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X-RAY FLUORESCENCE ANALYSIS OF 29 TRACE ELEMENTS IN ROCK AND MINERAL STANDARDS

RIASSUNTO. — Recentemente FRANZINI M. et Al. (1972) hanno proposto una metodologia in fluorescenza a raggi-X per la determinazione degli elementi in tracce nelle rocce e nei minerali. Questa metodologia prevede il calcolo della concentrazione di un elemento in tracce attraverso la relazione:

$$c_i = I_i \sum_{j=1}^{n} k_{i,j}\, c_j \qquad (1)$$

dove c_i e I_i sono rispettivamente le concentrazioni e l'intensità dell'elemento in tracce e $k_{i,j}$ coefficienti sperimentali che tengono conto degli effetti di matrice dovuti agli elementi maggiori H_2O, Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2 e Fe_2O_3) essendo gli effetti interelementari degli elementi in tracce trascurati. Attraverso la relazione (1) ed utilizzando per la misura delle intensità uno spettrometro automatico Philips PW1450 sono stati determinati Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Gd, Dy, Hf, Pb, Th e U in circa 35 standard internazionali di rocce e minerali. Per determinare i contenuti di V, Cr, Ni, Cu, Zn, Ga, Rb, Sr, Zr, Y, Nb, Ba, La, Ce e Pb sono stati utilizzati coefficienti $k_{i,j}$ già calcolati da FRANZINI M. et Al. (1972), mentre per i rimanenti elementi viene fornita una nuova serie di coefficienti.

Sulla base dei risultati conseguiti vengono inoltre discusse le possibilità analitiche della fluorescenza a raggi-X per l'analisi degli elementi in tracce nelle rocce e nei minerali.

ABSTRACT. — Utilizing powder pellets, thirty-five international standards of rocks and minerals have been analyzed for Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Gd, Dy, Hf, Pb, Th and U. Coefficients for matrix effects correction are given for the analytical lines of Sc, Co, As, Sn, Sb, Cs, Pr, Nd, Sm, Gd, Dy, Hf, Th and U being the coefficients for the characteristic lines of the other elements given by the authors in previous works.

The collected data point out that all the analyzed trace elements can be determined, by X-ray fluorescence tecniques, with a good accuracy, in a range of concentration comprised between 1-5 p.p.m. and about 5000 p.p.m..

Introduction

Utilizing powder pellets, as pointed out by FRANZINI M. et Al (1972), accurate trace element analysis by X-ray fluorescence can be achieved by a full matrix effect correction, provided that the major composition of the samples to be analyzed for trace elements is known.

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Following the analytical procedure outlined by the quoted authors we have determined the contents of Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Zr, Y, Nb, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Gd, Dy, Hf, Pb, Th and U on 35 international standards of rocks and minerals.

The choice of these elements is mainly dependent upon the limit of the X-ray fluorescence sensitivity. Practically, with the exclusion of some ligth elements as F, S and Cl, we have choosed all the trace elements whose amount in a rock can be greater than 1-2 p.p.m..

To overcome matrix effects the following relation (FRANZINI M. et Al., 1972) was applied:

$$I_i = \frac{C_i}{\sum_{j=1}^{n} k_{i,j} C_j} \qquad (1)$$

where, for a trace element *i*, I_i represents the intensity of the characteristic line, C_i the concentration and $k_{i,j}$ the coefficients that take into account the influence of the major components of a rock (H_2O, Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2, Fe_2O_3).

$K_{i,j}$ are experimental coefficients and, as pointed out by FRANZINI M. et Al. (1972) do not correspond exactly with mass absorption coefficients; they depend on: *a*) absorption of both incident and emergent beam; *b*) possible enhancement effects; *c*) instrumental conditions.

Experimental

The characteristic line intensities were measured utilizing a Philips PW1450 automatic X-ray spectrometer. The selected instrumental conditions for the analyzed trace elements are given in table 1.

To determine the contents of V, Cr, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pb we have utilized the $k_{i,j}$ coefficients previously determined by FRANZINI M. et Al. (1972) and LEONI L., SAITTA M. (1975).

