Fired pressed pellet as a sample preparation technique of choice for an energy dispersive X-ray fluorescence analysis of raw clays

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ARTICLE INFO

ABSTRACT

In this paper, the main subject concerns comparing different techniques to prepare raw clay samples for energy-dispersive X-ray fluorescence spectrometry (EDXRF). Three kinds of sample preparation procedures are examined, such as loose powder, pressed pellet, and fired pressed pellet. The fired pressed pellet approach was observed as a part of universal sample preparation for physic, mechanical, and instrumental analysis, which has not been previously tested as a solution in chemical analysis by the EDXRF method. The observed sample preparation techniques were compared by calculating the parameters of validation (recoveries, limit of detection - LOD, limit of quantification - LOQ, precision, and expanded uncertainties of measurements) of 11 elements (Si, Al, Fe, Ca, Mg, K, Na, Ti, P, Mn, and S) using 15 certified reference materials (CRMs). Calibration curves were created and evaluated using 30 reference materials (RM) for all three approaches. Results proved that the fired pressed pellet is the most practical and precise approach for sample preparation of raw clays.

1. Introduction

Clays are one of the oldest natural building materials in construction [1–3]. The ability to solidify after firing makes it possible to use clay for a variety of building products [4,5]. Clay is used in different industrial sectors such as construction, ceramics, pharmaceuticals, environmental remediation, conservation of historical mortars, etc. [6–8]. The choice of clay depends on its properties and cost. Further research on raw clay for physico-mechanical and chemical properties is critical for this purpose [9–11]. Clays from different sources have varying properties. Kaolinitic clays, which are pozzolanic materials, play an important role in hydration reactions because they contain mainly alumina and silica [12].

Traditional wet chemistry methods such as spectrophotometry and atomic absorption require the destruction of crystal lattices of minerals present in raw clays, which is labor-intensive and time-consuming. All of the principal digestion methodologies have been shown to contain flaws. For example, the method of hydrofluoric acid (HF) digestion is not precise for the determination of the content of Si [13]. The method of fusion with lithium tetra-borate combined with acid dissolution gives good results for all the elements, but for a large number of samples, this method is quite slow and requires additional equipment [14].

Dissolution of samples with Aqua Regia digestion is an unstable procedure and allows only partial digestion [14,15].

X-ray fluorescence (XRF) based techniques have been used in various fields because they can analyze solid and powder samples without sample dissolution. Recently, green chemistry analysis has been promoted and this includes, for instance, the techniques of energy-dispersive X-ray fluorescence (EDXRF) and wavelength dispersive X-ray fluorescence (WDXRF), which eliminate the use of concentrated and harmful chemicals. Other techniques, such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS), require sample dissolution and complex sample preparation. However, the use of an inadequate analytical method can give irregular results. XRF is sometimes used by people without knowledge of analytical chemistry because of the commercialization of this technique. As an additional difficulty, sometimes methods of sample preparation for XRF might require more attention to gain reliable results [16]. Furthermore, the sample preparation method differs in terms of its characteristic properties and the available XRF spectrometer instrument [17,18].

A few previously published studies have been conducted on the

various methods of preparation for the characterization of solid materials by energy-dispersive X-ray fluorescence (EDXRF). In addition, there are no studies related to this issue that deal with raw clay [16–18]. A study by Ichikawa and Nakamura [16] described approaches based on analytical depth to prepare solid samples for XRF. The authors explained theoretic instructions and tools for reliable analysis. Based on the analytical depth, solid samples should be processed by pulverization and homogenization to produce loose powder, powder pellet, or glass bead samples. The general conclusion was that solid samples such as soil and rock require destructive preparation (flatness, particle size, homogeneity, and thickness). The XRF results are determined to be representative if the particle size is lower than the analytical depth when the sample is homogenous and the surface of the sample flat. Another study by Ichikawa and Nakamura [17] gave an excellent overview of sample preparation techniques for XRF analysis. The authors described a micro glass bead technique developed to assay precious siliceous samples for geochemical and archaeological analyses, such as clays, soils, rocks, and sediments, to determine ten major oxides. An alternative fusion method was used to create synthetic calibration standards, which resulted in good agreement between the analytical and recommended values of six geochemical reference materials. The focus of the study by Croffie et al. [18] was sample preparation and calibrations to improve the results of EDXRF for soil tests. The EDXRF results of 41 raw clays were compared with Inductively coupled plasma optical emission spectrometry (ICP-OES) results. In conclusion, the EDXRF was found suitable for quantifying 13 elements in contaminated soils.

This study fills the literature gap while optimizing methods of sample preparation and constructing calibration curves for eleven elements (Si, Al, Fe, Ca, Mg, K, Na, Ti, P, Mn, and S). In this way, the applicable, useful, and relatively rapid EDXRF method for raw clay chemical content determination is developed. Another novelty of this work is the fact that fired pressed pellets were not previously considered in the available literature. Improving EDXRF analytical performance enhanced the ease of validating clay chemical determination methods.

