



Improvement and modification of the energy-dispersive X-ray fluorescence method for the determination of metal elements in cement leachates – A chemometric approach

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Abstract: A modification of an analytical procedure for the energy-dispersive X-ray fluorescence (EDXRF) quantification of ten chemical elements (As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn) in the leachates obtained from cement binders was developed. Twenty-nine testing samples were used in the experiment. All samples were based on Portland cement. Fly ash of different origin, zeolite and bentonite were employed as mineral additives in the cement binders. Distilled water was used as the leachate. Validation of the modified EDXRF procedure was conducted in terms of limits of detection and quantification, working range, linearity, selectivity, precision, trueness, and robustness. Traceability of the procedure was established using certified reference materials. Uncertainty of measurement was confirmed *via* an “in-house” laboratory validation approach. The expanded uncertainties for the ten analysed elements were obtained for the entire working range of the EDXRF method. Robustness of the modified EDXRF procedure was assessed by means of a chemometric in-house approach. The results obtained by the modified X-ray fluorescence method were additionally correlated to those acquired by inductively coupled plasma optical emission spectrometry to confirm that EDXRF could be used as an effective and reliable alternative method for analysis of cement leachates.

Keywords: in-house validation; mineral additives; cluster analysis; ICP-OES; EDXRF, building materials.

INTRODUCTION

Waste depots on which fly ash is being disposed are constantly producing significant amounts of waste water as a result of precipitation or contact with external water resources.¹ Fly ash leachates are characterized by high concentrations

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of toxic elements and high salinity.² The employment of fly ash as a component material in the construction industry is a successful means for the removal of potential pollutants from the natural environment.³⁻⁵ Addition of sorbent clays, such as zeolite and bentonite, in the mix-design of a construction material enables the immobilization of the toxic elements.⁴

Identification and quantification of the chemical elements contained in leachates can be acquired by various instrumental techniques: atomic absorption spectrometry (AAS),⁶ optical emission inductively coupled plasma spectrometry (ICP-OES),⁷ inductively coupled plasma-mass spectrometry (ICP-MS)⁸ and X-ray fluorescence spectrometry (XRF).⁹ The energy dispersive X-ray fluorescence (EDXRF) method is extensively being used in environmental protection¹⁰ and construction materials studies.¹¹⁻¹³ However, the application of EDXRF for simultaneous multi elemental analysis of liquid samples and leachates is sparsely investigated. For instance, S. Zhoua *et al.*¹⁴ successfully identified heavy metals in polluted water using a portable XRF. The authors indicated that at least two factors limit the application of this instrument for *in-situ* analysis of water samples, *i.e.*, high detection limits and water damage to the instrument. Marguí *et al.*¹⁵ proved that XRF instrument can be used for precise quantitative chemical analysis of leachates obtained from waste material rich in heavy metals. Pearsona *et al.*¹⁶ obtained highly comparable results from XRF analyses conducted on solid and liquid samples, thus proving the reliability of this non-destructive method.

The preparation of the XRF testing samples is rapid since a digestion procedure is not required, which makes XRF analysis low-cost and free of harmful chemicals.¹⁷ However, water-based samples (leachate, waste water, *etc.*) require a specific optimization procedure for their preparation and analysis.¹⁸ There is no standard method for EDXRF analysis of cement leachates. In addition, a fully validated EDXRF analytical methodology has not yet been established for the determination of toxic elements in leachates or wastewater. Therefore, the validation of multi elemental EDXRF analysis (As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn) of cement leachates was conducted in this study. Cement-based binders with mineral additives (fly ash, zeolite and bentonite) were used in the experiments. Validation included the statistical evaluation of data from the linear calibration range for each analysed element, as well as the limits of detection and quantification. Precision and trueness were evaluated at different concentration levels. Robustness was evaluated by application of multivariate statistics. The amount of sample used for the preparation for plastic container and the different thickness of polyester film were employed as the main process parameters for the determination of the robustness of the EDXRF technique for liquid samples. Traceability and measurement uncertainty were determined by an “in-house” validation approach. The results obtained by modified X-ray fluorescence

method were additionally correlated to those acquired by inductively coupled plasma optical emission spectrometry.

EXPERIMENTAL

Preparation and characterization of the cement binders

The chemical composition of the component materials (Portland cement CEM I 42.5R, Zeolite “Vranjska banja”, Bentonite “Šipovo”, Fly ash “Kolubara”, fly ash “Kostolac”, fly ash “TENT A” and fly ash “TENT B”) used for preparation of the cement binders is given in Table I. Chemical analyses were performed by EDXRF method.¹⁹

TABLE I. Chemical composition of the raw materials used in the mix-design of the cement binders; *LoI* – loss of ignition

