Determination of Boron, Lithium and Some Metals in Fly Ash by Laser Ablation – Inductively Coupled Plasma – Optical Emission Spectrometry

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Abstract

To avoid potentially harmful wet sample preparation is offered to use laser ablation (LA) – inductively coupled plasma – optical emission spectrometry (ICP-OES) as a method for the elemental analysis of fly ash for boron, lithium, and some metals. For this purpose, synthetic samples were prepared by spiking with dissolved standards. As a result, great stability of calibration curves was achieved. It was found that a particle diameter less than 80 μm in fly ash is enough to have a satisfying homogeneity for successful calibration in the method of standard additions. The average recovery test for reference materials used in the study was 16–77% of the certified values for the elements observed. The low results might be the effect of spiking with calibration samples in the liquid state. This type of analysis requires further investigation. According to the results of elemental analysis, the content of boron and lithium was determined for ZUK-2 and SO-1, which was not previously noticed in other papers.

1. Introduction

Coal is one of the resources to produce energy worldwide. Being formed during combustion, coal fly ash causes water [1] and air pollution [2] to increase. This waste contains a wide range of toxic elements that are harmful to people even at very low concentrations [3–4]. These toxic elements leach from coal fly ash into soil and groundwater. Due to the different mobility of these elements [5–6], it always needs to have special monitoring of their distribution in the environment in any particular case [7], even if the source of contamination is the same.

On the other hand, fly ash, as one waste, can be utilized to obtain various products such as catalysts [8] and cenospheres for different purposes [9–11], or to produce some valuable reagents, for instance, rare earth elements [12–14]. This branch also requires detailed chemical analysis to provide information about the economic efficiency of recycling and its eco-friendly production. However, the characterization of fly ash is not trivial owing to its heterogeneity and complex chemical compound.

The concentrations of the main ash-forming elements are usually determined by «wet» chemical methods such as atomic absorption spectrometry (AAS) [15] and inductively coupled plasma optical emission spectrometry (ICP-OES) [16–17]. In those cases, sample preparation leads to risks of contamination, sample loss, and dilution errors, totally spoils analysis for minor and trace quantities.

Alternatively, laser ablation inductively coupled plasma optical emission spectrometry (LA-ICP-OES) is a promising method not only to resolve the problem but also to reduce reagent and labour costs. Nevertheless, quantitative analysis is often limited due to a lack of suitable reference materials [18]; therefore, calibration may be a problem for LA-ICP-OES.

This study aims to develop a preparation technique for solid sampling and elemental analysis to improve analytical characteristics, have a possibility to determine B and Li (their content is a marker for usage as fertilizer and in power supply elements), detect some non-Fe metals (because of

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their harmful impact on the environment and potential use in industry to make chemicals).

Eventually, it is interesting to investigate the pros and cons of ICP-OES with solid sampling for the simultaneous quantification of light and «heavy» elements in fly ash.

2. Experimental

For analytical study, a New Wave UP-266 laser ablation system was employed with argon as carrier gas. The total volume of the system is less than 20 cm^3. The laser beam was focalized perpendicularly on the target surface.

The ablation cell was connected directly to ICP-source with tygone tube and special fitting. As ICP-OES spectrometer, a Thermo iCAP 6500 DUO was used in the mode of axial viewing. Experimental settings are listed in Table 1.

In this paper, three certified reference materials (CRMs) of fly ash are analysed. SO-1 is from Tomusinskaya State District Power Plant in the Kemerovo region, prepared by West Siberian Testing Centre (Russia). ZUK-1 is from Berezovskaya State District Power Plant of the Kansk-Achinsk Fuel and Energy Complex (KATEK). ZUK-2 is from Irsha-Borodinsky coal deposit of the KATEK. Vinogradov Institute of Geochemistry SB RAS produced the latter two CRMs.

All the pellets used in the investigation were prepared by mixing 200 mg of a sample with 200 mg of binder. Microcrystalline cellulose (Merk, Germany) was used as binder; it is free of traces and easy to handle.

