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M. FRANZINI, L. LEONI *

A FULL MATRIX CORRECTION IN X-RAY FLUORESCENCE ANALYSIS OF ROCK SAMPLES

Riassunto — Si mette in evidenza la possibilità di eseguire analisi chimiche di campioni di rocce, per mezzo della fluorescenza dei raggi X, attraverso una correzione degli effetti di matrice. L'analisi viene condotta direttamente su pasticche della roccia polverizzata. Il metodo consente la determinazione dei seguenti ossidi MgO , Al_2O_3 , SiO_2 , P_2O_5 , K_2O , CaO , TiO_2 , MnO , Fe_2O_3 ed è applicabile a tutte le rocce che, oltre i citati componenti ed H_2O e Na_2O , non contengono altri elementi quali costituenti maggiori. Il metodo consente, utilizzando uno spettrografo normale, di eseguire circa 50 analisi complete nel tempo di una settimana.

Si riportano i dati relativi a 28 standard internazionali di rocce e minerali, ed a 36 rocce analizzate in questo Istituto.

Summary — A new matrix correction method in X-ray fluorescence analysis is outlined. This method, utilizing powder pellets is applied to the analyse of the major elements Mg, Al, Si, P, K, Ca, Ti, Mn and Fe in rocks and minerals.

Data are reported for 28 international standards of rocks and minerals, and for 36 rocks chemically analyzed in our Institute.

INTRODUCTION

This account presents an extremely rapid method of chemical analysis by X-ray fluorescence of rocks and minerals for the major elements, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe.

The method has been developed as an application of a more comprehensive study of the matrix effects in X-ray fluorescence analysis. The first aim of our was effort in fact to verify the validity, from a practical point of view, of the well known formula:

(*) Istituto di Mineralogia e Petrografia dell'Università di Pisa. Lavoro eseguito con il contributo del C.N.R.

$$I = K \frac{C}{A_1 \csc \Theta_1 + \csc \Theta_2}$$

During this study we reached the conclusion that it is possible to make a full correction of matrix effects so that a routine analysis, utilizing powder pellets, is possible.

The method here outlined is applicable to rocks of widely differing compositions and therefore it is useful for studying whole series of rocks and minerals as well as for analyzing a single specimen.

A Philips PW 1540/₁₀ A manual X-ray spectrometer has been used. To achieve high precision, ratios have been taken of all measurements and related to one rock pellet that has been repeatedly measured after every three unknown ones (LEAK et al. [1969]).

No attempt will be made to outline the general principles of X-ray fluorescence spectrography.

TECHNIQUE

All the analyzed rock specimens have been carefully pulverized in an agate ball mill. The powders were sieved through a 250 mesh nylon bolting cloth and then homogenised. No biotite effect has been detected.

Pellets have been prepared in a brass ring and supported by boric acid. No binder has been used.

The operating conditions of the X-ray spectrometer are reported in Table I.

Matrix correction

Numerous investigators have shown that for infinitely thick specimens the fluorescence intensity, I_j , of the element j in a sample containing N elements, is related to the mass absorption coefficients of the sample by:

$$I_j = K_j \frac{C_j}{A_1 \csc \Theta_1 + A_2 \csc \Theta_2} \quad (1)$$

TABLE I - *Experimental condition for the measurements of X-ray fluorescence intensities.*

where c_j is the concentration of the element j ; A_1 and A_2 are the mass absorption coefficients of the sample to the exciting λ_1 and fluorescent λ_2 radiations, Θ_1 and Θ_2 are the angles the incident and emergent beams make with the surface of the specimen.

This relation holds in absence of enhancement effects. The aim of this work is however to see if the relation (1) holds true, from a practical point of view, even when there are enhancement effects, which will be regarded as negative absorption effects.

