Marco Lezzerini (*) (**), Marco Tamponi(*), Marco Bertoli(*)

CALIBRATION OF XRF DATA ON SILICATE ROCKS USING CHEMICALS AS IN-HOUSE STANDARDS

Abstract - *Calibration of XRF data on silicate rocks using chemicals as in-house standards.* X-ray fluorescence (XRF) is an accurate, rapid spectroscopic technique for chemical element determinations on rock samples. The aim of this research was to evaluate a calibration method based on the use of suitable mixtures of chemicals. X-ray fluorescence analysis of major elements (Na, Mg, Al, Si, K, Ca, Fe) was carried out using sample-lithium borate fusion mixtures (with a 1:9 sample/borate dilution). The accuracy of the proposed calibration method was tested on twenty-four international rock standards. Results are in good or excellent agreement with the literature recommended values.

Keywords - XRF; fused glass disc; major elements; calibration; chemicals.

Riassunto - *Calibrazione di dati XRF su rocce silicatiche usando prodotti chimici come standard.* La fluorescenza a raggi-X (XRF) è una tecnica spettroscopica accurata e rapida per la determinazione degli elementi chimici presenti in campioni di rocce. Lo scopo di questa ricerca è stato quello di valutare un metodo di calibrazione basato sull'uso di opportune miscele di prodotti chimici. L'analisi in fluorescenza a raggi-X degli elementi maggiori (Na, Mg, Al, Si, K, Ca, Fe) è stata effettuata utilizzando miscele di fusione campione/borato di litio (diluizione campione/borato 1:9). L'accuratezza del metodo proposto è stata testata su 24 standard internazionali di rocce. I risultati sono in ottimo o eccellente accordo con i valori raccomandati.

Parole chiave - XRF; disco di vetro fuso; elementi maggiori; calibrazione; reagenti chimici.

INTRODUCTION

Since the middle of the last century, X-ray fluorescence (XRF) is commonly considered as a fast and accurate spectroscopic technique for determining major, minor and some trace elements in rock samples (Bower & Valentine, 1986; Chappell, 1991; Lachance & Claisse, 1995; Beckhoff *et al.*, 2006). The main problems encountered in rock chemical analysis by XRF concern 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, by dissolving the sample in a lithium borate mixture. However, this methodology is almost exclusively used 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.

Matrix effects can be corrected by using appropriate experimental or calculated coefficients that take the influence of major components on the analytical lines of the elements to be analysed into account. The problem encountered in a similar calibration procedure is the strong dependence of the calibration parameters from the set of reference samples. From an analytical point of view, in fact, is formally incorrect to extend the value of the correction coefficients outside the compositional range of the standard set.

XRF analysis is the spectroscopic technique of choice for most petrologists and geochemists to obtain rock chemical compositions (Thomas & Haukka, 1978; Enzweiler & Webb, 1996; Beckhoff *et al.*, 2006), and in recent years it is widely used for studies in the field of conservation and restoration of stones, marbles, ceramics, mortars and other materials of cultural heritage (Franzini *et al.*, 2010; Mármol *et al.*, 2010; Tripati *et al.*, 2010; Fiori *et al.*, 2011; Browna *et al.*, 2013; Theodoridou *et al.*, 2013; Villagran *et al.*, 2013; Gliozzo *et al.*, 2014; Lezzerini *et al.*, 2014; Rolett *et al.*, 2015).

The main purpose of this paper is to evaluate a calibration methodology based on the use of in-house standards consisting of both suitable chemicals, and binary and ternary mixtures of them. A set of empirical coefficients correcting for matrix effects obtained using suitable in-house standards can be valid over the entire compositional range of each major component (from 0 to 100 wt%).

MATERIALS AND METHODS

Calibration of the method for measuring the main major elements of rocks (Na, Mg, Al, Si, K, Ca, Fe) was carried out on thirty-nine in-house standards, prepared by mixing pure chemical components in variable proportions; the list of the reference materials utilized for calibration is reported in Table 1.

