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Calibration of Intensity Data for X-Ray Fluorescence Silicate Rock Analysis

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Matrix correction factors for SiO_2, Al_2O_3, and CaO of silicate rock powder specimens are calculated from X-ray intensity data of standard rocks. The correction factors are used for 215 samples from the Grimstad granite, the difference between predicted and observed sums expressed as standard deviation is 0.9918.

Several attempts have been made to solve the matrix problem encountered in X-ray fluorescence analysis (see, *e.g.* Gillam and Heal,[1] Beattie and Brissey,[2] Gordon *et al.*,[3] Traill and Lachance [4]).

Some of the most important constituents of rocks are light elements and, consequently, matrix effects may interfere seriously with the analytical results. Fusing the sample in a fluxing agent such as borax or lithium tetraborate may reduce the matrix effect for some of the constituents but the disadvantage of this method is obvious: the concentration of phosphorus, manganese, and sometimes magnesium may be lowered to below the detection limit of a conventional X-ray spectrograph. Nevertheless the fluxing method has become routine in many laboratories.

In the present paper, correction methods for the matrix effects of unfused rock material and rock powder melted in smaller amounts of fluxing agents have been worked out. The aim of the present work is to examine the matrix effect, not the precision of the X-ray fluorescence method for silicate analysis, and the matrix correction factors for SiO_2, Al_2O_3, and CaO in silicate rocks in the range from amphibolites to granites have been calculated. The calculation is based upon intensity data from standard rocks, the composition of which are given in Table 1.

THEORETICAL OUTLINE

In an inert matrix the ratio of intensity of characteristic radiation of an element to its concentration in the studied sample is constant and equal to the intensity of the characteristic radiation of the pure element,

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Table 1. Observed values. Data for G-1, W-1, T-1, GR, and Sy-1a are taken from Ingamells and Suhr,[9] for NBS 4983 and NBS 70 from certificate of National Bureau of Standards. G-100, N-100, DI-100, GA-100, Antocord-100, NS-1, NS-2, A-100, and AGV-1 are analysed by wet chemical methods by B. Bruun, P_2O_5 has been determined by neutron activation methods by A. Brunfeldt.

	NBS 4983	G-1	Antocord -100	G-100	GR	N-100	Sy-1a	NS-2	NS-1	T-1	AGV-1	W-1	A-100	GA-100	DI-100	NBS 70
SiO_2	80.60	72.52	71.50	70.00	65.85	64.78	59.50	54.24	50.05	62.62	59.60	52.58	47.52	46.90	46.58	66.66
TiO_2	0.11	0.26	0.60	0.54	0.62	0.67	0.48	0.48	0.30	0.60	1.15	1.08	1.04	2.34	4.15	0.00
Al_2O_3	10.00	14.08	8.90	14.00	14.54	17.28	9.01	23.10	21.70	16.46	17.50	14.94	18.10	18.23	14.30	18.03
Fe_2O_3 (tot)	1.70	1.90	2.30	3.75	4.04	2.79	8.27	2.84	4.00	6.01	6.90	11.06	11.83	13.20	13.75	0.03
MgO	0.12	0.35	11.31	0.81	2.34	0.52	4.06	0.31	0.19	1.90	1.48	6.52	7.92	5.40	4.83	0.00
CaO	0.56	1.36	0.21	0.85	2.47	1.00	10.09	1.90	4.30	5.18	5.03	10.92	8.15	9.04	6.45	0.07
K_2O	4.00	5.52	1.05	5.25	4.50	6.24	2.70	8.20	7.85	1.23	3.01	0.63	0.56	0.81	1.88	12.58
Na_2O	2.62	3.29	0.32	3.70	3.73	5.93	3.38	7.76	7.57	4.40	4.28	2.15	2.88	3.00	4.36	2.38
P_2O_5	0.01	0.09	0.13	0.16	0.34	0.13	0.21	0.09	0.14	0.14	0.69	0.14	0.18	0.31	1.00	0.01

