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A fast and user-friendly software for quantitative chemical analysis through XRF

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Abstract. X-ray fluorescence (XRF) spectroscopy is a technique widely used for the study and conservation of cultural heritage materials. A Microsoft Excel spreadsheet to determine major (Na, Mg, Al, Si, K, Ca, Fe) and minor (P, Ti, Mn) elements in rocks and other materials by XRF is presented. The code is based on the analytical method proposed a few decades ago by Franzini et al., which is based on the algorithm: $C_i = I_i \cdot \Sigma K_{i,j} C_j$, where C_i is the concentration (expressed as wt%) of the chemical element “i”, I_i is the intensity of the characteristic line, C_j is the concentration of interfering elements, and $K_{i,j}$ are experimental coefficients that account for the matrix effects (absorption and enhancement). $K_{i,j}$ have the dimension of mass absorption coefficients and they may be calculated from a set of N reference samples using multivariate regression methods. The algorithm proposed by these authors is particularly suitable for processing samples prepared in the form of pressed powders. The Microsoft Excel spreadsheet allows you to: a) choose a set of reference samples (international or interlaboratory standards); b) evaluate the expected matrix effects on the basis of the XRF total mass absorption coefficients; c) calculate the correction coefficients $K_{i,j}$ through multivariable regression; d) calculate the analytical accuracy and graphically represent the results; e) choose five samples (monitors) for the correction of instrumental drift. Based on these steps, the software allows you to: i) enter the analytical intensities of major and minor elements measured on the monitors and on unknown samples (the loss on ignition must be determined separately); ii) calculate the correction of the instrumental drift; iii) determine the concentration of elements and express them as wt%.

1. Introduction

X-ray fluorescence (XRF) spectroscopy is a technique widely used for fast and accurate chemical analyses in industry and geology [1–3] and for the study and conservation of cultural heritage materials [4–13]. The main problems encountered in rock chemical analysis by XRF are related to the matrix effects (absorption and enhancements) due to the heterogeneity of samples (grain size, absorption, etc.). Sample heterogeneity effects can be drastically reduced by preparing the sample in the form of fused disks of pressed powders; in the last case, care should be taken to avoid coarse powders (the particle size must be $< 20 \mu\text{m}$). The pressed powder method has the advantage of preventing a considerable decrease of the peak/background ratio in fluorescence intensities, which is the typical problem encountered in samples prepared in the form of fused discs. This methodology allows us to obtain good results especially in the study of lithoid materials of monumental interest, where simplicity, speed of preparation, and high analytical accuracy are fundamental characteristics.



Matrix effects can be corrected by using appropriate experimental or calculated coefficients that consider the influence of major components on the analysed element analytical lines.

Over the past fifty years, various algorithms have been proposed to minimize matrix effects. One of the first methods was proposed by Franzini & Leoni [14] and Franzini et al. [15] in the mid-'70s, which in the following text will be referred to simply as FL. This method combines the advantage of considerable simplicity with that of a rigorous analytical approach, as the algorithm used represents a simplified form of the general formula of fluorescence radiation [14,15] and equation 2.25 in Lachance & Claisse [3].

The main purpose of this paper is to propose the use of the FL algorithm for the determination of major (Na, Mg, Al, Si, K, Ca, Fe) and minor (P, Ti, Mn) elements on building materials of historical and archaeological interest; a Microsoft Excel spreadsheet designed to allow easy application of the proposed methodology is also attached.

2. Theoretical background

The basic relation between the intensity of a characteristic line and an element's concentration is expressed by the equation (1) reported from various authors [3,14,15]:

$$I_i = K \cdot I_p \cdot \frac{\mu_i^{\lambda_p} \cdot C_i}{\mu_T^{\lambda_p} \operatorname{cosec} \Psi' + \mu_T^{\lambda_i} \operatorname{cosec} \Psi''} \quad (1)$$

where: I_p represents the intensity of the primary radiation emitted by the tube, C_i is the concentration (wt %) of element "i", $\mu_i^{\lambda_p}$ is the mass absorption coefficient of element "i" for primary radiation, $\mu_T^{\lambda_p}$ is the total mass absorption coefficients of the sample for primary radiation, $\mu_T^{\lambda_i}$ is the total mass absorption coefficients of the sample for characteristic radiation, Ψ' is the angle of incidence of primary radiation, Ψ'' is the emergency angle of characteristic radiation and K is the instrumental constant.