Since the $k_{i,j}$ coefficients for the analytical lines of these elements were evaluated starting by intensities collected with a different equipment (Philips PW1540 manual X-ray spectrometer) a preliminary calibration has been necessary. This calibration has been made comparing the intensities measured with the two different X-ray spectrometers; the following relation has been applied:

$$(k_{i,j})_2 = (k_{i,j})_1 \, H \qquad (2)$$

TABLE 1

Instrumental conditions

Element	Analytical line	X-ray tube	Crystal	Detector	Discrim.	Collimator
Sc	Kα	Cr(40 KV,60 mA)	LiF(200)	Flow.C.	yes	fine
Sn	Lα	Cr(90 KV,30 mA)	LiF(220)	Flow.C.	yes	fine
Sb	$L\beta_1$	Cr(90 KV,30 mA)	LiF(220)	Flow.C.	yes	fine
Cs	$L\beta_1$	Cr(40 KV,60 mA)	LiF(220)	Flow.C.	yes	coarse
V,Cr,Ni,Co	Kα	W (50 KV,45 mA)	LiF(220)	Flow.C.	yes	fine
As	Kα	W (50 KV,45 mA)	LiF(220)	Scint.	yes	fine
Ba,Ce	$L\beta_1$	W (60 KV,45 mA)	LiF(220)	Flow.C.	yes	fine
Dv	$L\beta_1$	W (60 KV,45 mA)	LiF(220)	F.C.+Scint.	yes	fine
Hf	$L\beta_1$	W (60 KV,45 mA)	LiF(220)	Scint.	yes	fine
Pb	$L\beta_{1,2}$	W (50 KV,45 mA)	LiF(220)	Scint.	yes	fine
La,Pr,Nd, Sm,Gd	Lα	W (60 KV,45 mA)	LiF(220)	Flow.C.	yes	fine
Cu	Kα	Ag(60 KV,20 mA)	LiF(220)	Scint.	yes	coarse
Zn,Ga,Rb,Sr Y,Zr,Nb	Kα	Ag(60 KV,20 mA)	LiF(220)	Scint.	yes	fine
Th,U	Lα	Ag(50 KV,30 mA)	LiF(220)	Scint.	yes	fine

were, for a trace element, $(k_{i,j})_1$ are the values of the coefficients reported by FRANZINI M. et Al. (1972) and by LEONI L., SAITTA M. (1975), $(k_{i,j})_2$ the coefficients utilized for the analysis and H a constant computed according to the following relation:

$$H = \left(\Sigma \frac{I_1}{I_2}\right) / n \qquad (3)$$

where I_1 and I_2 are rispectively the intensities (counts sec.) measured with the manual and the automatic X-ray spectrometers and n the number of standards utilized for the standardization.

For the other elements (Sc, Co, As, Sn, Sb, Pr, Nd, Sm, Gd, Dy, Hf, Th and U) the $k_{i,j}$ coefficients were experimentally determined following the same procedure as described by FRANZINI M. et Al. (1972).

The values of these coefficients are given in table 2. In table 3 are reported the intensities of the analitycal lines, measured on some international standards, of the elements for which the $k_{i,j}$ coefficients are given. These data are useful for other workers concerned with references standardization. Thus, to utilize the $k_{i,j}$ coefficients reported in table 2 it is necessary to compare the intensities (counts/sec.) collected on a different X-ray spectrometer with those reported in table 3. A relation similar to that previously described can be used.

All the measured intensities have been corrected for the background that was measured, generally, immediately before and after the angular position of each

TABLE 2

$k_{i,j}$ coefficients

	H_2O	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
Sc	0.00079	0.00191	0.00214	0.00238	0.00265	0.00829	0.00818	0.00139	0.00218
Co	0.00059	0.00138	0.00154	0.00165	0.00189	0.00613	0.00629	0.00649	0.00433
As	0.00032	0.00074	0.00086	0.00095	0.00106	0.00333	0.00342	0.00349	0.00646
Sn	0.00253	0.00423	0.00504	0.00516	0.00591	0.01562	0.01653	0.01730	0.03168
Sb	0.00284	0.00475	0.00567	0.00581	0.00664	0.01765	0.01858	0.01944	0.03560
Cs	0.00089	0.00199	0.00209	0.00233	0.00297	0.01499	0.01497	0.00163	0.00235
Pr	0.00394	0.00864	0.01013	0.01140	0.01372	0.03815	0.03806	0.01417	0.01122
Nd	0.00301	0.00719	0.00792	0.00922	0.01086	0.03182	0.03188	0.03270	0.00848
Sm	0.00265	0.00626	0.00705	0.00788	0.00936	0.02909	0.02937	0.03086	0.01411
Gd	0.00165	0.00429	0.00478	0.00513	0.00617	0.01865	0.01964	0.01953	0.01235
Dy	0.00114	0.00336	0.00383	0.00438	0.00534	0.01684	0.01717	0.01722	0.02562
Hf	0.00296	0.00666	0.00756	0.00766	0.00863	0.02285	0.02286	0.02310	0.02598
Th	0.00064	0.00186	0.00214	0.00221	0.00236	0.00728	0.00928	0.01076	0.01472
U	0.00071	0.00204	0.00236	0.00244	0.00260	0.00802	0.01022	0.01185	0.01622