Regarding enhancement effects as negative absorption effects, and assuming a prefixed set of operating conditions, it is easy to see that:

$$\frac{A_1 \csc \Theta_1 + A_2 \csc \Theta_2}{K_j} = \sum_{i=1}^N K_{j,i} c_i$$

Therefore the basic relation we assume to relate the fluorescent intensity I_j to the chemical composition of a given sample is of the type:

$$I_j = \frac{c_j}{\sum_{i=1}^N K_{j,i} c_i} \quad (2)$$

where c_i are the concentrations of the elements in the sample, N is the number of elements in the sample and $K_{j,i}$ are coefficients, with the meaning of absorption coefficients, which however cannot be computed from tables of mass absorption coefficients.

It is worthy to be noted that relation (2) holds true for infinitely thick specimens and that coefficients $K_{j,i}$ contains both absorption and enhancement effects.

A way to evaluate the practical validity of relation (2) is to select a number M ($M > N$) of rocks, of known chemical composition, to measure the fluorescence intensities $J_{l,j}$ ($l = 1 \dots M$, $j = 1 \dots N$) and to try to solve the N systems (for $j = 1 \dots, N$) of the type

$$\left| \sum_{i=1}^N K_{j,i} c_{l,i} = c_{l,j}/I_{l,j} \right| \quad (3)$$

$$(l = 1 \dots, M)$$

The computed set of $K_{j,i}$ enables, through relation:

$$(c_{l,j})_c = I_{l,j} \sum_{i=1}^N K_{j,i} c_{l,i} \quad (4)$$

to compute a set of calculated concentrations $(c_{l,j})_c$.

Relations (2) is true, from a practical point of view, if the differences

$$(c_{l,j})_c - (c_{l,j})_o$$

where $(c_{l,j})_o$ is the known chemical concentration of the element j in sample l , are sufficiently small.

In this instance not only we have proved the validity of the relation (2) but we have as well found a very good method of X-ray fluorescence analysis.

To compute the values of $K_{j,i}$ coefficients a least square program to solve systems (3) has been written for the IBM 7090 computer of the C.N.U.C.E computing center of the University of Pisa.

The $K_{j,i}$ values thus obtained have allowed to compute a first set of $(c_{l,j})_c$. Then the $K_{j,i}$ values were refined solving iteratively by a least square program the N equation systems (for $j = 1, \dots, N$)

$$\left| \sum_{i=1}^N [\delta(K_{j,i} c_{l,i}) / \delta(K_{j,i})] \Delta_{j,i} = (c_{l,j})_c - (c_{l,j})_o \right| \quad (l = 1, \dots, M)$$

and putting for every iteration

$$K_{j,i} = K_{j,i} + \Delta K_{j,i}$$

The iterations were stopped when a convergence of the $K_{j,i}$ values was obtained.

At this stage a new set of differences, $\Delta c_{l,j}$, between observed and calculated concentrations was computed:

$$\Delta c_{l,j} = (c_{l,j})_o - (c_{l,j})_c$$

The $\Delta c_{l,j}$ values were, at this stage, sufficiently small. Therefore we

feel confident that relation (2) may be utilized from a practical point of view.

Now the $K_{j,i}$ values and the $I_{l,j}$ measured intensities may be utilized to compute $(c_{l,j})_c$ values from relation (4).

To do this task a first set of computed concentrations, $(c_{l,j})_1$, is calculated from a relation of the type:

$$(c_{l,j})_1 = I_{l,j} B_j \quad (5)$$

where B_j is a linear coefficient whose value has been appropriately selected.

Next we compute

$$(c_{l,j})_2 = I_{l,j} \sum_{i=1}^N K_{j,i} (c_{l,i})_1 \quad (6)$$

and so on until we have:

$$| (c_{l,j})_{m+1} - (c_{l,j})_m | < \varepsilon$$

where ε is a small prefixed value and

$$(c_{l,j})_{m+1} = I_{l,j} \sum_{i=1}^N K_{j,i} (c_{l,i})_m$$

For every cycle of this computation we put

$$\sum_{i=1}^N (c_{l,i})_m = 100 \quad (7)$$

In what follows the $(c_{l,j})_c$ values are the values obtained from the computations now described.

