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REPRODUCIBILITY, PRECISION AND TRUENESS OF X-RAY FLUORESCENCE DATA FOR MINERALOGICAL AND/OR PETROGRAPHIC PURPOSES

Abstract - *Reproducibility, precision and trueness of X-ray fluorescence data for mineralogical and/or petrographic purposes*. Chemical data obtained by using XRF methodology appears to be suitable to solve many practical problems in the environment and cultural heritage fields. The aim of this research was to maximize the measurement sensitivity for the determination of major, minor and some trace chemical elements on building materials of historical and archaeological interest and to assess reproducibility, precision and trueness of measurement. X-ray fluorescence analysis of major and minor elements (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) and of some traces (Nb, Zr, Y, Sr, Rb, Ce, Ba, La, Ni, Cr, V, Co) was carried out using fused glass discs and pressed powder pellets, respectively. The analytical method has been calibrated by using fifty-two international rock standards, six chemicals, two inter-laboratory standards and twenty-two homemade samples, prepared by mixing some standard materials. With some exceptions, results are in good or excellent agreement with the recommended values.

Key words - XRF, Chemical analysis, Fused glass disc, Pressed powder pellet.

Riassunto - *Riproducibilità, precisione e accuratezza di dati di fluorescenza a raggi X per scopi mineralogici e/o petrografici*. I dati chimici ottenuti in XRF sono adatti per risolvere molti problemi pratici in campo ambientale e del patrimonio culturale. Lo scopo di questa ricerca è stato di massimizzare la sensibilità di misura per la determinazione degli elementi maggiori, minori e di alcuni elementi chimici in traccia sui materiali da costruzione di interesse storico ed archeologico e di valutare la riproducibilità, precisione ed accuratezza di misura. L'analisi in fluorescenza a raggi X di elementi maggiori e minori (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) e di alcuni elementi in traccia (Nb, Zr, Y, Sr, Rb, Ce, Ba, La, Ni, Cr, V, Co) è stata effettuata utilizzando, rispettivamente, dischi di vetro fuso e pasticche di polvere pressata. Il metodo analitico è stato calibrato utilizzando cinquantadue standard internazionali di roccia, sei sostanze chimiche pure, due standard interlaboratorio e ventidue campioni ottenuti mescolando alcuni standard. Con alcune eccezioni, i risultati sono in buono o eccellente accordo con i valori di riferimento.

Parole chiave - XRF, analisi chimica, disco di vetro fuso, pasticche di polvere pressata.

INTRODUCTION

Since 1950s, X-ray fluorescence spectrometry (XRF) is a widely used methodology for fast and accurate determinations of chemical composition in industry and in many other human activities (Lachance and Claisse, 1995). XRF data alone or combined with mineralogical and petrographic ones are useful for studying environment and cultural heritage issues. A large number of investigations and papers have dealt with the use of XRF analysis from a general point of view and specifically in archaeometric studies, and many interesting examples might be reported on its applications (Ferretti, 2000; Milazzo, 2004; Musílek *et al.*, 2012). Within the framework of archaeometric researches and studies at Department of Earth Science - University of Pisa, several building materials, cultural relicts and archeological finds have been investigated in the last years by means of this sensitive method for determining major, minor and some trace elements with the purpose of recognizing their constituent materials, their production technology, their provenance and trade route (Baldanza et. al., 2012; Lezzerini *et al.*, 2012; Riccardi *et al.*, 2007 and references therein).

Interesting samples of building materials for historical and archaeological investigations can be analyzed to evaluate their chemical compositions by XRF analysis in the form of both fused glass discs (FD) and pressed powder pellets (PP), each of them having specific advantages over the other. Usually, analyses are performed on FD for major elements and on PP for trace elements. The FD, which consists of dissolving the sample in a lithium borate, removes most of the effects of powder heterogeneity, and considerably reduces matrix effects. This methodology is, however, used almost exclusively for determining major and minor elements, since the dilution of the sample in a light matrix causes a considerable decrease of the peak/background ratio in fluorescence intensities. On the contrary, the determination of trace elements is usually performed on samples prepared in the form of PP, which are characterized by a higher peak/background ratio. Furthermore, samples containing higher than normal concentrations of elements like lead, tin, arsenic and/or antimony, as they can seriously damage the platinum crucibles as well as those which contain organic matter, are not suitable for FD preparation.