Powders of fly ash were spiked with standard solutions before pressing pellets to realize calibration process by the method of standard additions. The specimens were dried at 120 °C for 2 h, grinded in the agate mortar to make the mixture of standards and binder homogeneous, and then pressed into pellets at 10 MPa for 5 min.

The solutions were prepared by mixing single element standards (1 mg ml^{-1}) of boron, lithium, copper, cobalt, chromium, nickel, and vanadium in acid media. In the case of multi-standard calibration listed in the paper, the standard solution of Sc was used to make its concentration 100 μg g^{-1} as internal standard in each sample to make compensation for unavoidable matrix effects because of different ratios of Si, Ca, and Al in the CRMs. All the standard solutions were used immediately after preparation to avoid possible deterioration in stability.

Table 1
LA-ICP-OES parameters

Laser parameter (New Wave UP-266 laser)	
Wavelength	266 nm
Pulse duration	5 ns
Ablation rate	5 Hz
Spot size	500 μm
Fluence	22 J cm^{-2}
ICP-OES (Thermo iCAP 6500 Duo)	
RF power	1200 W
Viewing plasma	Axial
Argon make up flow rate	0.5 L min^{-1}
Argon flow rate (ablation transport gas)	0.8 L min^{-1}
Detection	Simultaneous
Optics	Echelle grating – cross dispersion
Integration time	10 s
Elements and wavelengths	B 208.559 nm Co 228.616 nm Cr 267.716 nm Cu 324.754 nm Li 670.784 nm Ni 231.604 nm V 290.882 nm

The additional concentration range of most elements was 12.5, 25 and 50 μg g^{-1}. To have a formidable statistic basis, it was decided to use six independent pellets and three rasters on the surface of every calibration sample. It makes it possible to work with eighteen measurements for a CRM. Taking into account all the additions, there were 72 samples and 216 measurements, including 648 sub-measurements, for three CRMs.

3. Results and discussions

It is possible to determine micro-component compound of fly ashes by ICP-OES after total digestion with HF/HNO$_3$ [16] or fusion within lithium tetraborate (Li$_2$B$_4$O$_7$) followed by dissolution of the melt in acid [19]. At the same time, required for monitoring the speed of analysis, as well as difficulties and errors with digestion, are important points in favour of LA-ICP-OES employment. Its application is also important to observe the effect of variation of the chemical and mineralogical composition of samples. Moreover, it is practically the only method to determine light elements, Li and B, in silicate materials. Therefore, it needs to develop a special LA-ICP-OES method for the analysis of fly ash.
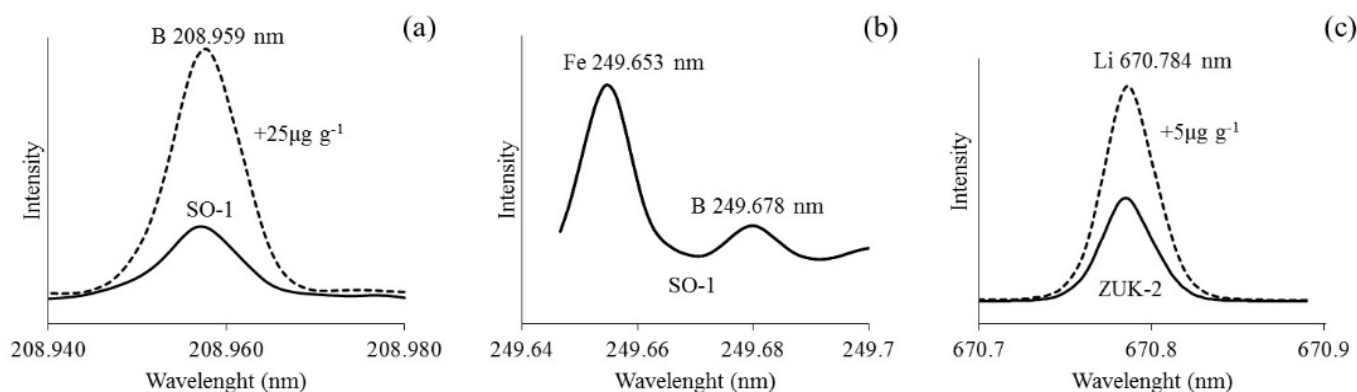
Fig. 1. Some analytical emission wavelengths analysed for employment in the study.