2. Materials and methods

2.1. Materials, sample preparation and instrumentation

Cereox wax (Fluxana GmbH, Bedburg-Hau, Germany) was used as a binder in the pressed pellet preparation with wax.

Forty-five certified reference materials (CRMs) and reference materials (RMs), which contained a clay and soil matrix, were used to estimate the validation parameters during the loose powders and pressed pellet preparation approaches. The CRMs used were: NCS DC CRM 60102 (clay), NCS DC CRM 60104 (clay), NCS DC CRM 60105 (clay), NCS DC CRM 60106 (clay), NIM–GBW07402 (soil), NIM–GBW07427 (soil), NIM–GBW07428 (soil), NIM–GBW07430 (soil), TILL–1 (soil), TILL–2 (soil), TILL–3 (soil), TILL–4 (soil), NIST 2709 (San Joaquin Soil), NIST 2710 (Montana soil) and NIST 2711 (Montana soil). The RM included thirty raw ceramic clays from the tertiary basin Crniljevo, Serbia [4]. The analysis of the reference materials was performed by the ICP-OES technique in three independent laboratories in Serbia (Table 1). All results concerning CRMs and RMs are given in an Excel file of Supplementary data (CRM and RM).

Table 1 presents the following parameters: minimum and maximum concentrations of the detected elements; average values; and standard deviation of all results given in the Supplement material (Excel file CRM and RM). Results of minimum and maximum values are used for the determination of the working range of calibration curves.

The samples were pulverized to a fraction below 0.5 mm for 1 min in a Herzog (Germany) vibration disk mill, after drying at 105 °C.

For the fired pressed pellet preparation (FPP) without binder wax, powdered homogenized samples or CRMs were weighed (20 ± 0.001 g), put in the 40 mm diameter mold, and then samples were pressed by using an automatic press. The pellets were pressed at 20 t for 3.0 min, then fired for 1 h at 1000 °C in a Carbolite Gero (Germany) laboratory furnace and analyzed in a vacuum atmosphere. All results by fired pressed pellet were normalized for loss on ignition at 1000 °C.

Loss on ignition (LOI) was determined by heating the clay powders in a furnace at 1000 °C for 1 h. The LOI determined at 1000 °C is corrected for the effect of oxidation. Namely, LOI is a characterization tool used to determine the presence of excess bound moisture content (difference between 250 °C and 550 °C) and organic matter access carbon dioxide (difference between 550 °C and 1000 °C). In the first reaction, organic matter is oxidized at 500–550 °C to carbon dioxide. In the second reaction, clay minerals dehydroxylate and carbon dioxide evolved from carbonate at 900–1000 °C, leaving oxide [19]. In this research, it is important to sum the LOI at 1000 °C because of the correction of results after firing. The remaining loss is assumed to constitute the sum of the common volatiles such as CO_2 and H_2O. The final sum including a volatile component, together with the major and minor elements, is ideally 100%. In this case, the result in Supplement material is presented as oxide form normalized to 100%. However, for the calculation of the validation parameters, the results are presented as elements because energy X-ray fluorescence measures the elemental form. Accurate knowledge of LOI is, however, essential for understanding combustion processes and the minimum requirement for proper interpretation of analyses of raw clay.

For the pressed pellet preparation (PPB) with binder wax, homogenized samples were weighed (5 ± 0.001 g) and mixed with (1 ± 0.001 g) binder wax (Cereox wax, Fluxana) into a Fluxana mixing container with a plastic ball. The samples were mixed at high speed for 120 s with a Fluxana MU-K Mixer, and after that, samples were put in the mold (40 mm in diameter), and then samples were pressed with an automatic press. The pellets were pressed at 20 t for 3.0 min and analyzed in a vacuum atmosphere.

For the loose powder preparation (LP), the homogenized samples were placed into a plastic sample cup with a plastic support film of 4 µm. To ensure infinite thickness for all of the elements of interest, the sample size was approximately half a cup (40 mm diameter). Samples with loose powder preparation analysis were analyzed in a helium atmosphere.

Each of the samples and CRMs was analyzed in triplicate. Fig. 1 presents the final appearance of the prepared sample using the three approaches.

The study was carried out with a Spectro Xepos (Germany) equipped with a 50 W and 60 V X-ray tube with a binary Co/Pd alloy thick target anode, controlled by the Software XRF Analyzer Pro, Version 2.2.2. The X-ray tube's excitation mode combined polarized and direct excitation. The unique radiation emitted by the components in the sample was

Table 1
ICP-OES results of RM (thirty raw ceramic clays from Serbia).