Parameter	Cement	Zeolite	Bentonite	Kolubara fly ash	Kostolac fly ash	TENT A fly ash	TENT B fly ash
$c_{SiO_2} / \%$	20.6±1.4	63.7±1.8	48.1±1.7	58.3±1.6	55.3±1.7	57.5±1.7	59.7±1.6
$c_{Al_2O_3} / \%$	5.6±0.7	13.4±0.6	11.6±0.7	18.9±0.5	17.4±0.5	17.7±0.5	21.0±0.5
$c_{Fe_2O_3} / \%$	2.6±0.4	1.4±0.3	3.1±0.4	6.8±0.5	10.3±0.4	10.5±0.4	6.0±0.5
$c_{K_2O} / \%$	0.8±0.1	1.6±0.3	0.7±0.1	1.2±0.2	0.6±0.1	0.6±0.1	5.8±0.1
$c_{Na_2O} / \%$	0.20±0.02	1.2±0.1	2.9±0.2	0.5±0.03	0.4±0.03	0.40±0.03	0.40±0.03
$c_{CaO} / \%$	61.6±1.3	3.5±0.8	3.5±0.8	8.7±0.9	7.9±0.9	7.0±0.8	5.8±0.7
$c_{MgO} / \%$	2.4±0.4	1.2±0.3	2.4±0.4	2.3±0.4	2.3±0.4	2.0±0.4	2.2±0.4
$c_{SO_3} / \%$	3.6±0.9	0.3±0.02	1.1±0.2	1.3±0.2	0.9±0.05	1.1±0.2	0.50±0.02
$c_{P_2O_5} / \text{mg kg}^{-1}$	1000±190	500±80	800±100	300±50	300±50	200±40	200±40
$c_{As} / \text{mg kg}^{-1}$	<0.03	<0.03	<0.03	182±50	10±2	11±2	17±3
$c_{Ba} / \text{mg kg}^{-1}$	<0.03	<0.03	<0.03	86±20	49±10	52±10	62±10
$c_{Cd} / \text{mg kg}^{-1}$	<0.03	<0.03	<0.03	0.20±0.01	0.20±0.01	0.10±0.01	0.20±0.01
$c_{Co} / \text{mg kg}^{-1}$	<0.01	<0.01	<0.01	15±3	5±1	8±1	7±1
$c_{Cr} / \text{mg kg}^{-1}$	<0.01	<0.01	<0.01	135±40	105±25	98±25	170±50
$c_{Cu} / \text{mg kg}^{-1}$	<0.01	<0.01	<0.01	36±4	54±5	53±5	30±4
$c_{Mo} / \text{mg kg}^{-1}$	<0.05	<0.05	<0.05	10±1	5±0.5	5±0.5	3±0.3
$c_{Ni} / \text{mg kg}^{-1}$	<0.01	<0.01	<0.01	51±5	24±2	22±2	32±3
$c_{Pb} / \text{mg kg}^{-1}$	<0.01	<0.01	<0.01	25±4	14±3	16±3	18±3
$c_{Zn} / \text{mg kg}^{-1}$	46±4	<0.01	<0.01	57±5	50±5	53±5	27±3
<i>LoI</i> / %	1.4±0.3	13.7±0.7	19.6±0.8	1.8±0.3	4.5±0.7	2.9±0.4	2.9±0.4

Twenty-nine samples of cement binders based on Portland cement were prepared for the experiment. Mineral additives (fly ash, zeolite and bentonite) were employed in the mix-design in different ratios. The mix-design of the cement binders is provided in Fig. 1. The experimental mixtures were prepared according to the standard procedure provided in SRPS EN 196-1:2017: Methods of testing cement – Part 1: Determination of strength. After 28 days of solidification, the samples were crushed and subsequently ground in a laboratory mill.

Leaching test

The leaching test was conducted according to SRPS EN 12457-4:2008.²⁰ The leachability of heavy metals for each sample was investigated on the mixtures of the testing samples and deionised water using a 1:10 liquid to solid ratio. The mixtures were prepared in a laboratory mixer manufactured by the Institute IMS, Centre for Laboratory equipment (volume 15 L and a mixing speed 10 rpm) at room temperature (20±2 °C) during 24 h,

according to the above-mentioned EN standard.²⁰ Afterwards, the leachate was filtered over a membrane filter (0.45 µm). The concentrations of metal elements in the leachates obtained from 29 samples were determined using EDXRF and ICP-OES analyses.

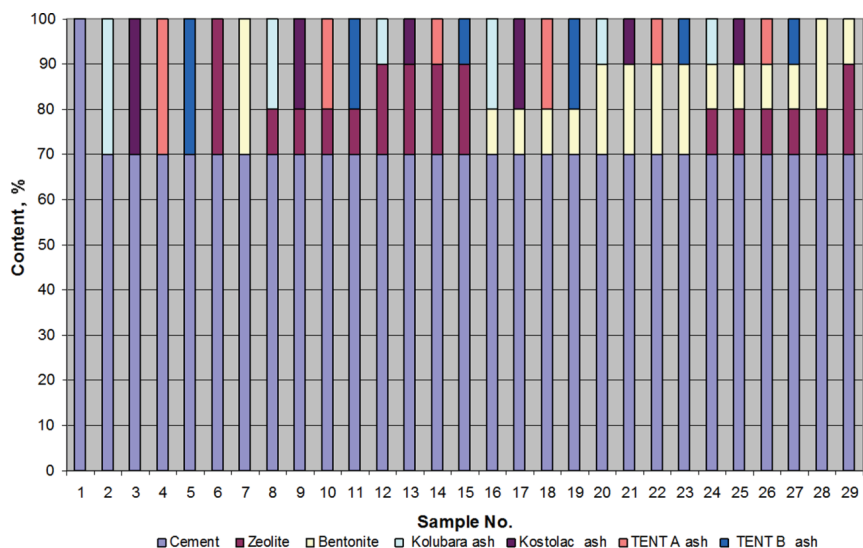


Fig 1. The mix-design of the cement binders.

