



Analytical Note

Rapid quantitative determination of major and trace elements in silicate rocks and soils employing fused glass discs using wavelength dispersive X-ray fluorescence spectrometry



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ABSTRACT

This paper introduces a calibration procedure and provides the data achieved for accuracy, precision, reproducibility and the detection limits for major (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, P) and trace (Ba, Cr, Cu, Hf, La, Nb, Ni, Pb, Rb, Sr, Ta, Th, U, Y, Zn, Zr) elements in the routine analysis of geological and environmental samples. Forty-two rock and soil reference materials were used to calibrate and evaluate the analytical method using a sequential wavelength dispersive X-ray fluorescence spectrometer. Samples were prepared as fused glass discs and analysis performed with a total measuring time of thirty-one minutes. Another set of twelve independent reference materials were analyzed for the evaluation of accuracy.

The detection limits and accuracy obtained for the trace elements (1–2 mg/kg) are adequate both for geochemical exploration and environmental studies. The fitness for purpose of the results was also evaluated by the quality criteria test proposed by the International Global Geochemical Mapping Program (IGCP) from which it can be deduced that the method is adequate considering geochemical mapping application and accuracy obtained is within the expected interval of certified values in most cases.

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1. Introduction

Silicate rocks, soils and sediments have a complex matrix composition and their multi-element chemical analysis is of interest in several geochemical and environmental applications [1]. Concerning the analytical technique for solid form multi-element analysis, probably X-ray fluorescence spectrometry is one of the most appropriate. But, analytical precision and the ultimate accuracy of the results depend on several factors: instrumental settings and stability, the calibration procedure, mineralogical and matrix effects, the reference materials used to calibrate the instrument, sample preparation and the strategy adopted to maintain the results within accepted limits [2].

In geochemistry, we often need accurate measurement of trace elements on a large number of samples, for example in order to study magmatic processes such as crystallization or partial melting. Usually L spectra have been used as the analytical line for heavy element analysis such as rare earth elements like Th and U, instead of the most intense K spectra, because of their excitation energy is higher than that of primary X-rays [3]. For the quantitative determination of major and trace elements the pressed pellet method is used, whilst the fused bead method is prescribed

for accurate analysis of matrix elements. Pressed pellets are prepared from a dried and fine grinded sample in the pellet press after mixing the sample with a binder such as wax. Fused discs are prepared using a fusion apparatus after addition of a suitable flux to the sample.

Many authors have examined the fusion techniques involving various samples to flux ratios such as 1:10 [4,5] 1:5 [6–9] and 1:2 [10–12]. The 1:10 dilution glass discs are suitable for major element analysis, but such a high dilution causes low fluorescent X-ray intensity and consequent difficulty in trace element analysis. The 1:5 and 1:2 dilution glass beads are available for both major and trace element analyses. In XRF analysis, borate fusion is particularly advantageous because the obtained result is based on a solid glass. In other physical-chemical methods like Atomic absorption (AA) and inductively coupled plasma (ICP) analysis-borate fusion competes with acid digestion techniques and is frequently an easier and simpler way to make liquid solutions. Further, the fused technique is well suited for accurate determination and sensitivities might be improved if the sample-to-flux ratio (dilution ratio) is lowered and the technique eliminates heterogeneity due to grain size and mineralogical effect. With this, a homogeneous molten glass with positive ions of the sample and flux in a cloud of oxygen atoms is formed after cooling to yield an amorphous homogeneous solid glass.

The purpose of the present study was to develop a quantitative analytical XRF method for the routine analysis of major and trace elements

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(SiO₂, TiO₂, Al₂O₃, Fe₂O₃(T), MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, Ba, Cr, Cu, Hf, La, Nb, Ni, Pb, Rb, Sr, Ta, Th, U, Y, Zn and Zr) in silicate rocks with ultramafic, mafic, felsic, calcic and alkaline compositions prepared as fused glass discs. For this purpose, we employed sample: flux ratio as 1:5 dilution glass beads, which is available to wide ranges of compositions and can be prepared more easily. Besides sample preparation, the final accuracy depends strongly on the calibration strategy, precision and reproducibility, which was evaluated by the analysis of 12 independent reference materials.

2. Experimental

2.1. Instrumentation

A Philips MagiX PRO, Model PW 2440 (Philips, Eindhoven, The Netherlands), sequential wavelength dispersive X-ray fluorescence spectrometer, coupled with an automatic sample changer PW 2540 and provided with suitable software SUPER Q 3.0, was used for this study. The MagiX PRO is a sequential instrument with a single goniometer based measuring channel covering the complete elemental measurement range from F to U in the concentration range from 1.0 ppm or mg/kg to % level, determined in vacuum media. The instrument is microprocessor controlled for maximum flexibility and consists of an end-window X-ray tube with an Rh anode and a maximum voltage/current of 60 kV/125 mA at a maximum power level of 4 kW. Table 1 shows the instrumental parameters on which the analytical program was developed using WDXRF. Measurement conditions were optimized to ensure best signal-to-background ratio and minimum line overlap.