(*) Dipartimento di Scienze della Terra, University of Pisa, Via S. Maria 53 - 56126 Pisa, Italy - E-mail: lezzerini@dst.unipi.it
(**) Laboratorio di Spettroscopia Laser Applicata, ICCOM-CNR, Via G. Moruzzi 1 - 56124 Pisa, Italy.

Tab. 1 - List of in-house standards (chemicals and mixtures of them).

Name	Description	Name	Description
1	$SiO_{2\ 100}$	21	$MgO_{25} + Al_2O_{3\ 25} + SiO_{2\ 50}$
2	$Al_2O_{3\ 100}$	22	$MgO_{25} + K_2O_{25} + SiO_{2\ 50}$
3	CaO_{100}	23	$MgO_{25} + CaO_{25} + SiO_{2\ 50}$
4	MnO_{100}	24	$MgO_{25} + Fe_2O_{3\ 25} + SiO_{2\ 50}$
5	$TiO_{2\ 100}$	25	$Al_2O_{3\ 25} + K_2O_{25} + SiO_{2\ 50}$
6	$Na_2O_{50} + SiO_{2\ 50}$	26	$Al_2O_{3\ 25} + CaO_{25} + SiO_{2\ 50}$
7	$MgO_{50} + SiO_{2\ 50}$	27	$Al_2O_{3\ 25} + Fe_2O_{3\ 25} + SiO_{2\ 50}$
8	$K_2O_{50} + SiO_{2\ 50}$	28	$K_2O_{25} + CaO_{25} + SiO_{2\ 50}$
9	$Fe_2O_{3\ 50} + SiO_{2\ 50}$	29	$K_2O_{25} + Fe_2O_{3\ 25} + SiO_{2\ 50}$
10	$P_2O_{5\ 50} + SiO_{2\ 50}$	30	$CaO_{25} + Fe_2O_{3\ 25} + SiO_{2\ 50}$
11	$Al_2O_{3\ 50} + SiO_{2\ 50}$	31	$Na_2O_{50} + Al_2O_{3\ 50}$
12	$CaO_{50} + SiO_{2\ 50}$	32	$CaO_{75} + Al_2O_{3\ 25}$
13	$TiO_{2\ 50} + SiO_{2\ 50}$	33	$CaO_{75} + SiO_{2\ 25}$
14	$MnO_{50} + SiO_{2\ 50}$	34	$CaO_{75} + K_2O_{25}$
15	$Fe_2O_{3\ 40} + SiO_{2\ 60}$	35	$CaO_{75} + Fe_2O_{3\ 25}$
16	$Na_2O_{25} + Al_2O_{3\ 25} + SiO_{2\ 50}$	36	$CaO_{50} + Al_2O_{3\ 50}$
17	$Na_2O_{25} + MgO_{25} + SiO_{2\ 50}$	37	$CaO_{50} + Si_2O_{2\ 50}$
18	$Na_2O_{25} + K_2O_{25} + SiO_{2\ 50}$	38	$CaO_{50} + Fe_2O_{3\ 50}$
19	$Na_2O_{25} + CaO_{25} + SiO_{2\ 50}$	39	$CaO_{40} + MgO_{40} + SiO_{2\ 20}$
20	$Na_2O_{25} + Fe_2O_{3\ 25} + SiO_{2\ 50}$		

The sample preparation technique and the fusion procedure are the same as those suggested by Claisse (1957). In particular, for the in-house standards, a mixture containing 0.700 g of pure oxides in variable proportions 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}-Au_5 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_3-Rh_2 plate and slowly cooled. After cooling, the glass disc (Φ = 32 mm) is directly used for analysis. For the rock standards (Table 2), the sample preparation is almost identical: the only difference consists in the pre-treatment of the sample powder by ignition at about 1000°C for 12 hours in order to eliminate the volatile components.