With some appropriate transformations, Franzini & Leoni [14] and Franzini et al. [15] expressed the equation (1) relationship in a simpler form (2):

$$I_i = \frac{C_i}{\sum_{j=1}^N C_j \cdot K_{i,j}} \quad (2)$$

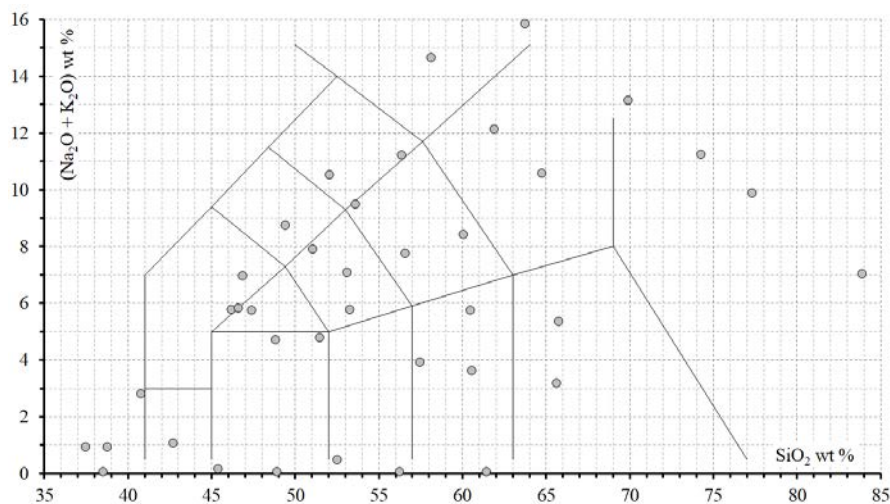
where C_i is the concentration (expressed as wt %) of the chemical element "i", I_i is the intensity of the characteristic line, C_j is the concentration of interfering elements, and $K_{i,j}$ are experimental coefficients that account for the matrix effects (absorption and enhancement). $K_{i,j}$ have the dimension of mass absorption coefficients and they may be calculated from a set of reference samples using multivariate regression methods.

3. Material and methods

Calibration of the method for measuring major (Na, Mg, Al, Si, K, Ca, Fe) and minor (P, Ti, Mn) elements of rocks was carried out on eighteen international standards of rocks samples and twenty-two additional homemade samples (from BT1 to BT22) prepared by mixing some reference materials in variable proportions; the list of the reference materials used for calibration is reported in Table 1. In Figure 1 the standards are plotted in a Total Alkali/Silica Scheme (TAS) [16].

Table 1. List of reference materials (for the identification see Govindaraju, App. 3 [17])

Name	Description	Name	Description
BT1	50% NIM-D + 50% NIM-S	DNC-1	Dolerite
BT2	40% NIM-D + 60% NIM-S	GSR-2	Andesite
BT3	29% NIM-D + 71% NIM-S	HE-1	Etna Basalt
BT4	83% NIM-D + 17% SiO ₂	MO-2	Basalt
BT5	71% NIM-D + 29% SiO ₂	MO-3	Gabbro
BT6	62.5% NIM-D + 37.5% SiO ₂	MO-6	Anorthosite
BT7	83% NIM-S + 17 SiO ₂	MO-7	Orthoclase Gabbro
BT8	71% NIM-S + 29% SiO ₂	MO-12	Andesite Basalt
BT9	62.5% NIM-S + 37.5% SiO ₂	MO-13	Olivine Basalt
BT10	44.5% NIM-S + 55.5% SiO ₂	MRG-1	Gabbro
BT11	83% MO-2 + 17% SiO ₂	MW-1	Miaskite
BT12	77% MO-2 + 23% SiO ₂	MY-1	Peridotite
BT13	67% MO-2 + 33 SiO ₂	NIM-D	Dunite
BT14	50% DNC-1 + 50% NIM-D	NIM-P	Pyroxenite
BT15	50% GSR-2 + 50% SGD-1a	NIM-S	Syenite
BT16	35% MO-7 + 65% MW-1	SDC-1	Mica Schist
BT17	50% MO-7 + 50% MW-1	SGD-1a	Gabbro
BT18	65% MO-7 + 35% MW-1	SGD-2	Gabbro
BT19	50% NIM-S + 50% SDC-1	SY-3	Syenite
BT20	50% NIM-S + 50% SY-3	For the identification of standards see Govindaraju (1994), App. 3.	
BT21	25% SGD-1a + 75% SY-3		
BT22	50% SGD-1a + 50% SY-3		

**Figure 1.** Total alkali-silica (TAS) diagram for reference materials

Specimens were prepared in the form of pressed powder pellets, obtained by homogenizing a mixture of both sample powder and binder (Licowax C®) in the ratio 2.5:1 for 30 minutes in a mechanical stirrer. The load used for pressing the powder was 200 MPa. The intensities of the elements were measured utilizing an ARL 9400 XP+ sequential X-ray spectrometer under the instrumental conditions reported in Table 2.