Generally, fly ash contains such elements as Fe and Mn in significant amounts. Hence, the atomic B 208.959-nm (Fig. 1a) wavelength was chosen as an analytical one for the determination of boron in fly ashes, as the more intensive lines B I 249.773 and 249.678 nm (Fig. 1b) are spoiled by interferences from Fe II 249.782 nm and Fe II 249.782 nm, accordingly [20–21]. The use of V II 311.071 nm [22] has been complicated by Mn I 311.068 nm [20]. Cr II 283.563 nm [22] interferes with Fe I 283.546 nm, Fe II 283.571 nm [21]. Ni II 221.647 nm employed in [23] has interference with Si I 221.667 nm [20].

In this paper, only free from spectral interference analytical lines are used (Table 1). Some of them are Li I 670.784 nm (Fig. 1c), Ni II 231.604 nm [24, 25, 26], Cr II 283.563 nm [23–25], V II 290.882 nm [24, 26, 27].

The element Si (its atomic 288.158-nm line) was used as internal standard because it is a macro-component with constant concentration in the sample analysed, which is helpful to compensate for inaccuracy in calibration because of possible aerosol transport instability, physical interferences, and for different rates of ablation during the analysis of samples [28].

Due to a lack of certified reference materials with the same matrix compound, the method of standard additions (addition calibration) was chosen to calibrate the spectrometer. This approach is considered as successful when using laser ablation with ICP-MS [29, 30].

Target homogeneity was controlled with all the samples investigated. For this purpose, at least three identical laser rasters were used on the surface of every pellet. The resulting relative standard deviation (RSD) of less than 10% indicates that there is no sufficient difference between the results of the analysis using the rasters. It means that the way of sample preparation used in this paper is efficacious for its aims.

Resulting calibration graphs for the elements determined in this investigation were linear within chosen calibration ranges. Examples are given in Fig. 2. Least squares regression correlation coefficients are better than 0.999 for B (Fig. 1b), Cu, Li, and Ni (Fig. 1a) and than 0.9999 for Cr (Fig. 1c), Co, and V. This fact allows considering this method appropriate to the analysis and indicates that the size of particles in the used CRMs (< 80 μm) is enough to have suitable material homogeneity for this analysis.

Limits of detection and quantification based on the 3 s and 10 s criteria, accordingly, are given in Table 2. They are an average of 18 independent measurements, which were calculated automatically via a special algorithm provided by [20]. Both of them are presented for convenience when making a comparison to other papers. The LOQ denotes the lowest concentration of an element in fly ash that is quantifiable using the referred instrument.

It was shown that the current method gives benefits in terms of lower limits of detection and quantification (Table 2). Unfortunately, there are not so many methodological papers published in the field of minor-trace elemental analysis of ashes and relative materials, probably due to the complexity of investigation samples.

Most of the studies used total decomposition of the matrix and "wet" form for analysis, therefore, conversion of LODs in solution to LODs in bulk material. It is important to note that the limits of detection and quantification were not predominantly calculated for matrix-matched solutions in those articles.

On the other hand, the calibration strategy using various reference materials [24] made those LODs much higher than in the other papers. Generally, because of significant disagreement between results of ICP-OES trace analysis and certified values for reference materials – it is a well-known fact – there is no benefit (in terms of precision) to using the same calibration graphs for samples with different matrices. Moreover, it was pointed out that different results were obtained for elements spiked in liquid form at least once in [28]: there was a systematic trend toward lower concentrations, and a reason for that phenomenon was not found.