Tab. 2 - List of rock international standards (reference values from Govindaraju, 1994).

n.	Name	Description
1	AC-E	Granite
2	BIR-1	Basalt
3	DR-N	Diorite
4	GS-N	Granite
5	GSR-2	Andesite
6	ISH-G	Trachyte
7	JA-3	Andesite
8	JB-2	Basalt
9	JB-3	Basalt
10	JG-1a	Granodiorite
11	JG-2	Granite
12	JG-3	Granodiorite
13	JGb-1	Gabbro
14	JR-1	Rhyolite
15	MA-N	Granite
16	MDO-G	Trachyte
17	MO-3	Gabbro
18	MRG-1	Gabbro
19	NIM-S	Syenite
20	SGD-1a	Gabbro
21	SGD-2	Gabbro
22	STM-1	Syenite
23	SY-3	Syenite
24	YG-1	Granite

The intensities of the main major elements of the rocks (Na, Mg, Al, Si, K, Ca, Fe) were measured utilizing an ARL 9400 XP+ sequential X-ray spectrometer under the instrumental conditions summarized in Table 3. 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 concentration of major elements, 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 are 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).

Tab. 3 - Instrumental conditions.

Parameter	Na, Mg	Al, Si	K, Ca, Fe
λ_E	K_α	K_α	K_α
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	10	10	10
CTB	10	10	10

λ_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).

RESULTS AND DISCUSSION

In Figure 1 the calibration plots, obtained by using the in-house standard set as calibration materials, are reported; for each major element, the average concentration (C_a, expressed as weight percentage of the oxide) and the relative standard error of estimate ($RSEE$) are also reported. In order to evaluate the accuracy of the adopted method, twenty-four international rock standards have been selected and analysed under the same analytical conditions of the in-house standards.