NBS 4983	Milford granite, Natl. Bureau of Standards	NS-1	Nepheline syenite, Stjernøy, Norway
G-1	Granite standard, U.S. Geol. Survey	T-1	Msusule Tonalite, Tanzania
Antocord-100	Anthophyllite-cordierite rock, Kragerø, Norway	AGV-1	Andesite standard, U.S. Geol. Survey
G-100	Grimstad granite, Norway	W-1	Diabase » » » »
GR	Granite standard, Nancy	A-100	Amphibolite, Kragerø, Norway
N-100	Nordmarkite, Grorud, Norway	GA-100	Gabbro » »
Sy-1a	Syenite rock standard, Canada	Di-100	Diabase » »
NS-2	Nepheline syenite, Stjernøy, Norway	NBS 70	Feldspar, Natl. Bureau of Standards

$$I_A/W_A = I_{A\,100} \tag{1}$$

Generally eqn. (2) may be used as an empirical approach for solving the matrix problem,

$$I_A^* = I_A\ (1 + \sum\mu_i W_i) \tag{2}$$

where I_A^* is the corrected intensity of the element A, μ_i the calculated matrix correction factor of the *i*th constituent present in the sample in the concentration W_i. Inserting I_A^* for I_A in eqn. (1) one arrives at the same matrix correction function as that used by Traill and Lachance: [4]

$$\frac{I_A\ (1 + \sum\mu_i W_i)}{W_A} = I_{A\,100}$$

The disadvantage of this approach lies in the fact that in order to estimate I_A^* the concentrations of all the other components have to be known, and consequently a large number of iterations have to be made on a computer in order to arrive at a satisfactorily result. Therefore, the general procedure for X-ray fluorescence analysis of silicate rocks would be to start with the determination of those components for which no matrix corrections are necessary, and the matrix correction of the remaining components should be based upon the simplest possible methods, reserving eqn. (2) for those components where other correction methods turn out to be unsatisfactorily.

It seems to be a general experience that eqn. (1), involving no matrix correction, can be used for both fused and unfused rock specimens for the components TiO_2, Fe_2O_3 (total) in concentrations below 10 %, MgO in concentrations below 2 %, and K_2O, and it was not necessary to produce matrix correction factors for these elements. Therefore, the data for unfused rock specimens of Table 3 do not cover all the available rocks of Table 1.

Matrix correction in fused and unfused samples has been made for Al_2O_3 and CaO; and SiO_2, Al_2O_3, and CaO, respectively. For P_2O_5 matrix correction has not been made because the P_2O_5 concentration in most silicate rocks is so low that lack of precision of the determination will not seriously influence the sum of oxides.

Table 2. Working conditions for the X-ray fluorescence spectrometer.

Element	Analyzing crystal	X-ray tube	kV	mA	Collimator	Counter
Si	EDDT	Cr	30	10	480μ	Flow prop. Discriminator
Ti	LiF	»	40	24	160 »	»
Al	EDDT	»	34	16	480 »	» Discriminator
Fe	LiF	W	28	8	160 »	Scintillation.
Mg	ADP	Cr	40	24	480 »	Flow prop. Discriminator
Ca	LiF	»	40	20	160 »	»
K	EDDT	»	26	14	160 »	»
P	EDDT	»	40	20	480 »	» Discriminator

Table 3. Predicted and observed concentrations for TiO_2, Fe_2O_3 (total), MgO, K_2O, and P_2O_5.

Unfused rock specimens *

		TiO_2				Fe_2O_3 (total)		
	obs.	pred.	diff.		obs.	pred.	diff.
DI-100	4.15	4.16	−0.01	DI-100	13.75	13.68	0.07
GA-100	2.34	2.35	−0.01	GA-100	13.20	12.96	0.24
A-100	1.04	1.03	0.01	A-100	11.83	12.77	−0.62
N-100	0.67	0.64	0.03	G-100	3.75	3.63	0.12
G-100	0.54	0.55	−0.01	N-100	2.79	2.78	0.01
NS-2	0.48	0.44	0.04				

