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Journal Pre-proof

Validation of energy-dispersive X-ray fluorescence procedure for determination of major and trace elements present in the cement based composites

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Abstract: Adjustment and subsequent validation of energy-dispersive X-ray fluorescence (ED-XRF) method for cement based binders with addition of mineral raw materials (fly ash, zeolite and bentonite) was conducted**.** Eighteen chemical elements present in the material composition were analyzed: ten major elements (Si, Al, Fe, Ca, Mg, S, Na, K, Ti, P) and eight trace elements (Cr, Zn, Cu, As, Ni, Pb, Sr, Mn). Thirty-five samples of either certified reference materials or reference materials of cement, fly ash and clay were utilized during adjustment and optimization of the investigated ED-XRF procedure. The method was consecutively validated in terms of selectivity, precision, working range, linearity, accuracy, robustness, limits of detection and quantification. Thirty-two samples in total, i.e. three certified reference materials and twenty-nine reference materials, were simultaneously analyzed by ED-XRF and inductively coupled plasma optical emission spectrometry (ICP-OES). Comparison of the outputs of monitored methods showed infinitesimally small differences, as correlation coefficients were extremely good (≈1), which highlighted ED-XRF as highly satiable alternative for ICP-OES for the chemical analysis of cement binders.

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Key words: *Quantitative analysis; Coupled plasma; Fly ash; Building materials; Multivariate analysis.*

Nomenclature	
ED-XRF	Energy-dispersive X-ray fluorescence
ICP-OES	Inductively coupled plasma optical emission spectrometry
AAS	Atomic absorption spectroscopy
PT scheme	Proficiency testing scheme
CRM	Certified reference material
RM	Reference material
LOD	Limit of detection, mg/kg
LOQ	Limit of quantification, mg/kg
SD	Standard deviation
RSD	Relative standard deviation, %
C_{Cal}	Calculated concentration, mg/kg
C_{CRM}	Certified or reference concentration, mg/kg

1. Introduction

Classic cement binders are still the main basis of contemporary building industry. Adequacy of conducted setting and hardening within cementitious material and consequently its mechanical performances are highly dependent on the chemical composition of the starting componential mixture. In order to decrease carbon footprint induced by cement manufacturing, a share of cement in binder is being replaced by a mineral raw material with pozzolanic characteristic [1]. Industrial waste materials such as fly ash are commonly used replacements due to high similarity with Portland cement regarding their chemical compositions and physico-mechanical characteristics [2]. However, coal combustion byproducts contain heavy metals prone to leaching [3]. The immobilization of these potential pollutants is conveyed by adding natural clayey materials (e.g. zeolite, bentonite) with adsorption capability to the mix-design of the cementitious binder [4].

Even though production technologies and performances of cement based binders are thoroughly investigated, there is still lack of detail studies on the chemical analysis methods which are employed in the testing of these materials [5, 6]. Identification of major and trace elements present in the cement can be conducted via classic laboratory volumetric and

gravimetric methods for chemical analysis [7] or instrumental methods such as: atomic absorption spectrometry (AAS) [8], energy dispersive or wavelength dispersive X-ray fluorescence (ED-XRF, WD-XRF) [5], optical emission inductively coupled plasma spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) [9]. Each method has its own advantages and disadvantages, but in contemporary material science and in the civil engineering practice, rapidity and precision of a method are the most valuated characteristics. All mentioned procedures, except XRF, require mineralization of the cement matrix in order to achieve the quantitative release of major and trace elements into solution. Chemical acids such as hydrofluoric acid are often necessary for destroying of the insoluble mineral matrix. However, the application of hydrofluoric acid disables precise determination of silicon content, which is the second most abundant cement component [10]. Contrariwise, ED-XRF analysis requires only pulverization of a cement sample followed by compressing of the powder into solid pellets, which can be repeatedly used for analytical purposes. Furthermore, despite longer and more complex sample preparation, AAS and ICP techniques show a lower limit of quantification than XRF. Also, AAS is a sequent method, since it allows determination of one element per time. ICP and XRF have multielement capability, i.e. ability to detect several elements at once [11-17]. Beside simple fast sample preparation without extra chemical waste, ED-XRF offers additional advantages regarding cement characterization such as: rapid low-cost analyzing procedure (no requirements regarding gases, acids and fume hoods) and possibility for in-situ analysis, i.e. at production site [18].

In this study ED-XRF was employed for the chemical analysis (quantification of Si, Al, Fe, Ca, Mg, S, Na, K, Ti and P as major elements and Cr, Zn, Cu, As, Ni, Pb, Sr and Mn as trace elements) of cement based binders with addition of fly ash, zeolite and bentonite. A standard ED-XRF method for cement was adjusted to fit the requirements of the investigated experimental composite materials. A novel stratagem to validation of in terms of selectivity,

precision, working range, linearity, accuracy, robustness, and limits of detection and quantification [19] was introduced. Uncertainty was measured using mathematical tools for empirical in-house validation approach [20] and robustness was evaluated during development phase of the method according to Youden's test [21]. The accuracy of ED-XRF method was confirmed by simultaneous comparison with inductively coupled plasma optical emission spectrometry (ICP-OES) conducted on thirty-two samples (three certified reference materials and twenty-nine reference materials). Multivariate analysis [22] was employed to explore differences between outputs of these two methods and to estimate if ED-XRF is a satiable alternative for ICP-OES for the chemical analysis of cement binders.

2. Materials and methods

2.1. Preparation of the experimental cement binders

Twenty-nine binders in total were prepared for the experiment. These samples were used for the validation of ED-XRF method and subsequent comparison with ICP-OES. All binders were based on Portland cement CEM I 42.5R (Lafarge). The binder M_0 contained only cement. The type and the ratio of mineral additives (fly ash, zeolite and bentonite) were altered in the mix designs of M_1-M_{10} binders (Table 1).

Table 1. *Mix design of experimental cement based binders.*

The binders with fly ash addition (M_1, M_4, M_5, M_6, M_7 and M_8) were prepared in four different sub-types (e.g. $M_{X\text{-}KOL}$, $M_{X\text{-}KOS}$, $M_{X\text{-}TA}$ and $M_{X\text{-}TB}$; where X is the number of a sample). Namely, the share of fly ash per sample was maintained the same, but the type of ash was alternated (Table 1). Fly ash originated from the lignite coal combustion process. It was obtained from filters of four power-plants located in the Republic of Serbia: *Kolubara*, *Kostolac*, *Nikola Tesla - A* and *Nikola Tesla – B.* Zeolite was acquired from *Vranjska banja* deposit, Republic of Serbia. Bentonite originated from *Šipovo* deposit, Bosnia and Herzegovina.