Raw clays	Si, %	Al, %	Fe, %	Ca, %	Mg, %	K, %	Na, %	Ti, %	P, %	*Mn,%	*S, %
Min	27.07	8.96	0.72	0.06	0.56	2.23	0.15	0.34	0.01	0.003	0.003
Max	32.94	15.08	7.61	0.21	0.85	3.52	2.45	0.48	0.05	0.013	0.374
Average	30.72	11.02	1.32	0.13	0.72	2.65	0.28	0.42	0.02	0.006	0.019
Standard deviation	1.39	1.02	1.20	0.04	0.07	0.29	0.41	0.03	0.01	0.002	0.066

All calculated values obtained were performed by the ICP-OES technique in three independent laboratories in Serbia. * The values for Mn and S are in three significant digits after the decimal point, as for certified concentration values in the standard samples in the Supplement material.

Fig. 1. Three approaches to the preparation of the samples: a) Loose powder preparation (LP), b) Pressed pellet preparation with binder wax (PPB), and c) Fired pressed pellet preparation without binder wax (FPP).

located using a silicon drift detector outfitted with a Peltier cooler device.

A laboratory hydraulic press (20 t), Specac (UK), was used to make the pellets with and without Cereox wax (Fluxana) as a binder.

The Mill Herzog (Germany) was used to pulverize samples to a fraction below 0.5 mm of raw clay for EDXRF analyses [4].

For fired pressed pellets, a Carbolite Gero laboratory furnace model RHF 1500 with a temperature range of 30 °C–1500 °C is used.

The ICP-OES analyzer Spectro Genesis (Germany) is equipped with a plasma generator (27.12 MHz; 1.700 KW power) used for RM analysis. The instrument system uses Smart Analyzer Vision software. The consumption of argon was 16 l/min 2400 points per millimeter make up a holographic grating. The wavelength range of the plasma, which was positioned radially, was 175–775 nm. The quartz system was cooled, the plasma was initiated, and it served as the carrier gas using high purity argon (99.9999%).

2.2. Evaluation and quantification of the limit of detection, trueness, precision, and uncertainty of measurement

This study used three approaches for sample preparation for testing clays by EDXRF (LP, PPB, and FPP). The obtained results were mutually compared and analyzed. Although EDXRF can be used for sample preparation techniques without using dissolution techniques, the process of preparation of solid samples needs to meet certain criteria of homogeneity and stability. Namely, there are many requests for testing of the ceramic clays, which include numerous samples and following the important parameters that characterize raw clay material and ceramic products' physical and mechanical parameters [4]. In laboratories that routinely deal with such studies, rapid analyzes are needed to test a large number of samples. Because of that, a fast method of sample preparation is to enable simultaneous testing for as many parameters as possible. In this case, it is a method of fired pressed pellet preparation without binder wax. Although this method is more difficult than using loose powder or pressed powder because it involves firing, it has several advantages, including homogeneous pellets, structural hardness, increased concentration of elemental ingredients, and reduced volume with decreased porosity and cracking [20]. This method of sample preparation is not represented in the literature as an option for chemical analysis, and neither of the manufacturers of XRF spectrometers gives calibrations for this approach. Consequently, the methodology of this study is based on the development and validation of an EDXRF method for the chemical determination of raw clay by the method of fired pressed pellet preparation without binder wax and a comparative study between those and the two traditional methods.

A methodology proposed in the previously published study [21] was used for the evaluation of the parametric validation strategy. The calibration curves for the determination of eleven elements (Si, Al, Fe, Ca, Mg, K, Na, Ti, P, Mn, and S) in this work were built up with 30 RMs (illitic-kaolinitic ceramic clays from Serbia).

The limits of detection (LODs) and the limits of quantification (LOQs) were calculated via calibration curves for all elements and all three approaches to the sample preparation (LP, PPB, and FPP). The LOD was expressed as a ratio of 3.3 standard deviations of the ordinate intercepts and the slope of the calibration curve [22]. The LOQ was expressed as a ratio of ten standard deviations of the ordinate intercepts and the slope of the calibration curve [22].

The results of the trueness (bias) study are given in the Excel file of Supplementary data (CRM and RM). The concentrations of all tested elements were compared with the certified reference values (15 CRMs) according to Eurachem network guides [23,24].

The precision (repeatability and reproducibility) in this study was evaluated by applying analysis of variance (ANOVA) by using Excel (Data Analysis). Three individual samples of CRMs prepared by each of the three examined approaches were tested by two different chemist analysts on three different days to ensure the objectivity of the results.

