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INDICE - *CONTENTS*

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M. Lezzerini (*), M. Tamponi (*)

X-RAY FLUORESCENCE ANALYSIS OF TRACE ELEMENTS IN SILICATE ROCKS USING FUSED GLASS DISCS

Abstract - *X-ray fluorescence analysis of trace elements in silicate rocks using fused glass discs.* X-ray fluorescence analysis of twelve trace elements in silicate rocks (V, Cr, Co, Ni, Rb, Sr, Y, Zr, Nb, Ba, La, Ce) was carried out by using fused glass discs prepared by mixing 0.700 g of powder rock samples with 3.150 g of lithium tetraborate and 3.150 g of lithium metaborate. The method was calibrated using one hundred and twenty-one in-house rock standards and the accuracy was tested using sixteen international rock standards. The errors range from 3 to 10% for abundances ranging from 0 to 2300 ppm. Overall, the quality of the analytical data obtained by the proposed method is similar to that one obtained by processing powder pellets. Since the samples prepared through this technique allows the determination of major elements too, with a high degree of accuracy, the proposed methodology is characterized by an excellent ratio of analytical quality and operating time.

Key words - XRF, trace elements, silicate rocks, fused glass discs, reproducibility, precision, accuracy.

Riassunto - *Analisi in fluorescenza a raggi X degli elementi in traccia in rocce silicatiche usando dischi di vetro fuso.* In questa nota viene proposta una metodologia analitica in fluorescenza-X per la determinazione di 12 elementi in tracce (V, Cr, Co, Ni, Rb, Sr, Y, Zr, Nb, Ba, La, Ce) in campioni di rocce silicatiche preparati secondo la tecnica della fusione. Le perle di fusione sono state ottenute fondendo una miscela contenente 0.700 g di polvere e 6.300 g di fondente (50% tetraborato di litio e 50% metaborato di litio). Per la messa a punto di questa metodologia sono stati utilizzati 121 standards di laboratorio e i risultati ottenuti sono stati testati mediante l'impiego di 16 standard internazionali. Gli errori inerenti la procedura analitica sono mediamente compresi tra il 3 e il 10% per concentrazioni dell'elemento comprese tra 0 e 2300 ppm. I risultati ottenuti indicano che la riproducibilità, la precisione e l'accuratezza dei dati analitici sono, per la maggior parte degli elementi, leggermente superiori a quelli ottenibili mediante l'impiego di polveri pressate. Poiché i campioni preparati secondo la tecnica della fusione consentono anche la determinazione degli elementi maggiori con un elevato grado di riproducibilità e accuratezza, la metodologia proposta risulta caratterizzata da un ottimo rapporto tra qualità analitica e rapidità di esecuzione.

Parole chiave - XRF, elementi in traccia, rocce silicatiche, perle di fusione, riproducibilità, precisione, accuratezza.

Introduction

Since few years, in most laboratory of all the world X-ray fluorescence (XRF) analysis of the major elements has been usually performed by using samples prepared in the form of fused glass discs. This method is based on the dilution of the sample in an appropriate quantity of lithium-rich flux and it is suggested to avoid the typical mineralogical and granulometric effects showed by powder pellets (Franzini & Leoni, 1972; Franzini *et al.*, 1975; Lachance & Claisse, 1995 and references therein). These effects can be a significant source of errors, which are barely correctable by calculations (Franzini *et al.*, 1975).

The fusion considerably reduces the matrix effects (Lachance & Claisse, 1995) and the residual effects of absorption and enhancement can be further reduced through appropriate mathematical algorithms.

In the last years, applied petrography and mineralogy researchers at Department of Earth Sciences – University of Pisa widely use XRF analyses to determine the chemical composition of marbles, stones, mortars and clay materials (Columbu *et al.*, 2014; Franzini & Lezzerini, 2003; Franzini *et al.*, 2001, 2002, 2010; Leoni *et al.*, 2010; Lezzerini *et al.*, 2012, 2014; Miriello *et al.*, 2013). However, specimens in form of powder pellets are generally preferred to determine trace elements, mainly due to the reduction of the net intensity of the elements analytical lines caused by the dilution of the sample with a flux during the preparation of the fused glass disc. The new XRF spectrometers allow to overcome this instrumental limitation and to obtain peak/background ratio that is 2 to 5 times higher than in the old instruments. This instrumental improvement has opened new developments in the measurement of trace elements on fused-disc specimens in which peak/background ratio is the main analytical criticality.