Fig. 1 - Calibration plots for the major elements of rocks.
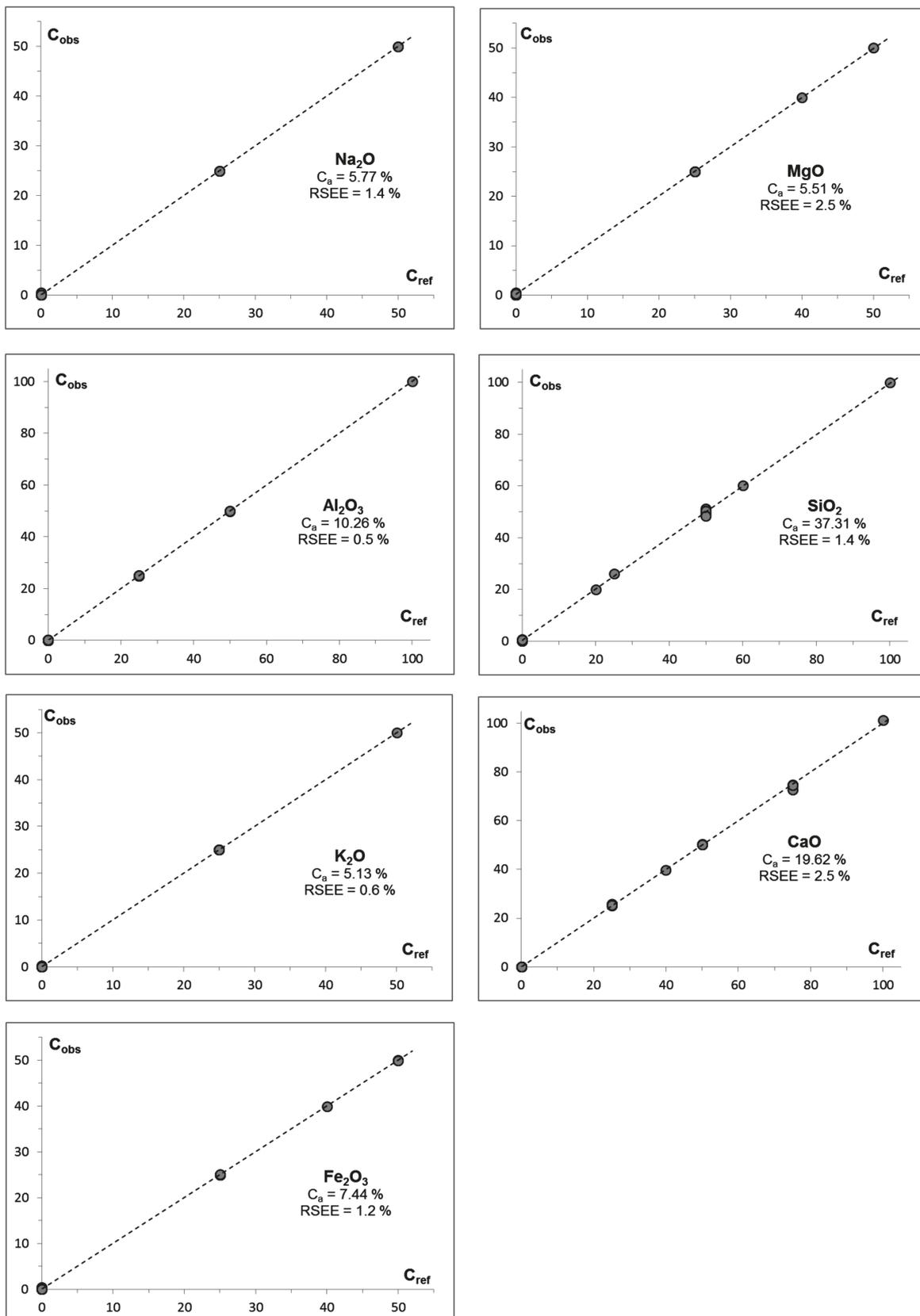
Fig. 2 - Accuracy in the determination of rock major elements.
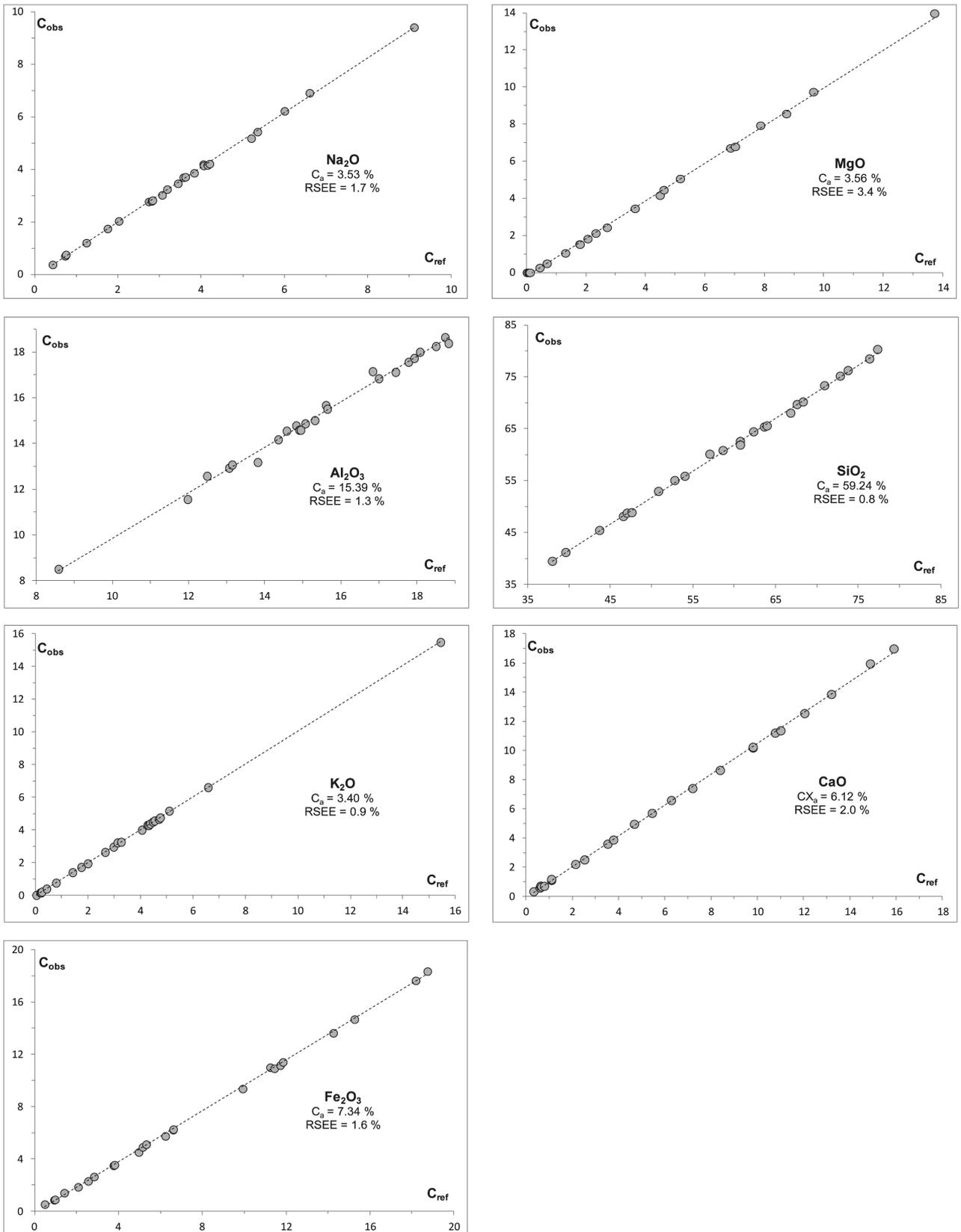
Tab. 4 - Accuracy in the determination of major elements.