Dry components for binders were homogenized in a laboratory pan mixer for 120 s. The water content needed for a self-flowing consistency was added during mixing. Thus, prepared green mixtures were poured into steel molds (20 × 20 × 20 mm) and preserved sealed in polyethylene bags for 48 hours (storing conditions: 20 ± 2 °C temperature, 95 ± 5 % humidity). Upon removing from the molds, the samples were kept under same conditions for the next 5 days. Until 28th day, the samples were stored at 20 ± 2 °C and 65 ± 5 % humidity, when they were crushed and pulverized for further analyses. Pulverization was conducted in a vibratory mill Herzog (Germany). Milling time was 1 min. Final particle size was 45 μm.

2.2. Instrumental analyses

The samples for ED-XRF analysis were prepared in accordance with the pressed powder method. Pulverized sample, i.e. hardened binder (5 g) or certified reference material (1 g) and binding agent (Cereox wax, Fluxana) were mixed. The 40 mm diameter pellets were formed in aluminum cups. The pellets were formed under 10 tones load applied during 2.5 min via a laboratory hydraulic press Specac (UK).

The solutions for ICP-OES analysis were prepared by digestion procedure. Approximately 0.1 g of a pulverized sample (cement binder) was weighed and fused at 1000 °C with 1 g of lithium tetra borate for 45 min. The fusion residue was dissolved with a 5 % HCl and brought up to 50 ml volume.

The characteristics of used techniques are provided in Table 2.

Table 2. *Characteristics and measurement conditions of applied instrumental techniques.*

2.3. Methodology of work: adjustment, optimization and validation of ED-XRF method for cement binders

The adjustment and subsequent validation of ED-XRF method for a cement based binder involves utilization of commercial products which are either same or similar to raw materials

used as starting components in the production of the analyzed binder (e.g. cement, lime stone, clay, etc.). In this study, untypical composite samples, made of cement with addition of clayey materials (zeolite and bentonite) and fly ash, were investigated. Since cement is the base for all experimental binders, the samples were analyzed with the built-in calibration curves provided by ED-XRF manufacturer. The calibration curves for determination of major (Si, Al, Fe, Ca, Mg, S, Na, K, Ti, P) and trace (As, Cu, Ni, Pb, Zn, Cr, Sr, Mn) elements covered a wide mass fraction range (from mg/kg to percentages) of elemental composition of cement sample. However, the results obtained for analyzed elements were accurate for concentrations of major elements but failed to produce correct results for the trace levels in the samples with mineral additives. Limits of detection for As, Cu, Ni and Pb were unexpectedly high, because cement normally contains low amounts of these metals. Therefore, the adjustment of ED-XRF method imposed as a necessity. Upon conducted adjustment, optimization and validation that followed an empirical approach [11] were conducted. The validation was performed by selectivity, linearity, limits of detection and quantification, precision, accuracy and robustness [22]. All certified reference materials (CRM) and reference materials (RM) used in this validation study are summarized in Table 3.

Table 3. *List of certified reference materials and reference materials used for validation.*

Eleven out of prepared twenty-nine experimental samples (i.e. binders) were used as matrix match reference materials (RM) for the calibration of ED-XRF method. The obtained analytes had to be the same in the experimental samples and reference materials (i.e. matrix match). Samples M_0, $M_{1\text{-KOL}}$, M_2, M_3, $M_{4\text{-KOL}}$, $M_{5\text{-KOL}}$, $M_{6\text{-KOL}}$, $M_{7\text{-KOL}}$, $M_{8\text{-KOL}}$, M_9, M_{10} were utilized for the calibration of major elements. $M_{X\text{-KOL}}$ samples were used because previously conducted characterization and analyses showed that *Kolubara* fly ash comprised the highest concentration of heavy metals [2, 4]. Ten different samples of *Kolubara* fly ash were used for forming of the calibration curves utilized for the trace elements analyses. Eight synthetic

reference materials made with pure chemical substances (CaO, SiO_2, TiO_2, MgO, Al_2O_3, Fe_2O_3, Na_2O, and K_2O) were prepared and used during validation procedure, as well as the cement RM that originated from the PT Scheme• [23].

2.4. Assessment of performance characteristics of ED-XRF method for cement binders.

The following parameters were used in validation testing of the ED-XRF method: selectivity (ability to unequivocally assess an analyte in the presence of components expected to occur in the sample, i.e. "matrix effect"), linearity, limit of detection (LOD), limit of quantification (LOQ), precision (repeatability and reproducibility), accuracy and robustness.

Selectivity is expressed as quotient of calculated concentration of analyte and concentration of certified reference material or reference material (C_{Cal}/C_{CRM}). CRM or RM which are not previously included in the calibration can be used in the selectivity determination. Calculated parameters of linearity are: series and energy of emission lines, correlation coefficients (*R*), Y-intercepts and slopes of linear function.

The equations used in the validation of the ED-XRF method are summarized in Table 4.

Table 4*. Equations used in the determination of validation parameters.*

Limit of detection and limit of quantification are calculated by equations Eq. 1 and 2, respectively [24, 25]. LOD data are provided by instrument's software (Spectro XRF Analyzer Pro, Xepos C Software) as concentrations that can be tested with acceptable trueness and precision [11]. LOQ is determined via ratio C_{Cal}/C_{CRM} with CRMs and RMs so the low concentrations can be tested with acceptable trueness and precision. LOQ data are employed to establish the working range. Obtained values of LOD and LOQ are confirmed by repeating measurements six times using a blank standard. Synthetic reference materials (Table 3) were applied as blank standard in this experiment.

• PT scheme refers the use of inter-laboratory comparisons for the determination of laboratory performances. The need for constant confidence inspection of laboratory performances is not only important for laboratories and their customers but also for other interested parties (laboratory accreditation bodies and other organizations that specify requirements for laboratories).

Evaluation of expanded uncertainties (combined standard uncertainty, contribution to the uncertainty from bias, and expanded uncertainties) is performed by formulae Eq. 3-5 [27]. According to GUM [26], all known sources of bias within the method have to be eliminated. Bias can vary depending on the changes in matrix and concentration, preparation of the samples and influence of the operator. The correction for an observed bias can be performed using "in-house validation" (i.e. Nord test) approach [27]. In this approach, the reproducibility within-laboratory *(Rw)* is combined with estimation of the method and laboratory bias *(Bias)*. Experimentally determined quality control (*QC*) is used for the estimation of uncertainty component of within-laboratory reproducibility (*u(Rw)*). Regularly repeated measurements of CRMs, as control samples, are used for the estimation of *u(Rw)*. A control sample has similar matrix and concentration as the test samples collected over a period of time. One pellet per each reference material is measured in triplicate in a long-term different analytical series. Ten series were run in this experiment. All samples and CRMs were prepared in exactly the same manner by two independent operators. Combined standard uncertainty is calculated according to Eq. 3 when *u(Rw)* and *u(Bias)* are known. *Bias* normally includes laboratory (RSM_{bias}) and procedural bias *u(Cref)*. In this case, uncertainty of *Bias* (*u(Bias)*) was calculated from the validation data (accuracy) of CRM and the data from the CRM certificate according to Eq. 4. The CRMs for estimation of *u(Bias)* were analyzed in 5 different analytical series on 5 different days in triplicate. The expanded uncertainties *U(x)* were calculated according Eq. 5 using Mathcad software.