This paper shows the analysis technique of trace elements on fused-discs specimens of stone materials that was developed at the Earth Sciences Department of the University of Pisa.

(*) Dipartimento di Scienze della Terra, University of Pisa (Italy) e-mail: lezzerini@dst.unipi.it

THEORETICAL OBSERVATIONS

The intensity I_i of the characteristic line of fluorescence emitted by an element *i* can be expressed as follows:

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

where C_i represents the concentration of the element *i* (in ppm), C_j the concentration of each interfering element, and $K_{i,j}$ coefficients that account for the matrix effects (absorption and enhancement) and having the dimension of mass absorption coefficients (Franzini *et al.*, 1975).

In order to determine concentration of trace elements, the algorithm proposed by Lucas-Tooth and Price (1961) was used:

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

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, 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. This algorithm is effective for processing samples dissolved in a moderately diluted lithium borate mixture (sample/flux dilution ratio from 1:5 to 1:12).

MATERIALS AND METHODS

Calibration of the proposed method for measuring twelve elements of rocks (V, Cr, Co, Ni, Rb, Sr, Y, Zr, Nb, Ba, La, Ce) was developed by using 121 in-house standards characterized by a wide chemical compositions, as shown in Figure 1 where the standards are plotted in a Total Alkali/Silica Scheme (TAS) (Le Maitre *et al.*, 1989).

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 been completely dissolved, 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. The fused glass discs were prepared following the method proposed by Claisse (1957). According to this procedure, the powder sample is ignited to about 1000°C for 1 hour to eliminate the volatile components. A mixture containing 0.700 g of specimen and 6.300 g of flux (50% lithium tetraborate $Li_2B_4O_7$ and 50% lithium metaborate $LiBO_2$) (Claisse®), correspondind to a 1:9 sample/ borate dilution, is carefully homogenised at 1000°C for twenty minutes in a Pt_{95}-Au_5 crucible using a Claisse Fluxer-Bis automatic apparatus. As non-wetting agent, a few drops of ammonium iodure are added. Then the produced melt is poured into a Pt_{95}-Au_3-Rh_2 plate and cooled. After cooling, the glass disc (φ = 32 mm) is directly used for trace elements analysis.

EXPERIMENTAL DATA

The analyses were carried out by using an ARL 9400 XP+ sequential X-ray spectrometer under the instrumental conditions summarized in Table 1.

The determination of the net intensities of the analytical lines is a particularly delicate phase due to the high values of the continuous radiation ("background") and because of the attenuation of the intensities of the lines caused by dilution (low peak/background ratio). For each analytical line, the background measurement was carried out by linearly extrapolating the background value assessed by two points arranged symmetrically with respect to the angular position of the peak. The correction of potential interferences of other analytical lines ("peak overlap") on the intensity of the characteristic line of the analyte *i* was carried out through the relation:

$$I_i^{CORR} = I_i - K \cdot I_j$$

where I_i represent the measured intensity corrected by the background, Ii^{CORR} the intensity corrected by the spectral interference of the analyte *i*, I_j the intensity of the characteristic line of the element *j* without interferences and *K* a constant calculated according to the relation:

$$K = \frac{I_j^{\lambda i}}{I_j}$$

in which $I^{\lambda i}_j$ is the net intensity of the characteristic line of the interfering element *j* measured in the same spectral area of the characteristic line of the element *i*. The constant *K* is an average value calculated on some samples that do not contain the element *i* and that are characterized by different compositions (Leoni & Saitta, 1976).

The evaluation of the reproducibility of this methodology was carried out on seven samples of different min-