Standard	Na$_2$O		MgO		Al$_2$O$_3$		SiO$_2$		K$_2$O		CaO		Fe$_2$O$_3$	
	C$_{ref}$	C$_{obs}$	C$_{ref}$	C$_{obs}$	C$_{ref}$	C$_{obs}$	C$_{ref}$	C$_{obs}$	C$_{ref}$	C$_{obs}$	C$_{ref}$	C$_{obs}$	C$_{ref}$	C$_{obs}$
AC-E	6,60	6,91	0,03	0,00	14,82	14,77	70,95	73,30	4,53	4,55	0,34	0,32	2,55	2,32
BIR-1	1,75	1,74	9,66	9,74	15,31	15,00	47,63	48,83	0,03	0,00	13,21	13,84	11,23	11,01
DR-N	3,06	3,02	4,50	4,16	17,92	17,72	54,05	55,84	1,74	1,71	7,21	7,39	9,92	9,38
GS-N	3,83	3,86	2,34	2,12	14,90	14,58	66,85	68,01	4,70	4,65	2,54	2,50	3,81	3,56
GSR-2	4,05	4,19	1,81	1,52	16,99	16,83	63,67	65,34	1,99	1,93	5,46	5,69	5,15	4,92
ISH-G	5,20	5,18	1,32	1,05	18,82	18,37	58,66	60,80	6,57	6,59	3,54	3,58	4,96	4,53
JA-3	3,18	3,24	3,66	3,45	15,60	15,66	62,36	64,40	1,41	1,39	6,29	6,57	6,60	6,24
JB-2	2,02	2,03	4,63	4,46	14,57	14,54	52,82	55,01	0,42	0,39	9,82	10,17	14,24	13,64
JB-3	2,81	2,79	5,18	5,06	16,83	17,14	50,85	52,92	0,78	0,75	9,82	10,22	11,84	11,42
JG-1a	3,44	3,46	0,70	0,49	14,35	14,16	72,85	75,14	4,05	3,99	2,15	2,19	2,07	1,87
JG-2	3,57	3,69	0,04	0,00	12,48	12,57	77,37	80,28	4,75	4,74	0,80	0,69	0,93	0,88
JG-3	4,06	4,14	1,80	1,53	15,64	15,50	67,63	69,67	2,65	2,63	3,79	3,86	3,76	3,51
JGb-1	1,24	1,20	7,88	7,93	17,77	17,55	43,72	45,40	0,24	0,20	12,05	12,53	15,25	14,69
JR-1	4,15	4,16	0,09	0,00	13,06	12,92	76,40	78,46	4,47	4,48	0,64	0,70	0,97	0,91
MA-N	6,00	6,22	0,04	0,00	18,07	17,99	68,36	70,16	3,26	3,25	0,61	0,57	0,48	0,55
MDO-G	5,35	5,43	2,07	1,82	18,49	18,24	57,06	60,09	4,26	4,28	4,69	4,94	6,23	5,76
MO-3	0,73	0,70	8,75	8,56	13,81	13,17	38,00	39,45	0,21	0,15	15,91	16,96	18,73	18,36
MRG-1	0,75	0,75	13,73	13,97	8,58	8,50	39,63	41,15	0,18	0,15	14,89	15,93	18,17	17,65
NIM-S	0,43	0,37	0,46	0,26	17,43	17,11	63,99	65,54	15,43	15,47	0,68	0,64	1,41	1,42
SGD-1a	2,83	2,82	7,03	6,79	14,94	14,58	46,60	48,08	2,97	2,95	11,02	11,35	11,71	11,17
SGD-2	2,74	2,77	6,87	6,71	15,06	14,86	47,05	48,73	3,12	3,21	10,78	11,19	11,43	10,93
STM-1	9,11	9,41	0,10	0,00	18,73	18,63	60,75	62,55	4,36	4,36	1,11	1,16	5,32	5,13