At this stage a new set of differences $\Delta c_{l,j}$ was computed. Then the linear correlation coefficients between $\Delta c_{l,j}$ and $(c_{l,j})_c$ were computed. All the correlation coefficients being very small, the computed $K_{j,i}$ values were regarded as satisfactory, meaning that the matrix effects due to the chemical composition of samples were satisfactory corrected for.

Experimental methods

To compute the $K_{j,i}$ values the X-ray fluorescence intensities were measured for nine elements (Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) in 64 rock samples. Of these 64 samples, 36 were analyzed by the Institute of Mineralogy and Petrology of the University of Pisa (F. Innocenti and R. Mazzuoli analysts), and 28 were international standards. The chemical analysis of the international standards are fully reported in Table II. Table III reports some data about the rocks of our Institute. A table with the complete chemical data is available on request. It is to be noted that we have not measured Na intensities, because our instrument is not equipped to measure such a light element.

Although there is not any theoretical impossibility to extend this method to the measurement of the Na also, it is clear that, to apply our data, the concentrations of Na_2O as well as H_2O , must be known before the X-ray fluorescence analysis can be done. Therefore to compute relations (5), (6) and (7), the H_2O^+ and Na_2O concentrations will be those that have been independently measured.

The computed $K_{j,i}$ values are reported in Table IV. The values of the columns relative to P and Mn have not been computed because these two elements are always in such a little concentration that they do not influence the intensities of the other elements.

The correlation coefficients between $\Delta c_{l,j}$ and $(c_{l,j})_o$ are reported in Table V.

For 64 samples a linear correlation coefficient equal to 0.25 means that there is no correlation at the level of 5% of confidence. We feel confident therefore that our $K_{j,i}$ coefficients assure an extremely efficient correction of the matrix effects due to the chemical composition.

DISCUSSION

For what concerns the precision of our results reference can be made to the discussion of LEAKE et al. [1969]. We have in fact utilized a technique of measurement very similar to the one of these authors.

For confirmation of the accuracy reference can be made to Table II which reports all the data computed for international standards.

TABLE II.1 - Comparison of Standard rocks for major elements (%).

	G - H (Granite)	GI-1 (Graniodor.)	G - A (Granite)	G - 2 (Granite)	GSP-1 (Graniodor.)
	(1)	(2)	(1)	(2)	(1)
H ₂ O	0.63	0.53	0.99	0.55	0.57
Na ₂ O	3.81	3.39	3.56	4.16	2.98
MgO	0.03	0.04	0.73	0.95	0.78
Al ₂ O ₃	14.53	14.27	14.26	13.68	12.20
SiO ₂	76.05	76.40	72.37	73.03	70.50
P ₂ O ₅	0.01	0.02	0.10	0.11	0.15
K ₂ O	4.80	4.70	3.94	3.93	4.04
CaO	0.65	0.68	2.20	2.12	2.45
TiO ₂	0.09	0.082	0.25	0.29	0.38
MnO	0.050	0.051	0.060	0.072	0.090
Fe ₂ O ₃	1.33	1.37	2.16	2.25	2.87

(1) Recommended or provisional values.

(2) X-ray calculated values.

TABLE II² - Comparison of Standard rocks for major elements (%).