Instrumentation and measurement conditions

The EDXRF analysis was performed using a Spectro Xepos system equipped with a 50 W and 60 V X-ray tube with a binary Co/Pd alloy thick target anode. The excitation mode of the X-ray tube was combined polarized/direct excitation. The characteristic radiation emitted by the elements present in the sample was detected by a silicon drift detector with Peltier cooler system. Spectro XRF Analyzer Pro, Xepos C Software was used. Liquid samples analysis was conducted in a helium atmosphere.

The multi element standard solution was diluted at different concentrations to obtain calibration standards. Stock solutions were prepared by a single dilution or series of dilutions in order to acquire a working concentration set in the range from 0.10 to 100.00 mg dm⁻³ for each element for the EDXRF technique. Liquid samples were packed in plastic containers. The diameter of the plastic container was 32 mm (24 mm inner diameter) with enough volume to cover the surface of the plastic container and give a depth of 10 mm (5 g for distilled water). The upper orifice of the container was covered with the polyester film (4.0 µm thickness) and with the help of two rings of the same material a taut wrinkle free sample support window was created.

An ICP-OES (Spectro Genesis, Germany) analyser equipped with a plasma generator (27.12 MHz; 1.700 KW power) was used. The argon consumption was 16 L min⁻¹. The holographic grating had 2400 point mm⁻¹. The plasma with a wavelength range of 175–775 nm was positioned radially. High purity argon (99.9999 %) was used for the plasma initiation, as a carrier gas, and for cooling of the quartz system. Smart Analyzer Vision software was used.

Commercially available 1000 mg L⁻¹ multi element standard solution in nitric acid (ICP multi element standard solution IV in 10 % nitric acid, Merck) containing Ag, Al, B, Ba, Bi,

Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Ni, Pb, Sr, Tl and Zn was used for the calibration of the ICP analysis. The calibration was performed for ten elements (As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn). The wastewater sample for the proficiency test (test code 586) and reference material (test code 500) were provided by ERA. Ultra-pure deionized water, $0.5 \mu\text{S cm}^{-1}$, obtained from a deionizer (Heming, Serbia) was used for dilution. Additional preparations of calibration standards, reference materials, and cement leachates were not necessary for the ICP-OES analysis.

Chemometric analysis

The applied experimental design corresponded to a 5×3 Latin square design with two factors (sample amount and different thickness of polyester film). All determinations were made in three repetitions and all data were averaged, expressed as mean \pm standard deviation (*SD*). Analysis of variance (ANOVA) was used to analyse the variations of the element contents in cement leachates. Pattern recognition techniques (cluster analysis – CA) was applied to the experimental data (used as descriptors) to characterize and differentiate among the observed samples. The data were processed statistically using the software package Statistica 12 (StatSoft Inc., Tulsa, OK, USA, 2012).

RESULTS AND DISCUSSION

A full validation of the modified EDXRF method for liquid samples included the characterization of calibration curves, linearity, selectivity, limit of detection (*LOD*), limit of quantification (*LOQ*), precision (repeatability and reproducibility), trueness and robustness. Traceability and uncertainty of the method were also determined. Limits of detection were determined as:

$$LOD = 3.3 \frac{\sigma}{S} \quad (1)$$

Limits of quantification were determined as:

$$LOQ = 10 \frac{\sigma}{S} \quad (2)$$

where: σ – standard deviation of blank; S – slope of regression line.

The equations for *LOD* and *LOQ* were used according to the International Union of Pure and Applied Chemistry (IUPAC) Procedures.²¹ The *LODs* and *LOQs* for the modified XRF method were determined for each metal element present in the cement leachates, *i.e.*, As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn. In order to experimentally confirm the *LOQ*, six standard solutions with concentrations close to the *LOQ* were prepared and analysed. The calibration parameters were determined using Merck multi-element standard stock solutions in the concentration range from 0.10 to 100.00 mg dm^{-3} . The concentration reference value in CRM for all elements was 100 mg dm^{-3} . The calibration curves for all chemical elements were constructed using seven nominal points (working standards 0.10, 1.00, 5.00, 10.00, 20.00, 50.00 and 100.00 mg dm^{-3}) with addition of a nominal blank. Calculations for mean concentration values for the calibration curve points were obtained as replicates of two series of triplicate measurements.

Calibration parameters for all analytes were employed in ANOVA (MS Excel) analysis for producing the calibration and residual. The emission wavelengths, *Y*-intercepts, slopes, coefficients of determination, *LOD* and *LOQ*, working range and selectivity of calibration curve for metal elements are given in Table II.

TABLE II. Parameters of calibration curves of 10 chemical elements found in cement leachates

Element	Emission lines series / <i>E</i> / keV	<i>Y</i> -intercept, mg dm ⁻³	Slope	<i>R</i> ²	<i>LOD</i> mg dm ⁻³	<i>LOQ</i> mg dm ⁻³	Working range mg dm ⁻³	Ratio <i>c</i> _{Cal} / <i>c</i> _{CRM}
As	K-α / 10.542	0.048	0.999	0.999	0.028	0.092	0.092–110	1.07
Ba	K-α / 32.188	0.045	0.999	0.999	0.024	0.079	0.079–103	1.08
Cd	K-α / 23.170	0.054	0.998	0.999	0.044	0.102	0.102–108	1.01
Co	K-α / 6.929	0.064	1.001	0.999	0.068	0.224	0.224–105	1.05
Cr	K-α / 5.414	0.048	0.999	1.000	0.024	0.079	0.079–115	1.28
Cu	K-α / 8.046	0.080	0.999	0.999	0.087	0.287	0.287–110	1.03
Mo	K-α / 17.476	0.046	1.000	0.999	0.031	0.102	0.102–105	1.07
Ni	K-α / 7.477	0.076	0.999	0.999	0.084	0.277	0.277–105	1.08
Pb	L-α / 10.550	0.039	0.999	0.999	0.022	0.073	0.073–108	0.98
Zn	K-α / 8.637	0.065	1.000	0.999	0.068	0.224	0.224–110	0.96

