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EX-SITU PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE MAJOR ELEMENTS DETERMINATION IN SILICATE GEOLOGICAL SAMPLES USING MATRIX-MATCHING STANDARDS FOR CALIBRATION

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ABSTRACT. An ex-situ method for determining the major elements in the high silicate matrix using portable XRF spectrometry (pXRF) was developed. The calibration is based on the dilution of a matrix-matched certified reference material BCS-CRM No. 376/1 Potash Feldspar with analytical grade SiO_2. Significant correlation coefficients for linear regressions were obtained for all major oxides. This approach of instrument calibration has as the principal advantage the use of a single certified reference material, which reduce the cost of analysis. The limits of detection were evaluated from measurement of SiO_2 considered as blank. The method accuracy of the developed calibration was checked in the recovery study of two certified reference materials (BCS-CRM No. 309 Sillimanite and BCS-CRM No. 375/1 Soda Feldspar), with geological matrix, and the recoveries rate were in the range of 85 – 110 %. The relative expanded uncertainties (*k = 2, P = 95%*) calculated from CRM analysis were of 6.99% for Al_2O_3, 3.56% for Fe_2O_3, 4.82% for CaO and 4.31% for K_2O. The proposed methodology is a green analytical method, allowing fast and accurate analysis of geological samples without use of chemical reagents.

Keywords: *X-ray fluorescence, major element, zeolite, instrument calibration, matrix-matching calibration, ex-situ procedure*

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INTRODUCTION

In general, the laboratory techniques used for the determination of the elements in solid samples require total or partial destruction for extraction of analytes into a liquid solution [1,2]. The sample digestion represents the main drawback of these techniques since it is time-consuming and requires hazardous and expensive reagents [3,4]. For geological sample characterization, usually is needed to know the total amount of constituents. Samples with higher silicate content are difficult to digest and most of the digestion methods are incomplete with an unsatisfactory extraction yield. The wet digestion procedures for silicate samples generally use mixtures of acids containing HF. The resulted solution cannot directly nebulized with the usual sample introduction systems of the spectrometric instruments, being necessary a supplementary neutralization step of HF with high quantities of boric acid [5].

A good alternative to the methods that involve sample digestion is the use of techniques that allow direct determination of elements in solid sample. X-ray fluorescence technique provides compositional data by exciting the sample with X-rays. This technique involves a loss of energy by emitting photons with energy equal to the difference in electron orbitals, specific for the element in question [6]. Energy Dispersive X-ray fluorescence (EDXRF) technique is used to obtain elemental information from different types of materials either in-situ or ex-situ approaches. Measurements made with portable X-ray fluorescence equipment (pXRF) have several advantages: can provide a large number of rapid on-site measurements; are non-destructive and cost-effective. Due to these advantages, the technique got increased attention, being applied to geochemical exploration [7,8] or to assess environmental contamination [9-13].

pXRF is typically used at concentrations between a few mg kg^{-1} to a few percent for elements with medium to high atomic mass (K, Z=19 to Pb, Z=82, and Th, Z=90 and U, Z=92), having more limitations for lightweight elements than laboratory XRF instruments [7], due to higher spectral background in the range of energy of these elements. However, new generation of pXRF have more sensitive X-ray detectors and/or an inert gas flow system (helium) to remove the air between the sample and the detector, that allow simultaneously determination of wide-ranging elements, including Mg (Z=12), Al (Z=13), Si (Z=14), P (Z=15), [7, 14]. Although pXRF has considerable advantages and there are many studies based on this technique [15-17], the obtained results could be influenced by possible matrix effects that can conduct to measurement bias, as quality control being extremely important. On most instruments, pXRF calibration principles differ for trace level elements (soil mode) and major level elements (mining mode).

In order to obtain reliable results, calibrations using matrix-matching CRMs, or techniques based on standard addition of analytes to a corresponding matrix were used [18]. Irenas-Islas and co-workers used for calibration of pXRF equipment a CRM diluted with pure calcium carbonate for analysis of samples with carbonate matrices [19].