The main purpose of the paper was to maximize the measurement sensitivity for the determination of major, minor and some trace chemical elements on building materials of historical and archaeological interest and to assess reproducibility, precision and trueness of measurement.

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MATERIALS AND METHODS

Fused glass discs (FD)

Calibration of the FD method for measuring major and minor elements was carried out on fifty-two reference standard materials, six chemicals and two interlaboratory standards; the list of the reference materials utilized for calibration is reported in Table 1.

The sample preparation technique and the fusion procedure are the same as those suggested by Claisse (1957). The sample powder is ignited to about 1000°C for 12 hours to eliminate the volatile components. A mixture containing 0.700 g of sample powder and 6.300 g of flux (50% lithium tetraborate, $Li_2B_4O_7$ and 50% lithium metaborate, $LiBO_2$, corresponding to a 1:9 sample/borate dilution) is carefully homogenized in a Pt$_{95}$-

Tab. 1 - List of standard materials.

Name	Description	Type of standard material	Sample preparation	Name	Description	Type of standard material	Sample preparation
AC-E	Granite	IS	FD	JB-2	Basalt	IS	FD
Al_2O_3	Aluminium oxide	CS	FD	JB-3	Basalt	IS	FD
BIR-1	Basalt	IS	FD	JDo-1	Dolomite	IS	FD/PP
BT01	NIM-D$_{50}$ - NIM-S$_{50}$	HS	PP	JF-1	Feldspar	IS	FD
BT02	NIM-D$_{40}$ - NIM-S$_{60}$	HS	PP	JF-2	Feldspar	IS	FD
BT03	NIM-D$_{29}$ - NIM-S$_{71}$	HS	PP	JG-1a	Granodiorite	IS	FD
BT04	NIM-D$_{83}$ + SiO$_{2\ 17}$	HS	PP	JG-2	Granite	IS	FD
BT05	NIM-D$_{71}$ - SiO$_{2\ 29}$	HS	PP	JG-3	Granodiorite	IS	FD
BT06	NIM-D$_{62.5}$ - SiO$_{2\ 37.5}$	HS	PP	JGb-1	Gabbro	IS	FD
BT07	NIM-S$_{83}$ - SiO$_{2\ 17}$	HS	PP	JLs-1	Limestone	IS	FD/PP
BT08	NIM-S$_{71}$ - SiO$_{2\ 29}$	HS	PP	JP-1	Peridotite	IS	FD
BT09	NIM-S$_{62.5}$ - SiO$_{2\ 37.5}$	HS	PP	JR-1	Rhyolite	IS	FD
BT10	NIM-S$_{44.5}$ - SiO$_{2\ 55.5}$	HS	PP	K_2CO_3	Potassium carbonate	CS	FD
BT11	MO-2$_{83}$ - SiO$_{2\ 17}$	HS	PP	MA-N	Granite	IS	FD
BT12	MO-2$_{77}$ - SiO$_{2\ 23}$	HS	PP	MDO-G	Trachyte	IS	FD
BT13	MO-2$_{67}$ - SiO$_{2\ 33}$	HS	PP	MgO	Magnesium oxide	CS	FD
BT14	DNC-1$_{50}$ - NIM-D$_{50}$	HS	PP	MO-12	Andesite-Basalt	IS	FD/PP
BT15	GSR-2$_{50}$ - SGD-1a$_{50}$	HS	PP	MO-13	Olivine-Basalt	IS	FD/PP
BT16	MO-7$_{35}$ - MW-1$_{65}$	HS	PP	MO-2	Basalt	IS	FD/PP
BT17	MO-7$_{50}$ - MW-1$_{50}$	HS	PP	MO-3	Gabbro	IS	FD/PP
BT18	MO-7$_{65}$ - MW-1$_{35}$	HS	PP	MO-6	Anorthosite	IS	FD/PP
BT19	NIM-S$_{50}$ - SDC-1$_{50}$	HS	PP	MO-7	Orthoclase-gabbro	IS	FD/PP
BT20	NIM-S$_{50}$ - SY-3$_{50}$	HS	PP	MRG-1	Gabbro	IS	FD/PP
BT21	SGD-1a$_{25}$ - SY-3$_{75}$	HS	PP	MW-1	Miaskite	IS	FD/PP
BT22	SGD-1a$_{50}$ - SY-3$_{50}$	HS	PP	MY-1	Peridotite	IS	FD/PP
$CaCO_3$	Calcium carbonate	CS	FD	Na_2CO_3	Sodium carbonate	CS	FD
CH-1	Marine sediment	IS	FD	NIM-D	Dunite	IS	FD/PP
COQ-1	Carbonatite	IS	FD/PP	NIM-P	Pyroxenite	IS	FD/PP
CRM 393	Limestone	IS	FD/PP	NIM-S	Syenite	IS	FD/PP
DR-N	Diorite	IS	FD	OU-3	Micrognanite	GS	FD
DT-N	Disthene	IS	FD	OU-6	Slate	GS	FD
DTS-1	Dunite	IS	FD	SDC-1	Mica Shist	IS	FD/PP
Fe_2O_3	Ferric oxide	IS	FD	SGD-1a	Gabbro	IS	FD/PP
GS-N	Granite	IS	FD	SGD-2	Gabbro	IS	FD/PP
GSR-2	Andesite	IS	FD/PP	SiO_2	Silicon dioxide	CS	FD
HE-1	Etna basalt	LS	FD/PP	SRM 1b	Argill. Limestone	IS	FD/PP
IC-1	Campanian ignimbrite	LS	FD	SRM 1c	Limestone	IS	FD/PP
ISH-G	Trachyte	IS	FD	STM-1	Syenite	IS	FD
JA-2	Andesite	IS	FD	SY-3	Syenite	IS	FD/PP
JA-3	Andesite	IS	FD	WS-E	Dolerite	IS	FD
JB-1a	Basalt	IS	FD	YG-1	Granite	IS	FD