The selectivity (*c*_{Cal}/*c*_{CRM}) was determined as the ratio of the obtained concentration of the observed element (in mg kg⁻¹) and its concentration in the certified reference material (CRM). If this ratio is close to 1.00, the selectivity for elements identified and quantified by developed the EDXRF method indicates that it can successfully assess the analyte in the presence of components that are expected to occur in the solution (Matrix effect).

Emission lines K-α type were used for all investigated elements. Only for lead, was the L-α emission line used. The calculated *Y*-intercepts for ten elements spanned from 0.039 mg dm⁻³ for lead to 0.080 mg dm⁻³ for copper. The steepest slope was obtained for cadmium (0.998), while cobalt (1.001) had the most even slope of the calibration curve. The obtained linearity was good for all investigated elements. Coefficients of determination (*R*²) were in satisfactory interval from 0.999 (As, Ba, Cd, Co, Cu, Mo, Ni, Pb and Zn) to 1.000 (Cr). The values obtained for *LOD* varied between 0.022 (Pb) and 0.087 mg dm⁻³ (Cu), while the *LOQ* was between 0.073 (Pb) and 0.287 mg dm⁻³ (Cu). The calculated values of *LOD* and *LOQ* are in conformity with the waste acceptance criteria for leachates obtained from inorganic wastes.²² The highest concentration limits obtained for the working ranges for the investigated elements were from 103 (Ba) to 115 mg dm⁻³ (Cr). The highest obtained selectivity value was for chromium (1.28). Zinc showed the lowest selectivity value (0.96). The high values of selectivity indicated that the matrix of the calibration standard corresponded adequately to the matrix of the tested cement leachates.

Traceability was determined using the results of the analyses of certified reference materials (CRM).²³ The precision was evaluated using the conditions that are normally employed for the determination of repeatability and reproducibility. Namely, the precision (which is expressed as repeatability and reproducibility) and trueness of the developed EDXRF method were evaluated through analysis of the certified reference materials for wastewater (ERA 500 and ERA 586). In addition, recovery tests for four levels of concentration (standard solutions of 0.05, 2.5, 30 and 80 mg dm⁻³) were performed. Trueness was expressed as the recovery percent (*R*). The mean recovery for each analyte was calculated according to the formula reported in Guidelines for the In-House Validation of Methods of Analysis, IUPAC.²⁴ The calculations of the above-mentioned parameters included 10 independent measurements of CRM during 2 h for repeatability and 20 independent measurements (two operators per 10 measurements) of CRM over two consecutive days. All measurements were performed in triplicate for different concentrations levels of the same working range. The obtained results for precision, trueness, and expanded uncertainty for 10 elements detected in the liquid samples for different concentration levels (low, medium, high) of the working range (0.05–80.0 mg dm⁻³) are given in Table III. “In-house” validation approach was used for the assessment of measurement uncertainties.²⁵

$$u_c = \sqrt{u(R_w)^2 + (u(\text{Bias}))^2} \quad (3)$$

where: u_c is the combined standard uncertainty; $u(R_w)$ is the uncertainty of the estimated within-laboratory reproducibility; $u(\text{Bias})$ is the uncertainty of the estimation of the laboratory and the method bias;

$$u(\text{Bias}) = \sqrt{RSM_{\text{Bias}}^2 + u(\text{Cref})^2} \quad (4)$$

where: $u(\text{Bias})$ is the contribution to the uncertainty from the bias; RMS_{Bias} is the root mean square of the individual bias values; $u(\text{Cref})$ is the standard uncertainty component for the certified or assigned value, *i.e.*, mean value of the individual uncertainties.

The CRM-s for the estimation the $u(\text{Bias})$ were analysed in at least 10 different analytical series (two operators on two consecutive days) in triplicate:

$$U(x) = k u(x) \quad (5)$$

where: $k = 2$ is the coverage factor corresponding to a 95 % confidence level.²⁵

This approach is quick, easy and straightforward because it uses data from the in-house validation process. Therefore, this approach was adopted for the uncertainty budget estimation of the concentration of 10 elements in leachates of cement binders for different concentration levels of the working range (0.05–80.0 mg dm⁻³).

TABLE III. Precision, trueness and expanded uncertainty for elements found in cement leachates