The uncertainty of measurement in this research encompasses the in-house data of method validation, data of precision, and trueness [25]. From the ANOVA results of precision (within-series and between-series variation), the bias and recovery are used for calculation. The uncertainty budget for EDXRF could contain the following contributions: sample preparation error given by Eq. (1) (milling (u_{mill}), pressing for PPB and FPP approaches (u_{press}), weighing (u_{weigh}), and analytical error. According to the Eurachem Guide [26], the random component of the measurement uncertainty is calculated by the combination of the sample preparation precision ($u_{s.p}$) and analytical precision ($u_{analytical}$). The analytical precision was obtained by 10 times measuring the CRMs in triplicate and including repeatability uncertainty (s_R) and the standard uncertainty of the recovery data (u_{bias}) (Eq. (2)). The total expanded uncertainty (U_{total}), a coverage factor corresponding to a 95% confidence level, requires this value to be multiplied by a coverage factor of 2 (Eq. (3)):

$$u_{s.p} = \sqrt{u_{mill}^2 + u_{weigh}^2 + u_{press}^2} \qquad (1)$$

$$u_{analitical} = \sqrt{u_{bias}^2 + s_R^2} \qquad (2)$$

$$U_{total} = 2 \cdot \sqrt{u_{s.p}^2 + u^2{}_{analytical}} \qquad (3)$$

3. Results and discussion

The influence of sample preparation methodology when different preparation techniques are used on the selected 15 CRMs (given in the Excel file of Supplementary data) are presented as trueness i.e. Recovery, % in Fig. 2.

The recoveries of the elements for the sample preparation techniques varied from 89 to 238%. A recovery rate of 80–120% was deemed satisfactory. The method's correctness was determined by a recovery of 100%, but a divergence of 20% was considered acceptable [18]. Outside those ranges (>120%) were the following results: Mg in all three approaches; Na in the case of LP and PPB; and S in LP. The sample preparation technique did not appear to show a significant influence on the determination of the main constituents such as Si and Al, but much better matches in concentrations with certified values were in the case of both pressed pellet approaches (PPB and FPP) (Fig. 2). However, as expected, sample preparation had a significant influence on light elements such as Mg and Na (Fig. 2) [18]. Concentrations of Mg and Na were significantly higher with the LP, compared to the pressed pellet approaches (PPB and FPP). Namely, pressed clay samples showed a higher signal-to-noise ratio and this allowed the detection of the lightest elements compared to their loose powder form, Fig. 3. This could be owing to particle size effects, which are more prevalent in high silica samples; larger particles diminish the intensity reaching the XRF detector, limiting the instrument's ability to precisely quantify these components [18]. However, in the LP technique, the fluorescence yield is very poor for light elements; while the analytical signals are easily absorbed in the film that covers the cup. Therefore, light elements have a weak signal and high errors of measurement. Ca and K concentrations did not differ in all the approaches, or when the certified values were compared (Fig. 2). The influence of the sample preparation is clearer in the case of S (Fig. 2). Thus, higher detected quantities of S were in the LP approach. However, those concentrations were relatively low (the second decimal of %) and, with the high associated uncertainty of measurement, the differences in results due to sample preparation are not
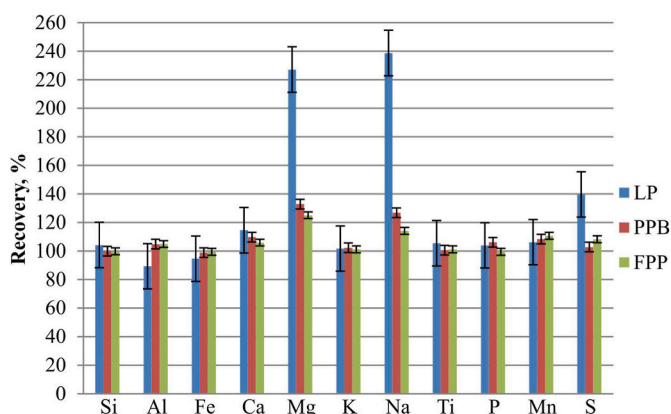

Fig. 3. Signal-to-noise ratio for CRM NCS DC 60104, brown line for the loose powders (LP) approach, blue line for the pressed pellet with the binder (PPB) approach, and red line for the fired pressed pellet without a binder (FPP) approach. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

significant for this element. Uncertainties in measurements ranged from 17% to 20% for S depending on the sample preparation technique ($U_S = 20.42\%$ for LP, $U_S = 17.69\%$ for PPB, and $U_S = 17.67\%$ for FPP). This issue will be discussed in depth later in this section (part of the uncertainties of measurements). All the uncertainties of measurements are given in Table 3. Other elements, such as Mn and Ti (Fig. 2), did not show deviations from certified values in all the sample preparation approaches. The obtained results showed similar trends as previously published in the case of mortars with the addition of clay [21].