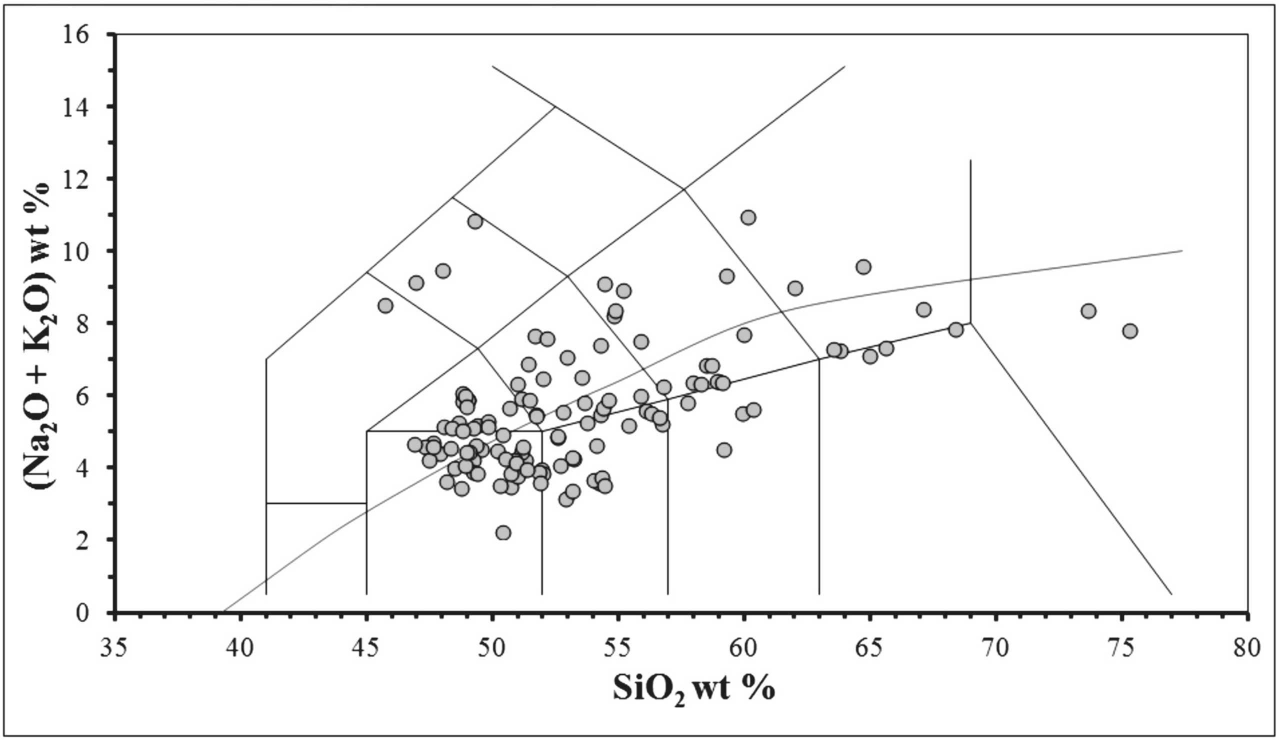

Fig. 1 - Total alkali-silica (TAS) diagram for in-house standards

Tab. 1 - 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
l$_{E}$	K□	K□	K□	K□1	L□1	L□1	K□
Tube	Rh	Rh	Rh	Rh	Rh	Rh	Rh
kV	30	30	30	60	60	60	60
mA	80	80	80	40	40	40	40
AC	AX06	PET	LiF200	LiF220	LiF220	LiF220	LiF220
DET	FPC	FPC	FPC	SC	FPC	FPC	FPC
COL	0.60°	0.60°	0.25°	0.15°	0.15°	0.15°	0.15°
CTP	10	10	10	100	100	100	100
CTB	10	10	10	50	50	50	50

l$_{E}$ = analytical line; **kV**, **mA** = voltage and current of X-ray tube; **AC** = analysing crystal (**AX06** = multilayer synthetic crystal, **PET** = pentaerytritol, **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)

eralogical and chemical compositions: 10 fused glass discs were obtained by each sample and these discs were independently measured. The evaluation of the analytical precision was determined by carrying out 10 measurements on each disc. The results are show in Table 2 in which are reported the detection limits *DL* (in ppm), the reference concentration (C_{ref}), the standard deviation of the 10 measurements carried out on each sample (RSD_I), and the standard deviation calculated on the measurements of the ten discs (RSD_{P+I}). The values measured for each sample are reported in increasing order of concentration.

Tab. 2 - Reproducibility on ten replicate fused glass disks of five selected international standards

	Nb				Zr				Y				Sr		
	(DL = 3 ppm)				(DL = 3 ppm)				(DL = 2 ppm)				(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				Ce				Ba				La		
	(DL = 3 ppm)				(DL = 15 ppm)				(DL = 10 ppm)				(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				Cr				V				Co		
	(DL = 2 ppm)				(DL = 2 ppm)				(DL = 3 ppm)				(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

C_{REF} = reference concentration (ppm) (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 ; **DL** = detection limit.