In the present study a new calibration strategy using pXRF was established to analyse major elements in silicate samples. Therefore, a calibration scheme that comprises the use of solid calibration standards obtained by mixing of a CRM with pure SiO_2 as diluent was developed. Figures of merit such as limits of detection and limits of quantification, repeatability and accuracy were also evaluated. The proposed methodology is a green analytical method that allows a fast and accurate analysis of complex silicate matrix samples without use of chemical reagents.

RESULTS AND DISCUSSION

Calibration curves for the pXRF

Compared to other more complex laboratory methods (including non-portable XRF analyzers), results obtained through this technique can be susceptible to measurement bias or to matrix effects [6]. To avoid this, the calibration with standards with an appropriate matrix is a more reasonably option than empirical or standardless approaches.

The use of CRMs with different levels of analyte concentrations as calibration standards is possible, although is difficult to find CRMs with similar matrices, and increasing concentrations of all analytes, equally distributed over the calibration range. Moreover, CRMs are expensive materials, which lead to an increased cost of analysis. The approach of standard addition of analyte from liquid solutions to prepare solid calibration standards can conduct to non-homogenous analyte concentrations, and it may not be the best option for calibration in this case. Therefore, in this study we used a different approach based on the dilution of an appropriate CRM (BCS-CRM 376/1 Potash Feldspar) with pure reagent of SiO_2. The study was conducted to evaluate the calibration parameters for Al_2O_3, Fe_2O_3, CaO and K_2O. Five calibration levels were prepared by mixing amounts of SiO_2 and CRM (BCS-CRM 376/1 Potash Feldspar) in order to have 10%, 20%, 40%, 60%, 70%, 80%, 90% and 100% CRM (w/w), with the calculated concentrations presented in Table 1.

Table 1. Concentrations (mg kg^{-1}) of Al_2O_3, Fe_2O_3, CaO and K_2O in the solid calibration standards

CRM content (m/m)	**Al_2O_3 mg kg^{-1}**	**CaO mg kg^{-1}**	**Fe_2O_3 mg kg^{-1}**	**K_2O mg kg^{-1}**
10%	18630	421	85	11590
20%	37260	842	170	23180
40%	74520	1684	340	46360
60%	111780	2526	510	69540
70%	130410	2947	595	81130
80%	149040	3368	680	92720
90%	167670	3789	765	104310
100%	186300	4210	850	115900

SiO_2 as blank and the calibration standards were measured, and the obtained signals were used to construct the calibration curves. As presented in Table 2, the correlation coefficients of the linear regressions, for the range of 10% – 100 % CRM, were below 0.9 for Al_2O_3, CaO and K_2O, and only in case of Fe_2O_3 the correlation coefficient was better than 0.9 (due to better detection of Fe emission lines, a direct consequence of higher atomic mass of Fe, Z=26). Graphical representation of the calibration curves appeared as a broken line in all cases. The poor linearity of the curves over the entire calibration range can be explained by the possible self-absorption.

Consequently, the calibrations ranges were divided in two different ranges: one for the amounts 10% – 60% CRM (10% CRM; 20% CRM; 40% CRM and 60% CRM), and the second for the range of 70% - 100% CRM (70% CRM; 80% CRM; 90% CRM; 100% CRM), these concentrations were measured, and linear regressions were constructed for the new ranges. The calibration parameters of the linear calibrations for Al_2O_3, Fe_2O_3, CaO and K_2O in the solid calibration standards over the all three ranges are presented in Table 2.

As presented in Table 2, the correlation coefficients for the range 10% – 60% CRM were significantly improved, being in all cases higher than 0.99. Also, the slope values were increased with a factor ranging between 1.60 for Fe_2O_3 to 2.75 for Al_2O_3, which means an increased sensitivity.

Also, the correlation coefficients for linear regressions over the range of 70 – 100% CRM are higher than 0.99 for all the analytes, but with significant lower sensitivity than in the case of lower domain of concentrations.