CRMs and standard solutions	ERA 500cal	ERA	Level 1 0.05 mg dm ⁻³	Level 2 2.5 mg dm ⁻³	Level 3 30 mg dm ⁻³	Level 4 80 mg dm ⁻³
As						
Repeatability ^a <i>RSD</i> , %	1.8	1.7	1.2	1.7	1.1	1.6
Reproducibility ^a <i>RSD</i> , %	2.5	2.3	2.1	2.4	2.2	2.4
Trueness ^a Recovery, %	95.3	99.1	98.1	98.0	98.8	99.1
Expanded uncertainty, %	11.0	10.2	13.9	13.7	11.6	9.9
Ba						
Repeatability ^a <i>RSD</i> , %	1.2	1.1	1.0	1.1	1.2	1.3
Reproducibility ^a <i>RSD</i> , %	1.8	1.7	1.9	1.7	1.9	1.9
Trueness ^a Recovery, %	99.2	100.3	98.8	98.9	102.2	103.2
Expanded uncertainty, %	10.1	11.9	12.1	10.3	10.5	11.3
Cd						
Repeatability ^a <i>RSD</i> , %	1.8	1.5	1.4	1.6	1.7	1.6
Reproducibility ^a <i>RSD</i> , %	1.9	2.1	1.9	1.7	2.1	1.9
Trueness ^a Recovery, %	101.3	100.5	97.7	98.3	99.8	97.9
Expanded uncertainty, %	11.4	14.9	13.1	14.0	11.1	12.0
Co						
Repeatability ^a <i>RSD</i> , %	1.3	1.5	1.7	0.8	0.7	0.7
Reproducibility ^a <i>RSD</i> , %	2.1	2.0	2.5	1.9	1.9	1.8
Trueness ^a Recovery, %	98.8	98.3	98.5	98.7	99.3	98.5
Expanded uncertainty, %	12.2	12.9	14.8	13.0	9.5	12.0
Cr						
Repeatability ^a <i>RSD</i> , %	0.8	1.6	1.0	1.2	1.8	1.3
Reproducibility ^a <i>RSD</i> , %	1.6	2.3	1.7	1.4	2.0	1.8
Trueness ^a Recovery, %	101.3	100.5	100.3	100.1	98.8	98.9
Expanded uncertainty, %	11.5	11.0	15.2	14.0	9.1	11.8
Cu						
Repeatability ^a <i>RSD</i> , %	2.5	2.4	2.8	3.1	2.8	3.4
Reproducibility ^a <i>RSD</i> , %	2.8	2.7	3.6	4.2	3.6	4.5
Trueness ^a Recovery, %	98.8	97.8	99.8	96.5	97.9	98.8
Expanded uncertainty, %	15.8	17.3	15.2	14.3	13.5	12.6
Mo						
Repeatability ^a <i>RSD</i> , %	2.7	2.8	2.9	2.1	2.8	2.3
Reproducibility ^a <i>RSD</i> , %	2.9	3.2	3.7	4.0	3.1	4.1
Trueness ^a Recovery, %	97.8	98.9	95.8	96.6	98.8	97.8
Expanded uncertainty, %	16.3	17.4	15.1	14.1	13.3	12.9
Ni						
Repeatability ^a <i>RSD</i> , %	0.9	1.7	1.8	1.9	1.9	1.8
Reproducibility ^a <i>RSD</i> , %	1.8	2.3	1.9	1.6	2.8	2.8
Trueness ^a Recovery, %	100.1	97.5	98.0	100.5	99.7	95.8
Expanded uncertainty, %	15.5	13.9	14.8	13.3	12.6	11.3

TABLE III. Continued

CRMs and standard solutions	ERA 500cal	ERA	Level 1 0.05 mg dm ⁻³	Level 2 2.5 mg dm ⁻³	Level 3 30 mg dm ⁻³	Level 4 80 mg dm ⁻³
Pb						
Repeatability ^a <i>RSD</i> , %	1.1	1.9	1.8	1.9	2.2	2.3
Reproducibility ^a <i>RSD</i> , %	2.6	2.4	2.7	2.4	2.8	3.8
Trueness ^a Recovery, %	99.3	98.5	98.7	97.3	95.8	100.5
Expanded uncertainty, %	11.6	11.1	18.2	13.3	12.6	16.3
Zn						
Repeatability ^a <i>RSD</i> , %	0.8	0.7	1.0	0.8	0.7	1.1
Reproducibility ^a <i>RSD</i> , %	1.5	1.3	1.2	1.3	1.3	1.6
Trueness ^a Recovery, %	98.3	100.1	99.5	98.8	100.1	97.7
Expanded uncertainty, %	9.2	10.3	19.1	18.0	15.2	12.4

^aIn triplicate

The obtained results for repeatability varied from 0.4 % for cobalt in the standard solution (80 mg dm⁻³) to 3.4 % for copper in the standard solution (80 mg dm⁻³). The values of *RSD* for reproducibility were from 1.2 % for zinc in the standard solution (0.05 mg dm⁻³) to 4.5 % for copper in the standard solution (80 mg dm⁻³). The investigated analytical method could be considered precise because the obtained precision parameters were below 10 %.²⁶ The recoveries varied from 95.3 % for As in CRM ERA 500 to 103.2 % for Ba in the standard solution (80 mg dm⁻³). The expanded uncertainties of the measurements, expressed as the percentage of the concentration of an analyte, were between 9.1 % for chromium in the standard solution (30 mg dm⁻³) and 19.1 % for zinc in the standard solution (0.05 mg dm⁻³). When the uncertainty is not defined in a regulation, an additional criterion for tolerance level (20–30 %) could be considered in order to acknowledge the variability of the uncertainty estimation process.²⁷ High values of the measurement uncertainty for low concentration of an element could be explained by its low concentration in the analysed test solutions.