CS = chemical, RPE-For analysis; GS = GeoPT international standard (www.geoanalyst.org); HS = homemade standard; IS = international geostandard (Govindaraju, 1994); LS = interlaboratory standard. FD = fused glass disk; PP = pressed powder pellet.

Au_3-Rh_2 crucible using a Claisse Fluxer-Bis!® automatic apparatus. As a non-wetting agent, ammonium iodure is added. The mixture is fused at 1000°C for about 20 minutes while continuously stirring the melt. When the sample has completely dissolved and any reactions ceased, the melt is poured into a Pt_{95}-Au_5 plate and slowly cooled. After cooling, the glass disc ($\phi = 32$ mm) is used directly for analysis.

The intensities of the major and minor elements (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) were measured utilizing an ARL 9400 XP+ sequential X-Ray spectrometer under the instrumental conditions reported in Table 2.

Tab. 2 - Instrumental conditions.

Parameter	Na, Mg	Al, Si, P	K, Ca, Ti, Mn, Fe	Nb, Zr, Y, Sr, Rb	Ce	Ba, La	Ni, Cr, V, Co
λ_E	$K\alpha$	$K\alpha$	$K\alpha$	$K\alpha1$	$L\beta1$	$L\alpha1$	$K\alpha$
Tube	Rh	Rh	Rh	Rh	Rh	Rh	Rh
kV	30	30	30	50	50	50	50
mA	80	80	80	50	50	50	50
AC	AX06	PET	LiF200	LiF220	LiF200	LiF200	LiF200
DET	FPC	FPC	FPC	SC	FPC	FPC	FPC
COL	0.60°	0.60°	0.25°	0.15°	0.25°	0.25°	0.25°
CTP	10	10	10	100	100	100	100
CTB	10	10	10	50	50	50	50

λ_E = analytical line; kV, mA = voltage and current of X-ray tube; AC = analysing crystal (AX06 = multilayer synthetic crystal, PET = pentaerythritol, LiF200, LiF220 = lithium fluoride); DET = detector (FPC = flow proportional counter; SC = scintillation counter); COL = collimator (0.60°, 0.25°, 0.15° = angle divergences); CTP = counting time of peak (s); CTB = counting time of background (s).

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

In order to determine major and minor elements on FD, the algorithm proposed by Lucas-Tooth and Price (1961) was used:

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

where D_i and E_i represent the parameters of the linear regression correlating the concentrations C_i (expressed as wt%) with the intensities I_i of the element «*i*», and $K_{i,j}$ are empirical coefficients correcting for matrix effects. The coefficients (D_i, E_i, $K_{i,j}$) may be calculated from a set of reference samples using multivariate regression methods. Lucas-Tooth and Price algorithm is particularly suitable for processing samples dissolved in a moderately diluted lithium borate mixture (sample/lithium borate dilutions from 1:5 to 1:10).

