Novel Approach for Determination of Potentially Toxic Elements via ICP–OES in Aqueous Solutions of Building Materials with Industrial Byproduct Addition

Nevenka Mijatović[1*)], Anja Terzić[1], Lato Pezo[2], Ljiljana Miličić[1], Aleksandra Milosavljević[3], Dragana Živojinović[4]

[1]Institute for Testing of Materials IMS, Vojvode Mišića Bl. 43, 11000 Belgrade, Serbia
[2]Institute of General and Physical Chemistry, University of Belgrade, Studentski Trg 12-16, 11000 Belgrade, Serbia
[3]Mining and Metallurgy Institute Bor, Zeleni Bulevar 35, Bor, Serbia
[4]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

Abstract:
New global tendencies for waste materials reusing in building materials are imposing the request for improved performances of chemical analysis methods and the improvements of matrices used. A new method for optical emission spectrometry with inductively coupled plasma (ICP-OES) is developed and validated for the chemical analysis (35 elements: Al, Be, Cd, So, Cr, Cu, Fe, Mn, Mo, Ni, V, Mo, Zn, Pb , Bi, Si, Zr, W, As, Se, Sb, Sn, Ti, Ba, B, Ag, Mg, Ca, K, Na, S, P, Ga, In, Li) in leachate of fly ash. Validation performances and the uncertainty of measurement were resolved. Uncertainty of measurements were resolved by three routes: validation procedure, participation in proficiency testing (PT) schemes and standard method. The obtained method is a new simple and effective analyzing route for determination of undesired trace elements and their quantity comprised in leachates of fly ash, and leachates of building materials with addition of fly ash (cement binders and mortars). In order to prove its accuracy and precision, the developed method was employed on laboratory samples of cement binders and mortars. Results were compared with limit values provided in the standard. Multivariate analyses, i.e. cluster analysis and principal component analysis, were applied to establish interrelations between analyzed samples, and to certify the developed ICP-OES method.
Keywords: Analytical procedures; Building materials; Waste materials; Leaching; Analytical modeling.

1. Introduction

With the rapid economic increase and the development of industry, increasingly more solid waste has been produced. Fly ash, secondary pollutant of the coal combustion in power plants has been classified as hazardous waste in many countries. High alkalinity and presence of heavy metals and soluble salts in fly ash have been focus of various studies [1-3]. The application of fly ash in the construction industry is one of the ways for successful reduction of its disposed quantities [3-5]. The immobilization of heavy metals comprised fly ash is required to prevent detrimental contamination in the natural environment. The leaching

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*) **Corresponding author:** nevenka.mijatovic@institutims.rs

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behavior of heavy metals is the main environmental risk of fly ash [1]. The leaching behavior of heavy metals is dependent on physical and chemical factors. Some of physical factors are shape and porosity of the particles, homogeneity of mineral phases, the size, wet/dry cycles, time frame, flow rate or liquid amount of leachant and degree of saturation, and temperature. Some of chemical factors are complexation processes, availability for leaching, related with pH and redox conditions, control mechanisms such as kinetic or equilibrium, and sorption processes [6]. Some elements, such as Si, Al, Ca and Fe are the major elements of fly ash which play important role on the leaching of toxic heavy metals. These elements directly affect on acid or alkaline properties of fly ash. The leaching of the heavy metals can be prevented by alkaline condition through precipitation or sorption [7].

   Leaching tests can be classified into the few categories: tests created to simulate the natural leaching of heavy metals to the environmental scenario (e.g., deinosed water or synthetic acid rain leach test), chemical extraction tests and tests which estimate fundamental leaching parameters [8]. In literature, there are many methods for leaching test in different conditions, but many studies have tried to simulate real-life scenario in environmental [8]. De-ionized water was used as leachate in this study.

   Validation of an analytical method includes the analytical procedures which is important for producing reliable and repeatable results for a routine analysis. A validation procedure contains the validation characteristics for evaluation of analytical method. There are: selectivity, accuracy, precision, detection limit, limit of quantification, sensitivity, working range and linearity, robustness and recovery [9]. The ICP-OES method is a routine analytical technique for metal determination. Validated methodology for the determination of multiple elements present in the leachate of fly ash cannot be found in the literature. Furthermore, statistical approach to validate analytical method [10-15] is relatively new method which provides a great challenge for research. There are various studies of ICP-OES, but they are related to matrices of waste materials, or they are predominantly dealing with metals determination in food [16-18] and pharmaceuticals [19].

   In this paper inductively coupled plasma optical emission spectrometry (ICP-OES) was used for the determination and validation of 35 elements (Al, Ve, Cd, So, Cr, Cu, Fe, Mn, Mo, Ni, V, Mo, Zn, Pb, Bi, Si, Zr, W, As, Se, Sb, Sn, Ti, Ba, B, Ag, Mg, Ca, K, Na, S, P, Ga, In, Li). Mathematical tools were used for the method validation and calculation of the measurement uncertainty on three solutions. One of three solutions is by in-house validation. The other two solutions are top-down approaches (data of participation in proficiency testing (PT) schemes and data given in standard method). The developed method is then employed on the leachate of fly ash, and subsequently affirmed on the leachates obtained on the crushed samples of cement binders and mortars. For a better understanding of the correlations between elements obtained upon analyzing leachates of fly ash and different building materials a chemometrics techniques were used. The experimental data were processed and interpreted by means of Principal Component Analysis (PCA) and Cluster Analysis (CA). These mathematical tools were applied to the experimental data (used as descriptors) to characterize and differentiate the observed samples [20].