The robustness evaluation of ED-XRF was performed using the method proposed by Youden [28]. Distance of robustness for the results of the factorial combinations (*RobDist*) was evaluated using RM samples of cement that participated in PT Scheme (Tab. 3). The content of SiO_2, as the second most abundant oxide in the cement composition, was determined in all factorial combinations. Also, ZnO and Cr_2O_3 are included in the robustness determination,

since Zn and Cu are elements which are present at lower concentrations in the composition of Portland cement. The main process parameters that affect the results of ED-XRF technique are: the amount of sample used for the preparation of pellets and the duration of a sample's milling. Therefore, small variations were induced in the nominal values of these two analytical parameters (5 different amounts and 5 milling times). 25 runs were performed in order to identify the influence of each parameter on the result. The effect of variation of sample's amount on the final result of the analyses was evaluated according to Eq. 6.

2.5. Multivariate analysis of ED-XRF and ICP-OES results.

Thirty-two samples which covered the full working ranges of ED-XRF and ICP-OES methods were selected. Twenty-nine testing samples were cement binders with mineral additives. Three samples were CRM: NIST CRM 1881a - Portland cement with addition of fly ash, NIST CRM 2689 - Fly ash, and NCS DC CRM 60102 - Clay. Eight samples were analyzed per day. The duration of each analysis was approximately 2 hours. Analyses via ED-XRF and ICP-OES were conducted parallelly.

Correlation coefficients between 32 outputs from ED-XRF and ICP-OES analyses were acquired via Statistica software version 12 (Statistica, StatSoft Inc. 2012, USA).

3. Results and discussion

Due to high diversity of cement based materials employed in the building sector, analytical procedures developed by manufacturers of the testing instruments cannot accurately cover entire range of chemical elements or chemical compounds present in these materials. Thereby adjustment followed by validation of employed method (i.e. ED-XRF) is necessary as well as the confirmation of its accuracy via comparison with other equally precise methods of analysis (ICP-OES in this case). In order to upgrade an existing method for quantitative chemical analysis cement, and apply it on composite cement binders, it is necessary to either modify or even synthesize a number of reference materials. Thereby, these reference

materials are able to cover extremely low concentrations of all present chemical elements, which is important for the validation procedure (especially precise calculation of LOQ, concentration ratio or establishing of the working range). The advantage of the applied novel approach to adjustment and validation of ED-ERF method is its ability to obtain the real values for parameters of validation as well as the possibility to widen the working range if that is required.

3.1. Selectivity, linearity, limits of detection and quantification, and analytical range of the ED-XRF method

The parameters of calibration curves (series and energies of the emission lines, Y-intercept, slope, LOD, LOQ, working range and C_{Cal}/C_{CRM} ratio) used for detection and quantification of 18 chemical elements comprised in the chemical compositions of the investigated cement binders are summarized in Table 5.

Table 5*. Parameters of calibration curves of chemical elements found in the experimental cement binders.*

Series of emission lines were K-α for all investigated elements, except Pb for which L-α emission line was used. Energies of emission lines ranged from the minimum obtained for Na (1.041) to maximal value for Pb (10.550). Calculated Y-intercepts for eighteen elements spanned from 1.2892×10^{-4} for As to 9.4984×10^{-8} for Ti. The highest slope was obtained for Fe, while Na had the smallest slope in the diagram. Correlation coefficient (R^2) values were in tight interval from 0.99932 (Si) to 0.99995 (Al). The correlation coefficients being close to 1 indicates the good linearity for all investigated elements.

Limits of detection ranged from minimal value for Al (0.0029 mg/kg) to maximum of 0.0333 mg/kg acquired for As. Limit of quantification was the smallest for Ti (0.0093 mg/kg) and the highest for As (0.1000 mg/kg). The obtained limits of quantification (LOQ) were not in agreement with the expected pattern which implies that the higher the atomic number is -

the lower LOQ is obtained [11-14]. Despite the LOD and LOQ trends of results not being as it was expected, all obtained values were smaller than 1 mg/kg, which is LOQ value established for Portland cement by ED-XRF manufacturers. This is valuable information for quantification of the trace elements such as As, Pb, Cu and Ni, because these elements normally do not participate in the cement chemical composition and therefore the accuracy of their identification by adjusted ED-XRF method is of utmost importance.

The main elements (Si, Al, Fe, Ca, Mg, S, Na, K, Ti, P) comprised in the experimental cement binders showed wider working ranges, while the trace elements (As, Cu, Ni, Pb, Zn) had significantly narrower working ranges. However, the working ranges were satisfactorily wide for all tested elements for ED-XRF method to perform their accurate identification.

Selectivity, i.e. C_{Cal}/C_{CRM} ratio, was high for all investigated elements. The highest selectivity value was acquired for Cr (1.18), while Si showed the lowest selectivity (0.93). The over-all high values of selectivity mean that all investigated elements are prone to being unequivocally assessed in analyte in the presence of components expected to occur in the sample of cement binder (the matrix effect).

3.2. Precision, accuracy and expanded uncertainty of the ED-XRF method

Precision and accuracy were assessed by repeating of the measurements of certified reference materials previously listed in Tab. 3. The calculations were conducted during the period of ten days by two independent operators. The acquired values were compared with the concentrations of the certified reference values. The results obtained on the same pellet by the same operator using calibration curves matched the standard deviations of the certified results. The same correlations between the standard deviations were obtained for the pellets made from the same material and prepared by two independent analysts.

Precision (i.e. *repeatability* – applied same conditions and *reproducibility* – applied different conditions) obtained as % RSD is given in Table 6. The accuracy is also provided in Tab. 6 as

the recovery value calculated from a CRM target value and an experimentally obtained value.

Table 6. *Precision, accuracy and expanded uncertainty for chemical elements found in the experimental cement binders.*

The results presented in Table 6 indicate that the intermediate precision is better when the mass fraction is increasing. RSD values for repeatability and reproducibility were below 5 %. Namely, the values for repeatability ranged from 0.3 % (Ti) to 3.8 % (Na). The lowest reproducibility was acquired for P (2.9 %), while the highest value (4.9 %) was obtained for Mg, Na and Cr. Recovery ranged in a narrow interval from 94 % for Zn to 104.1 % for Fe. Recoveries for all investigated elements were within ± 6 % of the target values.