EDXRF is known as a not completely precise technique for the determination of light elements, particularly when a loose powder sample preparation technique is used [16]. These types of samples are usually measured in a helium atmosphere to improve the light element measurement sensitivity. Generally, the factor that could affect the results of the concentration of the light elements was the critical analytical depth when X-ray photons are absorbed or escape from a sample [16, 27]. Critical analytical depth negatively influences the accuracy and trueness (recoveries) of light element concentrations determined by the XRF technique [17]. According to the study by Ichikawa and Nakamura [16], analytical depths are calculated. Analytical depths of different fluorescent X-rays for eleven elements in thirty reference materials with a density of 2.25 g cm-3 are: SiKα-11 μm; AlKα-9 μm; FeKα-100 μm; CaKα- 42 μm; MgKα-6 μm; KKα-32 μm; NaKα-4 μm; TiKα-11 μm; PKα-8 μm; MnKα-83 μm and SKα-5 μm. Other, heavy elements, show less impact on critical analytical depth. As X-ray energy and atomic number increase, the critical analytical depth for light elements such as Na, Mg, and S becomes shallower [16,27]. The influence of critical analytical depth on light elements measurement is expected to decrease after pulverization [27]. Namely, pulverization is done to gain homogeneity of the sample and decrease the particle size. Thus, by using the EDXRF

Fig. 2. Influence of sample preparation on the determined concentration of the major oxides using three different approaches: fired pressed pellet without a binder (FPP), press pellet with the binder (PPB), and loose powders (LP) preparation, for concentrations of Si, Al, Fe, Ca, Mg, K, Na, Ti, P, Mn, and S obtained with 15 CRM given as trueness (Recovery, %). The error bars indicate the standard deviation of the three replicated concentrations measured for the different sample preparations.
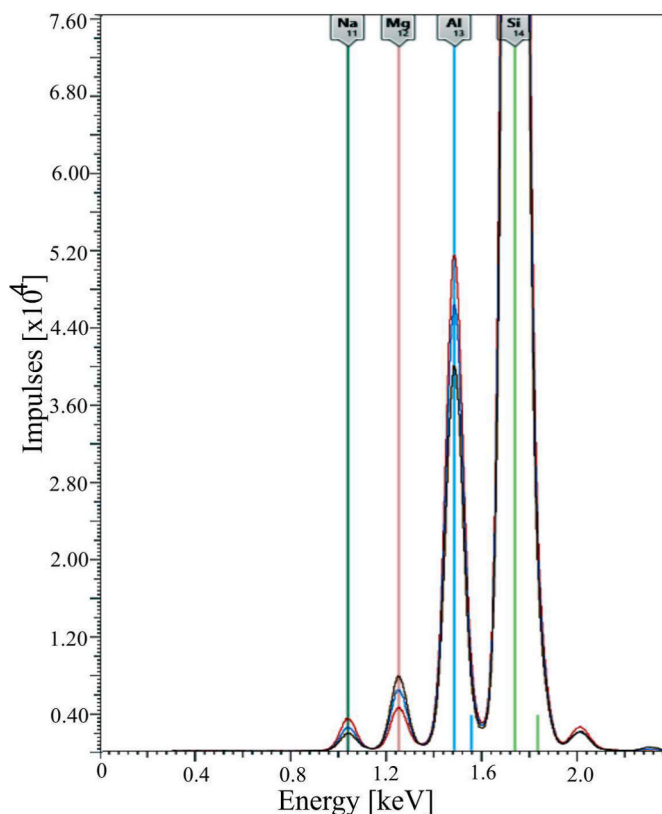
technique, it is possible to measure a high proportion of elements in finer fractions [27]. This may account for the differences in concentrations of Na and Mg between sample preparation approaches.

The influence of three sample preparation techniques on the recoveries of eleven elements (Si, Al, Fe, Ca, Mg, Na, K, Ti, P, Mn, and S) in the raw clay analyses has been highlighted in this study. The LP is the easiest preparation technique, but a problem with the quantification of Na, Mg, and S in clay due to the poor recoveries (>120%) is noticed. The pressed pellet with the binder (PPB) is more difficult to prepare than loose powder, but it enables gaining better results because the binder wax fills the spaces between the coarse grains, potentially reducing the effect of particle sizes and pores. Fired pressed pellet (FPP) is the most complicated technique of preparation in this study and requires the largest mass for the analysis of clays (20 ± 0.001 g). It is not a problem to prepare real clay samples, but the mass of CRMs samples is often limited. This may be a disadvantage of the proposed technique, but pellets made in this way are persistent and can be further used for testing the fired clay samples. Once made, fired pressed pellets can last for a long time, unlike pressed pellets with wax that usually crack. FFP gives the most precise recoveries because it achieves structural consistency, ensured by the firing, and fully oxidized elemental constituents. FPP is also suitable for performing other important experiments on ceramics [4,28].

Table 2 presents the working ranges, LOD, and LOQ, in %, of the method for EDXRF elemental analysis of raw and fired clay material.