2. Experimental Procedures
2.1. Materials

   The samples of five different materials were employed in the leaching test: fly ash (FA), Portland cement (CP), mixture of Portland cement and fly ash in the ratio 4:1 (CPFA), cement mortar (M) and cement mortar with the fly ash addition (MFA). Cement CEM I 42.5R, Lafarge was used. Fly ash is an aluminosilicate and a byproduct of lignite coal combustion. The samples were collected directly from the filter of power-plant plant "Kolubara" (Serbia). Particles size was in a range from 2.0 to 1250 μm [4].

The experimental cement binder (CP) was prepared from Portland cement and water via trial testing in order to acquire a self-flow consistency. Analogously, the cement binder with fly ash addition (CPFA) was prepared. Fly ash was used in the cement binder with the replacement coefficient 30 % (of total cement mass). Mortar samples were prepared and cured with respect to the method given in SRPS EN 196-1:2018 (Methods of testing cement - Part 1: Determination of strength). Portland cement was used as the binder in mortar in 30 wt.%, while the river sand was employed as the aggregate (70 wt.%). In the mix design of mortar with fly ash, 30 % replacement coefficient was applied. Water: binder ratio 0.5 was used for preparation of both mortar mixtures.

2.2. Leaching test

The samples for the leaching test were prepared in accordance to the Standard SRPS EN 12457-4:2008 (Characterization of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction)) [21]. Solidified samples of cement binders and mortars were crushed and micronized to the required particle size before applying the leaching test. The leachability of heavy metals from each of the sample (i.e. FA, CP, CPFA, M and MFA) was carried out by mixing the testing material with deionized water in liquid to solid ratio 1:10. The mixtures underwent subsequent and continuous shaking in a laboratory mixer at room temperature for the next 24 hours. The leachate was afterwards filtered by 0.45-μm filter. Metal concentrations in leachate were determined by ICP-OES method.

2.3. Calibration standards

Calibration standards were prepared from Merck standard solutions, i.e. multi-element standard for determination of 22 elements (in $mg \cdot dm^{-3}$): Al-998 ± 10, Cd-1001 ± 10 , Co-1000 ± 10 , Cr-998 ± 10, Cu-997 ± 10, Fe-1003 ± 10, Mn-1001 ± 10 , Ni-1000 ± 10, Sr-1000 ± 10, Zn-998 ± 10, Pb-1002 ± 10, Bi-1001 ± 10, Ba-998 ± 10, B-1003 ± 10, Ag-1001 ± 10, Mg-998 ± 10, Ca-1003 ± 10, K-1000 ± 10, Na-1001 ± 10, Ga-998 ± 10, In-998 ± 10, Li-998 ± 10. Standard solution for the determination of SO_4^{2-}, P, Se, Sb, Mo, As, Si, Ti, Be, Sn, V, Zr, W were (in $mg \cdot dm^{-3}$): SO_4^{2-} 1000 ± 2; P-1000±6, Se-992±8; Sb-971±7; Mo-1003±5; As-987±5; Si-9492±70; Ti-1000±2; Be-1000±2; Sn-1000±2; V-1000±2; Zr-1000±2; W-1000±2, respectively. Stock solutions were prepared by a single dilution or series of dilutions in order to acquire the working concentration set in the range from 0.50 $mg \cdot dm^{-3}$ to 100.00 $mg \cdot dm^{-3}$ for each element, except for Ca and S. Concentration range for Ca and S was set between 0.50 $mg \cdot dm^{-3}$ and 1000 $mg \cdot dm^{-3}$. De-ionized distilled water was used for the preparation all solutions.

2.4. Preparation of the matrix spike standards

Preparation of the matrix spike standards for all 35 elements (Al, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, V, Sr, Zn, Pb, Bi, Si, Zr, W, As, Se, Sb, Sn, Ti, Ba, B, Ag, Mg, Ca, K, Na, S, P, Ga, In, Li) was conducted by adding standard solutions with known concentration to real samples, i.e. fly ash leachates. Contents of some elements in spiked standards were higher than the standard calibration solutions for value of concentration each elements in the real samples.

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2.5. Instrumental analysis

An ICP analyzer, Spectro Genesis was used in the experiment. This apparatus is equipped with a plasma generator working at 27.12 MHz which allows the „robustness" of plasma. The device is capable of working with different solution densities without the plasma exhaustion. Generator power is 1.700 KW. The consumption of argon during analysis is 16 l/min. A holographic grating is 2400 point/mm. The plasma is positioned radially, with the wave length range of 175 - 775 nm. High purity argon (99.9999 %) is used for the plasma initiation, as a carrier gas, and for the cooling quartz system where the plasma develops. The instrumental system uses Smart Analyzer Vision software.

2.6. Statistical analysis

The data (mean values) collected upon leachate ICP analyses were statistically processed. The two pattern recognition methods, including the Cluster Analysis (CA) and Principal Component Analysis (PCA) were applied effectively to classify and separate the different samples. The assessment of CA and PCA of the acquired outcomes was performed using Statistica software version 12 (Statistica, StatSoft Inc. 2012, USA)®.

3. Results and Discussion
3.1. Validation method

According to EURACHEM 1998[•] the validation was performed by evaluating the selectivity, i.e. the ability to unequivocally assess the analyte in the presence of components that are expected to occur in the solution (Matix effect), linearity, limit of detection (LoD), limit of quantification (LoQ), precision (repeatability and reproducibility) and accuracy [22].

3.2. Selectivity, linearity, limit of detection (LoD) and limit of quantification (LoQ)

Parameters of calibration lines are: wavelength of the emission line (λ), limits of detection (LoD), limits of quantification (LoQ), correlation coefficients (R), Y-intercepts, slopes of linear function, proportion of two slopes of calibration lines - one for the original standard solution and the other for the derived spike standard solution. The working ranges for these parameters are given in Tab. I.