The data of the Table 2 shows that the reproducibility of the method (*RSD_{P+I}*) seems to be related mainly to the analytical accuracy (*RSD_I*) that depends primarily to the counting statistics. In particular, the reproducibility errors range from 2% to 11% for concentrations ranging from 20 to 100 ppm, and they range from 0.7 to 1.9% for concentrations exceeding 1000 ppm. Higher reproducibility errors (over 20%) are observable in concentrations under 20 ppm, close to the limits of detectability of all the analyzed elements.

The calibration curves of each elements are reported in Figures 2a and 2b and were obtained by using the in-house standards. The observed concentrations were calculated by processing the data of the net intensities of the analytical lines according to the algorithm of Lucas-Tooth & Price (1961) (see relation (2)) that significantly reduces the influences of the matrix effects.

Figures 2a and 2b report the relative standard error (*RSEE*) according to the following formula:

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

where where x and y represent the reference and calculated concentrations of each element in a single measurement (ppm) respectively, x_a and y_a the average concentrations for the interval of interest and n the number of the in-house standards.

As shown by Figures 2a and 2b, *RSEE* values are under 8 for almost all the samples, except for Ce and La, that are about 9. Those high values seems to be linked to the low analytical precision that is the consequence of a concentration range close to the detectability limit (almost 15 ppm for these elements) (Table 2). As regards Ni, the X-ray tube of the spectrometer emitted the typical line of this element (about 20 ppm) during the calibration phase. In case of low concentrations, the error produced by this line significantly modifies the calibration curve of Ni, in spite of the appropriate correction. Therefore, only concentrations over 50 ppm have been taken into account for this element. For all other elements the influence of the X-ray tube appears instead negligible for analytical purposes. The elements characterized by the highest concentrations reach very low *RSEE* values (Zr = 3.9, Sr = 2.2, Ba = 2.9) in agreement with the high statistical counting of their characteristic lines. It must be noticed the high linearity of the calibration curves of these elements in the whole compositional range.

Sixteen international standards of rocks (Table 3) were analyzed under the same instrumental condi-