TABLE 3

Intensities (count/s) of the analytical lines of the elements for which the $k_{i,j}$ coefficients are given

	Sc	Co	As	Sn	Sb	Cs	Pr	Nd	Sm	Gd	Dy	Hf	Th	U
G2	12.6	33.1	n.d	n.d	n.d	6.3	12.9	49.3	5.3	8.2	4.0	n.d	86.6	n.d
GA	25.3	40.2	10.5	2.5	n.d	17.6	5.0	22.2	5.1	14.7	7.3	n.d	52.0	14.3
GH	n.d	16.6	n.d	7.8	n.d	9.8	7.0	27.6	10.5	15.2	16.7	n.d	297.6	54.1
GM	15.1	23.7	32.2	2.4	1.4	30.3	5.4	24.2	4.1	7.3	9.8	n.d	122.4	22.5
NIM-G	n.d	23.8	109.9	4.7	2.0	7.8	19.0	70.0	13.5	23.8	23.5	11.9	193.3	60.4
GSP-1	21.0	39.5	6.9	6.1	2.1	8.0	40.9	166.6	19.2	22.7	4.7	14.8	323.7	n.d
JG-1	23.3	29.5	n.d	3.3	n.d	41.1	3.0	15.8	3.7	6.3	n.d	n.d	46.0	12.4
SY-1	27.6	80.8	21.4	6.8	n.d	10.8	40.2	185.9	40.6	63.9	73.0	70.3	2814.1	5413.8
SY-2	17.6	39.1	92.1	4.4	n.d	11.8	14.5	65.5	11.5	19.0	17.6	9.5	1028.2	704.0
AGV-1	43.6	69.8	13.6	5.0	3.0	n.d	3.9	26.5	6.5	9.9	9.4	n.d	20.9	n.d
TB	68.5	70.1	65.6	4.5	2.5	45.0	10.1	40.6	8.9	11.6	6.4	n.d	49.9	8.5
Len-X	n.d	26.5	16.1	2.1	n.d	11.1	22.4	81.7	10.4	14.4	10.0	11.6	45.9	15.1
DR-N	95.2	129.3	9.6	n.d	n.d	23.9	3.8	21.0	4.3	3.7	5.8	n.d	12.6	n.d
BCR-1	101.1	130.0	n.d	2.6	n.d	n.d	n.d	25.6	6.7	8.7	6.7	n.d	14.4	n.d
BR	58.8	190.8	9.2	4.0	n.d	n.d	9.8	50.4	8.6	9.5	4.7	6.5	20.7	n.d
BM	119.2	335.8	69.2	n.d	n.d	n.d	2.7	13.1	2.3	n.d	8.5	n.d	n.d	n.d
JB-1	74.5	138.8	13.7	2.2	n.d	n.d	3.3	22.1	5.6	3.9	6.2	n.d	25.0	n.d
NIM-N	119.5	215.2	n.d	1.8	n.d	n.d	n.d	3.1	n.d	n.d	n.d	n.d	n.d	n.d
NIM-L	n.d	15.3	141.9	5.3	n.d	16.4	18.2	47.9	n.d	n.d	n.d	210.5	156.0	39.0
PCC-1	38.9	560.5	n.d	2.3	3.5	n.d	n.d	n.d	n.d	n.d	n.d	8.1	n.d	n.d
DTS-1	13.3	656.6	n.d	n.d	3.0	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
NIM-D	21.6	887.3	n.d	n.d	2.3	n.d	n.d	n.d	n.d	n.d	n.d	9.0	n.d	n.d
NIM-P	116.6	402.2	n.d	n.d	1.9	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
UB-N	57.3	498.4	75.1	1.1	2.8	55.7	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Mic.Fe	49.1	79.9	14.4	68.7	1.9	779.1	27.5	115.5	16.5	19.6	12.1	23.6	233.5	112.5
Mic.Mg	1.9	103.4	n.d	n.d	n.d	209.5	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
KH	7.5	19.2	11.1	n.d	n.d	n.d	5.4	5.4	2.5	2.4	n.d	10.0	5.9	n.d

n.d = not detected

characteristic line (a value corresponding to the average of the two background measurements was taken). Sometime, owing to partially interferences of the peaks, the backgrounds were measured away more than 2-3° from the angular position of

the peak; in these cases the background curvature was taken into account. For a restricted range of 2 θ (about 7-8°) we have found experimentally that the background curvature is exprimible by an exponential function of the type:

$$I_B = e^{-a\lambda + b} \qquad (4)$$

where I_B is the background intensity, λ the wavelength, *a* and *b* two constant that depend on the instrumental conditions and on matrix composition. Table 4 a reports