		MgO				K_2O	
	obs.	pred.	diff.		obs.	pred.	diff.
T-1	1.90	1.87	0.03	NS-2	8.20	8.19	0.01
AGV	1.48	1.38	0.10	N-100	6.24	6.30	−0.06
G-100	0.81	0.93	−0.12	G-1	5.52	5.51	0.01
N-100	0.52	0.56	−0.04	G-100	5.25	5.20	0.05
G-1	0.35	0.28	0.07	A-100	0.56	0.58	−0.02
Milford	0.12	0.05	0.07				

		P_2O_5	
	obs.	pred.	diff.
DI-100	1.00	0.82	0.18
GR	0.34	0.21	0.13
GA-100	0.31	0.30	0.01
A-100	0.18	0.18	0.00
G-100	0.16	0.10	0.06
T-1	0.14	0.18	−0.04
N-100	0.13	0.09	0.04
G-1	0.09	0.05	0.04

Fused rock specimens

		TiO_2				Fe_2O_3 (total)	
	obs.	pred.	diff.		obs.	pred.	diff.
T-1	0.60	0.55	0.05	T-1	6.01	6.41	−0.40
N-100	0.67	0.64	0.03	N-100	2.79	2.88	−0.09
W-1	1.08	1.00	0.08	W-1	11.06	10.82	0.24
G-100	0.54	0.53	0.01	G-100	3.75	3.66	0.09
G-1	0.26	0.25	0.01	G-1	1.90	2.02	−0.12
GR	0.62	0.61	0.01	GR	4.04	4.42	−0.38
NBS 70	0.00	0.00	0.00	NBS 70	0.03	0.03	0.00
NS-1	0.30	0.31	−0.01	NS-1	4.00	4.15	−0.15
NS-2	0.48	0.50	−0.02	NS-2	2.84	2.92	−0.08
Milford	0.11	0.18	−0.07	Milford	1.70	1.83	−0.13
Sy-1a	0.48	0.44	0.04	Sy-1a	8.27	7.94	0.33
AGV-1	1.15	1.05	0.10	AGV-1	6.90	7.16	−0.26
Antocord	0.60	0.66	−0.06	Antocord	2.30	2.43	−0.13
A-100	1.04	1.02	0.02	A-100	11.80	11.92	−0.09
DI-100	4.15	3.99	0.16	DI-100	13.75	13.54	0.21
GA-100	2.34	2.66	−0.32	GA-100	13.20	13.18	0.02

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* Material selected to cover suitable ranges.

Table 3. Continued.

	MgO			K_2O			P_2O_5		
	obs.	pred.	diff.	obs.	pred.	diff.	obs.	pred.	diff.
T-1	1.40	1.76	0.14	1.23	1.29	−0.06	0.14	0.26	−0.12
N-100	0.52	0.35	0.16	6.24	6.12	0.12	0.13	0.06	0.07
W-1	6.52	6.15	0.37	0.63	0.76	−0.13	0.14	0.25	−0.11
G-100	0.81	0.53	0.28	5.25	5.32	−0.07	0.16	0.06	0.10
G-1	0.35	0.53	−0.18	5.52	5.47	0.05	0.09	0.01	0.08
GR	2.34	2.11	0.23	4.50	4.67	−0.17	0.34	0.22	0.12
NBS 70	0.00	0.00	0.00	12.58	12.24	0.34	0.01	0.01	0.00
NS-1	0.19	0.18	0.01	7.85	8.09	−0.24	0.14	0.09	0.05
NS-2	0.31	0.35	−0.04	8.20	8.36	−0.16	0.09	0.10	−0.01
Milford	0.12	0.18	−0.06	4.00	3.91	0.09	0.01	0.00	0.01
Sy-1a	4.06	3.52	0.54	2.70	2.81	−0.11	0.21	0.27	−0.06
AGV-1	1.48	1.45	0.03	3.01	3.04	−0.03	0.69	0.49	0.20
Antocord	11.31	11.60	−0.29	1.05	1.14	−0.09	0.13	0.09	0.04
A-100	7.92	8.09	−0.17	0.56	0.72	−0.16	0.18	0.23	−0.05
DI-100	4.83	5.10	−0.27	1.88	1.98	−0.10	1.00	1.04	−0.04
GA-100	5.40	5.27	0.13	0.81	0.95	−0.14	0.31	0.35	−0.04

PROCEDURE

Crystalline boric acid was used as binding material for the pellets. Unfused rock powders should be prepared according to Byström-Asklund [5] to prevent preferred stacking of mineral flakes.