Pressed powder pellets (PP)

Calibration of the PP method for measuring trace elements was carried out on twenty-four international standards of rocks and twenty-two additional homemade samples (from BT1 to BT22) prepared by mixing some reference materials in variable proportions (Table 1). PP specimens were obtained by homogenizing for 30 minutes in a mechanical stirrer a mixture of both sample powder and binder (Licowax C®) in the ratio 2.5:1. The load used for pressing the powder was 200 MPa.

The intensities of trace elements (Nb, Zr, Y, Sr, Rb, Ce, Ba, La, Ni, Cr, V, Co) were measured utilizing the same instrument used for measuring FD (ARL 9400 XP+ sequential X-Ray spectrometer) under the instrumental conditions reported in Table 2. Fluorescence intensities were corrected for background and peak overlap, and a blank sample was also used to evaluate the impurities of the binding agent.

For the trace element determinations on PP, the algorithm suggested by Franzini *et al.* (1975) has been adopted:

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

where C_i is the concentration (expressed as wt %) of the chemical element «*i*», I_i the intensity of the characteristic line, C_i 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. The algorithm proposed by Franzini *et al.* (1975) is particularly suitable for processing samples prepared in the form of pressed powders.

RESULTS AND DISCUSSION

Reproducibility and precision of measurement

In order to evaluate the reproducibility of the FD and PP sample preparation methods, five standard samples have been selected (GSR-2, Andesite; MRG-1, Gabbro; MW-1, Miaskite; SGD-1a, Gabbro; SY-3, Syenite). For each sample and method, ten specimens were prepared and measured. The results are summarized in Table 3a and 3b, where the reference concentrations of each analyzed element are also reported (see Govindaraju, 1994) together with the relative statistical counting error (RSD_I) and the total relative standard deviation (RSD_{P+I}), due to the counting standard error (I) and to the sample preparation (P).

Data of Table 3a indicate that the reproducibility of the FD method is essentially due to the sample prepa-

Tab. 3a - Reproducibility on ten replicate fused glass disks of five selected international standards.

Na_2O				MgO				Al_2O_3				SiO_2				P_2O_5			
	C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}
MRG-1	0.75	2.1	2.5	MW-1	0.35	1.9	5.0	GSR-2	0.55	0.4	1.2	MRG-1	39.63	0.2	1.1	MW-1	0.05	5.7	6.1
SGD-1a	2.83	0.8	1.2	GSR-2	1.81	0.8	2.3	MRG-1	8.58	0.3	0.9	SGD-1a	46.60	0.2	0.7	MRG-1	0.08	4.5	5.2
GSR-2	4.05	0.6	3.3	SY-3	2.72	0.8	0.8	SY-3	11.97	0.3	0.5	MW-1	58.34	0.2	0.7	GSR-2	0.13	2.2	3.5
SY-3	4.20	0.6	3.5	SGD-1a	7.03	0.4	2.0	SGD-1a	14.94	0.3	2.5	SY-3	60.76	0.1	0.4	SY-3	0.55	1.6	2.0
MW-1	8.55	0.4	0.6	MRG-1	13.73	0.2	0.9	MW-1	21.85	0.2	0.7	GSR-2	63.67	0.1	0.3	SGD-1a	1.01	1.1	2.0
K_2O				CaO				TiO_2				MnO				Fe_2O_3			
	C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}
MRG-1	0.18	1.9	2.3	MW-1	1.11	0.6	0.8	SY-3	0.15	1.6	5.1	GSR-2	0.08	1.5	1.7	GSR-2	2.15	0.2	0.9
GSR-2	1.99	0.4	0.7	GSR-2	5.46	0.3	0.6	MW-1	0.40	0.8	2.8	MW-1	0.13	1.1	1.2	MW-1	3.06	0.2	1.3
SGD-1a	2.97	0.4	0.9	SY-3	8.40	0.3	0.5	GSR-2	0.55	0.7	1.6	MRG-1	0.17	0.8	0.9	SY-3	6.61	0.1	0.7
SY-3	4.31	0.4	0.8	SGD-1a	11.02	0.2	0.8	SGD-1a	1.72	0.4	1.6	SGD-1a	0.17	0.7	1.4	SGD-1a	11.71	0.1	1.0
MW-1	6.16	0.4	0.7	MRG-1	14.89	0.2	0.6	MRG-1	3.82	0.3	1.0	SY-3	0.33	0.6	0.8	MRG-1	18.17	0.1	0.4

C_{REF} (wt%) = reference concentration (Govindaraju, 1994); RSD_I (wt%) = relative statistical counting error; RSD_{P+I} (%) = total relative standard deviation due to glass disc preparation and statistical counting error.