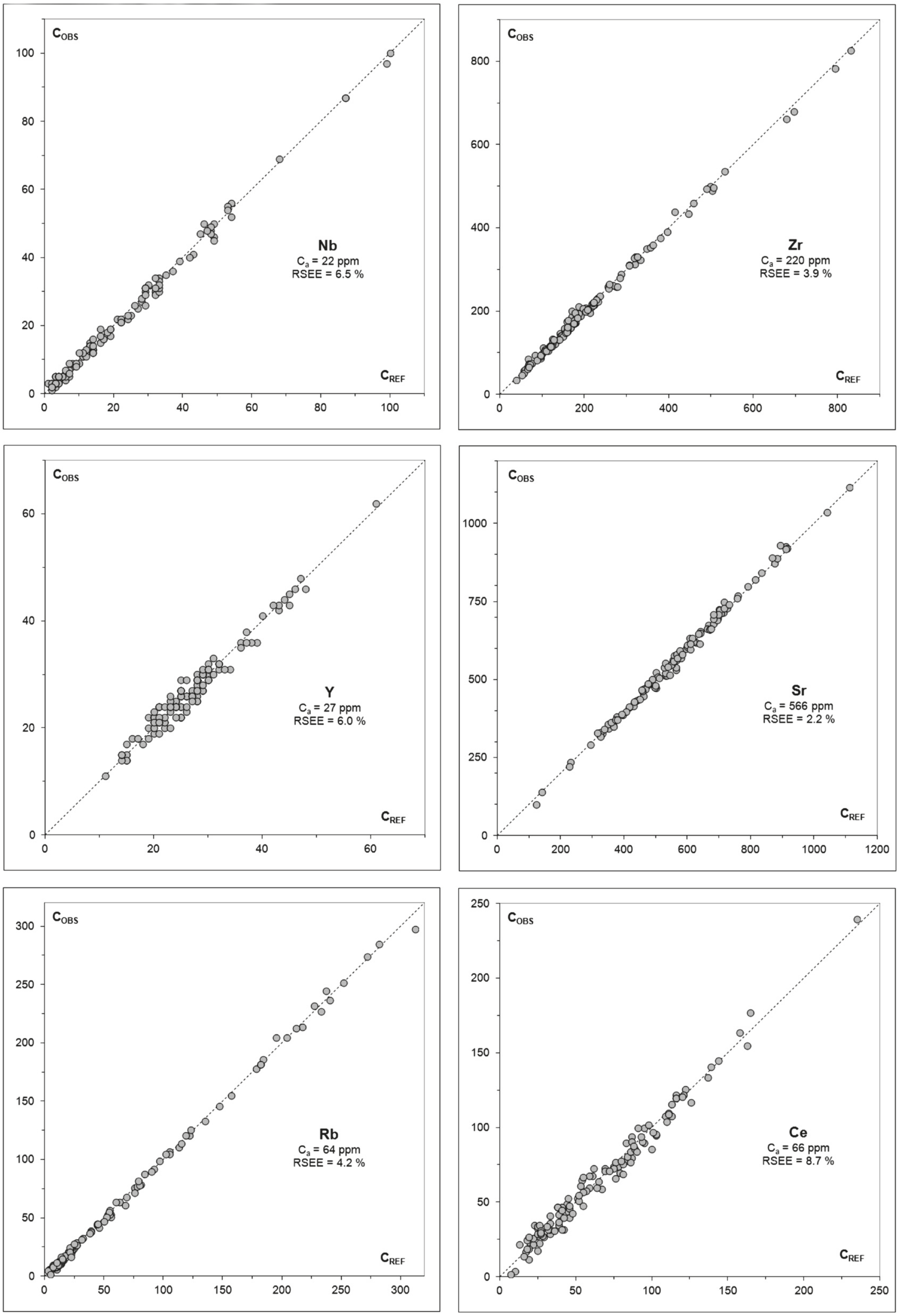

Fig. 2a - Calibration plots for Nb, Zr, Y, Sr, Rb, Ce

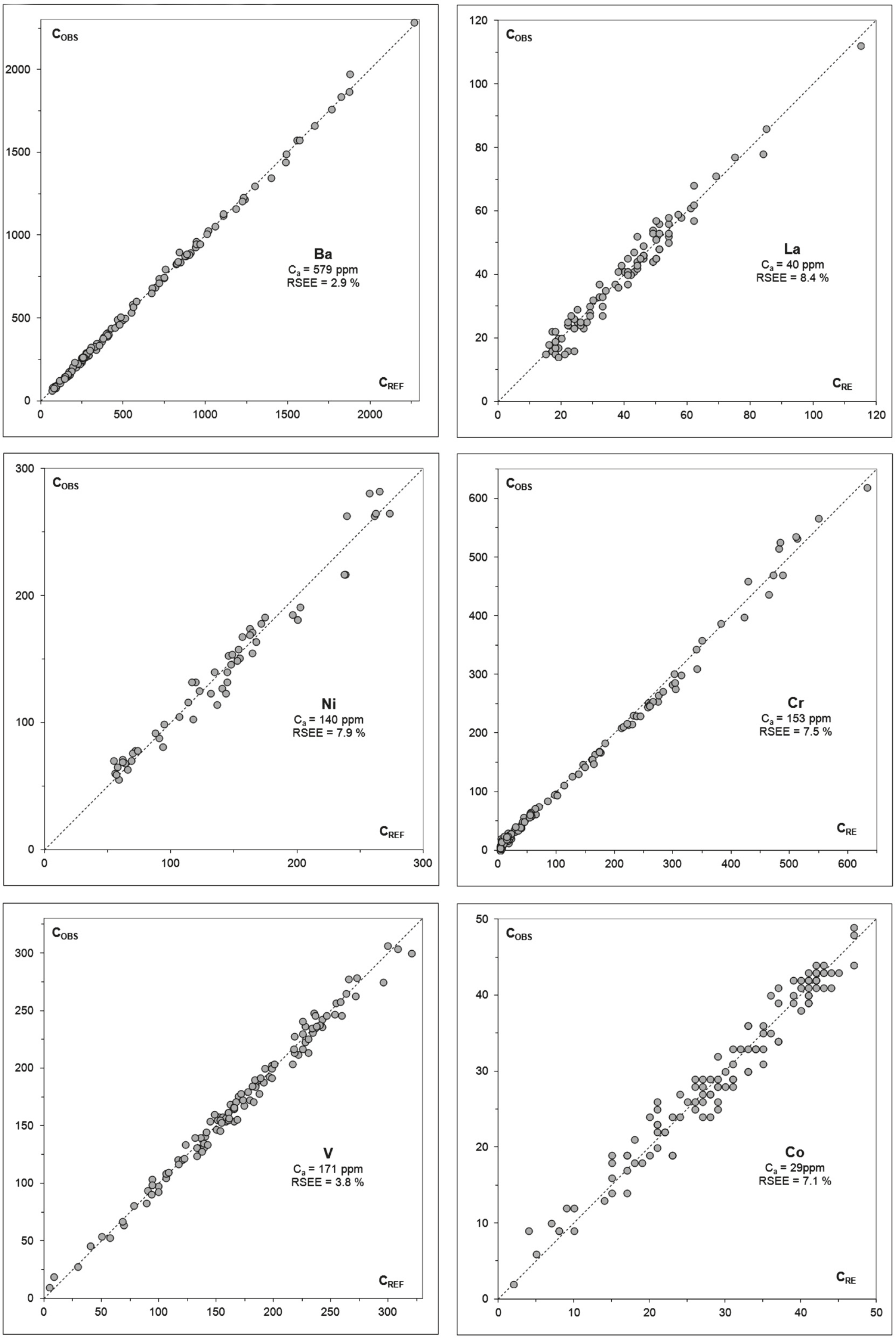

Fig. 2b - Calibration plots for Ba, La, Ni, Cr, V, Co tions used for the in-house standards to determine the accuracy of the proposed methodology. In Figures 3a and 3b the observed (C_{obs}) and reference (C_{ref}) concentration values (ppm) of each determined element, together the average concentration of the interval (C_a) and RSEE calculated according to the relation (5), are graphically. Therefore, *RSEE* data shows a valuation of the accuracy of the proposed methodology. Only the concentrations that range from the detectability limit (Table 2) and the highest calibration value were considered for the calculation. As regards Ni, in agreement to the calibration curve process, only the concentrations over 50 ppm were considered to reduce the influence of the X-ray tube emission.

As it can be observed, RSEE values ranges from 3.9 (Sr) to 9.8 (Ni and Co) and are quite similar (but slightly higher) to the corresponding values of Figures 2a and 2b (calibration curves from the in-house standards).

As results by the analysis of Figures 3a and 3b and Table 2, the accuracy of the proposed methodology depends essentially by the statistical counting. The errors resulting from the fused glass disc preparation (calcination of the samples before the fusion, weighing of the sample and flux, homogeneity of the melt, grain size of the powders) are quite negligible. This conclusion is exactly the opposite than that observed for the measurement of the major elements (Tamponi *et al.*, 2003; Lezzerini *et al.*, 2013).