The list of the international standards utilized for calibration purpose is reported in Table 2. The rock international standards (Govindaraju, 1994) were chosen to represent a wide range of lithological compositions: andesite (2), basalt (3), diorite (1), gabbro (5), granite (5), granodiorite (2), rhyolite (1), syenite (3) and trachyte (1).

The measured intensities on the rock international standards have been corrected for both background and peak overlap, and then processed using the calibration parameters derived from the in-house standard set. Data of accuracy are presented in Table 4 and Figure 2. Instead, Table 4 provides a comparison of the concentrations determined following the described procedure with the values recommended in the literature. In Figure 2, the observed (C_{obs}) and reference (C_{ref}) concentration values (expressed as weight percentage of the oxide) of each determined element, together with $RSEE$ values and the average concentration of the interval (C_a), are graphically reported. The $RSEE$ values, i.e. the accuracy achieved in the determination of major elements, were calculated according to the following equation:

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

where x and y represent the reference and calculated concentrations of each element in a single measurement (wt%) respectively, and x_a and y_a the average concentrations for the interval of interest.

Data of Figure 2 show that $RSEE$ values are better than 2% for all the measured elements (except for MgO), ranging from 0.8% (SiO$_2$) to 2.0% (CaO). The $RSEE$ value of MgO is considerably higher (3.4%). Data of Figure 2 also indicate that $RSEE$ values of Na$_2$O, MgO, Al$_2$O$_3$, K$_2$O and Fe$_2$O$_3$ are only slightly higher than those observed in the calibration plots. SiO$_2$ (0.8 vs 1.4%) and CaO (2.0 vs 2.5%) have even better values.

CONCLUSIONS

Within the compositional range of the studied reference materials, XRF determinations of major elements (Na, Mg, Al, Si, K, Ca, Fe) by utilising calibration parameters derived from in-house standards consisting of pure chemicals, yield accuracy of measurement which can be considered acceptable for many mineralogical and petrographic purposes. In fact, results are in good or excellent agreement with the recommended values proposed for international standard materials. The accuracy is better than 2% for all the elements except for MgO (3.4%). These results are comparable to those obtained by Tamponi *et al.* (2002) and Lezzerini *et al.* (2013) using international rock standards with limited compositional range. The advantage of the

methodology adopted in this article is to have valid calibration coefficients able to ensure good results of accuracy for wide compositional spectrum. Furthermore, it is not to be underestimated the fact that the empirical coefficients, which account for the matrix effects, are obtained on in-house standards, consisting of chemicals and mixtures of them. These standard materials are readily available commercially and are relatively inexpensive; in addition, the mixtures that can be obtained are virtually endless.

REFERENCES

BECKHOFF B., KANNGIESSER B., LANGHOFF N., WEDELL R., WOLFF H., 2006. Handbook of Practical X-Ray Fluorescence Analysis. Springer-Verlag, 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.

BROWNA F.H., NASH B.P., FERNANDEZ D.P., MERRICK H.V., THOMAS R.J., 2013. Geochemical composition of source obsidians from Kenya. *J. of Archaeol. Sci.* 40: 3233-3251.

CHAPPELL B.W., 1991. Trace element analysis of rocks by X-ray spectrometry. *Adv. X-Ray Anal.* 34: 263-275.