Light elements (Na, K, Si, Mg, and Al) show higher LOD and LOQ values. The highest values of LODs and LOQs were determined for elements with major elements (Si and Al). All 3 LODs and LOQs for all 3 methods exhibit similar trends. In the LP technique, values of LODs and LOQs are a few times higher than in the other two methods (PPB and FPP). LODs in the LP approach are in the range from 0.005% (Mn) to 1.56% (Si), while LOQs are from 0.02% (Mn) to 4.73% (Si). PPB and FPP have similar detection limits, with values ranging from 0.001% (Mn) to 0.61% (K) for the PPB approach and 0.001% (Mn) to 0.46% (Al) for the FPP approach. LOQs are in the range of 0.004% (Mn) to 1.86% (K) in the PPB approach and from 0.005% (Mn) to 1.42% (Al) in the FPP approach. The results of LODs and LOQs for light elements (Al, Si, K, Na, and Mg) in all three techniques are not surprising. The analytical depth of X-rays for light elements is extremely small, and the differences in LODs and LOQs between all the three techniques are lower than the LODs and LOQs for other elements. However, calibration reference materials in this research and concentrations of calibration reference materials of Si and Al are very high (Table 1). High values of calibration concentration are the reason for the high LODs and LOQs for Si, Al, K, Na, Fe, and Mg in this study. For the rest of the elements (Ca, Mn, Ti, P, and S), the concentration of working ranges were lower so the values of LODs and LOQs were nearer, too. The highest concentrations in the working range were

in the case of Si (27.07–32.94%), while the lowest concentration in the working range was in the case of Mn (0.003–0.013%). The LODs and LOQs in this study were higher when compared to the results of our previously published study on mortars with added clay [21]. The differences in results appeared since two different computational approaches were used. In this study, the LODs and LOQs were calculated using a calibration curve, while in the last study [21], the approach with blank samples was implemented.

Precision was determined by repeatability and reproducibility for all of the three approaches and expressed as the relative standard deviation (RSD) of the repeated measurements in triplicates using ANOVA (Excel, Data Analysis). Repeatability was estimated in the same conditions by measuring the same samples of CRMs for all three approaches (pellets, cups) on the same day in triplicate. Reproducibility was evaluated by measuring samples of CRMs in different conditions, which might vary if tested by two experimenters. Table 3 presents the repeatability and reproducibility of all three approaches, expressed as the relative standard deviation (RSD) of the three times repeated measurements.

Precision was determined as higher for elements in the 4th (K, Ca, Ti, Mn, and Fe) than elements in the 3rd period (Na, Mg, Si, Al, S, and P) of the Periodic Table of Elements. The precision of analyzes performed on the PPB and FPP samples showed somewhat more precise results than the LP, especially in the case of higher concentrations determined. This finding is useful and important in cases when there is a low amount of samples because it implies that the LP method could give reliable results. Using the binder wax improved the precision, especially for light elements. Fired pressed pellet of clayey material showed a slightly higher precision for light elements because the homogenization of the sample with the wax binder is in that case excluded. Homogeneity of the sample is even more important for the light elements because of the effect of critical analytical depth. In the case of heavier elements, homogeneity is not so important for the method's precision because X-rays of higher energy penetrate deeper layers of the pellets. As expected, reproducibility was higher than repeatability for all the elements in all three approaches because of different testing conditions (Table 2). The values of repeatability (RSD %) for the LP approach ranged from 0.27% (K) to 2.81% (Mg), while reproducibility (RSD %) in the same approach was from 0.71% (Ti) to 4.11% (P). Repeatability (RSD %) ranged from 0.23% (Ca and Mn) to 3.82% (Mg), and reproducibility (RSD %) from 0.42% (K) to 4.56% (S) in the PPB approach. The lowest value for repeatability (RSD %) was 0.11% (Ti) and the highest was 1.96% (S) in the FPP approach, while the lowest reproducibility (RSD%) ranged from 0.25% (Ti) to 3.53% (Na). When the precision and expanded uncertainties of measurements are compared to the previously published results [21], similar results on different materials are observed in both studies. This is expected given that both studies used the same approaches to calculate precision and measurement uncertainty.

Table 2

Working range, the limit of detection (LOD), and limit of quantification (LOQ) in % for eleven elements using three sample preparation techniques (loose powders (LP), pressed pellet approach with the binder (PPB), and fired pressed pellet (FPP)).

Element concentration, %	Working range, %	LP		PPB		FPP	
		LOD, %	LOQ, %	LOD, %	LOQ, %	LOD, %	LOQ, %
Si	27.07–32.94	1.56	4.73	0.25	0.76	0.11	0.32
Al	8.96–15.08	1.01	3.08	0.19	0.56	0.46	1.42
Fe	0.72–7.61	0.37	1.13	0.19	0.56	0.24	0.74
Mg	0.56–0.85	0.22	0.68	0.11	0.34	0.29	0.88
Ca	0.05–0.21	0.13	0.40	0.11	0.32	0.09	0.26
Na	0.15–2.47	0.41	1.24	0.14	0.41	0.11	0.32
K	2.23–3.52	0.29	0.89	0.61	1.86	0.17	0.52
Ti	0.34–0.48	0.10	0.32	0.03	0.09	0.04	0.11
P	0.01–0.05	0.01	0.02	0.01	0.03	0.01	0.03
[a]Mn	0.003–0.013	0.005	0.015	0.001	0.004	0.001	0.005
[a]S	0.003–0.374	0.010	0.030	0.005	0.016	0.005	0.013

[a] The values for Mn and S are in three significant digits after the decimal point, as for certified concentration values in the standard samples in the Supplement material.