For the fused samples lithium tetraborate was used as fluxing agents, two parts to one part by weight rock powder. The fusion was made in graphite crucibles at 1000°C for 30 min. Lithium tetraborate and graphite crucibles were delivered by Spex Industries Inc, P.O. Box 798, Metuchen N.J. 08841, USA. The fused beads were weighed to determine the ignition loss, and then crushed in agate mortar to ~200 mesh. The finegrained powder was finally pressed to pellets.

Working conditions for the X-ray spectrograph are given in Table 2. The X-ray intensities used for the calculation of predicted concentrations are mean values of at least four countings, the spread between the individual countings being less than 2 %.

RESULTS

By predicted values are understood values obtained by converting X-ray fluorescence intensity data to concentrations; observed values represent preferred concentrations of Table 1.

Determination without matrix correction

Predicted and observed concentrations for TiO_2, Fe_2O_3 (total), MgO, K_2O, and P_2O_5 are given in Table 3, for SiO_2 in Table 4.

Determination with matrix correction

Si_2O. The deviation from straight linearity of the intensity-concentration ratio of SiO_2 in unfused rock specimens is probably due to an absorption-enhancement effect and the procedure used for Al (eqn. (7)) would probably

be the best approach to the calibration of intensity data to concentrations. But SiO_2 is the prominent component of all silicate rocks, the most actual range being 45—75 %, and the variation is larger than the total content of the most abundant of the other constituents, Al_2O_3, which in turn is mostly constant within 16 ± 3 %. Among the remaining constituents, Fe_2O_3 (total), MgO, and CaO have the widest range of variation and they exhibit a strong negative correlation to SiO_2.

A similar negative correlation exists even for TiO_2 and P_2O_5 and this makes it possible to apply some function for the intensity-concentration relation of SiO_2 that is independent of the concentrations of the other constituents. As an approximation one may apply the equation

$$W_{\mathrm{Si}} = aI_{\mathrm{Si}}^2 + bI_{\mathrm{Si}} \qquad (3)$$

or

$$W_{\mathrm{Si}} = a\sqrt{I_{\mathrm{Si}}} + bI_{\mathrm{Si}} \qquad (4)$$

where I_{Si} is the measured intensity of the characteristic Si radiation and W_{Si} the weight fraction of SiO_2 in the sample.

It was empirically found during this work that the difference between observed and predicted values became smaller by using the equation

$$W_{\mathrm{Si}} = a\ (I_{\mathrm{Si}}^2 + \sqrt{I_{\mathrm{Si}}}) + bI_{\mathrm{Si}} \qquad (5)$$

and by the method of least squares reasonable values for the constants may be obtained. The square term of eqn. (5) gives a reduction of the SiO_2 values at concentrations below 0.5 (weight fraction) and above 0.8, and with the data used in the present study, the function of W_{Si} does not run asymptotically through the $I_{\mathrm{Si}\ 100}$ value at 1.00 SiO_2. Equations fulfilling this condition may easily be constructed, but in the present study this was not needed, and eqn. (5) gives satisfactory results within the range studied (Table 4).

For fused specimens eqn. (1) may be used for determination of SiO_2. The precision of SiO_2 determinations does not seem to be significantly improved by the use of eqns. (3), (4), or (5).

CaO. It was found that the deviation from straight linearity of the intensity-concentration ratio of CaO in unfused rock specimens may be related to the iron content of the rock according to eqn. (6a)

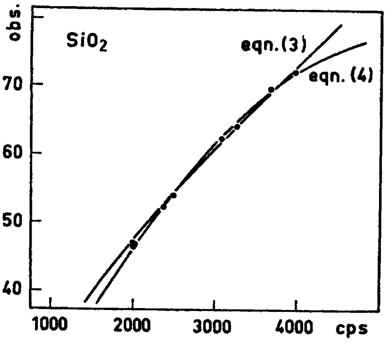

Fig. 1. Eqn. (3), eqn. (4), and observed intensities of Si radiation in the specimens of Table 4.