	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
	SY2 (Syenite)		AGV-1 (Andesite)		BCR1 (Basalte)		DNR (Diorite)		(Basalte) BJ-1	
H ₂ O	0.22	0.82			0.77		2.32		1.00	
Na ₂ O	4.22		4.37		3.30		3.00		2.79	
MgO	1.99	2.44	1.51	1.30	3.27	2.97	4.50	4.76	7.73	7.54
Al ₂ O ₃	11.34	12.32	17.18	16.74	13.60	13.61	17.40	16.88	14.64	15.64
SiO ₂	60.81	61.64	59.60	60.45	54.26	54.69	52.59	53.27	52.33	52.39
P ₂ O ₅	n.d.	—	0.49	0.49	0.36	0.38	0.27	0.22	0.26	0.23
K ₂ O	4.15	4.56	2.93	2.90	1.67	1.73	1.70	1.68	1.41	1.42
CaO	9.65	7.63	5.03	4.90	6.92	6.97	7.07	6.91	9.30	8.94
TiO ₂	0.14	0.13	1.09	1.10	2.22	2.28	1.11	1.11	1.36	1.32
MnO	0.330	0.348	0.099	0.109	0.169	0.194	0.209	0.236	0.151	0.160
Fe ₂ O ₃	7.15	6.49	6.87	6.84	13.45	13.12	9.84	9.63	9.04	8.91

(1) Recommended or provisional values.

(2) X-ray calculated values.

n.d. not detected.

TABLE II 3 - Comparison of Standard rock for major elements (%).

	PCC-1 (Peridotite)	DTS-1 (Dunite)	UBN (Serpentine)	BR (Basalte)	lb (Argill. Lim.)
	(1)	(2)	(1)	(2)	(1)
H ₂ O	4.69	0.46	12.58	2.42	41.20 ^(b)
Na ₂ O	0.05	0.04	0.10	3.08	0.04
MgO	43.44	43.33	50.35	35.01	14.42
Al ₂ O ₃	0.85	0.76	0.55	0.30	0.36
SiO ₂	41.75	47.47	40.25	39.54	11.30
P ₂ O ₅	0.014	0.027	0.012	0.010	1.12
K ₂ O	0.0014 ^(a)	0.0030	0.001 ^(a)	0.002	0.07
CaO	0.53	0.58	0.16	1.12	0.25
TiO ₂	0.023	0.060	0.023	0.060	0.17
MnO	0.122	0.128	0.125	0.120	0.046
Fe ₂ O ₃	8.51	8.95	8.80	8.49	0.046
					0.186
					0.20
					0.75
					0.81

(1) Recommended or provisional values.

(2) X-ray calculated values.

(a) values by Müller (1970).

(b) Co₂ taken as H₂O⁺.

TABLE II⁴ - Comparison of Standard rock for major elements (%).

	401 (Limestone)		402 (Limestone)		403 (Dol. Limest.)		400 (Dol. Limest.)		88a (Dol. Limest.)	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
H ₂ O	43.60 ^(b)		43.38 ^(b)		45.01 ^(b)		47.01 ^(b)		46.70 ^(b)	
Na ₂ O	0.02		0.02		0.03		0.04		0.01	
MgO	3.60	3.84	5.78	6.04	13.86	13.86	21.57	21.16	21.30	21.30
Al ₂ O ₃	0.22	0.27	0.53	0.59	0.43	0.56	0.029	0.027	0.18	0.36
SiO ₂	2.09	1.98	2.65	2.62	1.82	1.90	0.075	0.074	1.20	1.38
P ₂ O ₅	0.035	0.056	0.048	0.066	0.044	0.079	0.0	0.0	0.01	0.02
K ₂ O	0.060	0.066	0.161	0.162	0.141	0.132	0.010	0.015	0.12	0.11
CaO	50.14	49.55	46.94	46.71	38.20	38.07	30.61	31.00	30.15	29.77
TiO ₂	0.020	0.014	0.032	0.028	0.026	0.024	0.004	0.0035	0.020	0.013
MnO	0.011	0.015	0.019	0.015	0.018	0.019	0.0052	0.0038	0.030	0.020
Fe ₂ O ₃	0.199	0.185	0.372	0.340	0.310	0.311	0.053	0.058	0.28	0.29

(1) Recommended or provisional values.

(2) X-ray calculated values.

(b) Co₂ taken as H₂O⁺.

TABLE II 5 - Comparison of Standard rock for major elements (%).