Table 3
Repeatability and reproducibility for all three approaches (loose powders (LP), pressed pellet approach with the binder (PPB), and fired pressed pellet (FPP)) are expressed as the relative standard deviation (RSD) of the repeated measurements in triplicates.

El.	LP		PPB		FPP	
	Repeatability RSD, %	Reproducibility RSD, %	Repeatability RSD, %	Reproducibility RSD, %	Repeatability RSD, %	Reproducibility RSD, %
Si	1.85	2.35	1.57	2.15	0.41	0.75
Al	1.52	1.71	1.96	2.10	1.14	2.60
Fe	1.22	1.32	0.88	2.00	0.84	1.34
Mg	2.81	3.64	1.23	3.82	1.27	3.53
Ca	0.72	0.86	0.23	0.71	0.21	0.53
Na	1.48	1.78	1.25	1.26	1.37	2.04
K	0.27	0.85	0.30	0.42	0.31	0.36
Ti	0.47	0.72	0.43	0.49	0.11	0.25
P	2.09	4.11	0.64	1.89	1.43	2.25
Mn	0.63	1.26	0.23	0.46	0.72	0.79
S	2.01	2.61	2.16	4.56	1.96	2.70

Expanded uncertainties of measurements calculated by Eq. (1), Eq. (2) and Eq. (3) (section 2.2) for eleven elements and all the three approaches of sample preparation clays are given in Table 4.

As expected, the highest total uncertainties of measurements were in the LP approach for all the examined elements (from 5.65% for Fe to 35.21% for Na). In the other two approaches, PPB and FPP, the total uncertainties of measurements were from 3.64% for Fe to 25.54% for Na; and 4.35% for Fe and 20.34% for Na. Only one of the uncertainties was above 30% (LP approach for Na) and did not follow the Guide to the expression of uncertainty in measurement (GUM) and the International vocabulary of metrology (VIM) principles, while other results were below 30% [29,30].

The uncertainty of measuring the elemental concentrations in the different sample preparation was below 1% in all of the three approaches (Table 4). The uncertainties results related to the sample preparation technique were compared to analytical uncertainties in Fig. 4. The main contribution to the uncertainty in all the cases was the analytical error (see Fig. 4). The assumption of the origin of such a small error in sample preparation by EDXRF is that this technique does not require complicated sample preparation and there are small numbers of steps that can affect total uncertainties. In contrast to the uncertainty of the measurement for sample preparation technique, analytical measurement uncertainty is more dominant. Analytical uncertainties ranged from 2.77% for Fe to 17.59% for Na (LP approach), 1.69% for Fe to 12.74% for Fe (PPB approach), and 2.06%–10.14% for Fe (FPP approach).

4. Conclusions

Sample preparation techniques such as loose powder (LP), pressed pellet (PPB), and fired pressed pellet (FPP) without binder wax showed a relatively low extent of effects on multi-element EDXRF raw clay analysis. However, there are differences in recoveries between the approaches.

The main conclusions from the study are as follows:

1. For all the three sample preparation techniques, recoveries were predominantly allowed in the range from 80 to 120%, except for increasing recovery for light elements, Mg, Na, and S exclusively for the LP approach. Additionally, the FPP developed here appeared to be one of the most precise recoveries compared to the other two approaches (LP and PPB),
2. FPP gives the most precise recoveries because it achieves structural consistency, ensured by the firing, lowered porosity of the samples, and fully oxidized elemental constituents,
3. The LODs and LOQs for FPP are mostly the same as those obtained during the validation of the method with standard pellets (PBB approach). The LODs and LOQs for the LP approach are higher than for standard and fired pellets,
4. The precision and values of expanded uncertainties are similar in all three approaches for the majority of elements, but the lowest values were in the case of PPB and FPP,
5. Fired pressed pellets of clayey material had a slightly better precision for light elements because of the increased homogenization of the sample compared to the wax-bonded dry sample. This finding could be related to the highlighted advantages of the FPP approach as a sample preparation technique for clay for EDXRF analysis, and
6. The FPP is also suitable for testing other important physical and mechanical properties of the ceramics samples after the firing process. This method of preparation is multi-useful and facilitates the testing of clays in its entirety.

