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## THEORETICAL AND PRACTICAL APPROACH IN DETERMINING MATRIX EFFECTS IN QUANTITATIVE XRF ANALYSIS

**Abstract** - M. TAMPONI, S. PAGNOTTA, M. LEZZERINI, *Theoretical and practical approach in determining matrix effects in quantitative XRF analysis*.

Matrix effects are the main problems encountered in the chemical analysis of rocks by XRF. These effects can be corrected by using appropriate experimental or calculated algorithms, starting from a set of reference samples using multivariate regression methods.

In this work, we propose a simple method to evaluate the expected matrix effects for major elements, on the basis of the XRF total mass attenuation coefficients available in the literature.

The obtained results confirm that theoretically calculated matrix effects are compatible with those experimentally observed.

The proposed method makes it easier to choose an appropriate calibration set for routine analysis, allowing for a reduction in the number of standards to be used, or in case it is necessary to activate a new analytical line.

**Key words** - XRF, matrix effects, rock chemical analysis, mass attenuation coefficient

**Riassunto** - M. TAMPONI, S. PAGNOTTA, M. LEZZERINI, *Approccio teorico e pratico nella determinazione degli effetti di matrice nell'analisi XRF quantitativa*.

Gli effetti di matrice sono i principali problemi incontrati nell'analisi chimica delle rocce mediante XRF. Questi effetti possono essere corretti utilizzando opportuni algoritmi sperimentali o calcolati, partendo da un insieme di campioni di riferimento e utilizzando metodi di regressione multivariata.

In questo lavoro, proponiamo un semplice metodo per valutare gli effetti di matrice attesi per gli elementi maggiori sulla base dei coefficienti di assorbimento di massa totali XRF disponibili in letteratura.

I risultati ottenuti confermano che gli effetti di matrice calcolati teoricamente sono compatibili con quelli osservati sperimentalmente.

Il metodo proposto facilita la scelta di un set di calibrazione appropriato per le analisi di routine, consentendo di ridurre il numero di standard da utilizzare, o nel caso di attivazione di una nuova linea analitica.

**Parole chiave** - XRF, effetti di matrice, analisi chimica delle rocce, coefficiente di assorbimento di massa

### INTRODUCTION

X-ray fluorescence (XRF) spectroscopy is a technique widely used for fast and accurate chemical analyses in industry, geology and for the study of cultural herit-

age materials (Bower & Valentine, 1986; Lachance & Claisse, 1995; Beckhoff *et al.*, 2006; Lezzzerini *et al.*, 2013). The main problems encountered in rock chemical analysis by XRF are related to the effects due to the heterogeneity of samples (grain size) and to the matrix effects (absorption and enhancements) (Lachance & Claisse, 1995).

Sample heterogeneity effects are mathematically difficult to handle owing to the wide variability in mineralogical composition; these effects can be drastically reduced only by preparing the sample in the form of fused disks (Claisse, 1957). This method is based on the dilution of the sample in an appropriate quantity of lithium-rich flux (typically 1:5 to 1:10 sample/borate ratio). This technique also considerably reduces matrix effects as well. At such dilution levels, however, interelement corrections must still be applied to improve the quality of the analyses.

Matrix effects, on the other hand, can be corrected by using appropriate experimental or calculated coefficients that consider the influence of major components on the analytical lines of the element being analysed. These coefficients may be calculated from a set of reference samples using multivariate regression methods.

The main purpose of this work is to propose a simple method to evaluate, for a calibration set of reference samples, the expected matrix effects for major elements on the basis of the XRF total mass attenuation coefficients available in the literature. A comparison is also made between theoretical and experimental data.

### MATERIALS AND METHODS

The simplest form of the relation between the intensity of a characteristic line ( $I_i$ ) and an element's concentration ( $C_i$ ) is expressed by the equation (1)

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

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where  $C_j$  is the concentration of interfering elements, and  $K_{i,j}$  are experimental coefficients that account for the matrix effects (attenuation and enhancement) and having the dimension of mass attenuation coefficients (Franzini *et al.* 1972, 1975).