Tab. 3b - Reproducibility on ten replicate pressed powder pellets of five selected international standards.

Nb (DL = 3 ppm)				Zr (DL = 3 ppm)				Y (DL = 2 ppm)				Sr (DL = 3 ppm)			
	C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}
GSR-2	7	20.3	24.1	MRG-1	69	1.4	1.7	GSR-2	9	13.6	15.3	MW-1	89	1.0	1.0
SGD-1a	8	16.2	19.6	GSR-2	99	1.1	1.8	MW-1	11	10.3	9.7	MRG-1	266	0.7	0.9
MRG-1	20	7.4	11.3	SGD-1a	240	0.6	1.1	MRG-1	14	12.5	15.6	SY-3	308	0.6	1.1
SY-3	189	0.9	2.0	SY-3	330	0.5	1.0	SGD-1a	30	5.4	5.5	GSR-2	790	0.3	0.5
MW-1	201	0.8	1.6	MW-1	850	0.2	1.3	SY-3	781	0.3	0.4	SGD-1a	2300	0.2	0.8
Rb (DL = 3 ppm)				Ce (DL = 15 ppm)				Ba (DL = 10 ppm)				La (DL = 15 ppm)			
	C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}
MRG-1	9	15.9	22.6	MRG-1	26	14.1	16.0	MRG-1	61	2.9	5.9	MRG-1	< DL	-	-
GSR-2	38	5.6	6.4	GSR-2	40	11.7	16.1	MW-1	124	3.2	7.4	GSR-2	22	13.4	14.6
SGD-1a	73	2.7	3.3	MW-1	76	5.7	5.9	SY-3	435	1.5	2.6	MW-1	74	8.9	10.0
MW-1	189	1.0	1.8	SGD-1a	177	4.9	5.3	GSR-2	1020	0.8	0.8	SGD-1a	80	8.7	9.1
SY-3	206	1.0	1.2	SY-3	2206	0.5	0.8	SGD-1a	1300	0.7	1.9	SY-3	1383	0.6	0.7
Ni (DL = 2 ppm)				Cr (DL = 2 ppm)				V (DL = 3 ppm)				Co (DL = 1 ppm)			
	C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}		C_{REF}	RSD_I	RSD_{P+I}
MW-1	7	1.4	11.1	SY-3	4	8.2	8.8	MW-1	30	14.2	24.2	MW-1	5	16.7	19.9
SY-3	13	1.2	3.1	MW-1	12	7.2	10.0	SY-3	50	2.1	6.5	SY-3	12	16.3	16.7
GSR-2	17	1.4	3.6	GSR-2	32	3.2	4.9	GSR-2	96	2.8	3.1	GSR-2	13	15.0	15.2
SGD-1a	50	1.2	3.4	SGD-1a	55	2.6	4.3	SGD-1a	240	1.4	2.1	SGD-1a	40	7.0	7.5
MRG-1	193	0.7	2.7	MRG-1	430	0.6	1.2	MRG-1	526	0.9	0.9	MRG-1	87	3.5	4.1

All the measured data

Range	N.	C_{REF}	RSD_I	RSD_{P+I}
< 100	36	38	5.3	6.8
100-500	14	252	1.1	2.0
>500	9	1240	0.5	0.9
0-2300	*59*	*272*	*1.0*	*1.6*

C_{REF} (ppm%) = reference concentration (Govindaraju, 1994); RSD_I (ppm%) = relative statistical counting error; RSD_{P+I} (ppm%) = total relative standard deviation due to pressed powder preparation and statistical counting error; DL = detection limit.

ration (i.e. sample ignition, sample and flux weighing, sample-flux homogenization, melting procedure). In fact, RSD_I of the FD method are generally negligible (less than 1%), except for elements at concentrations levels below 1 wt%. The precision of measurement and the reproducibility of measurement, including sample preparation, determined on 50 specimens with a mean concentration of about 10 wt% are 0.2% and slightly higher than 1%, respectively. Overall, the reproducibility data of Table 3a are slightly better than those reported by Tamponi *et al.* (2003) due to improvement in the fusion procedure (50% lithium tetraborate + 50% lithium metaborate instead of 100% of lithium tetraborate).