TABLE 4

Interference between the characteristic lines of the analyzed elements and values of the constants K

Analytical line	Interfering line	Characteristic line utilized for correction and values of K	
		line	K
Sc Kα	Ca $K\beta_5$	Ca $K\beta_5$	0.0870
V Kα	Ti Kβ	Ti Kα	0.0500
Cr Kα	V $K\beta_1$	V Kα	0.0450
Co Kα	Fe $K\beta_1$	Fe $K\beta_1$	0.0860
As Kα	Pb Lα	Pb $L\beta_{1,2}$	0.5757
Ba Lβ	Ce Lα	Ce $L\beta_1$	0.5200
Gd Lα	Ce $L\gamma_1$	Ce $L\beta_1$	0.1150
Sm Lα	Ce $L\beta_2$	Ce $L\beta_1$	0.0450
Pr Lα	La $L\beta_1$	La Lα	0.2160
Y Kα	Rb $K\beta_1$	Rb Kα	0.2630
Zr Kα	Sr $K\beta_1$	Sr Kα	0.1100

the background values for different matrix in the region of continous spectrum comprised between $\lambda = 0.944$ Å and $\lambda = 0.732$ Å. The linear extrapolation has been made against the 2 θ values; the exponential extrapolation against the wavelength values.

The comparison between the observed background measurements and those evaluated by the two different extrapolations shows that the exponential one is more close to the observed background values.

In the intensities measurements of some characteristic lines it has been necessary to make corrections for line overlaps. Relations similar to those utilized by FRANZINI M. et Al. (1972) and by LEONI L., SAITTA M. (1975) have been applied to overcome these interferences, that is:

$$I_A' = I_A'' - I_B K \qquad (5)$$

where I'_A and I''_A are respectively the corrected intensity and the measured intensity (corrected for background) of the analyzed element (A), I_B the intensity of a characteristic line (free by interferences) of the interfering element (B) and K a constant computed according to the following ratio:

$$K = \frac{I'_B}{I_B} \qquad (6)$$

where I'_B is the intensity of the interfering line of the element B measured at the 2 θ value of the characteristic line of the analyzed element (A). I'_B and I_B are intensities referred to characteristic lines belonging to the same spectral serie and measured on samples absolutely free of the element A. In some cases, where the peak of the analyzed trace element is affected by the presence of the tail

TABLE 4 a

Background interpolation in the region of the continuos spectrum ranging from $\lambda = 0.944$ *to* $\lambda = 0.732$ *Å (X-ray tube: Ag operating at 60 KV and 20 mA; crystall LiF (220); detector: Scintillator with discriminator; fine collimator)*

			Background values (counts/s.)		
	2θ	λ	observed	Linear Extrap.	Expon.Extrap.
MgO	29.80	0.732	2488.0	2488.0	2488.0
	31.00	0.761	2142.4	2260.7	2147.0
	33.00	0.809	1676.9	1882.0	1662.0
	35.00	0.856	1301.9	1503.2	1293.0
	38.70	0.944	802.4	802.4	802.4
SiO_2			1630.4	1630.4	1630.4
			1420.4	1493.3	1422.8
			1136.7	1264.9	1141.1
			920.2	1036.5	919.4
			614.0	614.0	614.0
Fe_2O_3			342.2	342.2	342.2
			309.0	316.0	308.4
			252.3	272.4	255.5
			220.4	228.7	218.5
			148.0	148.0	148.0

of a peak of a major element (see for example Co Kα by Fe Kα or Sc Kα by Ca $K\beta_5$) the intensities I_B and I'_B of relation (6) are referred respectively to the maximum of the interfering peak and to the angular position (2 θ) of the peak of the analyzed element.

In table 4 are reported all the interferences encountered in the intensities measurements and the values of the K constants.

In the analyses of Cu, Cr and Ni it was necessary to take into account the presence of these elements either as trace in the target of the X-ray tube or in the material of the X-ray spectrometr cabinet. The amount of Cu, Cr and Ni due to these sources was evaluated on samples of pure Al_2O_3, SiO_2 (quartz) and $CaCO_3$ absolutely free of these elements. The following values (p.p.m.) were obtained:

	Cr	Ni	Cu
Al_2O_3	28	7.5	51
SiO_2	32	6.9	50
$CaCO_3$	30	6.6	49
$\bar{M}$	30	7.0	50

Table 5 reports the concentration of the trace element (p.p.m.) obtained on the analyzed international standards (U.S.G.S. standards: G2, GSP-1, AGV-1, BCR-1, PCC-1 and DTS-1; C.R.P.G. and A.N.R.T. standards: GA, GH, BR, Mica-Fe, Mica Mg, UB-N, DR-N, BX-N and DT-N; G.S.J. standards: JG-1 and JB-1; N.I.M. standards: NIM-D, NIM-G, NIM-L, NIM-N and NIM-P; C.S.R.M. standards: SY-1 and SY-2; N.B.W. standards: 69 a, 88 a and I b; Ingamels and Suhr carbonate standards: 401, 402 and 403; Len-X standard: Len-NS-1; Z.G.I. standards: BM, TB, GM and KH).