Silicon had the lowest value of expanded uncertainty (9.22 %). The highest expanded uncertainty (20.05 %) was acquired for zinc. All expanded uncertainties were below 21 %. These results are in accordance with GUM principles [29] which imply that the expanded uncertainty has to be smaller than the target value. The GUM principles also propose that if the target uncertainty is not defined in a regulation or specification, a tolerance of 20-30 % can be permitted in order to enable the variability of the uncertainty estimation process [29]. The mentioned tolerance interval is defined by the dependency of the usual degrees of freedom of standard uncertainties of measurements in chemistry and models of their variability. The obtained results are in accordance with the tolerance of 20-30 %.

Precision can be regarded as the main contributor to the standard uncertainty associated to the obtained results. Therefore, the precision and uncertainty of the measurements are consistent with the expected values for all elements, as seen in Tab. 6. Since the investigated ED-XRF method is going to be routinely applied on a wide rage of samples (i.e. cement based binders with different mineral additives – clayey materials, fly ash), the obtained values for precision and measurement uncertainty indicate that the results are reliable and thereby the developed method is trustworthy.

3.3. Robustness of the ED-XRF method

The amount of a sample taken for the preparation of pellets and the milling time until total pulverization of the observed sample are the main parameters of sample's preparation that could influence the results of the ED-XRF analysis. The milling time had been rarely tested in the studies because the commercial reference materials are already commonly received in the standard-sized powdery form. The preparation of experimental binders includes mixing of the mineral components of various grain diameters (i.e. often coarser grained materials) and their subsequent pulverization to the 45 μm sized powder.

A detailed experimental design was created for the testing of robustness of ED-XRF method for investigated experimental cement binders. Indicative values are given for SiO_2 content, since silicon dioxide is one of main constitutes of Portland cement (i.e. the second most abundant oxide). Also, ZnO and Cr_2O_3 are included in the quantification and the robustness determination. Zinc and copper are elements which are present at lower concentrations in the composition of cement, while heavy metals cannot be found in the pure Portland cement, therefore they could not be considered. Cement reference materials (Cement RM, Tab. 3) were used for testing of the robustness. The results obtained in the 25 runs on the cement sample are presented in Table 7.

Table 7. *Factorial combinations of SiO_2, ZnO and Cr_2O_3 contents for the robustness evaluation by Youden's test.*

Applying the criteria of Youden's test [30], which were previously explained in Chapter 2.4, adjusted ED-XRF method proved to be highly robust regarding the SiO_2, ZnO and Cr_2O_3 contents when variations of two analytical parameters were included. Namely, in order to evaluate the effect of each parameter (sample amount and milling time), the average of the five values corresponding to altered conditions was subtracted from the average of the five values obtained at the nominal conditions as demonstrated in Eq. 6 (Tab 4). Distance of

robustness (*RobDist*) for SiO_2 content varied from -0.02 % to 0.02 % regarding both analytical parameters. Distance of robustness for ZnO ranged from -6.0 mg/kg to -1.8 mg/kg regarding the sample amount and from -11.4 mg/kg to -1.6 mg/kg regarding the milling time. For Cr_2O_3, distance of robustness ranged from 0.8 mg/kg to 2.6 mg/kg and from -7.2 mg/kg to -2.4 mg/kg regarding the sample amount and milling time, respectively.

The lowest *RobDist* value for SiO_2 (-0.01 %) was obtained for the altered condition (6 g) when sample amount was the monitored parameter. In case of milling time as monitored parameter, the lowest *RobDist* value (-0.02 %) was obtained for two samples: altered condition (4 min) and altered condition (5 min). The highest value (0.02) was acquired for altered condition (7 g) and altered condition (8 g) in case of the sample amount as observed analytical parameter. In case of milling time as observed analytical parameter, the highest value (0.00) was acquired for altered condition (2 min).

The lowest *RobDist* value for ZnO was obtained for the altered condition (7 g) when sample amount was the monitored parameter. When the milling time was the monitored parameter, the lowest *RobDist* value for ZnO was obtained for altered condition (2 min). The highest value was acquired for altered condition (9 g) in case of the sample amount as observed analytical parameter. In case of milling time as observed analytical parameter, the highest value was acquired for altered condition (5 min). Regarding Cr_2O_3, the lowest *RobDist* value was obtained for the altered condition (6 g) when sample amount was the monitored parameter and for the altered condition (5 min) when the milling time was the monitored parameter. The highest values were acquired for altered condition (8 g) in case of the sample amount as observed analytical parameter and for altered condition (2 min) in case of milling time as observed analytical parameter.

As it can be seen, neither of the two observed analytical parameters made significant impact on the SiO_2 content. The variations regarding ZnO and Cr_2O_3 contents were also

comparatively small. The concentrations of SiO_2 were in agreement with the Youden's test for the obtained results in all tested conditions. The highest variation in the SiO_2 content was 0.02 %. These values are considerably low and therefore they are not regarded as significant in a routine chemical analysis [31].

3.4. Multivariate analysis and comparison of ED-XRF and ICP-OES results

The correlation coefficients slope and intersect obtained on the results of ED-XRF and ICP-OES methods via multivariate analysis are given in Table 8.

Table 8. *Linear regression parameters for the results of ED-XRF and ICP-OES analyses.*

The final evaluation of the ED-XRF method's performance was done by using robust statistics and by systematical comparison of ED-XRF and ICP-OES results. For all 18 investigated analytes (Tab. 8) the intercept was found not to be significantly different from 0, while the slope was close to 1. The correlation coefficients were in the range from 0.9595 to 1.0. Maximum of 1.0 was acquired for CaO and As. Higher correlation coefficients indirectly imply a good validation methodology of ED-XRF method. This is related to the detection limits of both methods, which means that a cross-calibration [32] between ED-XRF and ICP-OES techniques for different matrices is possible. Namely, the results obtained by these methods can be correlated in order to enable the recalculation of the results from ED-XRF to a more complex ICP-OES (better sensitivity and lower detection limits) if necessary.

The correlations for all outputs were extremely good (≈1.0) which means that developed XRF calibrations can be applied with high precision for the cement based materials. This is important because the major advantage of the ED-XRF technique compared to ICP-OES chemical analysis is that measurements can be carried out directly on solid samples in short time intervals which is a procedure that basically avoids the time consuming and complex sample preparation steps attributive to ICP-OES. The only disadvantages of ED-XRF analysis – the strong influence of the matrix effect is moderated by a suitable calibration set

comprising matrix matched samples spanning a wide range of concentrations [33] (in this case eleven reference materials).