The accuracy values are generally slightly higher than the ones that are commonly obtained by powder-pellet specimens (Franzini & Leoni, 1972; Franzini *et al.*, 1976; Haukka & Thomas, 1977; Thomas & Haukka, 1978; Bower & Valentine, 1986; Eastell & Willis, 1990; Chappell, 1991; Enzweilerand & Webb, 1996; Mori *et al.*, 1999; Beckhoff *et al.*, 2006; Lezzerini *et al.* 2013), and they are to be considered adequate for mineralogical and petrographic purposes. An improvement of data quality could be obtained by increasing the counting times or through the repetition of the measurement on each sample. The second way is probably to be preferred. In fact, in case of long analytical times, the low intensity of the fluorescence lines of the trace elements can compromise the stability of the instrumental conditions.

Tab. 3 - List of rock international standards

Name	Description	Reference
AMH-1	Mount Hood andesite	Thompson et al., 1999c
DNC-1	Dolerite	Govindaraju, 1994
GSR-2	Andesite	Govindaraju, 1994
JB-2	Basalt	Govindaraju, 1994
JP-1	Peridotite	Govindaraju, 1994
MRG-1	Gabbro	Govindaraju, 1994
MW-1	Miaskite	Govindaraju, 1994
OU-1	Bardon Volcanic Tuff	Thompson et al., 1998
OU-2	Belford dolerite	Thompson et al., 1999b
OU-3	Microgranite	Potts et al, 2000
SDC-1	Mica Schist	Govindaraju, 1994
SGD-1a	Gabbro	Govindaraju, 1994
SGD-2	Gabbro	Govindaraju, 1994
STM-1	Syenite	Govindaraju, 1994
SY-3	Syenite	Govindaraju, 1994
YG-1	Granite	Thompson et al., 1999a

CONCLUSIONS

In the compositional range of the analyzed samples, according to the proposed methodology, the reproducibility of V, Cr, Co, Ni, Rb, Sr, Y, Zr, Nb, Ba, La, Ce measurements depends mainly on the statistical counting error. The errors originated by the preparation of the fused glass discs are instead much less important. The obtained values shows that a data improvement can be reached by increasing counting times and the consequent reduction of the statistical counting errors.