As it is known, the mass attenuation coefficient  $\mu/\rho$  is the main cause of the matrix effects in XRF (attenuation and enhancements), and it is characterized by additive properties. Given a sample of known composition, we can calculate the total mass attenuation coefficient at a characteristic wavelength from the relation:

$$\left(\frac{\mu}{\rho}\right)_{tot} = \sum_{i=1}^N \left(\frac{\mu}{\rho}\right) \cdot C_i \quad (2)$$

where “ $C_i$ ” represents the fraction by weight of the “ $i^{th}$ ” atomic constituent.

A number of algorithms are available in the literature for computing the  $K_{i,j}$  values (Lachance & Claisse, 1995). The simplest is the one proposed by Lucas-Tooth & Price (1961):

$$C_i = D_i + E_i + I_i \cdot \left(1 + \sum_{i,j=1}^N C_i \cdot K_{i,j}\right) \quad (2)$$

where  $D_i$  and  $E_i$  represent the parameters of the linear regression line ( $I_i$  vs  $C_i$ ), and  $K_{i,j}$  may be calculated from a set of reference samples using multivariate regression methods. This algorithm is particularly suitable for analyses of samples prepared as fused discs.

In this work, the calibration of the method for determining major (Na, Mg, Al, Si, K, Ca, Fe) elements in silicate rocks was carried out on forty three reference standard materials and two interlaboratory standards, representative of a wide range of rocks and minerals. The list of the reference materials utilized for calibration is reported in Tab. 1. Reference values are from Govindaraju (1994), with the exception of HE-1 and IC-1, which are interlaboratory standards. Specimens were prepared in the form of fused discs (sample/borate dilution 1:9). The sample preparation technique and the fusion procedure are the same as those suggested by Claisse (1957) and described in Lezzzerini *et al.* (2013). The intensities of the major and minor elements were measured utilizing an ARL 9400 XP+ sequential X-ray spectrometer. The measured fluorescence intensities have been corrected for both background and peak overlap, and then processed using the Lucas-Tooth & Price algorithm.

Table 1. List of standard materials.

Name	Description	Name	Description
AC-E	Granite	JR-1	Rhyolite
BIR-1	Basalt	MA-N	Granite
CH-1	Marine sediment	MDO-G	Trachyte
DR-N	Diorite	MO-3	Gabbro
DT-N	Disthene	MO-6	Anorthosite
DTS-1	Dunite	MO-7	Orthoclase-gabbro
GS-N	Granite	MO-12	Andesite-Basalt
GSR-2	Andesite	MO-13	Olivine-Basalt
HE-1 *	Etna Basalt	MRG-1	Gabbro
IC-1 *	Campanian ignimbrite	MW-1	Miaskite
ISH-G	Trachyte	MY-1	Peridotite
JA-2	Andesite	NIM-D	Dunite
JA-3	Andesite	NIM-P	Pyroxenite
JB-1a	Basalt	NIM-S	Syenite
JB-2	Basalt	OU-3	Microgranite
JB-3	Basalt	OU-6	Slate
JF-1	Feldspar	SGD-1a	Gabbro
JF-2	Feldspar	SGD-2	Gabbro
JG-1a	Granodiorite	STM-1	Syenite
JG-2	Granite	SY-3	Syenite
JG-3	Granodiorite	WS-E	Dolerite
JGb-1	Gabbro	YG-1	Granite
JP-1	Peridotite		

\* Interlaboratory standards.