Table 2. Instrumental parameters. I_E = analytical line; kV, mA = voltage and current of X-ray tube; AC = analysing crystal (AX06 = multilayer synthetic crystal, PET = pentaerythritol, LiF200 = lithium fluoride); DET = detector (FPC = flow proportional counter); COL = collimator (0.60°, 0.25° = angle divergences); CTP = counting time of peak (s); CTB = counting time of background (s)

Parameter	Na, Mg	Al, Si, P	K, Ca, Ti, Mn, Fe
I_E	K_a	K_a	K_a
Tube	Rh	Rh	Rh
kV	30	30	30
mA	80	80	80
AC	AX06	PET	LiF200
DET	FPC	FPC	FPC
COL	0.60°	0.60°	0.25°
CTP	20	20	20
CTB	20	20	20

The measured intensities have been corrected for background, and correction with a blank sample was also applied to account for flux impurities.

4. Results

As mentioned above, the measured fluorescence intensities have been corrected for both background and peak overlap, and then processed using the FL algorithm. The results obtained measuring the analysed standards are reported in Figure 2 and Table 3. The concentration ranges (C), the number of analyses (N), the average concentration of the interval (X_a) and the relative standard error of estimate (RSEE) are reported for each element. The RSEE values, i.e. the trueness achieved when determining major and minor elements, were calculated according to the following equation (3):

$$RSEE = \frac{100}{x_a} \sqrt{\left[\sum (y - y_a)^2 - \frac{[\sum (x - x_a)(y - y_a)]^2}{\sum (x - x_a)^2} \right]} \quad (3)$$

where x and y represent the reference and calculated concentrations of each element in a single measurement (wt%), and x_a and y_a the average concentrations for the interval of interest. The collected data show that RSEE values are better than 6% for all the major elements, ranging from 1.5 (SiO₂) to 5.9% (MgO); the minor elements show slightly higher RSEE values, ranging from 3.9 % (MnO) to 6.5% (P₂O₅).