Chemometric analysis of the data obtained by modified EDXRF method

The robustness of the EDXRF method and the correlation between the obtained results and the experimental conditions were evaluated through the variation of two parameters: the amount of liquid sample and the thickness of the used polyester film. Samples were prepared with the following amounts of testing liquid (reference material ERA 500): 2.0, 3.0, 4.0, 5.0 and 6.0 g. The containers for liquid samples were covered with a polyester film of different thickness: 3.6, 4.0 and 5.0 µm. Fifteen tests on a XRF instrument were performed in order to monitor the influence of each input parameter on the final result. The results obtained from cups with 5.0 g of liquid sample and 4.0 µm thick polyester films (*i.e.*, calibration conditions) were adopted as optimal based on the manufacturer's instruction. The concentrations of metal elements in cement leachates

(modified XRF method) as an implication of the mass sample and film thickness are given in Table IV. Each value is the mean of three replicates. The standard deviation values are given in parentheses. The means in the same columns with different superscript letters are statistically different (at the level of statistical significance $p < 0.05$).

TABLE IV. The experimentally obtained metal element concentrations (mg dm^{-3}) using the XRF method on cement leachates depending on the mass of the sample and the film thickness

Sample amount, g	Polyester thickness, μm	Element									
		As	Ba	Cd	Co	Cr	Cu	Mo	Ni	Pb	Zn
2.0	3.6	482.3 (3.5) ^a	1232.7 (2.5) ^a	67.7 (2.5) ^{ab}	621.3 (1.5) ^a	392.0 (3.5) ^a	313.7 (11.8) ^a	42.3 (2.5) ^a	814.7 (12.7) ^a	546.0 (3.6) ^a	960.7 (3.1) ^a
2.0	4.0	492.3 (2.5) ^a	1296.0 (5.3) ^b	73.3 (3.1) ^b	618.3 (3.5) ^a	397.3 (0.6) ^{ab}	317.0 (12.0) ^a	45.0 (2.6) ^{ab}	823.3 (2.1) ^a	545.0 (2.6) ^a	956.0 (5.3) ^a
2.0	5.0	491.7 (4.5) ^a	1253.3 (7.6) ^a	66.3 (3.1) ^a	620.3 (0.6) ^a	394.0 (1.0) ^a	319.7 (1.5) ^a	41.3 (1.5) ^a	822.0 (2.6) ^a	551.7 (1.5) ^a	957.0 (3.0) ^a
3.0	3.6	504.7 (2.5) ^b	1476.7 (15.3) ^c	98.0 (2.0) ^c	659.0 (1.0) ^b	402.7 (2.5) ^{bc}	428.3 (4.7) ^b	54.0 (1.0) ^c	854.0 (3.6) ^b	569.3 (7.0) ^b	1000.3 (1.5) ^b
3.0	4.0	516.7 (3.1) ^c	1504.3 (4.0) ^{cd}	96.7 (1.5) ^c	662.3 (2.5) ^{bc}	403.3 (2.1) ^c	424.0 (3.6) ^b	52.7 (1.2) ^{bc}	851.7 (3.2) ^b	568.7 (1.5) ^b	1004.7 (0.6) ^{bc}
3.0	5.0	517.3 (5.0) ^c	1528.3 (20.2) ^d	99.0 (3.6) ^c	666.7 (1.5) ^c	403.7 (1.5) ^c	431.7 (1.5) ^b	53.3 (2.5) ^c	852.3 (2.1) ^b	587.7 (7.1) ^c	1009.7 (0.6) ^c
4.0	3.6	583.3 (3.5) ^d	1620.0 (17.4) ^e	114.7 (3.5) ^d	713.3 (1.5) ^{de}	593.3 (3.1) ^d	526.3 (5.5) ^c	109.0 (3.6) ^d	1219.7 (1.5) ^{cd}	751.7 (1.5) ^d	1158.0 (2.0) ^d
4.0	4.0	591.7 (1.5) ^{de}	1648.0 (11.3) ^e	112.3 (2.5) ^d	711.0 (1.0) ^d	598.3 (1.5) ^{def}	528.7 (5.0) ^c	115.0 (1.0) ^{de}	1204.0 (2.6) ^{cd}	751.7 (2.1) ^d	1158.3 (0.6) ^d
4.0	5.0	595.0 (1.0) ^e	1653.3 (25.2) ^e	118.0 (1.0) ^{de}	716.3 (1.5) ^{ef}	595.0 (1.7) ^{de}	529.3 (1.2) ^c	115.3 (2.5) ^{de}	1210.3 (2.5) ^c	757.0 (3.6) ^d	1161.7 (1.5) ^d
5.0	3.6	587.0 (2.6) ^{de}	1633.3 (7.6) ^e	124.7 (1.5) ^f	717.3 (1.5) ^{efg}	598.3 (1.5) ^{def}	523.7 (3.5) ^c	120.3 (2.5) ^{ef}	1215.3 (1.5) ^{cd}	751.7 (2.1) ^d	1160.3 (1.5) ^d
5.0	4.0	585.7 (2.3) ^{de}	1657.7 (6.8) ^e	124.7 (1.2) ^f	721.3 (1.5) ^g	598.0 (1.7) ^{def}	534.7 (5.0) ^c	124.7 (1.5) ^f	1223.0 (9.8) ^d	757.0 (2.6) ^d	1160.3 (1.5) ^d
5.0	5.0	591.0 (2.6) ^{de}	1637.7 (17.5) ^e	122.3 (1.2) ^{ef}	721.0 (1.0) ^{fg}	599.0 (1.0) ^{def}	531.0 (1.0) ^c	124.0 (1.0) ^f	1215.7 (1.5) ^{cd}	757.3 (4.9) ^d	1157.3 (1.2) ^d
6.0	3.6	590.3 (6.5) ^{de}	1643.0 (9.5) ^e	122.0 (1.0) ^{ef}	718.0 (1.0) ^{efg}	596.3 (1.2) ^{def}	525.7 (2.5) ^c	118.3 (6.5) ^{ef}	1222.3 (3.1) ^d	752.0 (1.0) ^d	1155.0 (5.0) ^d
6.0	4.0	591.0 (4.6) ^{de}	1659.3 (16.7) ^e	122.0 (1.0) ^{ef}	718.3 (0.6) ^{fg}	601.0 (1.0) ^{ef}	529.0 (1.7) ^c	117.3 (1.5) ^{ef}	1218.3 (8.6) ^{cd}	754.0 (1.0) ^d	1158.0 (2.0) ^d
6.0	5.0	593.7 (1.5) ^{de}	1630.0 (3.5) ^e	122.7 (1.5) ^{ef}	719.0 (1.0) ^{fg}	599.3 (2.1) ^f	527.0 (3.6) ^c	121.3 (2.5) ^{ef}	1210.7 (2.1) ^{cd}	751.7 (1.5) ^d	1156.3 (3.8) ^d

