

# PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE MAJOR ELEMENTS DETERMINATION IN SILICATE GEOLOGICAL SAMPLES

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## Introduction

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.

Samples with higher silicate content are difficult to digest and most of the digestion methods are incomplete with an unsatisfactory extraction yield. 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.

Although portable XRF (pXRF) has considerable advantages and there are many studies based on this technique, 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.

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<sub>2</sub> as diluent was developed.

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.

## Material and methods

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.

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.

SiO<sub>2</sub> 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, presented in Table 1.

Table 2. Calibration standards used for pXRF

CRM content (m/m)	Al <sub>2</sub> O <sub>3</sub> mg kg <sup>-1</sup>	CaO mg kg <sup>-1</sup>	Fe <sub>2</sub> O <sub>3</sub> mg kg <sup>-1</sup>	K <sub>2</sub> O mg kg <sup>-1</sup>
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

## RESULT and DISCUSSIONS

### Calibration curves for the pXRF

SiO<sub>2</sub> 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<sub>2</sub>O<sub>3</sub>, CaO and K<sub>2</sub>O, and only in case of Fe<sub>2</sub>O<sub>3</sub> the correlation coefficient was better than 0.9.

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<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO and K<sub>2</sub>O in the solid calibration standards over the all three ranges are presented in Table 2.

Table 2. Linear calibration curves parameters

Element	Intercept (a)	Slope (b)	Correlation coefficient (R)
<b>Range 10% - 100% CRM</b>			
Al <sub>2</sub> O <sub>3</sub>	8980	0.0061	0.792
CaO	11495	1.5985	0.846
Fe <sub>2</sub> O <sub>3</sub>	4151	6.4965	0.921
K <sub>2</sub> O	126122	1.3394	0.838
<b>Range 10% - 60% CRM</b>			
Al <sub>2</sub> O <sub>3</sub>	8395	0.0168	0.992
CaO	9462	2.9743	0.997
Fe <sub>2</sub> O <sub>3</sub>	2938	10.368	0.997
K <sub>2</sub> O	73235	2.5831	0.996
<b>Range 70% - 100% CRM</b>			
Al <sub>2</sub> O <sub>3</sub>	9110	0.0048	0.994
CaO	11408	1.4922	0.995
Fe <sub>2</sub> O <sub>3</sub>	6266	3.4859	0.990
K <sub>2</sub> O	199331	0.5557	0.993

### Figures of merit

For each element of interest, 10 repeated measurements were performed on the pure SiO<sub>2</sub>, 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 calculated LoDs were 81 mg kg<sup>-1</sup> for CaO, 48 mg kg<sup>-1</sup> for Fe<sub>2</sub>O<sub>3</sub> and 161 mg kg<sup>-1</sup> for K<sub>2</sub>O.

For precision study, BCS-CRM 375/1 Soda Feldspar certified reference material was measured 10 times and the results are listed in Table 3. The RSD% for repeatability was in the range of 1.83% - 2.53% indicating a good precision for this method for the analyzed oxides.

Table 3. Repeatability study for CRM sample (BCS-CRM 375/1 Soda Feldspar)

Element	Average (mg kg <sup>-1</sup> )	s <sub>r</sub> (mg kg <sup>-1</sup> )	RSD <sub>r</sub> (%)	r (%)
Al <sub>2</sub> O <sub>3</sub>	172530	3970	2.30	6.44
CaO	8091	148	1.83	5.12
Fe <sub>2</sub> O <sub>3</sub>	3044	77	2.53	7.08
K <sub>2</sub> O	13995	329	2.35	6.58

The trueness was evaluated by analyzing two CRMs with appropriate matrix (BCS-CRM 357/1 Soda Feldspar and BCS-CRM 309 Sillimanite), other than the CRM used for instrument calibration, and the results are presented in Table 4.

Table 4. Certified values of CRMs, measured concentrations, and recoveries

Components	Certified Values	Average values	Average Recovery
<b>BCS-CRM 357/1 Soda Feldspar</b>			
Al <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	0.291 ± 0.011	0.304 ± 0.006	105 ± 1.9
K <sub>2</sub> O	1.47 ± 0.03	1.40 ± 0.024	95.2 ± 1.6
<b>BCS-CRM 309 Sillimanite</b>			
Al <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	1.51 ± 0.03	1.45 ± 0.020	96.1 ± 1.4
K <sub>2</sub> O	0.46 ± 0.04	0.45 ± 0.004	98.7 ± 1.0

Measurement uncertainty was evaluated based on the bottom-up approach. The pooled relative expanded uncertainties (k = 2, P = 95%) were of 7% for Al<sub>2</sub>O<sub>3</sub>, 4% for Fe<sub>2</sub>O<sub>3</sub>, 5% for CaO and 4% for K<sub>2</sub>O, indicating a good confidence for this technique.

## CONCLUSION

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. 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

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