Parameters of linearity and selectivity were determined using the Merck standard stock solutions with the concentration range from 0.50 to 100.00 mg·dm^{-3}. Four of the most sensitive lines were selected for each element from the software wavelengths library. The working wavelengths with minimal spectral interference and the matrix effects of the sample were selected by comparing slopes of the proportion of two calibration lines - one of the original standard solution and the other which was derived from the spike standard solution (Tab. I). The selected wavelength from the available specter/database of wavelengths is one in which the ratio of these slopes is closest to 1.00. Upon selecting the appropriate wavelengths, the quantitative determination method was carried out manually. The background for each of the selected lines was corrected in order to achieve as many as possible relationships with the signal intensity. It was derived from the background of the element and the signal itself [23]. LoD, LoQ, correlation coefficients, Y-intercepts and slopes of linear function are automatically calculated by Smart Analyzer Vision software.

If correlation coefficient is close to 1 then the linearity of the method is better. Tab. I shows that the correlation coefficients are higher than 0.99. This highlights the fact that the

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[•] https://www.eurachem.org/index.php/publications/pubarch/143-gdmv98

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methods which were applied within the selected range of the concentrations gave the results that are directly proportional to the concentration of elements in the fly ash sample [24]. Values obtained for the LoD and LoQ that the targeted performance was achieved by application of this method. Target values for LoQ are adopted from the Standard SRPS EN ISO 11885:2011 (Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885:2007)).

Tab. I Parameters of calibration lines of 35 chemical elements found in fly ash leachate.

Element	Wave length, nm	Y-intercept cps	Slope, cps dm^3/mg	R^2	LOD, $mgdm^{-3}$	LOQ, $mgdm^{-3}$	Target value, $mgdm^{-3}$	Proportion slope cal/slope spike sample
Al	394.401	2.5341×10^{-5}	0.0052	0.99992	0.0028	0.0096	0.0100	0.92
Sb	206.883	9.5849×10^{-5}	0.4919	1.00000	0.0029	0.0098	0.0100	0.98
As	189.042	1.6497×10^{-4}	0.0405	0.99999	0.0036	0.0120	0.0180	1.09
Ba	455.404	8.2659×10^{-8}	0.0081	0.99999	0.0001	0.0004	0.0060	1.12
Be	313.042	1.5763×10^{-7}	0.0210	0.99999	0.0003	0.0012	0.0020	1.10
Bi	190.241	2.4285×10^{-4}	0.0224	1.00000	0.0030	0.0101	0.0400	1.15
B	249.773	6.4484×10^{-6}	0.0057	1.00000	0.0011	0.0037	0.0040	1.11
Cd	226.502	7.5416×10^{-6}	0.0350	0.99998	0.0002	0.0008	0.0040	1.07
Ca	317.833	9.4984×10^{-8}	0.2107	0.99992	0.0021	0.0071	0.0260	1.06
Cr	205.552	1.5949×10^{-5}	0.1918	0.99999	0.0002	0.0006	0.0010	1.03
Co	228.616	1.4980×10^{-5}	0.1804	0.99999	0.0016	0.0055	0.0060	0.97
Cu	324.754	4.5598×10^{-6}	0.2239	0.99999	0.0015	0.0054	0.0090	0.98
Ga	417.206	8.9710×10^{-6}	0.0111	0.99999	0.0145	0.0482	0.0500	1.16
In	230.606	1.2892×10^{-4}	0.2404	0.99999	0.0131	0.0439	0.0500	1.12
Fe	259.941	5.4508×10^{-6}	0.0477	0.99979	0.0017	0.0060	0.0060	1.06
Pb	220.353	1.3169×10^{-4}	0.2294	0.99999	0.0031	0.0103	0.0140	1.04
Li	670.780	1.3731×10^{-6}	0.1575	0.99999	0.0015	0.0058	0.0060	0.97
Mg	279.079	9.1418×10^{-6}	0.4919	0.99995	0.0096	0.0323	0.0330	0.99
Mn	259.373	1.5278×10^{-6}	0.2378	0.99999	0.0002	0.0008	0.0010	0.90
Mo	202.095	1.5598×10^{-6}	0.2341	0.99999	0.0010	0.0036	0.0300	0.97
Ni	231.604	2.5065×10^{-5}	0.4055	0.99996	0.0036	0.0119	0.0150	0.97
P	213.618	1.4806×10^{-5}	0.4647	0.99998	0.0035	0.0192	0.0500	1.04
K	766.491	2.0712×10^{-4}	0.0613	1.00000	0.0092	0.0306	0.0660	1.11
Se	196.090	1.9653×10^{-4}	0.1300	0.99999	0.0333	0.1000	0.1000	1.12
Si	288.158	3.5882×10^{-5}	0.3960	0.99999	0.0086	0.0287	0.0300	0.96
Ag	328.068	5.0701×10^{-6}	0.1781	0.99999	0.0019	0.0035	0.0200	1.03
Na	585.502	$7,8290 \times 10^{-6}$	0.5188	0.99998	0.0146	0.0398	0.0930	1.07
Sr	460.733	1.0766×10^{-5}	0.3004	0.99998	0.0020	0.0080	0.0100	1.08
S	182.034	1.9909×10^{-4}	0.6526	1.00000	0.0087	0.0291	0.0390	1.06
Sn	242.949	4.6390×10^{-4}	0.1429	0.99998	0.0277	0.0923	0.1000	1.05
Ti	336.121	1.4184×10^{-6}	0.3767	0.99999	0.0017	0.0056	0.0100	1.03
W	207.911	5.9536×10^{-5}	0.0017	0.99991	0.0010	0.0032	0.0300	0.99
V	292.464	9.8196×10^{-6}	0.0704	1.00000	0.0030	0.0096	0.0100	1.03
Zn	213.856	5.4978×10^{-6}	0.2391	0.99999	0.0007	0.0023	0.0030	0.98
Zr	339.198	1.3639×10^{-6}	0.0636	0.99993	0.0100	0.0320	0.0500	1.05

3.3. Accuracy and precision

Accuracy and precision of the proposed method were tested by the determination of the content of each of the analyzed elements and also by comparing these values with the concentration of the certified standard solutions. This step of the validation was determined by the contents of each of the analyzed elements using Merck standard stock solutions. The 2.00 mg·dm^{-3} concentration was applied for all of the elements, with exception of Ca, S, Al, Si, K and Na. Standard stocks of 100.00 mg·dm^{-3} were used for Ca and S. 20.00 mg·dm^{-3} concentration was used for Al, Si, K and Na. These standard solutions were selected for the determination of accuracy and precision on basis of the approximate contents of the mentioned elements in real fly ash samples.