Table 6 reports for each analyzed trace element the detection limit and the precision at a level of concentration of 10 p.p.m.; both these parameters are referred to a matrix of pure SiO_2 and have been evaluated for a counting time of 200 sec..

Data listed in table 6 are indicative and depend, the detection limit in particular, on the matrix composition.

With the exception of the elements that have been analyzed with the Ag X-ray tube (we have utilized an Ag X-ray tube of 1600 W of power) for the other elements the values relative to the detection limits given in table 6 represent, at present, substantially a limit for X-ray fluorescence analysis of the trace elements in a rock.

Conclusions

On the basis of the results reported in table 5 we can conclude that the method proposed by the authors is sufficiently accurate for petrographical and geochemical researches. With some exceptions generally the agreement between our data and literature ones is good.

The precision of the method depends substantially on the standard counting error. Accuracy depend on the $k_{i,j}$ values.

TABLE 5 (a)

Results of the trace elements analyses on the international standards

	G2	GA	GH	GM	NIM-G	GSP-1	JG-1
Sc	3.7(3.7)	7.3(7.0)	n.d	4.4(5.1)	n.d	5.0(6.3)	6.7(6.5)
V	35.3(35.4)	38.0(36.0)	n.d(5)	11.4(11)	n.d(2)	49.7(52.9)	24 (24)
Cr	10.0(7.0)	8.0(10)	3 (6)	12 (10)	9 (12)	11 (12.5)	59 (50)
Co	7.2(5.5)	8.7(5)	3.5(1.5)	5 (3.5)	5.1(6)	9 (6.4)	6.4(4)
Ni	6.0(5.1)	7.0(7)	4 (3)	8 (7.5)	4 (11)	10 (12.5)	10 (10)
Cu	20.9(11.7)	20.7(14)	20.4(12.0)	20.3(13)	20.4(15)	28.2(33.3)	10 (3.3)
Zn	80.0(85)	62 (75)	56 (80)	28 (40)	45 (60)	94 (98)	37 (36)
Ga	26.3(22.9)	17.1(16)	25 (22)	18.4(15)	30 (32)	22 (22)	18 (20)
As	n.d(0.3)	1.4	n.d	4.1(4)	14.2	n.d(0.1)	n.d
Rb	174 (168)	173 (175)	398 (390)	259 (250)	324 (274)	249 (254)	179 (185)
Sr	498 (479)	307 (305)	9 (10)	133 (133)	11.4(13)	233 (233)	188 (184)
Y	12.9(12)	23 (18)	88 (70)	29 (26)	121 (100)	30 (30.4)	32.7
Zr	333 (300)	153 (140)	171 (160)	146 (145)	298 (300)	566 (500)	118 (160)
Nb	12.6(13.5)	13.6(13)	105 (85)	24 (17)	60 (50)	26 (29)	13
Sn	n.d(1.5)	2 (4)	5.2(10)	1.6(4.6)	3.2	4.6(6.3)	2.3(3)
Sb	n.d(0.1)	n.d	n.d	1.1(0.5)	1.5(0.4)	1.8(3)	n.d
Cs	2.2(1.4)	6.3(5)	3.4	10.6(7.6)	2.7(3)	2.9(1)	14.5(10.3)
Ba	1787 (1870)	819 (850)	37 (22)	319 (328)	136 (179)	1254 (1300)	454 (450)
La	97 (96)	39 (36)	22 (25)	35 (35)	118 (85)	165 (191)	17 (25)
Ce	175 (150)	76	58	68 (60)	224 (160)	394 (394)	36 (42)
Pr	19 (19)	7.3	10	8 (9)	28	61 (50)	4.4
Nd	58 (60)	26	32	28 (27)	82 (60)	200 (188)	18.5(19.5)
Sm	6.4(7.3)	6.2	12.4	5 (6)	16 (20)	24 (27.1)	4.5(4.6)
Gd	5.7(5)	10.2	10.2	5 (6)	16 (10)	16 (15)	4 (4)
Dy	2.6(2.6)	4.7	10	6 (6)	15 (17)	3.2(5.4)	n.d(3.2)
Hf	n.d(7.4)	n.d	n.d	n.d(5)	12 (12)	16 (16)	n.d(3.5)
Pb	34 (31)	34	49	37 (30)	42 (38)	57 (51)	28 (24)
Th	26 (24)	16 (15)	83	35 (35)	56 (62)	106 (104)	14 (13)
U	n.d(2)	4.8	17	7 (7)	19 (14)	n.d	4 (3.3)