On the contrary, data of Table 3b indicate that the reproducibility of the PP method is due essentially to the analytical precision which depends in large degree by the statistical counting. In particular, the errors of reproducibility vary from 1 (Sr determined on ten MW-1 specimens) to 10.0% (La determined on ten MW-1 specimens) for concentrations ranging between 50 and 100 ppm, from 0.4 (Y determined on ten SY-3 specimens) to 7.4% (Ba determined on ten MW-1 specimens) for concentrations ranging between 100 and 1000 ppm, and from 0.7 (Sr and La determined on SGD-1a and SY-3 specimens, respectively) to 1.9% (Ba determined on ten SGD-1a specimens) for concentrations above 1000 ppm. Some higher errors of reproducibility (up to over 20%) have been observed for concentrations lower than 50 ppm (Nb, Rb and V). Measurement precision and measurement reproducibility taking all the collected data into account, i.e. 59 specimens with a mean concentration of 272 ppm, are 1.0% and slightly higher than 1.5%, respectively.

Trueness of measurement

As mentioned above, the measured intensities on FD samples have been corrected for both background and peak overlap, and then processed using the algorithm of Lucas-Tooth and Price (1961). For sake of comparison, the results obtained measuring the analysed standards on FD specimens are divided into several concentration ranges (*C*); for each range, the number of analyses (*N*), the average concentration of the interval (X_a) and the relative standard error of estimate (*RSEE*) are reported in Table 4a. The *RSEE* values, i.e. the trueness achieved in the determination of major and minor elements on FD specimens, were calculated according to the following equation:

$$RSEE = \frac{100}{x_a} \cdot \sqrt{\frac{1}{(n-2)}\left[\sum (y - y_a)^2 - \frac{\left[\sum (x - x_a)(y - y_a)\right]^2}{\sum (x - x_a)^2}\right]}$$

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.

Data of Table 4a show that *RSEE* values decrease with increasing concentrations. For concentrations above 1% by weight, the *RSEE* values are below 3%, except for Na_2O and CaO which are characterised by higher values (4.1 and 4.4% with average concentrations of 3.17 and 2.29 wt%, respectively). Trueness of measurement taking all the collected data into account, i.e. the values of 51 samples for P, 52 samples for K, Ti, Mn and 53 samples for Na, Mg, Al, Si, Ca and Fe, with a mean concentration ranging from 0.13 (MnO) to 100 wt% (MgO and Fe_2O_3), are better than 2% for MgO, Al_2O_3, SiO_2, K_2O, Fe_2O_3 and ranging from 6.3 (MnO) to 2.8% (Na_2O) for the other determined chemical components.

The *RSEE* values determined on PP specimens relate to the full range of concentrations are reported in the

Tab. 4a - Trueness in the determination of major and minor elements on fused glass disks.