	1011 (Cem. Portl.)		69a (Bauxite)		70a (K. Feldsp.)		Or-1 (K. Feldsp.)		Ab-1 (Na. Feldsp.)	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
H ₂ O	1.15		29.67		0.40		0.08		0.06	
Na ₂ O	0.08		0.01		2.55		1.15		9.07	
MgO	1.14	1.45	0.02	0.015	0.0	0.0	0.0	0.0	0.0	0.0
Al ₂ O ₃	5.48	4.09	55.23	54.76	17.91	17.48	18.74	17.83	28.84	21.37
SiO ₂	21.04	21.31	6.04	6.10	67.14	67.22	64.95	65.30	65.68	65.38
P ₂ O ₅	0.33	0.20	0.08	0.08	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	0.26	0.33	0.01	0.016	11.85	12.07	15.05	15.51	2.39	2.28
CaO	67.79	68.83	0.29	0.34	0.11	0.13	0.0	0.0	1.93	1.90
TiO ₂	0.25	0.26	2.79	2.88	0.010	0.016	0.0	0.0	0.0	0.0
MnO	0.0	0.0	0.010	0.010	0.0	0.0	0.0	0.0	0.0	0.0
Fe ₂ O ₃	2.11	2.14	5.85	6.10	0.075	0.127	0.033	0.020	0.033	0.040

(1) Recommended or provisional values.

(2) X-ray calculated values.

TABLE II⁶ - Comparison of Standard rock for major elements (%).

	99a (Na. Feldsp.)		Mica-Fe (Biotite)		Mica-Mg (Phlogopite)	
	(1)	(2)	(1)	(2)	(1)	(2)
H ₂ O	0.26		4.72		4.86	
Na ₂ O	6.22		4.25		0.12	
MgO	0.0	0.0	4.50	4.95	20.85	21.18
Al ₂ O ₃	20.57	20.24	19.17	17.87	15.40	
SiO ₂	65.45	65.84	33.80	33.41	38.03	37.05
P ₂ O ₅	0.02	0.04	0.48	0.33	0.028	0.020
K ₂ O	5.22	5.24	8.65	8.64	9.92	9.68
CaO	2.15	2.08	0.49	0.48	0.095	0.02
TiO ₂	0.007	0.012	2.51	2.59	1.65	1.65
MnO	0.0	0.0	0.364	0.359	0.256	0.240
Fe ₂ O ₃	0.065	0.076	25.17	26.04	9.47	9.07

(1) Recommended or provisional values.

(2) X-ray calculated values.

TABLE III - Some data on the rocks of Institute of Mineralogy and Petrology of Pisa.

	Concentration range		
MgO	0.22	—	39.07
Al ₂ O ₃	2.45	—	18.97
SiO ₂	7.72	—	93.59
P ₂ O ₅	0.04	—	0.63
K ₂ O	0.03	—	7.57
CaO	0.84	—	48.65
TiO ₂	0.04	—	2.29
MnO	0.03	—	0.21
Fe ₂ O ₃	0.97	—	16.29

TABLE IV - Calculated values of $K_{j,i}$ coefficients.

	H ₂ O	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
MgO	0.8630	2.3350	0.9140	1.5700	0.4349	1.1509	1.9233	1.6413	2.9036
Al ₂ O ₃	0.1716	0.3032	0.5100	0.1299	0.1300	0.1056	0.1157	0.1199	0.1900
SiO ₂	0.1914	0.3688	0.7897	1.0370	0.3493	0.3631	0.4773	-1.1251	0.9690
P ₂ O ₅	0.0035	-0.0184	0.0008	0.0031	0.0076	0.0087	0.0	0.0825	-0.0062
K ₂ O	0.0081	0.0132	0.0257	0.0283	0.0427	0.0605	0.0312	0.0344	0.0387
CaO	0.0127	0.0285	0.0595	0.0623	0.0642	0.1732	0.0806	0.0903	0.1175
TiO ₂	0.0029	0.0045	0.0084	0.0104	0.0132	0.0285	0.0340	0.0284	0.0119
MnO	0.0003	0.004	0.0005	0.0012	0.0014	0.0018	0.0026	0.0028	0.0015
Fe ₂ O ₃	0.0112	0.0202	0.0450	0.546	0.0652	0.1516	0.1901	0.1904	0.1452

TABLE V - Correlation coefficients between $\Delta c_{l,j}$ and $(c_{l,j})_o$.