-- =not determined
n.d = not detected
In brackets : Literature data (F.J.Flanagan,1972)

TABLE 5 (b)

	SY-1	SY-2	AGV-1	TB	Len-X	DR-N	BCR-1
Sc	8.9(14)	5.6(7)	12.8(13.4)	18.4(13.4)	n.d	28.0(31.5)	29.6(33.0)
V	80.7(89)	45 (50)	122.9(125)	120.3(106)	n.d	229 (225)	459 (399)
Cr	53 (56)	9 (10)	12 (12.2)	109 (80)	n.d	41 (45)	21 (17.6)
Co	21.1(19)	9.8(10)	16.4(14.1)	15 (13)	6	32 (35)	34 (38)
Ni	35 (43)	8.5(10)	18 (18.5)	43 (40)	n.d	18 (16)	14 (15.8)
Cu	14.3(23)	15	45 (59.7	37 (50)	16.3	40 (52)	23 (18.4)
Zn	224 (219)	224	83 (84)	91 (95)	112	137 (150)	117 (120)
Ga	25 (20)	29	23.5(20.5)	29 (25)	35.5	24 (25)	21 (20)
As	3.8	15.2	2.2(0.8)	10 (11)	2.3	1.7	n.d(0.7)
Rb	179 (195)	221	66 (67)	183 (178)	214	71 (75)	43 (46.6)
Sr	192 (286)	263	661 (657)	165 (155)	1588	395 (400)	324 (330)
Y	402 (441)	126	18.3(21.3)	35 (39)	33.7	26	34 (37)
Zr	3211 (3030)	275	224 (225)	190 (175)	577	123	178 (190)
Nb	192 (150)	27	15 (15)	21 (12)	202	7.5	13 (13.5)
Sn	6.3(11)	3.8(3)	4.2(4.2)	5 (9)	1.6	n.d	2.7(2.6)
Sb	n.d(2.2)	n.d	2.8(4.5)	2.2(3.3)	n.d	n.d	n.d(0.7)
Cs	4.6	5	n.d(1.4)	14 (6.8)	4	9	n.d(0.9)
Ba	320 (282)	451 (450)	1269 (1208)	775 (725)	1255	411 (360)	775 (675)
La	166 (233)	72 (90)	43 (35)	52 (56)	142	22	29 (26)
Ce	449 (512)	167	71 (63)	101 (103)	259	45	61 (54)
Pr	64 (139)	23	6 (7)	14 (15)	32	5.6	n.d(7)
Nd	240 (314)	83	32 (39)	45 (50)	97	25	31 (29)
Sm	56 (245)	15	8 (5.9)	10 (9)	13	5.6	9 (6.6)
Gd	52 (65)	15	7.4(5.5)	8 (11)	10	2.9	7 (6.6)
Dy	61 (118)	14	7 (3.5)	4.4(4)	6.8	4.7	6 (6.3)
Hf	86	11	n.d(5.2)	6 (4.8)	12.3	n.d	n.d(4.7)
Pb	447 (445)	91 (80)	39 (35)	9 (7)	12	60	20 (18)
Th	1181 (1305)	395 (264)	8 (6.4)	17 (19)	15	5.2	7 (6)
U	2503 (2520)	298 (280)	n.d(1.9)	3.2(3)	5.5	n.d(1.5)	n.d(1.7)

TABLE 5 (c)