Na_2O				MgO				Al_2O_3				SiO_2				P_2O_5			
C	N	X_a	RSEE	C	N	X_a	RSEE	C	N	X_a	RSEE	C	N	X_a	RSEE	C	N	X_a	RSEE
< 1	15	0.17	19.1	< 1	17	0.20	20.9	< 1	7	0.23	18.6	< 1	3	0.34	3.6	< 1	45	0.14	9.3
1-5	30	3.17	4.1	1-5	14	2.43	2.7	1-5	4	2.13	0.2	1-5	2	4.21	0.0	1-5	6	1.56	1.1
5-25	7	6.63	1.4	5-25	16	8.17	2.2	5-25	40	16.18	1.3	5-25	1	6.87	0.0	5-25	-	-	-
25-50	-	-	-	25-50	5	40.52	0.7	25-50	-	-	-	25-50	16	44.18	1.2	25-50	-	-	-
50-100	1	58.48	0.0	50-100	1	100.00	0.0	50-100	2	80.19	0.0	50-100	31	63.47	0.8	50-100	-	-	-
0-100	*53*	*3.82*	*2.8*	*0-100*	*53*	*8.88*	*1.4*	*0-100*	*53*	*15.43*	*1.2*	*0-100*	*53*	*50.77*	*0.9*	*0-100*	*51*	*0.30*	*4.4*
K_2O				CaO				TiO_2				MnO				Fe_2O_3			
C	N	X_a	RSEE	C	N	X_a	RSEE	C	N	X_a	RSEE	C	N	X_a	RSEE	C	N	X_a	RSEE
< 1	22	0.29	10.6	< 1	12	0.43	11.1	< 1	33	0.25	7.6	< 1	52	0.13	6.3	< 1	11	0.42	14.7
1-5	23	3.17	0.7	1-5	12	2.29	4.4	1-5	19	1.78	1.8	1-5	-	-	-	1-5	11	3.17	2.3
5-25	6	9.80	1.4	5-25	22	10.38	1.1	5-25	-	-	-	5-25	-	-	-	5-25	30	10.57	1.6
25-50	-	-	-	25-50	2	41.20	0.0	25-50	-	-	-	25-50	-	-	-	25-50	-	-	-
50-100	1	68.16	0.0	50-100	5	53.70	1.0	50-100	-	-	-	50-100	-	-	-	50-100	1	100.00	0.0
0-100	*52*	*3.96*	*1.5*	*0-100*	*53*	*11.54*	*3.2*	*0-100*	*52*	*0.81*	*3.1*	*0-100*	*52*	*0.13*	*6.3*	*0-100*	*53*	*8.62*	*1.5*

C (wt%) = range of concentration; N = number of analysed samples; X_a (wt%) = average concentration in the range; RSEE (%) = relative standard error of estimate.

Tab. 4b - Trueness in the determination of trace elements on pressed powder pellets.

Nb				Zr				Y				Sr			
C	N	X	RSEE	C	N	X	RSEE	C	N	X	RSEE	C	N	X	RSEE
0-3900	43	115	1.6	2-850	45	139	9.2	0-718	44	59	5.0	25-12000	46	770	4.4
Rb				Ce				Ba				La			
C	N	X	RSEE	C	N	X	RSEE	C	N	X	RSEE	C	N	X	RSEE
0-530	44	120	1.3	0-2230	44	230	9.5	1-7480	45	1066	7.6	0-1340	44	122	6.6
Ni				Cr				V				Co			
C	N	X	RSEE	C	N	X	RSEE	C	N	X	RSEE	C	N	X	RSEE
0-2050	44	306	5.9	0-24000	44	982	2.1	3-960	43	129	8.5	0-210	44	48	7.5

C (ppm) = range of concentration; N = number of analysed samples; X (ppm) = average concentration in the range; RSEE (%) = relative standard error of estimate.

Table 4b. The collected data show that *RSEE* values are better than 10% for all the measured traces, ranging from 9.5 (Ce) to 4.4% (Sr) for Ce, Zr, V, Ba, Co, La, Y, Ni, Sr and from to 2.1 (Cr) to 1.3% (Rb) for Cr, Nb and Rb.

Based on data here not reported, but according to those of previous authors (Franzini and Leoni, 1972; Franzini *et al.*, 1976; Haukka and Thomas, 1977; Thomas and Haukka, 1978; Bower and Valentine, 1986; Eastell and Willis, 1990; Chappell, 1991; Enzweiler and Webb, 1996), the fusion glass disk method offers major advantages over the pressed powder pellets method in terms of trueness of measurement for major and minor elements, essentially in the determination of light elements such as Na and Mg. On the contrary, the method of pressed powder pellets offers the advantage of a quick and easy preparation and, on samples grounded as fine as possible, a better trueness of measurement for trace element determination in respect to fusion glass disk method.

CONCLUSIONS

Within the composition range of the studied reference materials, chemical determinations by XRF of Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe, Nb, Zr, Y, Sr, Rb, Ce, Ba, La, Ni, Cr, V, Co yield reproducibility, precision and trueness of measurement which can be considered acceptable for mineralogical and petrographic purposes. In fact, results are in good or excellent agreement with the recommended values proposed for international standard materials. Measurement trueness is better than 6% in the determination of major and minor elements and better than 10% for trace elements; chemical concentrations of MgO, Al_2O_3, SiO_2, K_2O, Fe_2O_3, Cr, Nb and Rb are determined better than about 2%.

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