4. Conclusions

Adjustment and validation of ED-XRF method for cement based binders were successfully conducted as a solution to a problem regarding the lack of analytical procedures developed by testing instrument manufacturers for accurate quantification of the complete range of chemical elements present in these materials. Obtained validation parameters for the adjusted ED-XRF method were extremely satisfactory. Limits of detection and quantification were below 1 mg/kg, which is the value established for Portland cement by ED-XRF manufacturers. High values of selectivity mean that all investigated elements are prone to being unequivocally assessed in analyte in the presence of components expected to occur in the sample of cement (i.e. matrix effect). Precision (repeatability and reproducibility) as the main contributor to the standard uncertainty associated to the obtained results was below 5 %. Recovery for all elements was within ± 6 % of a target value. The SiO_2 concentrations (max. 0.02 %.) correspond to the Youden's test in altered testing conditions (milling time and sample amount). The variations regarding ZnO and Cr_2O_3 contents were comparatively small. The obtained values for precision and measurement uncertainty indicate that the results are reliable and thereby the developed ED-XRF method is trustworthy.

The precision of ED-XRF method was confirmed by comparison with ICP-OES. The correlations between outputs were extremely good (≈1.0) which means that modified ED-XRF calibrations can be used with high precision for cement based materials (i.e. cements with mineral additives). Therefore, this highly-precise, validated and verified ED-XRF method for cement binders is rapid and easy technique which has the potential to replace commonly used laboratory analysis such as ICP-OES.

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6. References

[1] I. Yuksel, T. Bilir, O. Ozkan, Durability of concrete incorporating non-ground blast furnace slag and bottom ash as fine aggregate, Build. Environ. 42 (2007) 2651–2659.

[2] A. Terzić, L. Pezo, N. Mijatović, J. Stojanović, M. Kragović, Lj. Miličić, Lj. Andrić, The effect of alternations in mineral additives (zeolite, bentonite, fly ash) on physico-chemical behavior of Portland cement based binders, Con. Build. Mat. 180 (2018) 199-210.

[3] L. Zeyuan, Y. Yang, L. Ming, Z. Jia, S. Fucheng, H. Xin, Z. Jizhi, Q. Guangren, Comprehension of heavy metal stability in municipal solid waste incineration fly ash with its compositional variety: A quick prediction case of leaching potential, Waste Manag. 84 (2019) 329–339.

[4] A. Terzić, L. Pezo, Lj. Miličić, N. Mijatović, Z. Radojević, D. Radulović, Lj. Andrić, Thermal and mechanical behavior of composite mortars containing natural sorptive clays and fly ash, Sci. Sin. 51 (2019) 39-56

[5] C. García-Florentino, M. Maguregui, E. Marguí, L. Torrent, I. Queralt, J. Manuel Madariaga, Development of total reflection X-ray fluorescence spectrometry quantitative methodologies for elemental characterization of building materials and their degradation products, Spectrochim. acta Part B. 143 (2018) 18–25.

[6] C. García-Florentino, M.Maguregui, E.Marguí, I. Queralt, J.A. Carrero, J.M.Madariaga, Development of X-ray fluorescence quantitative methodologies to analyze aqueous and acid extracts from building materials belonging to cultural heritage, Anal. Chem. 89 (2017) 4246–4254.

[7] ASTM C114-18, Standard test methods for chemical analysis of hydraulic cement, ASTM

International, West Conshohocken, PA, 2018.

[8] O. Wah-Law, L. Lam, S.Fai-Luk, Analysis of cement and cement raw meal by atomic absorptionn spectrophotometry using a new fusion agent, Talanta 42 (1995) 1265-1271.

[9] M. Elfaham,U. Eldemerdash, Advanced analyses of solid waste raw materials from cement plant using dual spectroscopy techniques towards co-processing, Opt laser technol. 111 (2019) 338-346.

[10] D. Knotter, Etching mechanism of vitreous silicon dioxide in HF-based solutions, J. Am. Chem. Soc. 122 (2000) 4345–4351.

[11] Y. Fiamegos, M. Beatriz, Validation strategy for an ED-XRF method to determine trace elements in a wide range of organic and inorganic matrices based on fulfiment of performance criteria, Spectrochim. acta Part B. 150 (2018) 59–66.

[12] L. Perring, M. Nicolas, D. Andrey, C. Fragniere Rime, J. Richoz-Payot, S. Dubascoux, E. Poitevin, Development and validation of an ED-XRF method for the fast quantification of mineral elements in dry pet food samples, Food anal. method. 10 (2017) 1469–1478.

[13] L. Perring, A. Tschopp, Determination of ash content of milk-based powders by Energy Dispersive X-ray Fluorescence, Microchem. J. 145 (2019) 162-167.

[14] D.Andrey, J.P.Dufrier, L.Perring, Analytical capabilities of Energy Dispersive X-Ray Fluorescence for the direct quantification of iron in cocoa powder and powdered cocoa drink, Spectrochim. acta Part B. 148 (2018) 137-142.

[15] L. Perring, D. Andrey, Multi-elemental ED-XRF determination in dehydrated bouillon and sauce base products, Food anal. method 11 (2018) 148–160.

[16] M.N. Hepp, I.C. James, Application of high-energy polarized energy-dispersive x-ray fluorescence spectrometry to the determination of trace levels of As, Hg, and Pb in certifiable color additives, X-Ray Spectrom. 45 (2016) 330–338.

[17] R. Milani, M. Morgano, S. Cadore, A simple and reliable method to determine 16 trace

elements by ICP-OES in ready to drink beverages, Food anal. method., 11 (2018) 1763–1772.

[18] M. Bouchard, J. Anzelmo, S. Rivard, A. Seyfarth, Global cement and raw materials fusion/XRF analytical solution, Adv. X-Ray Anal. 53 (2009) 263-279.

[19] F. Peters, O. Drummer, F. Musshoff, Validation of new methods, For. Sci. Int. 165 (2007) 216–224.

[20] N. Ashill, D. Jobber, Measuring state, effect, and response uncertainty: Theoretical construct development and empirical validation, J. Manag. 36 (2009) 1278-1308.

[21] E. Karageorgou, V. Samanidou, Youden test application in robustness assays during method validation, J. Chrom. A. 1353 (2014) 131-9.

[22] S. Haswell, A. Walmsley, Multivariate data visualization methods based on multielemental analysis of wines and coffees using total reflection X-ray fluorescence analysis, J. Anal. At. Spectrom. 13 (1998) 131–134.

[23] M. Thompson, S. Ellison, R. Wood, The international harmonized protocol for the proficiency testing of analytical chemistry laboratories (IUPAC Tehnical Report), Pure.Appl.Chem. 78 (2006) 145-196.

[24] V. Barwick, S. Ellison, E. Gjengedal, B. Magnusson, O. Molinier, M. Patriarca, L. Sibbesen, N. Vanlaethem, I. Vercruysse, Method validation in analytical sciences: discussions on current practice and future challenges, Accred Qual Assur. 22 (2017) 253-263.

[25] A. Shrivastava, VB. Gupta, Methods for the determination of limit of detection and limit of quantitation of the analytical methods, Chron Young Sci. 2 (2011) 21-5.