CLAISSE F., 1957. Accurate X-ray fluorescence analysis without internal standards. *Norelco Reporter* 4: 3-17.

ENZWEILER J., WEBB P.C., 1996. Determination of trace elements in silicate rocks by X-ray fluorescence spectrometry on 1:5 glass discs: comparison of accuracy and precision with pressed powder pellet analysis. *Chem. Geol.* 130: 195-202.

FIORI C., VITALI D., CAMURRI E., FABBRI B., GUALTIERI S., 2011. Archaeometrical study of Celtic ceramics from Monte Bibele (Bologna, Italy). *Appl. Clay Sci.* 53: 454-465.

FRANZINI M., LEZZERINI M., ORIGLIA F., 2010. Marbles from the Campiglia Marittima area (Tuscany, Italy). *Eur. J. Mineral.* 22: 881-893.

GLIOZZO E., IACOVIELLO F., FORESI L.M., 2014. Geosources for ceramic production: The clays from the Neogene-Quaternary Albegna Basin (southern Tuscany). *Appl. Clay Sci.* 91-92: 105-116.

GOVINDARAJU K., 1994. 1994 compilation of working values and sample description for 383 geostandards. *Geostandards Newsletter* 18, Issue Supplement S1, 1-158.

LACHANCE G.R., CLAISSE F., 1995. Quantitative X-ray Fluorescence Analysis. John Wiley & Sons, Chichester, 402 pp.

LEZZERINI M., LEGNAIOLI S., LORENZETTI G., PALLESCHI V., TAMPONI M., 2014. Characterization of historical mortars from the bell tower of St. Nicholas church (Pisa, Italy). *Constr. Build. Mater.* 69: 203-212.

LEZZERINI M., TAMPONI M., BERTOLI M., 2013. Reproducibility, precision and trueness of X-ray fluorescence data for mineralogical and/or petrographic purposes. *Atti Soc. Tosc. Sci. Nat. Mem.,* Serie A 120: 67-73.

LUCAS-TOOTH H.J., PRICE B.J., 1961. A mathematical method for the investigation of interelements effects in X-ray Fluorescence Analysis. *Metallurgia* 64: 149-152.

MÁRMOL I., BALLESTER P., CERRO S., MONRÓS G., MORALES J., SÁNCHEZ L., 2010. Use of granite sludge wastes for the production of coloured cement-based mortars. *Cement Concrete Comp.* 32: 617-622.

MIRAGLIA L., 2013. Determinazione degli elementi maggiori in rocce silicatiche mediante fluorescenza ai raggi x su dischi fusi (perle). *Rapporti tecnici INGV* 261: 5-8.

ROLETT B.V., WEST E.W., SINTON J.M., IOVITA R., 2015. Ancient East Polynesian voyaging spheres: new evidence from the Vitaria Adze Quarry (Rurutu, Austral Islands). *J. Archaeol. Sci.* 53: 459-471.

TAMPONI M., BERTOLI M., INNOCENTI F., LEONI L., 2003. X-ray fluorescence analysis of major elements in silicate rocks using fused glass discs. *Atti Soc. Tosc. Sci. Nat. Mem.,* Serie A 108: 1-8.

THEODORIDOU M., IOANNOU I., PHILOKYPROU M., 2013. New evidence of early use of artificial pozzolanic material in mortars. *J. Archaeol. Sci.* 40: 3263-3269.

THOMAS I.L., HAUKKA M.T., 1978. XRF determination of trace and major elements using a single-fused disc. *Chem. geol.* 21: 39-50.

TRIPATI S., MUDHOLKAR A., VORA K.H., RAO B.R., GAUR A.S., SUNDARESH, 2010. Geochemical and mineralogical analysis of stone anchors from west coast of India: provenance study using thin sections, XRF and SEM-EDS. *J. Archaeol. Sci.* 37: 1999-2009.

VILLAGRAN X.S., SCHAEFER C.E.G.R., LIGOUIS B., 2013. Living in the cold: Geoarchaeology of sealing sites from Byers Peninsula (Livingston Island, Antarctica). *Quatern. Int.* 315: 184-199.