## RESULTS

Fig. 1 represents the variation of the total mass attenuation coefficient (calculated according to relation 2 and expressed as s %) as a function of sample dilution. We can observe a drastic decrease of  $\mu/\rho_{tot}$  up to dilution values of about 1:10, and a sharp reduction of the rate of decrease at higher dilutions. This means that by strongly diluting the sample, the matrix effects are strongly attenuated. High dilutions, on the other hand, have the disadvantage of significantly attenuating the intensity of the analytical lines of the elements to be determined, thus drastically reducing the instrumental sensitivity. The analyst's ability is therefore to find a good compromise between sample dilution and analytical sensitivity: a sample/borate dilution from 1:5 to 1:10 is an almost universally accepted compromise (1:9 in this study).

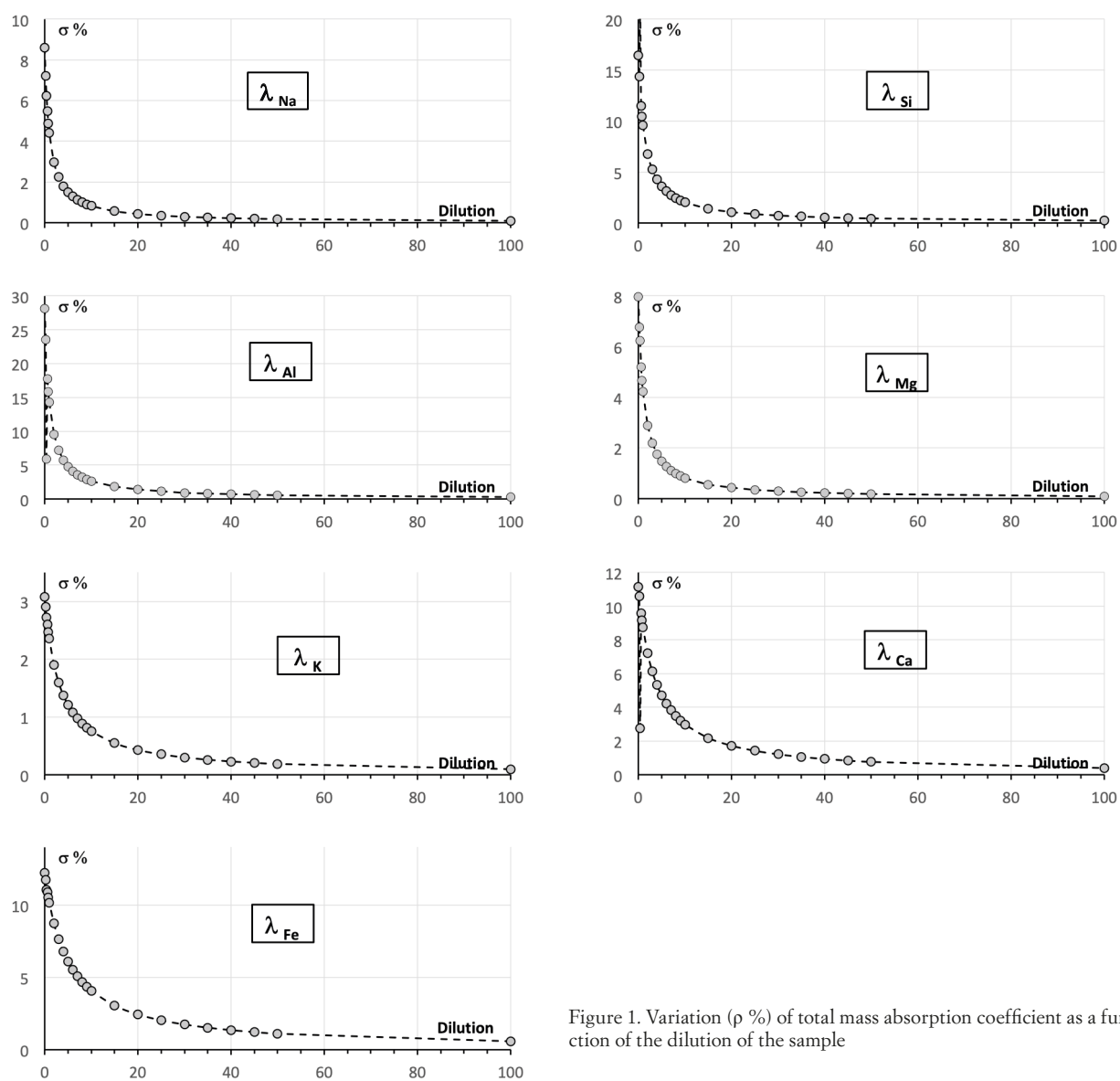


Figure 1. Variation ( $\rho$  %) of total mass absorption coefficient as a function of the dilution of the sample

Table 2. Values of the mass attenuation coefficient ( $\mu/\rho$ ) as a function of photon energy, for elemental media (values obtained from Hubbell and Seltzer data, 2004).

	Li	B	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
<b>Na Ka</b>	206	1090	4110	586	834	1065	1413	1722	3665	4398	5309	7339	8248
<b>Mg Ka</b>	116	635	2497	4676	509	653	869	1062	2296	2769	3366	4714	5323
<b>Al Ka</b>	69	385	1577	3219	4044	412	549	671	1467	1777	2176	3091	3509
<b>Si Ka</b>	42	243	1032	2232	2782	3340	359	438	957	1163	1434	2067	2360
<b>P Ka</b>	27	158	692	1552	1937	2417	2682	295	635	772	957	1400	1608
<b>K Ka</b>	6	35	167	373	498	734	780	864	168	190	229	332	390
<b>Ca Ka</b>	4	25	121	263	362	560	570	657	1135	150	174	241	284
<b>Ti Ka</b>	2	13	64	136	198	340	309	389	688	787	120	141	163
<b>Mn Ka</b>	1	5	24	64	90	179	134	180	333	391	451	92	97
<b>Fe Ka</b>	1	4	17	58	75	152	109	141	265	313	363	90	92