	H ₂ O	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
MgO	-0.114	0.191	-0.205	0.086	0.158	0.061	-0.045	-0.035	-0.03
Al ₂ O ₃	0.040	-0.206	0.095	0.038	-0.101	0.064	0.079	-0.171	-0.109
SiO ₂	0.182	-0.302	0.262	-0.190	-0.261	-0.238	0.140	0.177	0.178
P ₂ O ₅	0.070	-0.060	-0.010	-0.037	-0.149	-0.080	0.266	-0.108	-0.037
K ₂ O	-0.061	0.124	0.061	0.026	0.048	-0.066	-0.106	0.149	0.058
CaO	-0.100	0.308	-0.271	0.126	0.323	0.281	-0.311	-0.119	-0.087
TiO ₂	0.009	-0.015	0.072	-0.160	-0.016	0.086	0.125	-0.306	-0.233
MnO	0.142	-0.111	-0.057	0.010	-0.147	0.026	0.115	0.216	0.017
Fe ₂ O ₃	-0.086	0.197	-0.013	0.046	0.028	-0.077	-0.032	0.215	0.066

Table VI reports the mean relative error and the mean difference for 64 rocks. The mean relative error is defined as follows:

$$\varepsilon_j = \frac{\sum_{l=1}^M \left| (\Delta c_{l,j}) / (c_{l,j})_o \right|}{M}$$

The mean difference Δ is defined as follows:

$$\Delta_j = \frac{\sum_{l=1}^M \left| (c_{l,j})_o - (c_{l,j})_c \right|}{M}$$

TABLE VI - *Values of mean relative error ε_j and mean differences Δ_j for the 64 rocks.*

	Mean relative error ε	Mean difference Δ (%)
MgO	15.6	0.490
Al ₂ O ₃	7.8	0.510
SiO ₂	1.8	0.570
P ₂ O ₅	28.0	0.037
K ₂ O	12.7	0.127
CaO	10.0	0.290
TiO ₂	18.0	0.085
MnO	27.0	0.019
Fe ₂ O ₃	9.7	0.250

TABLE VII - *Values of ϵ_j and Δ_j for prefixed intervals of concentrations.*

	Concentration range %	Mean relative error %	Mean difference
MgO	0 - 5	19.9	0.362
	5 - 15	10.0	0.750
	15 - 45	2.0	1.034
Al ₂ O ₃	0 - 10	22.9	0.364
	10 - 55	3.6	0.546
SiO ₂	0 - 10	5.9	0.216
	10 - 95	1.2	0.623
P ₂ O ₅	0 - 0.1	53.7	0.0153
	0.1 - 1	18.6	0.0539
K ₂ O	0 - 1	57.0	0.0296
	1 - 5	37.	0.0965
	5 - 15	37.	0.258
CaO	0 - 1	30.9	0.133
	1 - 10	7.7	0.273
	10 - 68	0.9	0.375
TiO ₂	0 - 0.1	34.8	0.0060
	0.1 - 2.8	14.9	0.111
MnO	0 - 0.1	29.8	0.018
	0.1 - 1	14.2	0.024
Fe ₂ O ₃	0 - 1	27.0	0.111
	1 - 10	5.7	0.244
	10 - 26	3.3	0.478

More interesting are the data of Table VII where the value of ϵ_j and Δ_j are reported for prefixed intervals of concentrations.

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