2.2. Sample preparation

Reference samples were prepared as received with particle size 74 μ, without extra grinding to avoid any contamination. The standard reference bottles were manually rolled and mixed thoroughly before sub-

samples were taken. Glass discs for each sample were prepared by fusion of 2.0 g of the standard sample with 10.0 g of lithium metaborate:tetraborate (4:1) (Spectroflux 100B, Johnson Matthey, USA), using Pt-Au crucibles and moulds employing fusion equipment supplied with gas burners (Fluxy, Claisse, Canada). A Claisse M4 Fluxer is a three position fluxer, specially developed for automatic ignition and flame watching system for increased safety and backfire control. The burners with supply of liquefied petroleum gas (LPG) was maintained at input pressure of 69 ± 7 kPa (10 ± 1 PSI) and maximum burner pressure of 3.5 PSI for superior flame stability at low and high temperatures. There are three burners with maximum gas consumption of 18.4 L/min and maximum heat dissipation: 29 kW. The voltage ranges from 100 to 115 V with 50–60 Hz frequency at 100 W power.

2.3. Calibration

The spectrometer was calibrated after measuring intensities in the following forty two international reference materials: ASK-1, ASK-2 (larvikite, schist, ASK, Norway); BHVO-1, GXR-4, RGM-1, DTS-2, DTS-1, RGM-2, SDC-1, PCC-1, G-2, DNC-1, AGV-2, W-2, BIR-1, BCR-2 (basalt, soil, rhyolite, dunite, dunite, rhyolite, cody shale, peridotite, granite, dunite, andesite, diabase, basalt, basalt, USGS, rseton); SRM-2710 (soil, NIST, USA); JA-3, JP-1, JB-2, JG-2, JR-1, JR-2, JR-3, JA-1, JB-3, JGB-2, JGB-1, JG-1A (andesite, peridotite, basalt, granite, rhyolite, rhyolite, andesite, basalt, gabbro, gabbro, granodiorite, GSJ, Japan); NIM-L, NIM-D, NIM-P, NIM-S (lujaravite, dunite, pyroxinite, syenite, MINTEK, South Africa); SO-2, STM-1, SY-3 (soil, syenite, syenite, CCRMP, Canada); MA-N, ANG, BEN (GIT-IWG, Groupe International de Travail-International Working Group); UB-N (serpentine, ANRT, Paris); GSR-1, GSR-4 (granite, sandstone, IGGE, China). The criteria to select these samples were the required interval of concentration, the quality of the known data for each reference material, and also previous calibration tests. Source/reference for the certified values were taken from Govindaraju 1994 [13]. Table 2 provides the interval of concentration of each analyte in

Table 1
Instrumental parameters used in wavelength dispersive X-ray fluorescence spectrometer (WDXRF).

Element	Line	Crystal	Detector	kV	mA	Peak 2 (°)	Bkg 2 (°)	Counting time (s) 'peak + background'	Line overlap/correction
Traces									
Ba	Lα	PX9	Duplex	40	90	87.1508	0.9652	60 + 40	–
Cr	Kα	PX9	Duplex	40	70	69.3876	0.771	60 + 40	–
Cu	Kα	LiF 220	Duplex	40	90	65.5022	0.8652	60 + 40	–
Hf	Lα	PX9	Duplex	60	66	45.8716	0.2384	60 + 40	–
La	Lα	PX9	Duplex	40	70	82.8976	–0.4458	60 + 40	–
Nb	Kα	PX9	Scint.	40	70	21.3524	0.4046	60 + 40	–
Mo	Kα	LiF 220	Duplex	40	90	28.8422	0.8064	60 + 40	V/alpha
Ni	Kα	LiF 220	Duplex	40	80	71.2262	0.8594	60 + 40	–
Pb	Lα	PX9	Duplex	40	90	33.8972	0.9486	60 + 40	–
Rb	Kα	LiF 220	Duplex	40	80	37.9122	0.6884	60 + 40	–
Sr	Kα	LiF 220	Scint.	60	66	35.7714	0.9226	60 + 40	Y/alpha
Ta	Lα	PX9	Duplex	60	66	44.4060	0.2318	60 + 40	–
Th	Lα	LiF 220	Scint.	60	66	39.2058	0.8344	60 + 40	–
U	Lα	LiF 220	Duplex	60	66	37.2436	–0.6448	60 + 40	Rb/alpha
Y	Kα	LiF 220	Duplex	40	90	33.8118	0.7838	60 + 40	Zr/alpha
Zn	Kα	PX9	Duplex	40	80	41.7432	0.9124	60 + 40	–
Zr	Kα	LiF 220	Duplex	40	80	32.0112	0.814	60 + 40	Ba/alpha
Major									
Si	Kα	PE 002-C	Flow	40	60	108.9726	2.4836	20 + 10	–
Al	Kα	PE 002-C	Flow	40	60	144.843	2.6008	20 + 10	–
Fe	Kα	PX9	Scint.	30	40	57.4932	0.9372	20 + 10	–
Mn	Kα	PX9	Scint.	40	80	62.9406	0.9482	20 + 10	–
Mg	Kα	PX1	Flow	40	60	23.0708	2.3298	20 + 10	–
Ca	Kα	PX9	Flow	40	70	113.1196	–1.0578	20 + 10	–
Na	Kα	PX1	Flow	40	70	27.9086	2.3194	20 + 10	–
K	Kα	PX9	Flow	50	40	136.6522	1.99	20 + 10	–
Ti	Kα	PX9	Flow	40	70	86.1484	0.9272	20 + 10	–
P	Kα	Ge 111-C	Flow	40	70	141.0412	1.8622	20 + 10	–

Duplex = flow proportional and sealed xenon counter; scint. = scintillation counter.

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