The significant differences in sensitivity between the two calibration ranges can be explained by different measurement mode of the instrument using different acquisition parameters and calibration coefficients (soil mode for lower concentrations and mining mode for higher concentrations) [7].

The results obtained in the linearity of the calibration curves assay demonstrate that the pXRF can be reliably used to measure major oxides in silicate matrices.

Table 2. Linear calibration curves parameters for the ranges of 10% – 100%; 10% – 60%; and 70% – 100% CRM BCS-CRM 376/1 Potash Feldspar

Element	Intercept (a)	Slope (*b*)	Correlation coefficient (R)
Range 10% – 100% CRM			
Al_2O_3	8980	0.0061	0.792
CaO	11495	1.5985	0.846
Fe_2O_3	4151	6.4965	0.921
K_2O	126122	1.3394	0.838
Range 10% – 60% CRM			
Al_2O_3	8395	0.0168	0.992
CaO	9462	2.9743	0.997
Fe_2O_3	2938	10.368	0.997
K_2O	73235	2.5831	0.996
Range 70% – 100% CRM			
Al_2O_3	9110	0.0048	0.994
CaO	11408	1.4922	0.995
Fe_2O_3	6266	3.4859	0.990
K_2O	199331	0.5557	0.993

Limits of detection (LoDs)

The LoDs for pXRF depend on instrumental characteristics, such as tube and detector specifications, sample matrix and/or emission lines [7]. Thus, each instrument has its own specific element range, for a specific application [17].

The LoD is commonly assessed as three times the standard deviation of replicate analysis of blank standards of the analyte [20, 21]. In our study, we adapted this approach to estimate LoDs of elements in the matrix of SiO_2. For each element of interest, 10 repeated measurements were performed on the pure SiO_2, and the signals were registered. LoDs were calculated as the ratio between three-time standard deviations and slopes of the calibration curves for each element. The obtained LoDs are significant for silicate matrices.

The calculated LoDs were 81 mg kg^{-1} for CaO, 48 mg kg^{-1} for Fe_2O_3 and 161 mg kg^{-1} for K_2O. These values are in the range of those reported by Lemiere et al. [7] for elements as being characteristic for performing pXRF instruments. Also, the LoDs obtained in our study were in similar domains with those reported by Hall et al. [18] for major elements. A higher LoD of about 0.25% was evaluated in our study for Al_2O_3 that can be explained by the high concentrations of this element in the used standards for equipment calibration, in the range of 37260 – 186300 mg kg^{-1}.

Precision and Trueness

BCS-CRM 375/1 Soda Feldspar certified reference material was measured 10 times and the results are listed in Table 3. The concentrations of K_2O were measured on the calibration curve at lower range of concentrations, while Al_2O_3, CaO and Fe_2O_3 were measured on the the calibration curves at high range of concentrations. Since the values for CaO and Fe_2O_3 were higher than those in the most concentrated standard, appropriate dilutions with SiO_2 were used.

Table 3. Repeatability study for CRM sample (BCS-CRM 375/1 Soda Feldspar (n=10 parallel determinations)

Element	**Average (mg kg^{-1})**	**s_r (mg kg^{-1})**	**RSD$_r$ (%)**	**r (%)**
Al_2O_3	172530	3970	2.30	6.44
CaO	8091	148	1.83	5.12
Fe_2O_3	3044	77	2.53	7.08
K_2O	13995	329	2.35	6.58

s_r – standard deviation of repeatability; RSD$_r$ – relative standard deviation of repeatability; r – limit of repeatability (2.8x RSD$_r$)

The RSD% for repeatability was in the range of 1.83% - 2.53% indicating a good precision for this method for the analyzed oxides. The trueness was evaluated by analyzing two CRMs with appropriate matrix (BCS-CRM 357/1 Soda Feldspar and BCS-CRM 309 Sillimanite), other that the CRM used for instrument calibration, and the results are presented in Table 4. The concentrations of oxides were measured on the appropriate calibration curves according to theirs concentrations. After the measurement of CRMs the absolute difference (Δm) between the mean measured values and the certified values were calculated. Also, the expanded uncertainty was calculated (for k=2) from the combined uncertainty (UΔ) estimated using Equation (1).

$$U_{\Delta} = \sqrt{U_m^2 + U_{CRM}^2} \qquad (1)$$

where U_m is the measured uncertainty expressed as standard deviation obtained from repeated determinations, and U_{CRM} is the specified uncertainty in the CRM certificate.