Moreover, the accuracy of this methodology can be considered acceptable for mineralogical and petrographic studies, and it is comparable to that obtained on powder pellets. The results are in fact in good agreement with the reference values of the international standards. The relative error is ever under 10%, ranging from 3.9% (Sr) and 9.8% (Ni and Co).

Furthermore, the proposed methodology is characterized by both high analytical quality and short operating time due to the possibility of performing also the measurement of the major elements on the same sample, much to the advantage of the management of the XRF laboratory.

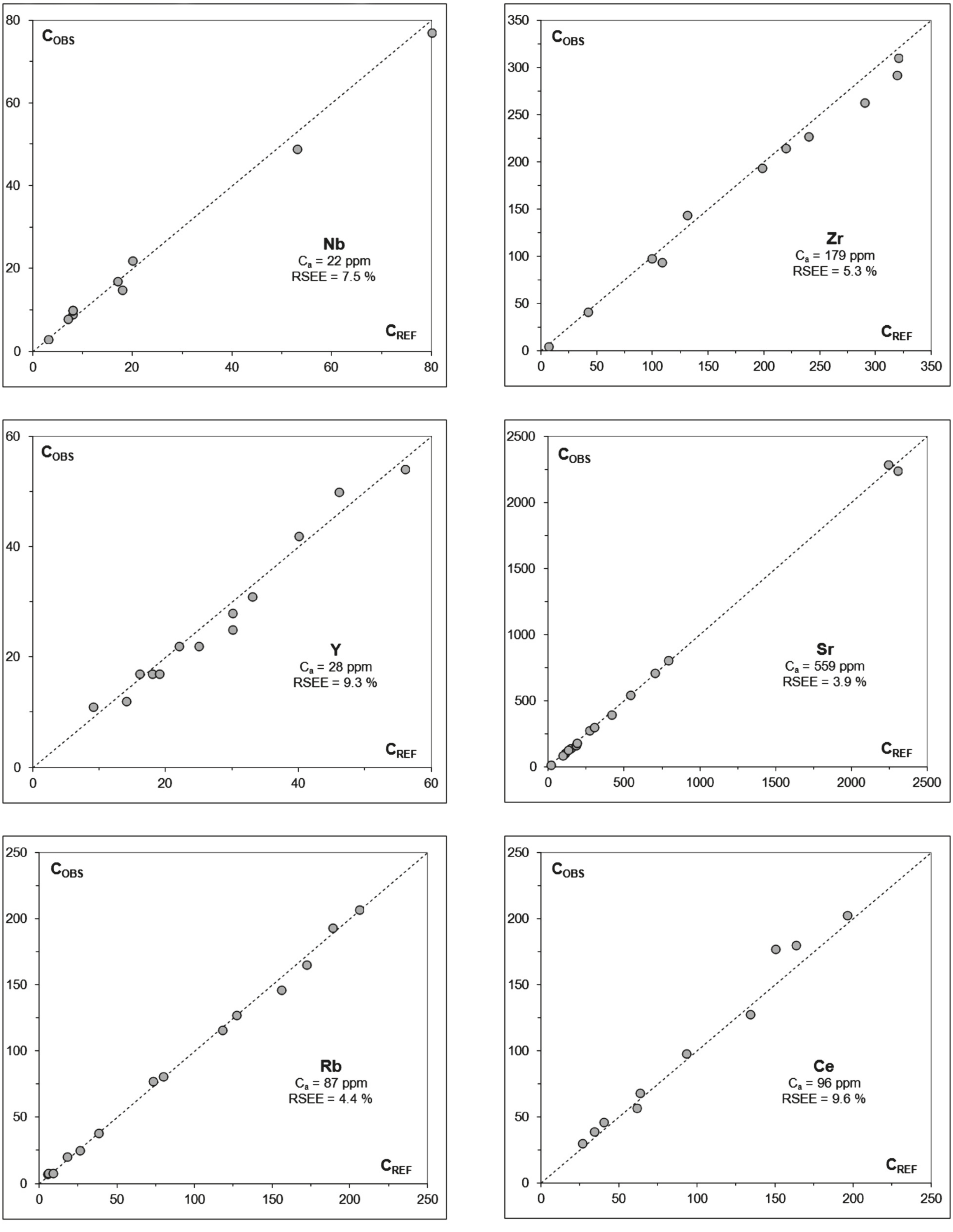

Fig. 3a - Analytical accuracy for Nb, Zr, Y, Sr, Rb, Ce

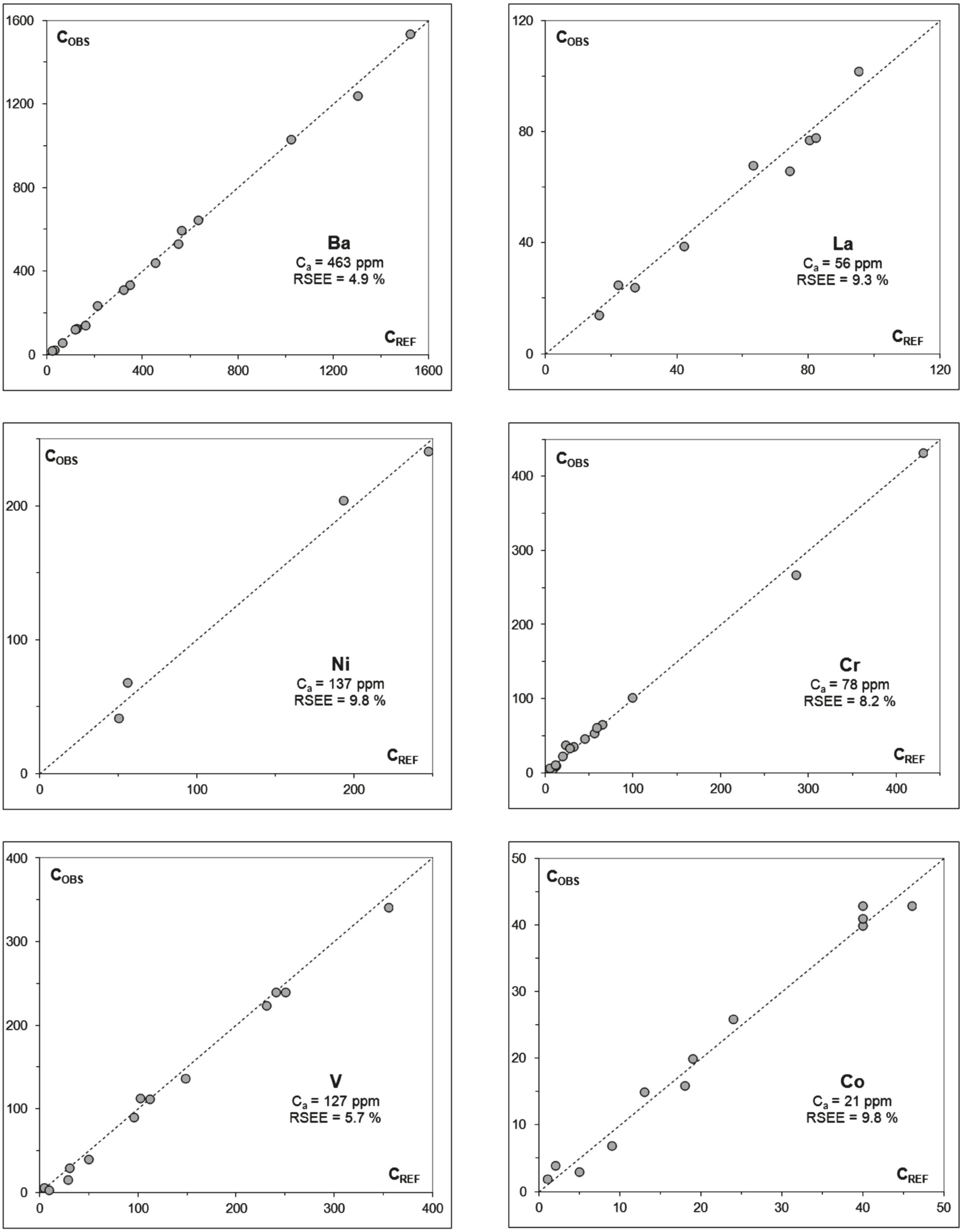

Fig. 3b - Analytical accuracy for Ba, La, Ni, Cr, V, Co

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