As could be seen from Table IV, there was highly significant differences (level $p < 0.05$) between samples obtained using different sample amounts and polyester thicknesses. Grouping of the samples was presented by cluster analysis (CA) and the results are illustrated in Fig. 2. The dendrogram was obtained by

grouping variables using the Complete linkage method - City-block (Manhattan) distances.

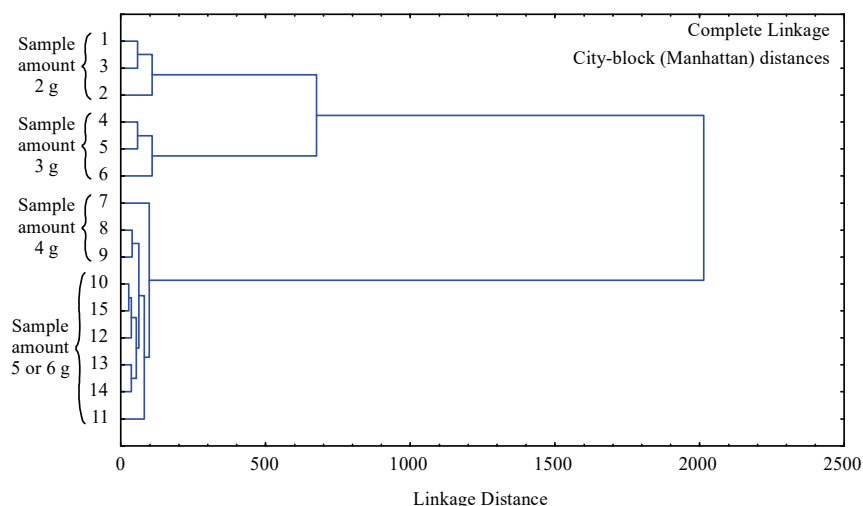


Fig. 2. Dendrogram for robustness of EDXRF data for liquid samples.

Four groups of samples were formed (4 clusters). The first group contained 2 g samples, the second group contained 3 g samples, and the third group contained samples prepared with 4 g samples, while the fourth cluster contained samples with 5 and 6 g samples. The shortest distance, *i.e.*, the strongest correlation was achieved between the first and the second group.

ANOVA exhibits the significant effect of independent variables as well as the interactions of these variables (Table V). This analysis revealed that the linear terms of sample amount (SA) in the second order polynomial (SOP) model were found statistically significant at $p < 0.01$ level, for each metal element calculations. The quadratic terms of the sample amount in the SOP models were statistically significant for Ba, Cd, Co, Cu and Zn calculation, statistically significant at $p < 0.01$ level, while the influence of the quadratic terms of sample amount in the SOP models for As, Mo and Pb calculation was statistically significant at the $p < 0.05$ level.

All SOP models had an insignificant lack of fit tests, which means that all the models represented the data satisfactorily.

Comparison of EDXRF and ICP-OES results by the linear regression method

Results obtained by the EDXRF and ICP-OES methods applied on cement leachates were compared and correlated *via* linear regression analysis. Linear regression parameters for the concentrations of metal elements in the analyzed leachates are presented in Table VI.

Table V. ANOVA table of the yield evaluation (sum of squares) for each element content in the leachates samples (df - degrees of freedom, PT- polyester thickness); SA – sample amount, g; PT – polyester thickness (μm); significant at level: $+p < 0.01$, $*p < 0.05$, $**p < 0.10$; error terms statistically insignificant

	SA	SA ²	PT	PT ²	SA \times PT	Error	r ²
df	1	1	1	1	1	9	
As	22828.5 ⁺	3080.0*	168.1	40.5	9.9	2758.96	0.907
Ba	236038.9 ⁺	81664.4 ⁺	940.9	2187.6	502.2	6125.4	0.982
Cd	5116.6 ⁺	1023.5 ⁺	0.2	0.3	0.6	51.288	0.992
Co	18807.7 ⁺	3777.8 ⁺	20.5	0.4	0.2	455.55	0.981
Cr	106476.4 ⁺	9103.2**	6.9	21.1	0.3	23834.6	0.833
Cu	79441.6 ⁺	22773.4 ⁺	44.1	11.7	5.2	1495.0	0.986
Mo	14483.5 ⁺	1329.8*	12.8	6.9	10.0	2009.62	0.889
Ni	390389.8 ⁺	37640.2**	22.5	0.2	63.7	78372.2	0.849
Pb	100809.2 ⁺	12058.8*	120.2	2.3	47.1	17996.0	0.866
Zn	88579.5 ⁺	13849.1 ⁺	5.9	0.1	1.6	11044.8	0.905