The values of column 5 in Tab. 3 represent the RSDs calculated from relation (2) by using the set of reference materials of Tab. 1. The mass attenuation coefficient values used for the calculations were calculated using the NIST database (Hubbell and Seltzer, 2004) and are reported in Tab. 2. The variation of the total mass attenuation coefficients (expressed as relative standard deviation) therefore gives us an estimate of the expected matrix effects with the chosen calibration set. As can be seen from the examination of these values, the matrix effects are not negligible, especially for Al, Ca and Fe and therefore make a reduction by algorithm.

The trueness (RSEE) and reproducibility ( $RSD_{REP}$ ) in the determination of major elements are summarized in the columns 2 and 4 of Tab. 3.

The reproducibility values of the method are derived from Lezzzerini *et al.* (2013). The results reported in column 4 of Tab. 3 express the sum of two causes: sample preparation and statistical counting error. We can interpret these values as the unavoidable errors that contribute to the final accuracy of the measurements, expressed in column 2 of Tab. 3.

The values in column 3 of Tab. 3 ( $RSEE_{LIN}$ ) are the relative standard errors of estimate from linear arrangement intensity/concentration (i.e. before correcting the matrix effects).

The values of columns 2 and 4 appear substantially low and they are significantly lower than those of column 3. This means that the matrix effects have been almost completely corrected by the Lucas-Tooth & Price (1961) algorithm. The values of column 5 also confirm that theoretically calculated matrix effects are compatible with those experimentally observed (differences between columns 2 and 3).

Table 3. Trueness, reproducibility and expected matrix effects in the determination of major elements on fused glass disks.