[26] W. Bich, Revision of the "Guide to the Expression of Uncertainty in Measurement". Why and how, Metrologia. 51 (2014) 155-158.

[27] T. Näykki, A. Virtanen, L. Kaukonen, B. Magnusson, T. Väi sän e n, I. Leito, Application of the Nordtest method for real-time uncertainty estimation of on-line field measurement, Environ. Monit. Assess. 187 (2015) 630.

[28] W. Youden, E. Steiner, Statistical manual of AOAC – Association of official analytical chemistry, AOAC-I, Washington, 1975, pp. 88.

[29] International Organization for Standardization, Guide to the expression of uncertainty in measurement (GUM), JCGM 100:2008.

https://www.bipm.org/en/publications/guides/gum.html

[30] E. Karageorgou, V. Samanidou, Youden test application in robustness assays during method validation, J. Chrom. A. 1353 (2014) 131-139.

[31] M. Thompson, Towards a unified model of errors in analytical measurement, The Analyst. 125 (11) (2000), 2020-2025.

[32] K. Chojnacka, M. Samoraj, Ł. Tuhy, I. Michalak, M. Mironiuk, M. Mikulewicz, Using XRF and ICP-OES in Biosorption Studies, Molecules. 23 (2018) 2076 https://doi.org/10.3390/molecules23082076.

[33] G. Guild, J. Stangoulis, Non-matrix matched glass disk calibration standards improve XRF micronutrient analysis of wheat grain across five laboratories in India, Front. Plant. Sci. 7 (2016) 1-10.

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Declaration of interests

(YES) The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

(No, not applicable) The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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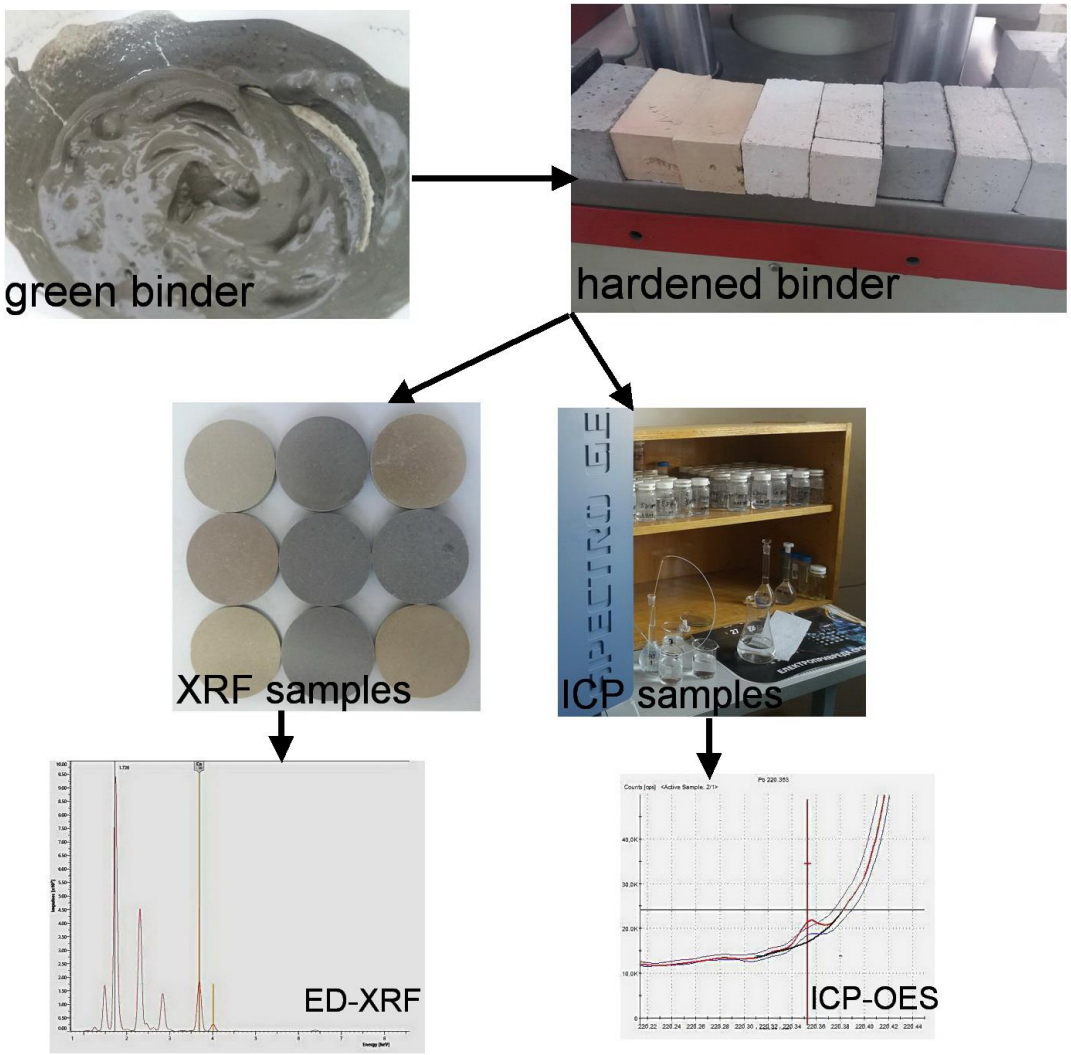
green binder
hardened binder
XRF samples
ICP samples
ED-XRF
ICP-OES

Table 1. Mix design of experimental cement based binders.

Binder / Raw material	M_0*	$M_{1\text{-KOL}}$** $M_{1\text{-KOS}}$ $M_{1\text{-TA}}$ $M_{1\text{-TB}}$	M_2	M_3	$M_{4\text{-KOL}}$** $M_{4\text{-KOS}}$ $M_{4\text{-TA}}$ $M_{4\text{-TB}}$	$M_{5\text{-KOL}}$** $M_{5\text{-KOS}}$ $M_{5\text{-TA}}$ $M_{5\text{-TB}}$	$M_{6\text{-KOL}}$** $M_{6\text{-KOS}}$ $M_{6\text{-TA}}$ $M_{6\text{-TB}}$	$M_{7\text{-KOL}}$** $M_{7\text{-KOS}}$ $M_{7\text{-TA}}$ $M_{7\text{-TB}}$	$M_{8\text{-KOL}}$** $M_{8\text{-KOS}}$ $M_{8\text{-TA}}$ $M_{8\text{-TB}}$	M_9	M
Cement, %	100	70	70	70	70	70	70	70	70	70	7
Fly ash, %	0	30	0	0	20	10	20	10	10	0	
Zeolite, %	0	0	30	0	10	20	0	0	10	10	2
Bentonite, %	0	0	0	30	0	0	10	20	10	20	1

**M_X – label of the cement binder; where X (X=0-10) is the ordinal number of the sample whose mix-design is presented in the Tab.1*

*** Binders made with fly ash from different origin/power plants: KOL-Kolubara; KOS-Kostolac; TA-Nikola Tesla A; TB-Nikola Tesla B.*

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Table 2. Characteristics and measurement conditions of applied instrumental techniques.