Table 4. Observed and predicted concentrations of SiO_2.

Unfused rock specimens. Corrected according to eqn. (5) and (4).

		Eqn. (5)		Eqn. (4)	
	obs.	pred.	diff.	pred.	diff.
G-1	72.52	72.68	−0.16	73.19	−0.67
G-100	70.00	69.52	0.48	69.53	0.47
N-100	64.78	64.93	−0.15	64.51	0.27
T-1	62.62	62.57	0.05	62.07	0.58
NS-2	54.24	54.58	−0.34	54.26	−0.02
W-1	52.58	52.72	−0.14	52.53	0.05
A-100	47.52	46.42	1.00	46.79	0.73
GA-100	46.90	47.07	−0.17	47.38	−0.48
DI-100	46.58	46.91	−0.33	47.23	−0.65
Sum of squared differences			*1.56*		*2.27*

Fused rock specimens

	obs.	pred.	diff.
Milford	80.60	81.74	−0.14
Antocord	71.50	71.95	−0.45
G-1	72.52	71.95	0.57
G-100	70.00	70.53	−0.53
NBS 70	66.66	67.85	−0.67
GR	65.85	66.00	−0.15
N-100	64.78	63.26	1.52
T-1	62.62	61.95	0.67
AGV-1	59.60	58.97	0.63
Sy-1a	59.50	60.28	−0.78
NS-2	54.24	52.89	1.35
W-1	52.58	51.69	0.89
NS-1	50.05	51.10	−1.05
A-100	47.52	47.64	−0.12
GA-100	46.90	47.52	−0.62
DI-100	46.58	47.88	−1.30

$$I_{\mathrm{Ca}}{}^{*} = I_{\mathrm{Ca}}\left(1 - \frac{[\mathrm{Fe}] - 4.70}{44.5}\right) \tag{6a}$$

for positive values of the numerator where I_{Ca} is the measured intensity and [Fe] the concentration of total Fe as Fe_2O_3 in per cent. This relation is most probably quite empirical but still useful for the purpose of silicate rock analysis. For mineral analysis and rocks high in potash, the correction should take variations in K_2O content in consideration as well. When applying eqn. (6a) to counting data from instruments other than the one used by us the figures 4.70 and 44.5 may need to be adjusted.

The measured Ca intensity corrected according to eqn. (6a) may be inserted in eqn. (1). The predicted values of Table 5 are in reasonable agreement with the observed ones over the compositional range studied, but additional work is needed before this equation can be applied to rocks of more extreme compositions or to minerals.

Table 5. Observed and predicted values for CaO.

Unfused rock specimens. Corrected according to eqn. (6a).	obs.	pred.	diff.
GA-100	9.04	8.61	0.43
A-100	8.15	8.41	−0.26
DI-100	6.45	6.39	0.06
T-1	5.18	5.39	−0.21
AGV-1	5.03	5.08	−0.05
NS-2	1.90	1.95	−0.05
G-1	1.36	1.33	0.03
N-100	1.00	1.00	0.00
G-100	0.85	0.82	0.03
DTS-1	0.20	0.16	0.04

Fused rock specimens. Corrected according to eqn. (6b).	obs.	pred.	diff.
T-1	5.18	5.09	0.09
N-100	1.00	0.96	0.04
W-1	10.92	10.90	0.02
G-100	0.85	0.73	0.12
G-1	1.36	1.15	0.21
GR	2.47	2.34	0.13
NBS 70	0.07	0.01	0.06
NS-1	4.30	4.29	0.01
NS-2	1.90	1.87	0.03
Milford	0.56	0.51	0.03
Sy-1a	10.10	10.01	0.09
AGV-1	5.03	4.98	0.05
Antocord	0.21	0.16	0.05
A-100	8.15	8.16	−0.01
DI-100	6.45	6.58	−0.13
GA-100	9.04	9.02	0.02