	RSEE	$RSEE_{LIN}$	$RSD_{REP}$	$RSD(\mu/\rho)_{tot}$
<b>Na<sub>2</sub>O</b>	3,7	3,8	1,9	0,8
<b>MgO</b>	1,7	2,0	1,3	1,0
<b>Al<sub>2</sub>O<sub>3</sub></b>	1,4	2,1	1,2	1,1
<b>SiO<sub>2</sub></b>	0,9	1,1	1,0	2,1
<b>K<sub>2</sub>O</b>	1,9	2,1	0,8	0,8
<b>CaO</b>	2,4	3,5	3,3	2,9
<b>Fe<sub>2</sub>O<sub>3</sub></b>	1,8	6,2	0,7	4,0

RSEE = accuracy expressed as relative standard error of estimate;  $RSD_{REP}$  = reproducibility expressed as total relative standard deviation (sample preparation + statistical counting error);  $RSEE_{LIN}$  = relative standard error of estimate before correcting the matrix effects;  $RSD(\mu/\rho)_{tot}$  = relative standard deviation of  $(\mu/\rho)_{tot}$  distribution.  $RSD_{REP}$  values are from Lezzzerini *et al.* (2013).

## CONCLUSIONS

The estimation of the matrix effect in unknown samples has always been one of the thorny issues in spectroscopy. We have always tried to evaluate and quantify this effect a posteriori. In this work, we tried to work in a priori way, if our samples have a well-defined matrix, it is easier and faster to be able to carry out an analysis knowing what the second order effects could be determined by the matrix of a sample.

The variation of the total mass attenuation coefficients (expressed as relative standard deviation), calculated on a set of calibration samples, provides a simple and reliable estimate of the expected matrix effects.

The preliminary evaluation of the matrix effects is of particular importance for the choice of an appropriate calibration set for routine analysis, or when it is necessary to proceed with the activation of a new analytical line.

Establishing one or more analytical protocols for determining the matrix effect helps to reduce the number of standards to be used, avoiding the introduction of an analytical error due to the presence of reference standards with matrices other than those of the analyte.

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## REFERENCES

- BECKHOFF B., KANNGIESSER B., LANGHOFF N., WEDELL R., WOLFF H., 2007. *Handbook of practical X-ray fluorescence analysis*, Springer Science & Business Media, Berlin - Heidelberg, 878 pp.
- BOWER N.W., VALENTINE G., 1986. Critical comparison of sample preparation methods for major and trace element determinations using X-ray fluorescence. *X-Ray Spectrom*, 15: 73-78.
- CLAISSE F., 1957. Accurate X-ray fluorescence analysis without internal standards. *Norelco Reporter*, 4, 3-17.
- FRANZINI M., LEONI L., 1972. A full matrix correction in X-ray fluorescence analysis. *Atti della Società Toscana di Scienze Naturali, Memorie, Serie A* 74: 7-22.
- FRANZINI M., LEONI L., SAITTA M., 1975. Revisione di una metodologia analitica per fluorescenza-X, basata sulla correzione completa degli effetti di matrice. *Rend. Soc. It. Mineral. Petrol.* 31: 365-378.
- GOVINDARAJU K., 1994. Compilation of working values and sample description for 383 geostandards. *Geostandard Newslett.* 18: 1-158.

- HUBBELL J.H., SELTZER S.M., 1995. *Tables of X-ray mass attenuation coefficients and mass energy-absorption coefficients 1 keV to 20 MeV for elements Z = 1 to 92 and 48 additional substances of dosimetric interest*. National Institute of Standards and Technology, Gaithersburg (MD).
- LACHANCE G.R., CLAISSE F., 1995. *Quantitative X-ray Fluorescence Analysis*, John Wiley & Sons, Chichester.
- LEZZERINI M., TAMPONI M., BERTOLI M., 2013. Reproducibility, precision and trueness of X-ray fluorescence data for mineralogical and/or petrographic purposes, *Atti della Società Toscana di Scienze Naturali, Memorie, Serie A* 120: 67-73.
- LUCAS-TOOTH H.J., PRICE B.J., 1961. A mathematical method for the investigation of inter-elements effects in X-ray Fluorescence Analysis. *Metallurgia* 64: 149-152.

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