ED-XRF	
Manufacturer	Spectro Xepos, Germany
Excitation	X-ray tube, Binary Co/Pd alloy thick-target anode (50W/60kV)
Excitation mode	Combined polarized/direct excitation.
Gas	Helium (applied for samples prepared via cups only)
Detector	Silicon drift detector (SDD)
Cooling system	Peltier coolers
Software	Spectro XRF Analyzer Pro, Xepos C Software
ICP-OES	
Manufacturer	Spectro Genesis, Germany
Excitation	Plasma torch
Excitation mode	Radial plasma
Generator power	1.7 KW
Frequency	27.12 MHz
Gas (plasma initiation, carrier and cooling gas)	High purity argon (99.9999 %)
Gas consumption	16 l/min
Charge	Coupled Devices (CCD)
Software	Smart Analyzer Vision software

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Table 3. List of certified reference materials and reference materials used for validation.

No.	Name of CRM and RM	Matrix	Application
1.	NIST CRM 1889a	Portland cement	Working range, linearity, selectivity, precision, accuracy for major elements (Si, Al, Fe, Ca, Mg, S, Na, K, Ti, P, Mn, Sr) and trace elements (Cr and Zn) in binders. LOD and LOQ for trace elements (As, Pb, Ni, Cu).
2.	NIST CRM 1887a		
3.	NIST CRM 1888a		
4.	NIST CRM 1881a		
5.	NIST CRM 2689	Fly ash	Working range, linearity, selectivity, precision, accuracy for major elements (Si, Al, Fe, Ca, Mg, S, Na, K, Ti, P) and trace elements (Cr, Zn, Cu, As, Ni, Pb) in binders.
6.	NIST CRM 2690		
7.	NIST CRM 2691		
8.	NCS DC CRM 60106	Clay	Working range, linearity, selectivity, precision, accuracy for major elements (Si, Al, Fe, Ca, Mg, S, Na, K, Ti, P, Mn,) in binders. LOD and LOQ for trace element (As, Pb, Ni, Cu).
9.	NCS DC CRM 60102		
10.	NIST CRM 2711	Montana II Soil	Working range, linearity, selectivity, precision, accuracy for trace elements (As, Pb, Ni, Cu).
11.	NIST CRM 2710	Montana I Soil	
12.	NIST CRM 2709	San Joaquin Soil	
13.	NIST CRM 2586	Soil	
14.	NIST CRM 1633b	Coal fly ash	
15.	RM M_0	Binders	Built in the calibration curve for major elements*.
16.	RM $M_{1\text{-KOL}}$		
17.	RM M_2		
18.	RM M_3		
19.	RM $M_{4\text{-KOL}}$		
20.	RM $M_{5\text{-KOL}}$		
21.	RM $M_{6\text{-KOL}}$		
22.	RM $M_{7\text{-KOL}}$		
23.	RM $M_{8\text{-KOL}}$		
24.	RM M_9		
25.	RM M_{10}		
26.	RM *Kolubara* fly ash	Fly ash	Built in the calibration curve for trace elements.
27.	Synthetic RM-1	CaO, SiO_2, TiO_2, MgO, Al_2O_3, Fe_2O_3, Na_2O and K_2O	LOD and LOQ for major elements (Si, Al, Fe, Ca, Mg, S, Na, K, Ti, P, Mn).
28.	Synthetic RM-2		
29.	Synthetic RM-3		
30.	Synthetic RM-4		
31.	Synthetic RM-5		
32.	Synthetic RM-6		
33.	Synthetic RM-7		
34.	Synthetic RM-8		
35.	Cement RM**	Portland cement	Testing of robustness.

**Calibration of RM samples was simultaneously conducted in three different independent laboratories.*
***Cement RM originates from PT scheme conducted for 11 laboratories.*

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Table 4. Equations used in the determination of validation parameters.

Eq. no.	Validation parameter	Equation	Symbols used in equations
(1)	Limit of detection	$LOD = 3.3 \cdot \frac{\sigma}{S}$	σ - SD of blank, SD of ordinate intercept, or residual SD of linear regression; S - slope of regression line
(2)	Limit of quantification	$LOQ = 10 \cdot \frac{\sigma}{S}$	
(3)	Combined standard uncertainty	$u_c(\%) = \sqrt{(u(R_w))^2 + (u(Bias))^2}$	*u(Rw)* - uncertainty of the estimated within-laboratory reproducibility; *u(Bias)* - uncertainty of the estimation of laboratory and method bias
(4)	Contribution to the uncertainty from bias	$u(Bias) = \sqrt{RSM_{Bias}{}^2 + u(Cref)^2}$	RSM_{bias} - laboratory bias *u(Cref)* - procedural bias from certificate
(5)	Expanded uncertainties	$U(x) = k \cdot u(x)$	*k* - coverage factor corresponding to a 95 % confidence level
(6)	Distance of robustness	$RobDist = \frac{R1+R2+R3+R4+R5}{5} - \frac{R6+R7+R8+R9+R10}{5}$	R1-R10 - results of the factorial combinations

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Table 5. Parameters of calibration curves of chemical elements found in the experimental cement binders.

Element	Emission lines (series, energy), KeV	Y-intercept, cps	Slope, cps, mg/kg	R^2	Matrix effects and overlapping corrections*	LOD, mg/kg	LOQ, mg/kg	Working (WR), m
Si	K-α, 1.740	$2.9660x10^{-6}$	0.9885	0.99932	Linear (Mg, Fe)	0.0033	0.0100	0.01-100
Al	K-α, 1.486	$4.9289x10^{-7}$	0.9638	0.99995	Linear (Fe)	0.0029	0.0098	0.0098-10
Fe	K-α, 6.403	$2.9210x10^{-6}$	1.3345	0.99959	Linear (Mn)	0.0036	0.0120	0.012-10
Ca	K-α, 3.691	$4.7567x10^{-8}$	1.1659	0.99947	Linear (Al, Si, Fe)	0.0031	0.0094	0.0094-10
Mg	K-α, 1.253	$1.6778x10^{-6}$	0.9608	0.99967	Linear (Si)	0.0033	0.0100	0.01-100
S	K-α, 2.306	$2.4285x10^{-4}$	1.1068	0.99962	No correction	0.0030	0.0101	0.0101-10
Na	K-α, 1.041	$5.5769x10^{-6}$	0.8712	0.99977	Linear (Si)	0.0033	0.0100	0.01-100
K	K-α, 3.310	$7.5416x10^{-6}$	1.0263	0.99978	No correction	0.0032	0.0098	0.0098-10
Ti	K-α, 4.504	$9.4984x10^{-8}$	0.9175	0.99942	No correction	0.0031	0.0093	0.0093-10
P	K-α, 2.012	$1.5949x10^{-5}$	0.9480	0.99952	No correction	0.0032	0.0096	0.0096-10
Mn	K-α, 5.898	$2.0237x10^{-5}$	0.9658	0.99969	Linear (Fe)	0.0036	0.0108	0.0108-5
Sr	K-α, 14.163	$4.5598x10^{-6}$	1.0136	0.99929	No correction	0.0035	0.0105	0.0105-5
Cr	K-α, 5.414	$8.9710x10^{-6}$	0.9175	0.99942	No correction	0.0045	0.0135	0.0135-
As	K-α, 10.542	$1.2892x10^{-4}$	1.1721	0.99949	No correction	0.0333	0.1000	0.1-12
Cu	K-α, 8.046	$5.4508x10^{-6}$	0.9583	0.99979	No correction	0.0317	0.0951	0.0951-
Ni	K-α, 7.477	$1.3169x10^{-4}$	1.0439	0.99969	No correction	0.0311	0.0933	0.0933-
Pb	L-α, 10.550	$1.3731x10^{-6}$	1.3111	0.99959	No correction	0.0332	0.0996	0.1-10
Zn	K-α, 8.637	$1.9210x10^{-5}$	0.9852	0.99989	No correction	0.0299	0.0897	0.0897-