For fused rocks $I_{\mathrm{Ca}}{}^*$ is calculated according to the equation

$$I_{\mathrm{Ca}}{}^* = I_{\mathrm{Ca}} (1 + \mu_{\mathrm{Fe-Ca}} W_{\mathrm{Fe}} + \mu_{\mathrm{K-Ca}} W_{\mathrm{K}}) \tag{6b}$$

which is only a special case of eqn. (2) by which the matrix effect is ascribed to the elements Fe and K. $I_{\mathrm{Ca}}{}^*$ is inserted in eqn. (1) for calculation of W_{Ca}. Using the value 28.700 for $I_{\mathrm{Ca}\,100}$ we obtained the values -0.1829 and $+ 2.407$ for $\mu_{\mathrm{Fe-Ca}}$ and $\mu_{\mathrm{K-Ca}}$, respectively. The results are given in Table 5.

Al_2O_3. Estimation of the concentration of $\mathrm{Al_2O_3}$ from unfused rock powders according to eqn. (1) gives results of extremely poor precision. It is supposed that this is due to interelement absorption-enhancement effects which for $\mathrm{Al_2O_3}$ are so strong that an equation of type (2) must be employed. The concentration of Al was estimated from

$$W_{\mathrm{Al}} = \frac{I_{\mathrm{Al}}}{I_{\mathrm{Al}\,100}} (1 + \mu_{\mathrm{Si-Al}} W_{\mathrm{Si}} + \mu_{\mathrm{Fe-Al}} W_{\mathrm{Fe}} + \mu_{\mathrm{Mg-Al}} W_{\mathrm{Mg}} + \mu_{\mathrm{Ca-Al}} W_{\mathrm{Ca}} + \mu_{\mathrm{Na-Al}} W_{\mathrm{Na}} + \mu_{\mathrm{K-Al}} W_{\mathrm{K}} + \mu_{\mathrm{P-Al}} W_{\mathrm{P}}) \tag{7}$$

where μ_{Si-Al} is the correction factor (being negative for the enhancement effect and positive for the absorption effect) accounting for the absorption-enhancement effect of Si upon the characteristic Al radiation, μ_{Ti-Al} for the effect of Ti upon the Al radiation, etc. It should be noted that the effect of, *e.g.*, Si upon the characteristic Al radiation is calculated in terms of SiO_2 and Al_2O_3 contents, not in terms of Si and Al atomic percentage.

Table 6. Matrix correction constants, μ, for determination of Al_2O_3 in unfused and fused rock specimens. These values are valid only for the specifications given in Table 2 for Al. The μ values should be determined anew for instruments other than the one used in the present study.

	Unfused specimens	Fused specimens
μ_{Si-Al}	-0.0095	-0.1095
μ_{Ti-Al}	$+0.3291$	-2.6017
μ_{Fe-Al}	-3.0410	$+1.1854$
μ_{Mg-Al}	$+6.8169$	$+0.7336$
μ_{Ca-Al}	$+1.3356$	-0.0668
μ_{Na-Al}	$+3.7351$	-0.3258
μ_{K-Al}	-0.8901	$+0.6136$
μ_{P-Al}	$+18.0366$	$+10.4354$

The high value for μ_{P-Al} (Table 6), which is the last one to be calculated in our computer program, may indicate that the μ values may be adjusted when more accurate Al_2O_3 values of silicate analyses are available. It should be noted that high μ values should be avoided since inaccuracies in the determination of the other constituents may amplify the inaccuracy of the Al_2O_3 determination. In our experience μ values up to 10 000 and even more may be obtained if the calculation of the correction factors are based upon analyses with inferior Al_2O_3 determinations. Such μ values are, of course, useless.

There is an obvious lack of coincidence of the μ values given in Table 6 and the absorption measured from transmission of X-rays through thin metal foils. Again it should be emphasized that the correction factors of Table 6 are based upon the concentration values of the oxides.

There is also lack of coincidence of the μ values for unfused samples and for the corresponding components in the fused samples. In the unfused specimens the oxides less Al_2O_3 make up about 85 % by weight of the specimen, in the fused ones only about 25 %. As oxygen may contribute to the total matrix effect, a correlation between the μ values for fused and unfused specimens is not to be expected either. Furthermore the influence of coordination shielding in the crystal lattices of the minerals of the unfused samples may contribute to the lack of correlation between the two sets of μ values.

