cd, Hg, Pb, etc. would be easily performed using this instrumentation when employing some of the more conventional sample preparation procedures ensuring quantitative release of desired analytes from the sample matrix as for the elements above 80 amu the spectral effects are significantly less important.

ACKNOWLEDGMENTS

REFERENCES

1. Ahmaruzzaman, M., *Prog. Energ. Combust.*, 2010, vol. 36, no. 3, p. 327.
2. Yao, Z.T., Ji, X.S., Sarker, P.K., Tang, J.H., Ge, L.Q., Xia, M.S., and Xi, Y.Q., *Earth-Sci. Rev.*, 2015, vol. 141, no. 1, p. 105.
3. Lachas, H., Richaud, R., Jarvis, K.E., Herod, A.A., Dugwell, D.R., and Kandiyoti, R., *Analyst*, 1999, vol. 124, no. 2, p. 177.
4. Wang, J., Nakazato, T., Sakanishi, K., Yamada, O., Tao, H., and Saito, I., *Talanta*, 2006, vol. 68, no. 5, p. 1584.
5. Depoi, F.S., Pozebon, D., and Kalkreuth, W.D., *Int. J. Coal Geol.*, 2008, vol. 76, no. 3, p. 227.
6. Marrero, J., Polla, G., Rebagliati, R.J., Pla, R., Gomez, D., and Smichowski, P., *Spectrochim. Acta, Part B*, 2007, vol. 62, no. 2, p. 101.
7. Smichowski, P., Polla, G., Gomez, D., Espinosa, A.J.F., and Lopez, A.C., *Fuel*, 2008, vol. 87, no. 7, p. 1249.
8. Chang, C.Y., Wang, C.F., Mui, D.T., and Chiang, H.L., *J. Hazard. Mater.*, 2009, vol. 163, nos. 2−3, p. 578.
9. Pontes, F.V.M., Mendes, B.A.D., de Souza, E.M.F., Ferreira, F.N., da Silva, L.I.D., Carneiro, M.C., Monteiro, M.I.C., de Almeida, M.D., Neto, A.A., and Vaitsman, D.S., *Anal. Chim. Acta*, 2010, vol. 659, nos. 1−2, p. 55.
10. Ilander, A. and Vaisanen, A., *Ultrason. Sonochem.*, 2009, vol. 16, no. 6, p. 763.
11. Ilander, A. and Vaisanen, A., *Anal. Chim. Acta*, 2007, vol. 602, no. 2, p. 195.
12. Huang, S.J., Chang, C.Y., Mui, D.T., Chang, F.C., Lee, M.Y., and Wang, C.F., *J. Hazard. Mater.*, 2007, vol. 149, no. 1, p. 180.
13. Low, F. and Zhang, L., *Talanta*, 2012, vol. 101, no. 1, p. 346.
14. Iwashita, A., Nakajima, T., Takanashi, H., Ohki, A., Fujita, Y., and Yarnashita, T., *Talanta*, 2007, vol. 71, no. 1, p. 251.
15. Rodushkin, I., Axelsson, M.D., and Burman, E., *Talanta*, 2000, vol. 51, no. 4, p. 743.
16. Wang, H., Nakazato, T., Sakanishi, K., Yamada, O., Tao, H., and Saito, I., *Anal. Chim. Acta*, 2004, vol. 514, no. 1, p. 115.
17. Xu, Y.H., Iwashita, A., Nakajima, T., Yamashita, H., Takanashi, H., and Ohki, A., *Talanta*, 2005, vol. 66, no. 1, p. 58.
18. Laitinen, T., Revitzer, H., and Tolvanen, M., *Fresenius' J. Anal. Chem.*, 1996, vol. 354, no. 4, p. 436.
19. Bettinelli, M., Spezia, S., Baroni, U., and Bizzarri, G., *Microchem. J.*, 1998, vol. 59, no. 2, p. 203.
20. Fernandez-Perez, V., Garcia-Ayuso, L.E., and de Castro, M.D.L., *Analyst*, 2000, vol. 125, no. 2, p. 317.
21. Mketo, N., Nomngongo, P.N., and Ngila, J.C., *Int. J. Environ. Anal. Chem.*, 2015, vol. 95, no. 5, p. 453.
22. Smolka-Danielowska, D., *Pol. J. Environ. Stud.*, 2006, vol. 15, no. 6, p. 943.
23. Xie, H.L., Tang, Y.G., Li, Y.J., and Li, L.B., *J. Cent. South Univ. Technol. (Engl. Ed.)*, 2007, vol. 14, no. 1, p. 68.
24. Swami, K., Judd, C.D., Orsini, J., Yang, K.X., and Husain, L., *Fresenius' J. Anal. Chem.*, 2001, vol. 369, no. 1, p. 63.

25. Das, A.K. and Chakraborty, R., Guardia Mde, L., Cervera, M.L., and Goswami, D., *Talanta*, 2001, vol. 54, no. 5, p. 975.

26. Li, X., Dai, S.F., Zhang, W.G., Li, T., Zheng, X., and Chen, W.M., *Int. J. Coal Geol.*, 2014, vol. 124, no. 1, p. 1.

27. Antes, F.G., Duarte, F.A., Mesko, M.F., Nunes, M.A.G., Pereira, V.A., Mueller, E.I., Dressler, V.L., and Flores, E.M.M., *Talanta*, 2010, vol. 83, no. 2, p. 364.