Repeatability and reproducibility, as the most common precision measurements, were assessed on the daily basis. Also, the variations between daily measurements were estimated. The results obtained for the repeatability were conducted on six parallel samples by a single operator using the same equipment. Precision (repeatability) was expressed as % RSD (Tab. II). Accuracy is given as the difference in recovery of the CRM target value and the obtained value (Tab. II).

Tab. II Accuracy (mean spike recovery %) and precision (repeatability as %RSD) for 35 elements found in fly ash leachate.

Element	$\overline{X} \pm SD$, mg$\cdot$dm^{-3}	Recovery, %	RSD, %	Element	$\overline{X} \pm SD$, mg$\cdot$dm^{-3}	Recovery, %	RSD, %
Al	19.07±0.148	95.3	0.7	Mn	1.909±0.065	95.0	3.4
Sb	1.900±0.023	95.0	1.2	Mo	1.977±0.076	98.5	3.8
As	2.081±0.064	104.0	3.1	Ni	1.962±0.089	90.0	4.5
Ba	1.942±0.045	97.0	2.3	P	1.862±0.076	93.0	4.1
Be	1.971±0.053	98.5	2.7	K	20.051±0.187	100.3	0.9
Bi	1.920±0.052	96.0	2.7	Se	1.891±0.065	94.5	3.4
B	1.962±0.076	98.0	3.8	Si	20.011±0.187	100.1	0.9
Cd	2.023±0.071	101.0	3.5	Ag	1.931±0.067	96.5	3.4
Ca	96.984±0.265	96.9	0.3	Na	19.972±0.176	99.9	0.9
Cr	1.935±0.049	96.5	2.5	Sr	1.894±0.056	94.5	2.9
Co	1.954±0.056	97.5	2.7	S	101.635±0.298	101.6	0.3
Cu	1.963±0.054	98.0	2.8	Sn	1.955±0.045	97.5	2.3
Ga	2.064±0.067	103.0	3.2	Ti	1.927±0.056	96.0	2.9
In	1.975±0.039	98.5	1.9	W	1.948±0.052	97.0	2.7
Fe	1.942±0.045	97.0	2.3	V	1.929±0.050	96.0	2.6
Pb	1.981±0.076	99.0	3.8	Zn	1.976±0.038	98.5	1.9
Li	1.920±0.068	96.0	3.5	Zr	1.980±0.058	94.5	2.9
Mg	1.892±0.076	94.5	4.0				

Results that are given in Tab. II show that the recoveries for all elements were generally within ±7 % of the target values. The set targets for 2.00 mg·dm^{-3} concentrations were relative standard deviations of repeatability below 5 %. RSD was below 1 % for 20.00 mg·dm^{-3} concentrations. RSD-s for Ca and S were 0.3 % for 100.00 mg·dm^{-3} concentration.

3.4. Measurement uncertainty

Three procedures for the measurement uncertainty evaluation were used. The first procedure was based on the data of validation (i.e. in-house validation approach). The second procedure was based on the data of the participation in proficiency testing (PT) schemes and the third procedure was based on the data given in standard method (i.e. top-down approaches).

3.5. Measurement uncertainty calculated by validation data

Measurement of the uncertainty was calculated by Nord test concept, i.e. recovery test approach [25]. In this approach, the sources of uncertainty are grouped into two major groups of components: precision and trueness. The two major components in the single laboratory validation and QC approach are the within-laboratory reproducibility and bias. This approach uses the data of quality control (*u(Rw)*) and data of validation (*u(Bias)*) to estimate measurement uncertainty for routine analyses according the equation (1):

$$u_c \ (\%) = \sqrt{u(Rw)^2 + (u(Bias))^2} \qquad (1)$$

where: u_c is combined standard uncertainty, $u(Rw)$ is uncertainty of the estimate within-laboratory reproducibility, and $u(Bias)$ is uncertainty of the estimate of the laboratory and the method bias.

The uncertainty component for within-laboratory reproducibility ($u(Rw)$) was estimated using repeated measurements of a control sample (similar matrix and concentration as the test samples) over a long period of time. *Rw* includes repeatability and between-days (runs).

Bias includes both - laboratory and procedural bias. In this case, uncertainty of *Bias* was calculated from the validation data (accuracy) of the spike recovery and data from the certificate of calibration of reference materials and volumetric glassware (volumetric flasks, pipettes) according to the equation (2):

$$u(Bias) = \sqrt{RMS_{Bias}^2 + u(Cref)^2} \qquad (2)$$

where: *u(Bias)* is contribution to the uncertainty from bias, and $u(Cref)$ uncertainty component from the certified or nominal value.

The main sources of measurement uncertainty in this case were: uncertainty of the calibration of reference materials, uncertainty of measured intensities of the reference solutions, uncertainty of the delivered volumes and recovery of the method. Recovery eliminates possible interferences in the method for the samples of selected matrix. After estimation, all sources of uncertainty were combined and converted in order to combine the standard uncertainty $u(x)$. The final result was given as the expanded uncertainty $U(x)$, which was calculated as $U(x)=k \cdot u(x)$, where k is the coverage factor corresponding to a 95 % confidence level. Calculations were made by using Mathcad software which was checked and validated before application. The results of the measurement uncertainty by data of validation for 35 elements in leachate from the fly ash sample are summarized in Tab. III.