Having analysed the reference fly ashes for this investigation, LA-ICP-OES results showed that the measured values (RSD < 10%) of B, Li, Co, Cr, Cu, Ni and V in all three samples are not well consistent with the certified. All the results are listed in Table 3. The best coincidence in the measured concentrations was obtained for ZUK-1.
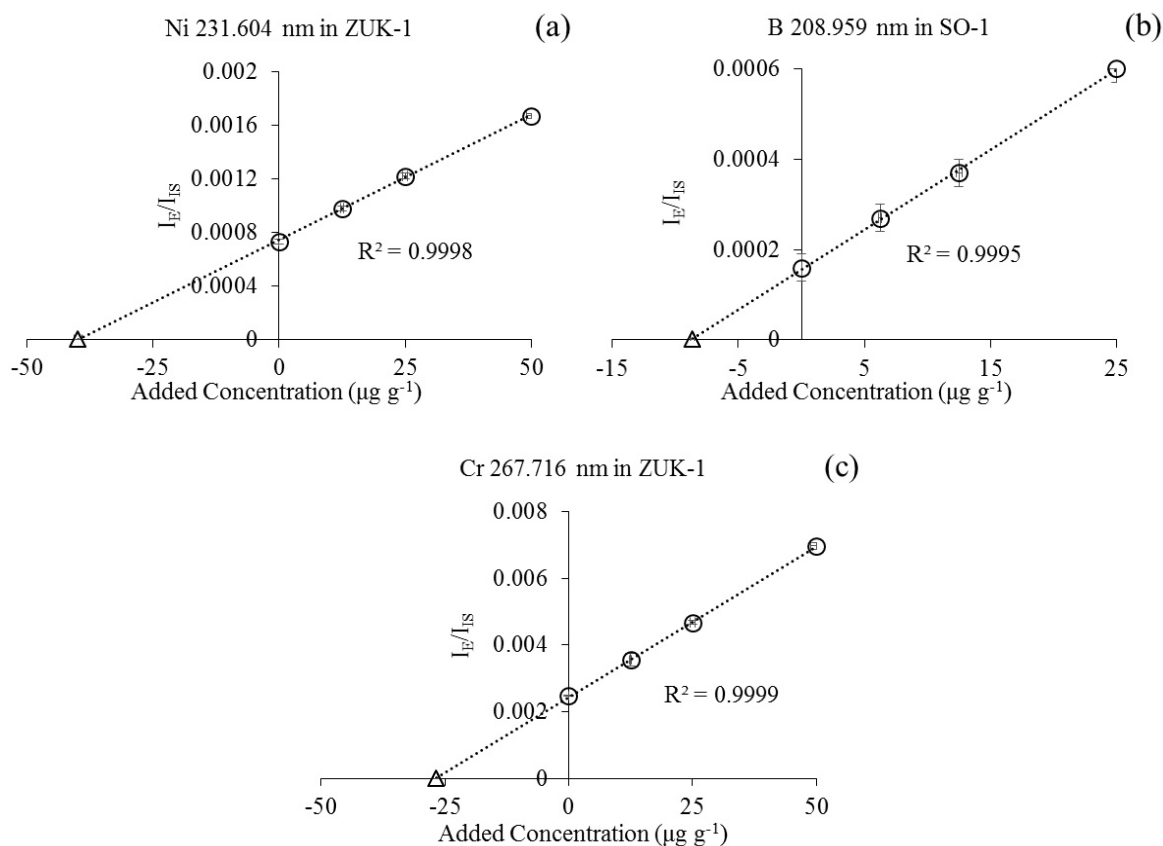

Fig. 2. Examples of calibration made by the method of standard additions for samples (CRMs) under consideration, using internal standardisation (Si I 288.158 nm)

Table 2
Limits of detection and quantification (μg g^{-1}) calculated for this study and from references