	BR	BM	JB-1	NIM-N	NIM-L	PCC-1	DTS-1
Sc	18.7	32.7(34)	23 (26)	37.5(38)	n.d	9 (6.9)	3.1(3.6)
V	253 (240)	233 (180)	223 (300)	227 (225)	79 (76)	33.4(30)	10 (10.3)
Cr	374 (420)	150 (123)	478 (417)	39 (40)	18 (20)	2733 (2730)	3585 (4000)
Co	54 (50)	78	35 (39)	55 (65)	3.7(4)	107 (112)	127 (133)
Ni	276 (270)	68 (57)	143 (139)	123 (78)	4 (11)	2428 (2339)	2338 (2269)
Cu	51 (70)	36 (45)	46 (52)	23 (13)	12 (15)	12.8(11.3)	11 (7)
Zn	151 (160)	120 (107)	81 (83)	57 (80)	377 (320)	44 (36)	45 (45)
Ga	18 (20)	20 (15)	20 (17)	18 (19)	53 (55)	n.d(0.4)	n.d(0.2)
As	1.9	12 (14)	2.5	n.d	25	n.d(1)	n.d(1)
Rb	45 (45)	8 (12)	39 (41)	2 (9)	187 (183)	n.d(0.1)	n.d(0.1)
Sr	1299 (1350)	225 (230)	443 (438)	257 (254)	4155 (4480)	n.d(0.4)	n.d(0.4)
Y	26 (27)	26 (26)	22	5.6(7)	14.2(30)	n.d(5)	n.d(0.1)
Zr	238 (240)	102 (105)	129 (300)	8.2(25)	8966	3.3(7)	1.6(3)
Nb	100	5 (10)	35	1.3(2)	907 (980)	n.d(2)	1.5(3)
Sn	4.3(8)	n.d(1.7)	2 (2.3)	1.7	4.8	1.8(1)	n.d(1)
Sb	n.d	n.d(2)	n.d(0.2)	n.d(0.4)	n.d(0.3)	3 (1.4)	2.6(0.5)
Cs	n.d	n.d(1.7)	n.d(1)	n.d	6 (6)	n.d	n.d(0.6)
Ba	1263 (1050)	269 (263)	548 (400)	107 (90)	392 (448)	10 (1.2)	9 (2.4)
La	96 (85)	7 (8.6)	46 (36)	6 (3)	229 (170)	n.d(0.2)	n.d(2)
Ce	156	21 (23)	69 (67)	9 (14)	299 (240)	n.d(0.1)	n.d(0.1)
Pr	15.4	3.7(3.5)	5	n.d	26	n.d	n.d(2)
Nd	67	15 (16)	28 (25)	4 (8)	56 (70)	n.d	n.d(2
Sm	13	3 (4)	7.6(5.9)	n.d	n.d	n.d(2)	n.d(2)
Gd	8	n.d(6)	3.1(4.8)	n.d	n.d	n.d	n.d(3)
Dy	4.4	6.6(4)	5.1(4.1)	n.d	n.d	n.d(5)	n.d(3
Hf	8.7	n.d(3.1)	n.d(3.5)	6 (5)	245 (250)	8.1	n.d(5)
Pb	12	20 (12)	11 (14)	6	46 (45)	13 (13)	13 (14)
Th	10.4	n.d(3)	10 (9.4)	n.d(0.5)	63 (69)	n.d(2)	n.d(2)
U	n.d	n.d(1)	n.d(1.8)	n.d(0.5)	17 (13)	n.d(2)	n.d(2)

TABLE 5 (d)

	NIM-D	NIM-P	UB-N	Mica-Fe	Mica-Mg	DT-N	BX-N
Sc	5.1(7)	30 (35)	13	14.3	0.6	2	67
V	48 (65)	288 (225)	71 (100)	135 (135)	87	--	--
Cr	3044 (2900)	2.38%	2498 (2200)	123 (90)	104	--	--
Co	192	89 (70)	93 (110)	24 (20)	26	18.6	38
Ni	1856 (2120)	503 (470)	1996 (2000)	32 (35)	112	--	--
Cu	12 (8.8)	19 (17)	19 (30)	10 (4)	19	18.7	16
Zn	93 (90)	97 (100)	78	1377 (1350)	277	26	85
Ga	n.d	8 (13)	2.3	105 (95)	21	34	73
As	n.d	n.d	10.4	4	n.d	n.d	109
Rb	n.d	n.d(4)	2.4	2242 (2300)	1298 (1250)	3.4	2.2
Sr	3.4(5)	29 (40)	7.4(10)	4.4(6)	27 (25)	34	114
Y	n.d	2	1.9	86	26	7	115
Zr	3.6(50)	11 (20)	5.2	852	15	402	561
Nb	1.7(3)	n.d(3)	n.d	313	129	42	59
Sn	n.d	n.d	n.d	97 (70)	n.d	n.d	24
Sb	2.6(0.6)	1.9(0.8)	2.4	3	n.d	1.5	10
Cs	n.d	n.d(7)	13.8	291 (300)	80	n.d	2.7
Ba	15 (20)	48 (56)	37	190 (140)	4186 (4700)	165	71
La	n.d	2.3(4)	n.d	174	n.d	96	483
Ce	n.d	n.d(85)	n.d	308	n.d	154	682
Pr	n.d	n.d	n.d	40	n.d	20	65
Nd	n.d	n.d	n.d	142	n.d	54	189
Sm	n.d	n.d	n.d	24	n.d	7.8	13
Gd	n.d	n.d	n.d	18	n.d	5.6	30
Dy	n.d	n.d	n.d	14.5	n.d	4.7	23
Hf	11	6	17	37	n.d	11	21
Pb	5.7	6.4	n.d	14	9.7	30	152
Th	n.d	n.d(1)	n.d	151	n.d	11	56
U	n.d(0.5)	n.d(0.5)		80		n.d	4.6