3.6. Measurement uncertainty calculated by the data of participation in proficiency testing (PT) schemes

In case of measurement uncertainty calculation via data from proficiency testing (PT) schemes, reproducibility standard deviation of a measurement from inter-laboratory comparisons (s_R) are used directly for each compared element as an approximation of $u(x)$. The expanded uncertainty $U(x)=2 \cdot s_R$ is calculated for each element. The results of the measurement of uncertainty for 17 compared elements are also listed in Tab. III. This method may over-estimate the uncertainty depending on the quality of the laboratory (i.e. worst case scenario). It may also under-estimate the uncertainty due to the sample's inhomogeneity or matrix variations.

3.7. Measurement uncertainty calculated by data provided in the standard method

In this case, reproducibility standard deviation of a measurement (s_R), given in standard method was directly used and the expanded uncertainty was calculated as $U(x) = 2 \cdot s_R$ for each investigated element. The results of the uncertainty measurements calculated by data given in standard method are given in Tab. III.

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Expanded uncertainties of the measurements, calculated by in-house validation approach are lower than 10 %. These values are lower than values obtained via two other methods. Since the uncertainty should be smaller than the target value, the GUM proposes that if the target uncertainty is not defined in a regulation or specification, an additional tolerance of 20-30 % can be considered in order to allow the variability of the uncertainty estimation process [26]. The tolerance of 20-30 % is defined considering the usual degrees of freedom of standard uncertainties of measurements in chemistry and models of their variability. All values in Tab. III are below 30 %, which is in accordance with GUM principles. Variability of the uncertainty estimation process is illustrated with the variability of the estimation of the standard deviation of a population obtained through different ways.

Tab. III Measurement uncertainty for 35 elements found in the fly ash leachate.

Element	Working range	Measurement uncertainty via validation data,%	Measurement uncertainty via PT data, %	Measurement uncertainty via standard method data, %
Al	0.05-10	±9.04	±12.04	±17.44
Be	0.05-10	±9.22	-	±17.02
Cd	0.05-10	±9.98	-	±14.95
Co	0.05-10	±9.04	-	±12.04
Cr	0.05-10	±9.06	±24.14	±11.36
Cu	0.05-10	±9.08	-	±12.28
Fe	0.05-10	±9.02	-	±13.32
Mn	0.05-10	±9.57	-	±12.97
Mo	0.05-10	±9.42	±18.21	±12.32
Ni	0.05-10	±9.32	-	±12.32
V	0.05-10	±9.48	±19.91	±11.08
Sr	0.05-10	±4.91	±5.52	±10.21
Zn	0.05-10	±8.42	±20.91	±11.72
In	0.05-10	±9.94	-	±11.93
Pb	0.05-10	±9.68	-	±10.80
Bi	0.05-10	±9.18	-	±12.18
Si	0.05-10	±4.02	±4.62	±10.88
Zr	0.05-10	±9.01	-	±14.61
W	0.05-10	±9.09	-	±11.19
As	0.05-10	±8.75	±16.09	±10.95
Se	0.05-10	±6.29	±7.12	±11.29
Sb	0.05-10	±9.07	-	±10.67
Sn	0.05-10	±9.15	-	±11.19
Ti	0.05-10	±9.37	-	±11.57
Ba	0.05-10	±9.67	±25.21	±11.57
B	0.05-10	±9.32	±14.03	±13.72
Ag	0.05-10	±9.10	-	±13.90
Ga	0.05-10	±9.42	-	±16.42
Mg	0.1-100	±9.36	±19.93	±16.41
Ca	0.1-100	±9.01	±14.08	±11.11
K	0.1-100	±4.56	±5.95	±7.96
Li	0.1-100	±9.35	±12.41	±15.85
Na	0.1-100	±5.16	±6.18	±7.56
S	0.1-100	±7.25	±8.02	±12.55
P	0.1-100	±9.07	-	±12.07

Standard deviations of a population obtained via data of PT and via data given in standard method are usually higher than the standard deviation of a population via validation

method, because standard deviation of a population in PT and standard method are related to the increasing number of laboratories and different procedures. Different approaches for the evaluation of measurement uncertainty evaluation can be selected, depending on the purpose and the available data, but when data are available in the laboratory (validation, quality control), a possible approach is single laboratory validation and quality control data. However, in most of the cases, if detailed knowledge of the different uncertainty components is not needed, a laboratory using a standard method within its scope should use the inter-laboratory approach. The results of the validation and comparison of different approaches for estimation of the uncertainty measurement gave unique, significant and original contribution to the development and application of ICP-OES method for the analysis of metal elements present in samples of the fly ash leachate. The improvements to this method for chemical analysis, which is widely used in the building materials industry, facilitate and speed up the process of trace metals determination in the aqueous solutions of fly ash and similar waste materials.

4. Application of the developed ICP–OES method on leachates of building materials with industrial byproduct addition

The method that was developed and validated for the analysis of the contents of 35 metals in the leachate obtained from fly ash sample can be applied for the testing of leachates of other building materials (e.g. binders or mortars) that contain fly ash as an additive. Thereby, the concentrations of 35 elements were determined on the fly ash leachate and leachates obtained from experimental binders (cement (CP) and cement with fly ash (CPFA)) and mortars (cement mortar (M) and mortar with fly ash addition (MFA)) via procedure described in the Chapter 2.2. The acquired values given in Tab. IV are compared with the limit values for certain elements where it was possible. Namely, according to the Waste Acceptance Criteria [27], leaching limit values for Sb, As, Ba, Cd, Cr, Cu, Pb, Mo, Ni and Se are proposed in order to classify a waste material as hazardous or non-hazardous.