28. Bettinelli, M., Spezia, S., Baroni, U., and Bizzarri, G., *At. Spectrosc.*, 1998, vol. 19, no. 3, p. 73.

29. Stankova, A., Gilon, N., Dutruch, L., and Kanicky, V., *J. Anal. At. Spectrom.*, 2011, vol. 26, no. 2, p. 443.

30. Zhang, Y.F., Jiang, Z.C., He, M., and Hu, B., *Environ. Pollut.*, 2007, vol. 148, no. 2, p. 459.

31. Vieira, M.A., Ribeiro, A.S., and Curtius, A.J., *Microchem. J.*, 2006, vol. 82, no. 2, p. 127.

32. Ni, J.L., Liu, C.C., and Jiang, S.J., *Anal. Chim. Acta*, 2005, vol. 550, nos. 1−2, p. 144.

33. Chen, C.C., Jiang, S.J., and Sahayam, A.C., *Talanta*, 2015, vol. 131, no. 1, p. 585.

34. Maia, S.M., Pozebon, D., and Curtius, A.J., *J. Anal. At. Spectrom.*, 2003, vol. 18, no. 4, p. 330.

35. Hu, Z.C., Gao, S., Liu, Y.S., Hu, S.H., Zhao, L.S., Li, Y.X., and Wang, Q., *J. Anal. At. Spectrom.*, 2010, vol. 25, no. 3, p. 408.

36. Srogi, K., *Anal. Lett.*, 2007, vol. 40, no. 2, p. 199.

37. Aldabe, J., Santamaria, C., Elustondo, D., Lasheras, E., and Santamaria, J.M., *Anal. Methods*, 2013, vol. 5, no. 2, p. 554.

38. Stankova, A., Gilon, N., Dutruch, L., and Kanicky, V., *Fuel*, 2010, vol. 89, no. 11, p. 3468.

39. Brenner, I.B. and Zander, A., *Fresenius' J. Anal. Chem.*, 1996, vol. 355, nos. 5−6, p. 559.

40. Yu, Z.S., Robinson, P., and McGoldrick, P., *Geostand. Newslett.*, 2001, vol. 25, nos. 2−3, p. 199.

41. Bacon, J.R. and Davidson, C.M., *Analyst*, 2008, vol. 133, no. 1, p. 25.

42. Nobrega, J.A., Trevizan, L.C., Araujo, G.C.L., and Nogueira, A.R.A., *Spectrochim. Acta, Part B*, 2002, vol. 57, no. 12, p. 1855.

43. Al-Harahsheh, M. and Kingman, S.W., *Hydrometallurgy*, 2004, vol. 73, nos. 3−4, p. 189.

44. Armenta, S., Garrigues, S., and de la Guardia, M., *TrAC, Trends Anal. Chem.*, 2008, vol. 27, no. 6, p. 497.

45. Sah, R.N. and Brown, P.H., *Microchem. J.*, 1997, vol. 56, no. 3, p. 285.

46. Mann, S., Geilenberg, D., Broekaert, J.A.C., and Jansen, M., *J. Anal. At. Spectrom.*, 1997, vol. 12, no. 9, p. 975.

47. Hu, Z. and Gao, S., *Chem. Geol.*, 2008, vol. 253, nos. 3−4, p. 205.

48. Kozono, S., Yagi, M., and Takashi, R., *Anal. Chim. Acta*, 1998, vol. 368, no. 3, p. 275.

49. Husakova, L., Urbanova, I., Sidova, T., Cahova, T., Faltys, T., and Sramkova, J., *Int. J. Environ. Anal. Chem.*, 2015, vol. 95, no. 10, p. 922.

50. Hoenig, M., *Talanta*, 2001, vol. 54, no. 6, p. 1021.

51. Sturgeon, R.E., Lam, J.W.H., and Saint, A., *J. Anal. At. Spectrom.*, 2000, vol. 15, no. 6, p. 607.

52. Reed, N.M., Cairns, R.O., Hutton, R.C., and Takaku, Y., *J. Anal. At. Spectrom.*, 1994, vol. 9, no. 8, p. 881.

53. Husakova, L., Urbanova, I., Audrlicka-Vavrusova, L., Sramkova, J., Cernohorsky, T., Bednarikova, M., and Pilarova, L., *Microchim. Acta*, 2011, vol. 173, nos. 1−2, p. 173.

54. Husakova, L., Urbanova, I., Sidova, T., and Mikysek, T., *Anal. Methods*, 2015, vol. 7, no. 12, p. 5019.

55. Husakova, L., Urbanova, I., Sramkova, J., Cernohorsky, T., Krejcova, A., Bednarikova, M., Frydova, E., Nedelkova, I., and Pilarova, L., *Food Chem.*, 2011, vol. 129, no. 3, p. 1287.

56. Husakova, L., Urbanova, I., Sramkova, J., Konecna, M., and Bohuslavova, J., *Talanta*, 2013, vol. 106, p. 66.

57. Krishna, M.V.B., Chandrasekaran, K., and Karunasagar, D., *Anal. Methods*, 2012, vol. 4, no. 5, p. 1401.

58. Anastas, P.T. and Kirchhoff, M.M., *Acc. Chem. Res.*, 2002, vol. 35, no. 9, p. 686.

59. Box, G.E.P., Hunter, W.G., and Hunter, J.S., *Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building*, New York: Wiley, 1978.

60. Montgomery, D.C., *Design and Analysis of Experiments*, New York: Wiley, 1991.

61. Husakova, L., Cernohorsky, T., Sramkova, J., and Urbanova-Dolezalova, I., *Anal. Chim. Acta*, 2009, vol. 634, no. 1, p. 22.

62. Rakov, E.G. and Mel'nichenko, E.I., *Russ. Chem. Rev.*, 1984, vol. 53, no. 9, p. 851.

63. Walker, T.R., Young, S.D., Crittenden, P.D., and Zhang, H., *Environ. Pollut.*, 2003, vol. 121, no. 1, p. 11.