To evaluate accuracy, Δ_m was compared with U_{Δ}. Since $\Delta_m \leq U_{\Delta}$ there was no significant difference between the measurement result and the certified value.

Table 4. Certified values of CRMs, measured concentrations (n = 10 parallel determinations) and the average recovery degree (%)

Components	**Certified Values ± U** (mass %)	**Average values ± CI** (mass %)	**Average Recovery ± CI** **(%)**
BCS-CRM 357/1 Soda Feldspar			
Al_2O_3	17.89 ± 0.08	17.25 ± 0.28	96.4 ± 1.6
CaO	0.78 ± 0.03	0.81 ± 0.011	104 ± 1.4
Fe_2O_3	0.291 ± 0.011	0.304 ± 0.006	105 ± 1.9
K_2O	1.47 ± 0.03	1.40 ± 0.024	95.2 ± 1.6
BCS-CRM 309 Sillimanite			
Al_2O_3	61.1 ± 0.2	60.98 ± 0.71	99.8 ± 1.2
CaO	0.22 ± 0.02	0.22 ± 0.003	102 ± 1.2
Fe_2O_3	1.51 ± 0.03	1.45 ± 0.020	96.1 ± 1.4
K_2O	0.46 ± 0.04	0.45 ± 0.004	98.7 ± 1.0

U = expanded uncertainty; CI – confidence interval for repeated determinations

The recovery rates were in the range of 95.2% and 105%. The differences between the certified and measured values for all the analyzed oxides were smaller than the expanded uncertainties (*U*, *k*=2) calculated from the combined uncertainties.

Estimation of measurement uncertainty

Measurement uncertainty was evaluated based on the bottom-up approach. The identified main sources of measurement uncertainty were assumed to come from uncertainty of calibration reference materials, uncertainty of weighted CRMs for standards preparation, uncertainty of measured signals of the calibration standards, bias obtained in accuracy study in CRM analysis, and are presented in Figure 1. In our study for the estimation of measurement uncertainty, it was assumed that two main components affect the method uncertainty: bias in CRM analysis and standard deviation obtained in repeated CRM analysis. The combined uncertainties (u_c) were calculated using Equation (2), then were calculated the expanded uncertainties (*U*) for a cover factor k = 2 (P = 95%).

$$u(B) = \sqrt{B^2 + u(C_R)} \tag{2}$$

where B is bias from the CRM analysis and $u(C_R)$ is the standard deviation of parallel measurements of CRM.

The pooled expanded uncertainty (*U%*) for the method was calculated by combining the expanded uncertainties (U_1 and U_2) of each CRM analysis, according to Equation (3) [22]:

$$U(\%) = \sqrt{\frac{U_1^2 + U_2^2}{2}} \tag{3}$$

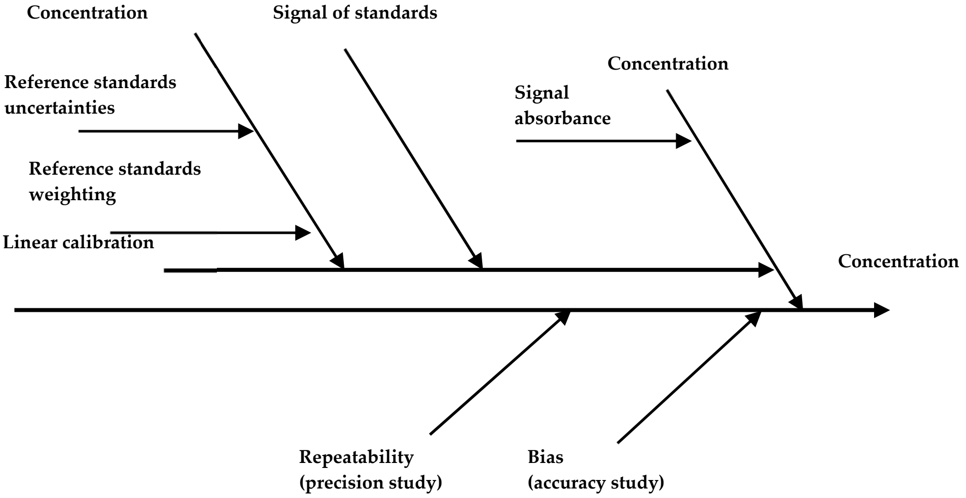

Figure 1. Cause and effects diagram of uncertainties in measurements by XRF

The pooled relative expanded uncertainties (*k = 2, P = 95%*) were of 7% for Al_2O_3, 4% for Fe_2O_3, 5% for CaO and 4% for K_2O, indicating a good confidence for this technique.

CONCLUSIONS

In this study, a new approach for calibration of pXRF for the determination of major elements in geological samples with high silicate matrices was used. Calibration curves were built for determination of Al_2O_3, Fe_2O_3, CaO and K_2O. Correlation coefficients better than 0.9 for linear regressions were obtained for all major oxides. This approach of instrument calibration has as the main advantage the use of a single certified reference material, in a non-destructive way (thus allowing virtually unlimited reuse), which reduces the cost of analysis. The method accuracy of the developed calibration was checked in the recovery study of two certified reference materials (BCS-CRM No. 309 Sillimanite and BCS-CRM No. 375/1 Soda Feldspar) with good results. The proposed methodology is in the line of green analytical methods, permitting fast and accurate analysis of geological samples without the use of chemical reagents.

EXPERIMENTAL SECTION

Analyses were performed with a Bruker Tracer 5i portable X-ray fluorescence with a 5kV and 4-watt X-ray source, 8 μm Be window and 8 mm spot collimator. The pXRF device was used for all measurements in a desktop stand (laboratory) configuration. Between the instrument's window and the detector, no special conditions were created (air atmosphere). Samples were placed in a Chemplex® container covered with polyester Mylar® film (offering minimal X-ray absorption, but safely separating the sample from the instrument internal volume).

For Fe analysis, a voltage of 50 kV and a current of 6 μA were used, no filters were used. For the rest of the elements (Al, K, Ca), a voltage of 15 kV and a current of 20 μA were used, also with no filter. A 30-minute time was dedicated for signal acquisition for each sample. Data was acquired using Bruker's Artax software (v8.0.0.476) and the signal values (in counts) for each corresponding peaks were exported to Microsoft Excel for further processing.

SiO_2 powdered reagent (Merck, Darmstadt, Germany) was used as diluent for the certified reference material BCS-CRM No. 376/1 Potash Feldspar (Bureau of Analysed Samples Ltd, United Kingdom), with particle size < 60 μm, in order to obtain the calibration standards. Before using, the SiO_2 was dried at 70 °C in an oven for 2 hours, and then the solid mixtures were prepared using different weight percentages of SiO_2 and BCS-CRM 376/1, according to the data presented in Table 1. The final dry weight of each of the 11 mixtures used for the calibration curve was 6.0 g.

Simple linear regression analyses were carried out using Microsoft Excel® program. The detection limits for each element measured with the pXRF were calculated as 3 times the standard deviation (SD) measured in pure SiO_2 (considered as blank).

For the recovery study, two Certified Reference Materials, CRM BCS-CRM 357/1 Soda Feldspar (particle size < 60 μm) and BCS-CRM No. 309 Sillimanite (particle size < 90 μm) from Bureau of Analysed Samples Ltd (United Kingdom) were used. The samples (CRMs) were analysed as powders with the granulation provided by producers.

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