Element	B	Co	Cr	Cu	Li	Ni	V	Reference
	0.32*	**0.18**	**0.069**	**0.030**	**0.0018**	**0.20**	**0.093**	Present
LOD (μg g^{-1})		0.5	0.5	0.4			0.5	[22]
			0.213	2.85		1.01		[23]
			6.8	6.3		7.1	12.4	[24]
	1.0	0.63	**0.23**	**0.10**	**0.0061**	**0.67**	0.31	Present
		0.2	0.5	0.5		1.0		[25]
LOQ (μg g^{-1})		0.09	0.4	0.3	0.02**	0.9	0.5	[26]
		0.2	0.5	0.5		1.0	**0.1**	[27]
* Minimal values are in bold; ** Quantified with ICP-MS								

Its average recovery test is about 77%. The second on the list is ZUK-2 with more than 55%. The least one is SO-1 with more than 16% of the recovery. It should be noted that in the closest similar study [24], recovery was 78–109% for LA-ICP-OES and 51–342% for LA-ICP-MS because of some interferences and calibration with different-matrix samples.

With the presented investigation, it has been found that ZUK-2 and SO-1 contain boron and lithium. The last one is in almost equal quantity. The boron component in ZUK-2 is near the same in ZUK-1.

According to the certificates for these materials, reference values for elements were measured by different techniques such as atomic absorption spectrometry (AAS), optical emission and mass-spectrometry with inductively coupled plasma (ICP-OES and ICP-MS), atomic spectroscopy analysis (ASA), and neutron activation analysis (NAA). This set of methods is enough for the precise determination of microelements in fly ashes. In the case of SO-1, it was used only one ASA technique with spectrographs, graphite electrodes, photo-plates and mixtures of oxides as standards

for calibration [31]. Probably, the latter fact is the most crucial in this disagreement between values in the certificate and those obtained in this paper. Moreover, comparatively low sensitivity did not allow having results that are more precise for Cu and V in the certificate.

The average recovery for ZUK-1 shows that the determined concentration values are in good concordance with their certificate ones, taking into account possible deviations between various laboratories and their ways of analysis (30%). The difference revealed in the data of LA-ICP-OES and the listed range of methods employed for ZUK-2 requires further investigation as well as in the case of SO-1.

It is worth emphasizing the fact that calibration plots with new concentrations in the CRMs are well as straight lines, which made the differences between the practical and certified values more intriguing. In Fig. 3 several examples of the calibration curves can be found for Co (Fig. 3a), Cr (Fig. 3b), Ni (Fig. 3c), and V (Fig. 3d). To offset differences of a matrix in the CRMs, Sc standard solution was applied as described for spiking in Experimental Section.
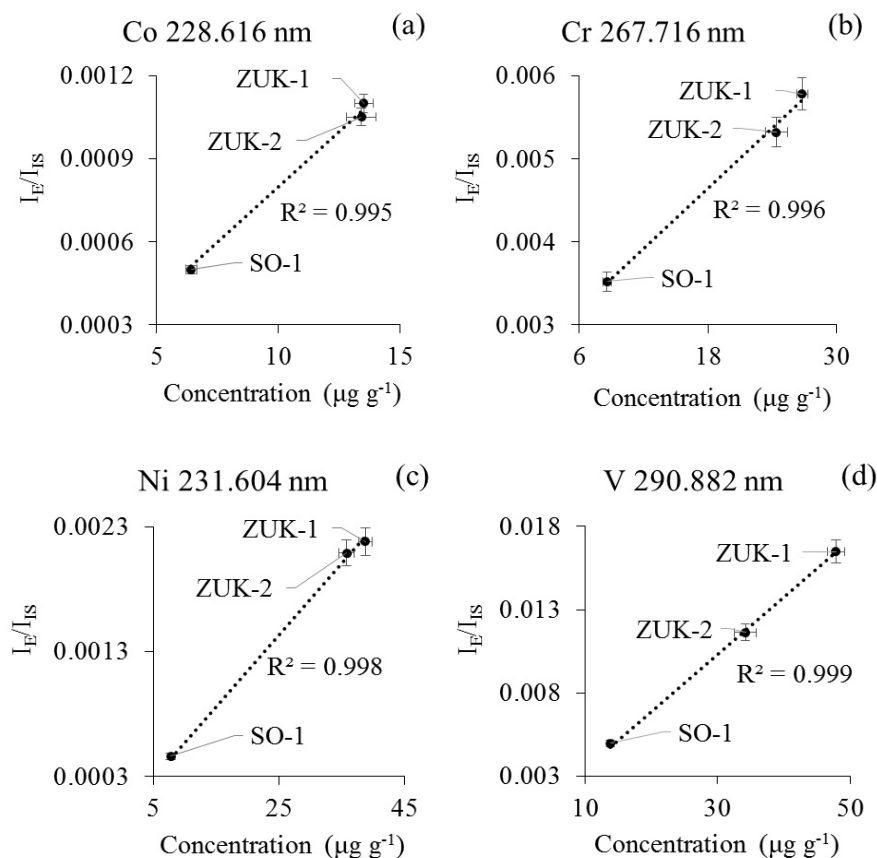
Fig. 3. Calibration plots obtained from different fly ash samples (CRMs). LA-ICP-OES measurements are made using new concentrations of elements analysed and internal standardisation (100 µg g^{-1} of Sc at 361.384 nm).