This study shows the validation of the EDXRF method for raw clay analysis by selecting the appropriate and novel sample preparation. In addition, laboratory EDXRF could be a possible confirmatory technique for verifying the chemical content of raw clays.
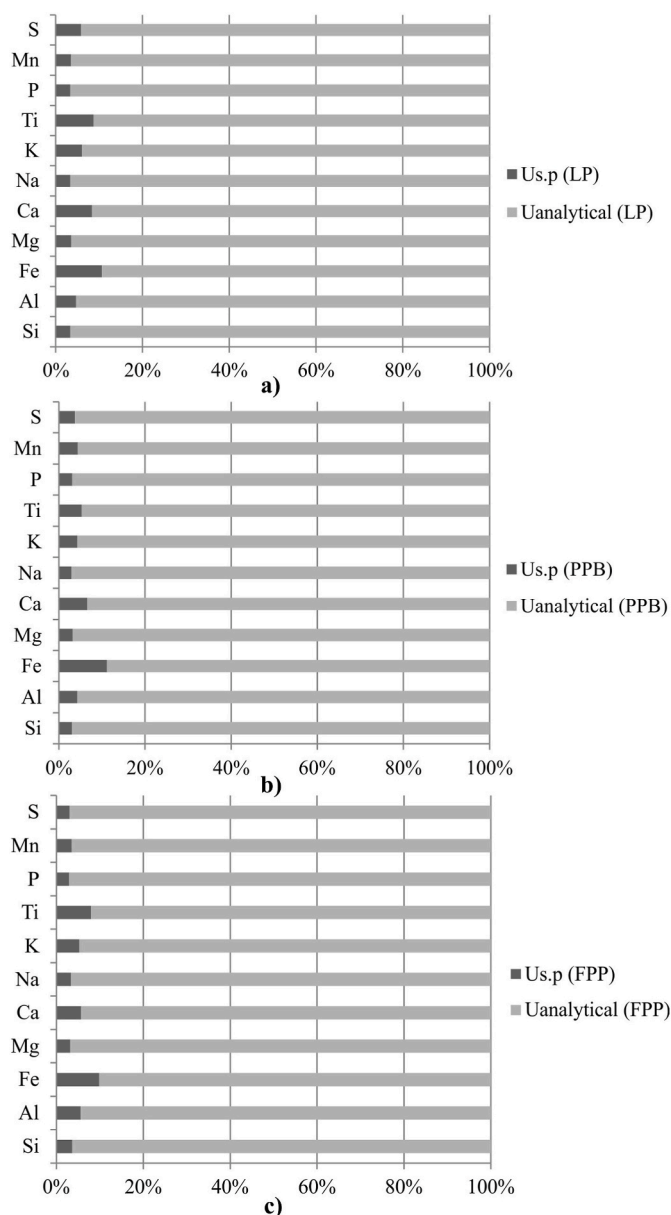
Table 4
Uncertainty values are calculated for sample preparation ($u_{s,p}$), analysis ($u_{analytical}$), and total expanded uncertainties (U_{total}) of measurements (k = 2) for eleven elements and all three approaches (loose powders (LP) pressed pellet approach with the binder (PPB), and fired pressed pellet (FPP)) in clay.

El	LP			PPB			FPP		
	Uncertainty of measurement, %								
	$u_{s,p}$	$u_{analytical}$	U_{total}	$u_{s,p}$	$u_{analytical}$	U_{total}	$u_{s,p}$	$u_{analytical}$	U_{total}
Si	0.32	9.10	18.23	0.42	6.65	13.37	0.47	6.14	12.35
Al	0.35	7.14	14.33	0.38	4.28	8.65	0.43	3.61	7.34
Fe	0.33	2.77	5.65	0.45	1.69	3.64	0.47	2.06	4.35
Mg	0.53	14.16	28.36	0.66	9.91	19.88	0.57	8.56	17.18
Ca	0.43	4.73	9.56	0.47	3.27	6.69	0.38	3.11	6.35
Na	0.61	17.59	35.21	0.78	12.74	25.54	0.71	10.14	20.34
K	0.55	8.55	17.16	0.69	7.63	15.36	0.75	6.71	13.53
Ti	0.53	5.55	11.19	0.49	4.32	8.76	0.67	3.81	7.79
P	0.44	12.65	25.34	0.65	10.09	20.24	0.56	9.30	18.66
Mn	0.28	7.60	15.24	0.48	5.13	10.36	0.47	6.35	12.78
S	0.63	10.18	20.42	0.69	8.81	17.69	0.55	8.80	17.67

Fig. 4. Uncertainty contribution of sample preparation ($u_{s,p}$). and analysis ($u_{analitical}$) for target elements in clays obtained for a) loose powders (LP) approach, b) pressed pellet approach with the binder (PPB) approach, and c) fired pressed pellet FPP approach.

Credit author statement

Nevenka Mijatović; : Conceptualization, Methodology, Validation, Writing – original draft, Writing – review & editing, Visualization. Milica Vasić; : Conceptualization, Writing – review & editing. Ljiljana Miličić; : Investigation, Resources. Milena Radomirović; : Formal analysis, Investigation,. Zagorka Radivojević: Investigation Writing – review & editing.

Declaration of competing interest

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2022.123844.

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