As it can be seen from the results given in Tab. IV, the values of all leached elements (i.e. where comparable values exist) are below the proposed leaching limit values for the waste to be classed as hazardous [27]. The only element whose concentration (0.970 mg/kg) in the fly ash leachate was above its leaching limit value (0.500 mg/kg) is arsenic. Since arsenic normally condenses on the surface of fly ash particle as sparingly soluble arsenate species, the obtained leachability of as highlighted its potentially high mobility. However, As concentrations found in leachates of CPFA and MFA are far below concerning value, therefore fly ash can be regarded as non-hazardous material for usage as additive in building materials (binders and mortars). The amounts of the leached Ca vary from 2020 mg/kg to 4120 mg/kg, however calcium is not regarded as an element of concern, i.e. toxic/hazardous component in a building material. High amount of calcium present in all leachates including the fly ash leachate is of particular significance, because Ca participates in the cement hydration and formation of ettringite and other secondary Ca-hydrated phases that are likely to incorporate and retain certain elements such as As, S, Sr, V and B, and to prevent them from migrating into environment [28]. If FA leachate and leachates of CPFA and MFA were to be compared, it can be concluded that the concentrations of Si, Mg and Li were also reduced in CPFA and MFA samples because these elements were immobilized within the microstructure of binder and/or mortar during the cement process hydration. The concentrations of Sb, Be, Bi, Cd, Cr, Co, Cu, Ga, In, Pb, Mn, Mo, Ni, P, Se, Ag, Sn, Ti, W, Zn and Zr were, in all leachates, below the limit of quantification (LoQ), therefore they can be regarded as non-harmful [29]. The concentrations of aluminium in leachates obtained from crushed binders and mortar samples increased with fly ash addition. The addition of fly ash did not significantly influence quantity of Ba, K, Na and Fe in the observed samples of

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building materials. Also, the concentrations of barium in all leachates were far below its upper limit value (20 mg/kg) [30].

The results presented in Tab. IV indicate that heavy metals contents contained in the fly ash leachate are higher than the adequate values obtained on the leachates of cement binders and mortars. This can be explained by the fact that during the cement hydration process heavy metals are bound and trapped within the crystalline structure of newly formed cement minerals, as it is reported by various authors in the literature [30-32].

Tab. IV Contents of metal elements in leachates of fly ash, experimental binders and mortars.

Element, mg/kg*	Fly ash (FA)	Binders		Mortars		Limit values (LIM)
		Cement binder (CP)	Cement binder with fly ash (CPFA)	Cement mortar (M)	Mortar with fly ash (MFA)	
Al	28.344±0.016	21.444±0.018	27.534±0.020	21.157±0.035	28.134±0.054	-
Sb	<0.010	<0.010	<0.010	<0.010	<0.010	0.060
As	0.970±0.014	<0.010	<0.010	<0.010	<0.010	0.500
Ba	3.108±0.017	3.273±0.018	3.175±0.010	3.089±0.011	3.093±0.015	20.00
Be	<0.010	<0.010	<0.010	<0.010	<0.010	-
Bi	<0.010	<0.010	<0.010	<0.010	<0.010	-
B	21.177±0.023	0.251±0.004	0.252±0.003	0.293±0.003	0.331±0.003	-
Cd	<0.010	<0.010	<0.010	<0.010	<0.010	0.040
Ca	2020.575±0.592	3718.124±0.362	4120.325±0.312	3855.245±0.112	4679.155±0.302	-
Cr	<0.100	<0.100	<0.100	<0.100	<0.100	0.500
Co	<0.100	<0.100	<0.100	<0.100	<0.100	-
Cu	<0.100	<0.100	<0.100	<0.100	<0.100	2.000
Ga	<0.020	<0.020	<0.020	<0.020	<0.020	-
In	<0.500	<0.500	<0.500	<0.500	<0.50	-
Fe	0.657±0.044	0.573±0.011	0.575±0.015	0.557±0.012	0.558±0.015	-
Pb	<0.100	<0.100	<0.100	<0.100	<0.100	0.500
Li	4.945±0.017	2.294±0.007	3.632±0.009	<0.100	<0.100	-
Mg	17.158±0.124	<0.030	<0.030	<0.030	<0.030	-
Mn	<0.030	<0.030	<0.030	<0.030	<0.030	-
Mo	<0.100	<0.100	<0.100	<0.100	<0.100	0.500
Ni	<0.100	<0.100	<0.100	<0.100	<0.100	0.400
P	<0.100	<0.100	<0.100	<0.100	<0.100	-
K	118.890±0.327	116.147±0.525	113.136±0.327	118.025±0.176	116.165±0.136	-
Se	<0.050	<0.050	<0.050	<0.050	<0.050	0.100
Si	26.596±0.124	3.181±0.121	1.157±0.059	1.345±0.060	1.173±0.089	-
Ag	<0.030	<0.030	<0.030	<0.030	<0.030	-
Na	87.744±0.397	86.123±0.089	85.325±0.097	87.321±0.037	85.358±0.017	-
Sr	16.481±0.286	8.079±0.057	9.032±0.067	5.325±0.017	5.225±0.027	-
S	1597.957±5.482	166.325±0.017	166.385±0.020	168.023±0.018	166.589±0.020	-
Sn	<0.070	<0.070	<0.070	<0.070	<0.070	-
Ti	<0.300	<0.300	<0.300	<0.300	<0.300	-
W	<0.060	<0.060	<0.060	<0.060	<0.060	-
V	1.509±0.012	<0.010	<0.010	<0.010	<0.010	-
Zn	<0.300	<0.300	<0.300	<0.300	<0.300	4.000
Zr	<0.200	<0.200	<0.200	<0.200	<0.200	-

*Values are expressed as milligrams per kilogram (mean ± standard deviation of five replicates).