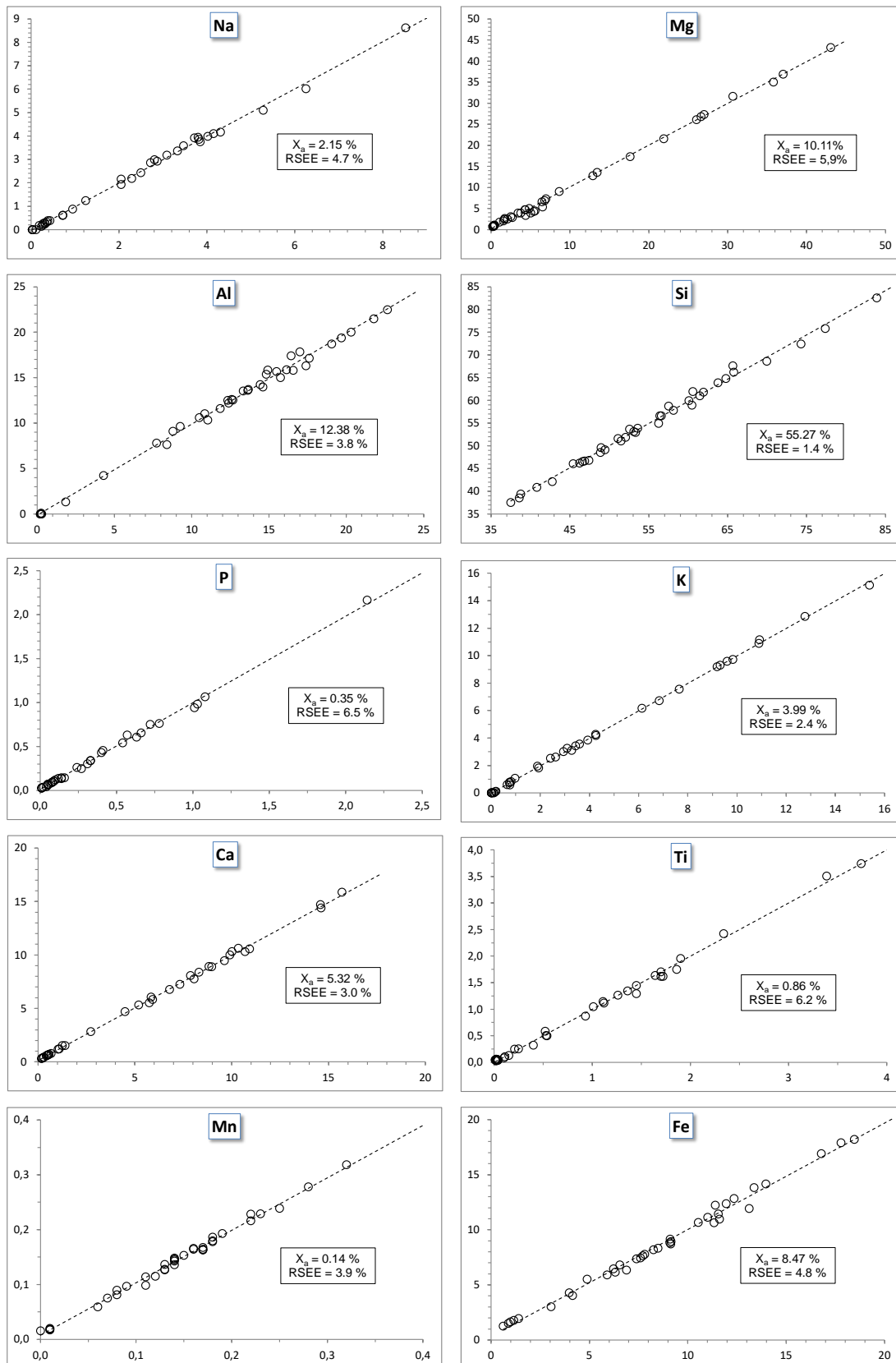


Figure 2. Trueness in the determination of rock major and minor elements

Table 3. Trueness in the determination of rock major and minor elements

	C (wt%)	X _a	RSEE
Na₂O	0-9	2.15	4.7
MgO	0-44	10.11	5.9
Al₂O₃	0-23	12.38	3.8
SiO₂	38-83	55.27	1.4
P₂O₅	0-2	0.35	6.5
K₂O	0-15	3.99	2.4
CaO	0-16	5.32	3.0
TiO₂	0-4	0.86	6.2
MnO	0-0,3	0,14	3.9
Fe₂O₃	0-18	8.47	4.8

Such accuracy values are slightly worse than those obtainable on samples prepared in the form of fused discs [1,3,18–23], but are perfectly usable for the study of cultural heritage materials. The method of pressed powder pellets offers the advantage of quick and easy preparation and, on samples grounded as fine as possible, a good accuracy useful for chemical characterization of both stone [24–26] and mortar [12, 27–28] samples.

5. Excel spreadsheet

A Microsoft Excel spreadsheet to determine major (Na, Mg, Al, Si, K, Ca, Fe) and minor (P, Ti, Mn) elements in rocks and other materials by XRF through the FL algorithm is available on request at the Earth Science Department of University of Pisa.

The spreadsheet allows you to: a) choose a set of reference samples (international or interlaboratory standards); b) evaluate the expected matrix effects on the basis of the XRF total mass absorption coefficients; c) calculate the correction coefficients $K_{i,j}$ through multivariable regression; d) calculate the analytical accuracy and graphically represent the results; e) choose five samples (monitors) for the correction of instrumental drift. Based on these steps, the software allows you to: i) enter the analytical intensities of major and minor elements measured on the monitors and on unknown samples (the loss on ignition must be determined separately); ii) calculate the correction of the instrumental drift; iii) determine the concentration of elements and express them as wt%.

The minimum number of reference samples to be used must be 14 (2 for the parameters of the calibration line, 10 for the number of elements to be analysed, 2 for the L.O.I. and the binder), but it is recommended to oversize the system at least 2-3 times (28 or 42 standards). If we assume that the influence of the minor elements (P, Ti, Mn) and the L.O.I. on the larger ones it is negligible, and that the binder is a constant, the minimum number of reference samples to be used is reduced to 9, and by oversizing the system 2-3 times, 18-27 standards would be sufficient. The accuracy achievable with the proposed method also depends on the compositional variability of the standards used in the calibration set. A large variability allows users to obtain a large calibration range, useful for routine samples characterized by high compositional variability; for routine samples with limited compositional variability (e.g. basaltic, granite, carbonate rocks, etc.) it is possible to use more targeted calibration sets and, therefore, obtain higher accuracy.

6. Conclusion

More than 4 decades after its presentation, the method proposed by Franzini & Leoni [14] and Franzini et al. [15] proves to be still valid in determining the major elements through XRF. Within the composition range of the studied reference materials, chemical determinations of Na, Mg, Al, Si, P, K,

Ca, Ti, Mn, Fe, yield trueness of measurement which can be considered acceptable for mineralogical and petrographic purposes, namely for the characterization of stone materials of monumental construction. The results are in a good agreement with the recommended values proposed for international standard materials. Measurement trueness is lower than 6% when determining major elements and lower than 7% for minor elements; chemical concentrations of Al₂O₃, SiO₂, K₂O and CaO are determined lower than about 2%. A further improvement in the quality of the analyses can be obtained with more stringent control of the particle size of the powder.

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