* Calibration RMs are matrix-matching standards, i.e. calibration RMs and samples were chosen to match their matrices as close as possible. Matrix effects were thereby minimized. Additional corrections for matrix effects are provided where it was necessary. Performed overlapping corrections are listed.

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Table 6. Precision, accuracy and expanded uncertainty for chemical elements found in the experimental cement binders.

Element	Used CRM and RM	Repeatability* (RSD), %	Reproducibility* (RSD), %	Recovery, %	Expanded uncertainty, %
Si	NIST CRM 1889a/1887a/ 1888a/1881a/2689/2690/2691, NCS DC CRM 60106/60102	0.8	3.4	95.4	9.22
Al		1.3	3.9	95.1	10.97
Fe		3.2	4.5	104.1	11.96
Ca		2.3	4.2	97.2	12.82
Mg		2.7	4.9	98.5	13.25
S		2.7	3.5	96.1	11.81
Na		3.8	4.9	98.0	12.01
K		2.6	3.5	101.1	13.83
Ti		0.3	3.9	96.8	10.87
P		1.6	2.9	96.6	18.74
Mn	NIST CRM 1889a/1887a/1888a/1881a, NCS DC CRM 60106/60102	1.7	3.3	97.5	11.53
Sr	NIST CRM 1889a/1887a/1888a/1881a	1.8	4.3	98.0	19.55
Cr	NIST CRM 1889a/1887a/1888a/1881a/ 2689/2690/2691	2.2	4.9	103.0	19.37
As	NIST CRM 1889a/1887a/1888a/1881a/2689/ 2690/2691/2711/2710/ 2709/2586/1633b NCS DC CRM 60106/60102	1.9	4.7	98.5	19.38
Cu		2.3	4.6	97.0	19.20
Ni		0.7	4.4	99.0	19.78
Pb		1.2	4.8	96.0	19.80
Zn	NIST CRM 1889a/1887a/ 1888a/1881a	0.9	4.5	94.0	20.05

* in triplicate

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Table 7. Factorial combinations of SiO_2, ZnO and Cr_2O_3 contents for the robustness evaluation by Youden's test.

Factorial combination	Analytical parameter		Oxide content		
	Sample amount, g	Milling time, min	SiO_2, %	ZnO, mg/kg	Cr_2O_3, mg/kg
1	5	1	20.86	668	172
2		2	20.89	680	174
3		3	20.83	670	178
4		4	20.85	669	176
5		5	20.90	670	180
6	6	1	20.86	669	171
7		2	20.85	681	173
8		3	20.88	678	176
9		4	20.91	679	177
10		5	20.89	671	179
11	7	1	20.84	672	170
12		2	20.83	685	174
13		3	20.89	679	175
14		4	20.86	678	176
15		5	20.84	673	178
16	8	1	20.84	670	170
17		2	20.87	680	172
18		3	20.85	679	175
19		4	20.85	674	176
20		5	20.86	672	174
21	9	1	20.87	671	170
22		2	20.88	681	172
23		3	20.85	671	175
24		4	20.86	671	176
25		5	20.88	672	178

	*RobDist***	SiO_2, %	ZnO, mg/kg	Cr_2O_3, mg/kg
Analytical parameter	Sample amount			
	NC (5 g) – AC (6 g)*	-0.01	-4.2	0.8
	NC (5 g) – AC (7 g)	0.02	-6.0	1.4
	NC (5 g) – AC (8 g)	0.02	-3.6	2.6
	NC (5 g) – AC (9 g)	0.00	-1.8	1.8
	Milling time			
	NC (1 min) – AC (2 min)	0.00	-11.4	-2.4
	NC (1 min) – AC (3 min)	-0.01	-5.4	-5.2
	NC (1 min) – AC (4 min)	-0.02	-4.2	-5.6
	NC (1 min) – AC (5 min)	-0.02	-1.6	-7.2

*NC - nominal condition; AC - altered condition

***RobDist* of oxide = average value obtained at NC - average value obtained at AC

Table 8. Linear regression parameters for the results of ED-XRF and ICP-OES analyses.

Oxide/element	Correlation coefficient*	Slope	Intercept
SiO_2	0.99990	1.00427	0.10067
Al_2O_3	0.99990	0.99358	-0.08748
Fe_2O_3	0.99990	0.99661	0.01793
CaO	1.00000	0.99900	-0.00343
MgO	0.99950	1.02527	-0.02855
SO_3	0.99890	1.00004	0.00472
Na_2O	0.99710	1.03219	-0.00833
K_2O	0.99720	0.98627	0.03747
TiO_2	0.99870	0.98028	-0.00431
P_2O_5	0.95950	0.89799	0.01208
MnO	0.99910	1.00185	-0.07940
SrO	0.99050	1.00086	0.02168
Cr	0.99950	0.98528	-0.04549
As	1.00000	0.94568	-0.01952
Cu	0.99990	0.92179	0.05104
Ni	0.99990	0.98536	-0.03061
Pb	0.99980	0.91162	0.06335
Zn	0.99740	0.97185	-0.03443

*Correlations are significant at $p<0.01$

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Highlights

- Adjustment and validation of ED-XRF method for cement based materials
- Repeatability and reproducibility values are below 5 %
- Limit of quantification ranges from 0.0093 mg kg^{-1} for Ti to 0.1 mg kg^{-1} for As
- Robustness of ED-XRF method is confirmed by Youden's test
- ED-XRF is satiable alternative for ICP-OES for chemical analysis of cement binders

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