TABLE VI. Linear regression parameters for the results of EDXRF and ICP-OES analyses; correlations significant at level: $p < 0.01$; slope and intercept values statistically significant at the $p < 0.01$ level

Oxide/element	Determination coefficient	Slope	SD	Intercept	SD
As	0.9994	1.00357	0.01000	-0.01432	0.00014
Ba	0.9995	1.00045	0.00838	-0.02958	0.00029
Cd	0.9996	0.99894	0.00914	0.019277	0.00019
Co	0.9998	1.00102	0.00771	-0.03803	0.00038
Cr	0.9995	1.00701	0.00999	0.00226	0.00002
Cu	0.9994	1.00016	0.00826	0.00989	0.00010
Mo	0.9971	1.00042	0.00902	-0.00665	0.00007
Ni	0.9982	0.99527	0.00833	1.00101	0.01000
Pb	0.9989	0.99939	0.00769	0.00035	0.00000
Zn	0.96998	0.99889	0.00910	0.01008	0.00010

The obtained determination coefficients for the analysed chemical elements were within the confidence interval at a level of 95 %. The determination coefficients were in the range from 0.96998 (Zn) to 0.9998 (Co).

The determination coefficients (≈ 1.0) indicated that there were no significant differences between the outputs of the applied analyses methods. The statistical parameters of the intercepts and the slopes for the ten studied elements showed that the intercepts were in the range from -0.03803 (Co) and 1.00101 (Ni). The slopes (0.99527 for Ni-1.00701 for Cr) were not significantly different from 1. The regression parameters verified a good correlation between EDXRF and ICP-OES results, which means that both of techniques are adequate for the determination of metal elements in leachate of cement-based binders.

Regarding the analytical performances, the proposed and validated EDXRF method features a straightforward quantification method in which periodic recal-

ibration is not required. On the other hand, the ICP-OES method shows superior detection capabilities for low concentrations of elements. The cost of analyses, reagents and personnel expenses undoubtedly support the application of both ICP-OES and EDXRF techniques for liquid samples. However, on-site analyses support the EDXRF method.

CONCLUSIONS

A modified EDXRF analytical procedure for multi elemental determination of As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn in leachates of cement binders with additions of fly ash, zeolite and bentonite was successfully developed. The modified analytical technique proved to be a reliable tool for the analysis of a wide variety of building materials based on cement. The former statement could be substantiated with faster unattended analysis of samples within a wide range of concentrations and matrices, different states of matter are applicable and simultaneous multi-trace detection is feasible. The obtained values for the detection limits were within the range from 0.022 (Pb) to 0.080 mg·dm⁻³ (Cu). Measurement uncertainty for the developed method ranged from 9.1 for Cr to 19.1 % for Zn. The robustness of the EDXRF technique for liquid samples was successfully evaluated in altered testing conditions (sample amount and variable film thickness). It was highlighted that different thickness of film did not significantly influence the final results unlike the amount of the liquid sample that induced significant variations in the outputs of EDXRF analysis. The precision of EDXRF method for liquid samples was confirmed by the high values obtained for coefficients of determination (≈ 1) in comparison with the ICP-OES results. This means that the modified EDXRF calibrations could be used with high precision in the analysis of the leachate of cement-based materials with mineral additives and that this validated EDXRF method could be a good and reliable alternative for the commonly used laboratory technique: ICP-OES.

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ИЗВОД

УНАПРЕЂЕЊЕ И МОДИФИКАЦИЈА ЕНЕРГЕТСКИ ДИСПЕРЗИВНЕ РЕНДГЕНСКЕ ФЛУОРЕСЦЕНЦИЈЕ ЗА ОДРЕЂИВАЊЕ МЕТАЛА У ЕЛУАТУ ЦЕМЕНТНИХ ВЕЗИВА – ХЕМОМЕТРИЈСКИ ПРИСТУП

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У овом раду извршена је модификација аналитичке методе енергетски дисперзивне рендгенске флуоресценције (EDXRF) за квантификацију десет хемијских елемената (As,

Va, Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn) у елуатима цемента. У експерименту је коришћено 29 узорка за тестирање. Сви узорци су на бази Портланд цемента. Као минерални додаци у цементним везивима коришћени су: летећи пепео различитог порекла, зеолит и бентонит. Дестилована вода је коришћена као медијум излуживање метала. Валидација модификованог поступка EDXRF извршена је у смислу границе детекције и квантификације, радног распона, линеарности, селективности, прецизности, истинитости и робусности. След поступка утврђен је коришћењем сертификованих референтних материјала. Несигурност мерења потврђена је „интерним“ лабораторијским приступом валидације. Проширене несигурности за десет анализираних елемената добијене су за цео радни опсег EDXRF методе. Робусност модификованог EDXRF поступка процењена је хеометријским интерним приступом. Резултати добијени модификованом методом рендгенске флуоресценције додатно су корелисани са онима добијеним методом оптичке емисионе спектрометрије са индуктивно спрегнутом плазмом (ICP-OES) применом регресионе анализе како би се утврдило да се EDXRF може користити као алтернативна метода за анализу елуата цемента.

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