4.1. Cluster analysis (CA)

Fig. 1 indicates the dendrogram of CA for the observed samples (explained by the element concentration variables). The complete linkage algorithm and City block (Manhattan) distances are used as the measure of similarity between the samples [33]. City block distances (appeared on ordinate axis) are measured as the average distinction over the dimensions of the observed samples. The similarities of the samples are presented by the distance on the dendogram. Samples CP, M, CPFA and MFA could be considered as the members of one cluster, which shared the similar chemical composition, while samples FA and LIM were distinct, having different characteristics.
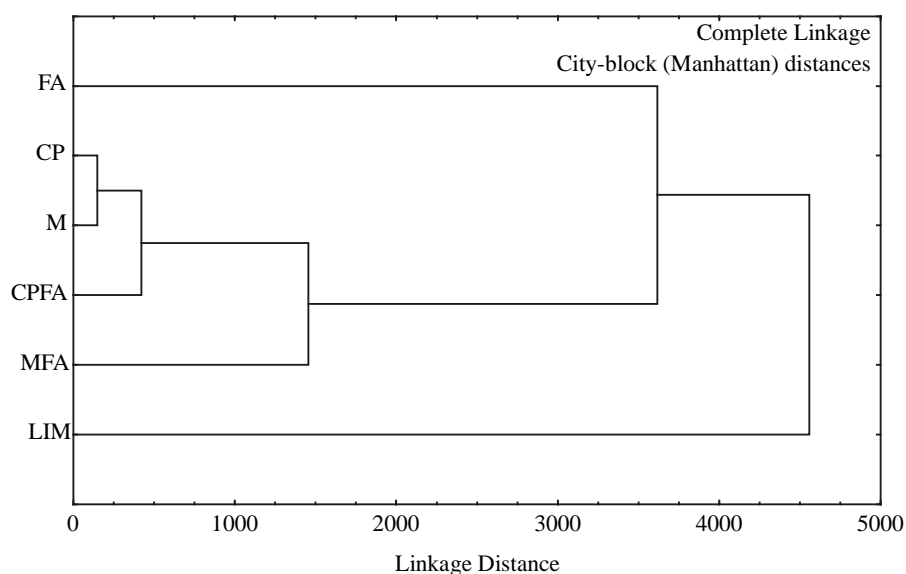
Fig. 1. Tree diagram for leachates of fly ash, binders and mortars.

Similarities of the investigated samples are illustrated in the Fig. 1. The first cluster is separated and it comprises only FA. The second cluster consists of the samples CP, M, CPFA and MFA. It can be concluded that significantly less quantities of heavy metals have been leached out by de-ionized water during leaching trial from the experimental samples of building materials (binders and mortars) than from the original fly ash sample. This is consistent with the theory that certain heavy metals comprised in fly ash sample have been immobilized in the crystalline structures of binders and mortars during cement hydration. The LIM cluster being separated indicates that results of leaching tests conducted on the ash additive and building materials are different than set limit values (LIM), i.e. quantities of heavy metals are far below their upper limit. Thereby the investigated materials can be classified as safe, i.e. non-harmful for application in civil engineering. Thereby, Fig. 1 showed three different groups of results and confirms that validated ICP-OES method can be applied for all tasted leachates.

4.2. Principal component analysis

Principal component analysis is a mathematical procedure used as a central tool in exploratory data analysis [34, 35]. The PCA, applied to the given data set, Tab. IV, has shown a differentiation between the samples according to the observed parameters. Quality results show that the first two principal components, accounting for 78.55 % of the total variability for leachate samples can be considered sufficient for data representation (Fig. 2).

Considering the map of the PCA (Fig. 2) performed on the data, the variables contributed negatively according to the first principal component were the concentrations of: Fe, Al, Sn, Ga, Be, W, Mn, K, Na, Ti, In, P, Ag, Bi and Co (all of these variables contributed between 3.5 and 3.7 %, based on the correlations). The variables which showed the positive influence towards the first principal component were: Ba, Cr, Cd, Se, Sb, Zn, Pb, Mo, Ni and Cu (their contributions were almost equal, close to 3.7 %). The concentrations of: As, B, V, Sr, Si, Mg and *S* showed the positive impact on the second principle component (these variables contributed between 7.0 and 14.8 %, based on the correlations), while the concentration of Ca (3.3 %) showed the negative influence on the second principal component calculation. PCA graphic showed quite good discrimination between samples of leachate of fly ash, mortars and cement binders.

The points shown in the PCA graphics, which are geometrically close to each other, indicate the similarity of patterns that represent these points. The orientation of the vector describing the variable in factor space indicates an increasing trend of these variables, and the length of the vector is proportional to the square of the correlation values between the fitting value for the variable and the variable itself. The angles between corresponding variables indicate the degree of their correlations (small angles corresponding to high correlations).