Table 3
Comparison of reference values (µg g⁻¹) to concentrations determined for standard reference materials

	SO-1			ZUK-1			ZUK-2		
	Reference (µg g⁻¹)	Determined (µg g⁻¹) RSD (%)*	Recovery (%)	Reference (µg g⁻¹)	Determined (µg g⁻¹) RSD (%)*	Recovery (%)	Reference (µg g⁻¹)	Determined (µg g⁻¹) RSD (%)*	Recovery (%)
B	-	9.41 2.5	-	97±14	105.0 1.9	108	-	92.0 4.3	-
Co	20±5	6.42 3.7	32.1	16±2	13.5 1.7	84.4	26±2	13.4 1.7	51.5
Cr	90±10	8.6 4.6	9.5	45±5	26.8 1.8	59.6	42±4	24.4 2.0	59.1
Cu	(70)**	9.1 6.5	(13)	45±7	32.0 6.2	71.1	51±7	45.0 6.6	88.2
Li	-	4.45 3.8	-	32±4	20.3 1.9	63.4	-	3.65 3.2	-
Ni	50±10	7.77 2.7	15.5	49±6	38.8 2.5	79.2	68±8	35.8 1.9	52.6
V	(100)	13.8 2.1	13.8	61±8	47.9 2.7	78.5	63±7	34.2 4.6	54.3

* for 18 independent measurements; ** non-certified values are given in parenthesis

To conclude, it is necessary to say that there is no significant difference in analytical character-istics or laser ablation between light and "heavy" elements in the method of standard additions, based on the recovery tests, calibration behaviour and signal stability.

4. Conclusions

The application of the described technique enables the possibility of solid-phase analysis for trace elements in powder fly-ash samples by LA-ICP-OES. This procedure avoids the disadvantages of melting and acid digestion for target preparation, which leads to reduced costs and analytical errors.

The analytical procedures can be accomplished with synthetic samples prepared by spiking with dissolved standards. This approach showed great stability of calibration curves. The trace elements must be distributed homogeneously in the powder samples with a particle diameter lower than 80 µm.

The suggested method is appropriate for the determination of boron and lithium in fly ashes (necessary for fertilizers and power supply elements). In ZUK-2 and SO-1 content of boron and lithium was quantified. It is also found that there were no obvious features that any difference between light and "heavy" elements in the addition calibration during the process of ablation.

The low results observed, especially for SO-1 and ZUK-2, might be the effect of liquid spiking with solid calibration samples, and detailed studies of this phenomenon are required.

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