TABLE 5 (c)

	69a	KH	88a	1b	401	402	403
Sc	8.9	3.4(2.3)	n.d	2	n.d	0.9	n.d
V	--	--	--	--	--	--	--
Cr	--	--	--	--	--	--	--
Co	3.5	6.8(4)	3.4	5	4.2	4	4
Ni	--	--	--	--	--	--	--
Cu	9	15 (10)	11.4	13.6	14.2	13.8	11
Zn	11	25 (11)	2.8	16.2	9.1	10.1	10
Ga	119	4.2(3)	n.d	n.d	n.d	n.d	n.d
As	12.2	2.2(1)	n.d	2.8	n.d	1.4	2.5
Rb	n.d	22 (30)	n.d	8.7	n.d	3	1.5
Sr	49	555 (490)	41	1164	122 (152)	90 (101)	362 (363)
Y	16	10.4	2.3	6.7	8.4	7.7	5.6
Zr	1285	21 (30)	6.6	n.d	7.7	7.8	1.7
Nb	59	3	n.d	1.6	1.2	1.7	1.3
Sn	8	n.d	2.1	n.d	n.d	1.8	n.d
Sb	3.1	n.d	n.d	n.d	n.d	n.d	n.d
Cs	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Ba	73	70 (49)	28	n.d	1080	46	55
La	71	14 (15)	2.2	114	4.3	6.6	6.8
Ce	94	18 (19)	4.8	10.7	10.7	5.6	5.6
Pr	5.4	3.2(3)	n.d	4.5	n.d	n.d	n.d
Nd	28	10 (15)	n.d	2.9	3.6	4.8	3.5
Sm	5.1	4.8(2.5)	n.d	6.4	4	2.7	3.5
Gd	3.2	2.6(2)	n.d	2.2	n.d	2.9	n.d
Dy	4.5	n.d(1)	n.d	n.d	n.d	n.d	n.d
Hf	33	14 (0.8)	n.d	n.d	n.d	n.d	n.d
Pb	37	10	3	9	6	8	7
Th	94	3 (3)	n.d	n.d	n.d	n.d	n.d
U	6.2	n.d(1)	n.d	n.d	n.d	n.d	n.d

TABLE 6

Detection limits and precision at a concentration level of about 10 *p.p.m.. These parameters have been evaluated on a matrix of pure* SiO_2 *(quartz) for a counting time of* 200 *s.*

	Detection limit (p.p.m.)	Precision (p.p.m.)		Detection limit (p.p.m.)	Precision (p.p.m.)
Sc	0.6	10 ± 0.4	Sn	1.0	0.5
V	1.0	0.5	Sb	1.1	0.7
Cr	1.0	0.5	Cs	1.0	0.5
Co	0.6	0.4	Ba	3.0	1.3
Ni	0.6	0.4	La	2.0	0.9
Cu	1.0	0.6	Ce	3.0	1.5
Zn	1.3	0.6	Pr	2.0	1.0
Ga	1.5	0.7	Nd	2.0	1.0
As	1.0	0.3	Sm	2.0	1.2
Rb	0.9	0.4	Gd	3.0	1.2
Sr	0.9	0.4	Dy	3.0	2.0
Y	0.9	0.4	Hf	5.0	2.0
Zr	0.8	0.4	Pb	2.0	0.9
Nb	0.7	0.3	Th	2.0	0.8
			U	2.0	0.8

The method is applicable to rocks of widely different composition and in a great range of concentrations of the trace elements (from 1-2 to about 5000 p.p.m.), provided that the concentration of the major components is known. At present, this is not a serious limitation; in fact regression method, based on a full matrix correction allows to carry out analysis of rocks for major components by X-ray fluorescence, in a very short time (about 15 minutes for a rock).

Even operating with instrumental conditions different from those used in this work, the $k_{i,j}$ coefficients for the characteristic lines of Sc, Co, As, Sn, Sb, Cs, Pr, Nd, Sm, Gd, Dy, Hf, Th and U can be used, with a preliminary calibration, by other authors.

We observe in fact that the use of the $k_{i,j}$ coefficients obtained by FRANZINI M. et Al. (1972) and LEONI L., SAITTA M. (1975) with a different X-ray spectrometer ($k_{i,j}$ coefficients for the characteristic lines of Cr, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, La, Ce and Pb) have given good results.

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