The influence of variables can be observed in Fig. 2. Samples CP, MFA, CPFA and M are located at the bottom left corner of the PCA graph, these samples are similar to each other, according to the increased concentration of Fe, Al, Sn, Ga, Be, W, Mn, K, Na, Ti, In, P, Ag, Bi, Co and Ca. Sample FA is located at the upper part of the graph, showing the increased concentration of Sr, S, Si, B, V, Mg and As, while the LIM values are located at the right part of the graph, showing the increased concentrations of Ba, Cr, Cd, Se, Sb, Zn, Mo, Ni, Pb and Cu.
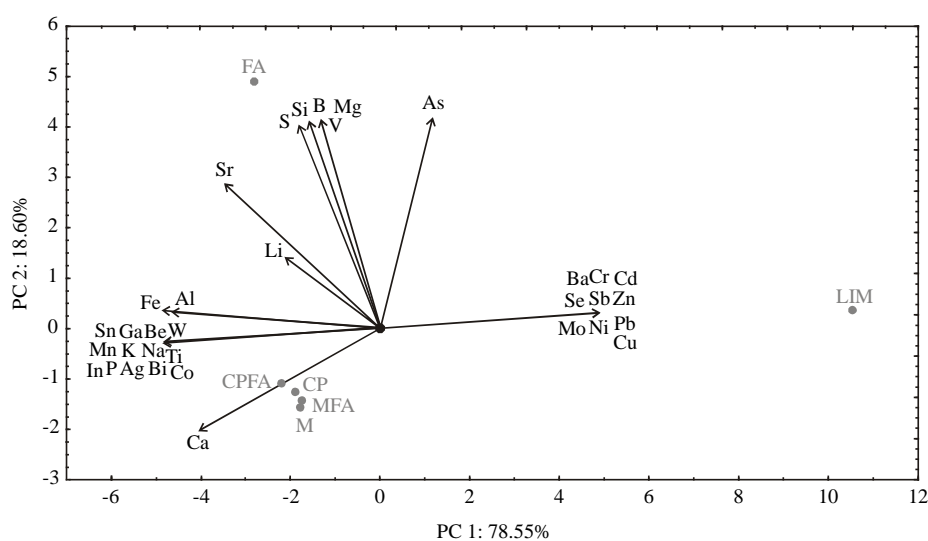
Fig. 2. Biplot graphic of leachates of fly ash, binders and mortars.

The PCA diagram illustrated in Fig. 2 shows similarity with the results of CA analysis for the classification of materials. Ca, Al and Fe are positioned at lower left side of the PCA diagram. Their disposition indicates that these elements are characteristic for binders and mortars (CP, CPFA, M, MFA). Similarly, Si is positioned at upper left side of the PCA plot, which is in accordance with chemical composition on fly ash. Namely, fly ash is alumoslicate, thereby both Al and Si are situated at the left side of the diagram with FA. Analogously, cement binders and mortars are positioned on the left due to the abundance of Si, Al and Ca in their compositions. Trace elements such as V, B, Sr, Li, Sn, Ga, Be, W, In, P, Ag, Bi and Co are also on the left side, which means that their content in Fa, CP, CPFA, M and MFA is detectable, but still significantly lower than proposed limit values. Namely, LIM point is positioned at the opposite, i.e. right side of the PCA graph. The group of trace elements (Ba, Cr, Cd, Se, Sb, Zn, Mo, Ni, Pb) are on the right side of the diagram, which indicates that their content is scarce in leachates of all investigated samples.

PCA analysis made clear distinction between fly ash leachate and leachates obtained on the samples of building materials, by positioning them at opposite sides: FA at the upper side of the graph, CP, CPFA, M and MFA at the bottom of the diagram. These points out to the fact that certain heavy metals present in the fly ash are more readily leachable from the ash sample itself, than from the structure of cementitious material in which fly ash is incorporated. PCA and CA analyses confirmed excepted different leachability of heavy

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metals from the samples of fly ash and building materials. Established chemometric correlations between samples of investigated materials indicates that validated ICP-OES method for quantification of trace elements in the leachate of fly ash could be utilized for quantification of the same elements in leachates of other cementitious materials.

5. Conclusion

A fully validated novel method for metal analysis conducted on fly ash leachate and leachates of cement binders and mortars was established in this paper. It is verified that this ICP-OES method is reliable and accurate for quantification of 35 selected metals in leachate of samples. Satisfactory validated performances of method such as a low LoQ, good linearity and high accuracy and precision is very important for reliably results of samples. All uncertainty results were below 30%, which is in accordance with GUM principles. The development of this method facilitates and speeds up the process of trace metals identification and quantification in the leachates obtained from the samples of building materials, industrial by-products used as additives in civil engineering and composite materials with these industrial by-products in their composition.

Chemometric analysis (CA and PCA) of the leaching test results indicated that heavy metals present in the fly ash are more readily leachable from the ash sample itself, than from the structure of cementitious material in which fly ash is incorporated. Both of multivariate analyses confirm that validated ICP-OES method was successfully applied to determine multi-element in leachates of industrial by-products and materials that include these secondary raw resources in their composition.

Acknowledgments

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Садржај: Нове глобалне тенденције да се отпадни материјали поново користе као грађевински материјали намећу захтев за побољшаним перформансама хемијских метода у различитим матриксима. Нова метода за оптичку емисиону спектрометрију са индуктивно спрегнутом плазмом (ICP-OES) је развијена и валидована за хемијске анализе (35 елемената: Al, Be, Cd, So, Cr, Cu, Fe, Mn, Mo, Ni, V, Mo, Zn, Pb , Bi, Si, Zr, W, As, Se, Sb, Sn, Ti, Ba, B, Ag, Mg, Ca, K, Na, S, P, Ga, In, Li) у елуатима пепела. Израчунате су валидационе перформансе и мерна несигурност. Мерна несигурност је израчуната на три начина: валидације поступка, на основу параметара добијених из PT шема и на основу података из стандарда методе. Објављена метода је нова, једноставна и ефикасна за рутинске анализе одређивања садржаја нежељених елемената у траговима у елуатима пепела и елуатима грађевинских материјала са додатком летећег пепела (цементне пасте и малтери). Да би се доказала тачност и прецизност, развијена метода је примењена на лабораторијским узорцима цементних везива и малтера, а резултати су упоређени са граничним вредностима наведеним у стандарду. Мултиваријационе анализе односно кластер анализа и анализа главних компоненти, су примењене да успоставе однос између анализираних узорака, као и да потврде примену развијене ICP-OES методе.

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Кључне речи*: Аналитичке процедуре, Грађевински материјали, Отпадни материјали, Лужење, Аналитичко моделовање.*