If corresponding values for the correction factors are required the matrix effect should be studied on the basis of variation in atomic percentage rather than variation in oxide percentage. The latter was chosen by us for practical reasons and in order to find an empirical solution to the matrix problem rather than a theoretical one, whereby the effect from coordination shielding could be disregarded.

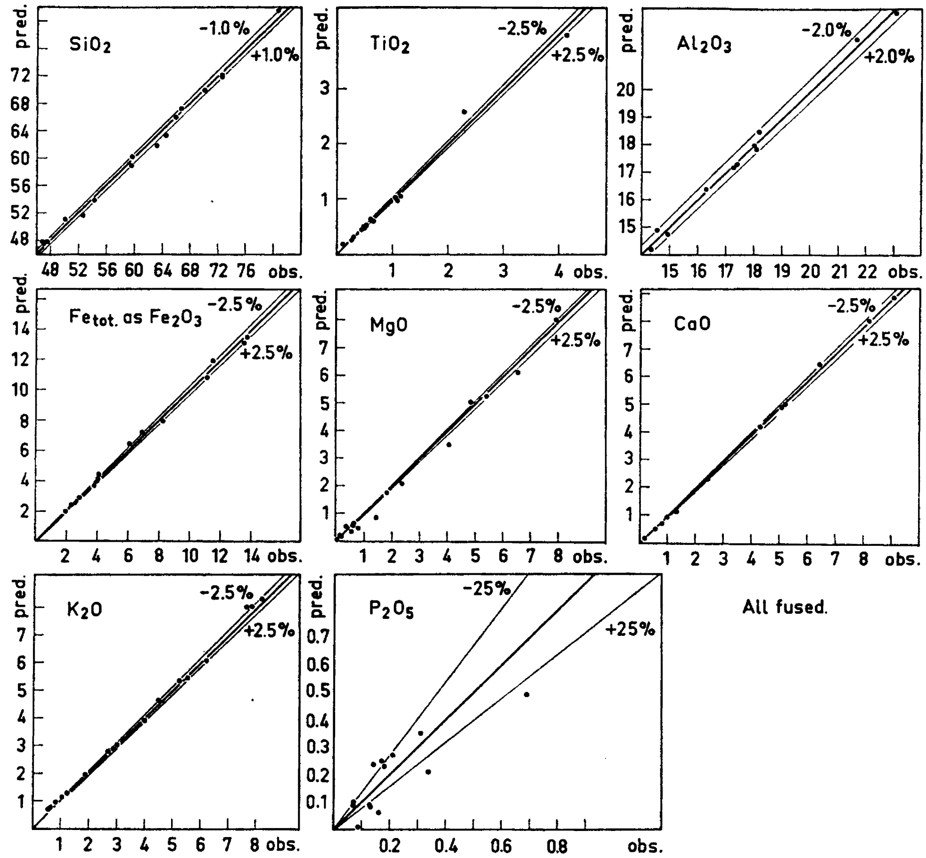

Fig. 2. Observed and predicted values for fused samples.

APPLICATION OF THE CALIBRATION METHOD FOR UNFUSED ROCKS

The calibration outlined for unfused rock samples, involving the use of eqn. (1) for TiO_2, Fe_2O_3 (total), MgO in concentrations below 2 %, K_2O and P_2O_5, eqn. (4) for SiO_2, eqn. (6a) for CaO, and eqn. (7) for Al_2O_3, was used for a set of 215 specimens from the Grimstad granite (Christie *et al.*[6]). The average sum of the analyses where H_2O was not determined is 99.00 % for granitic rocks. Within the Grimstad granite several rock types occur which are remnants of inclusions showing a wide range of chemical compositions.

Assuming that the water content shows a linear increase from 1 % in rocks of 80 % SiO_2 to 2.5 % in rocks of 40 % SiO_2 the predicted sum for analyses where water has not been determined is

$$\sum_{\text{pred}} = 99.0-(0.8000-W_{\text{si obs}}) \times 3.75 \qquad (8)$$

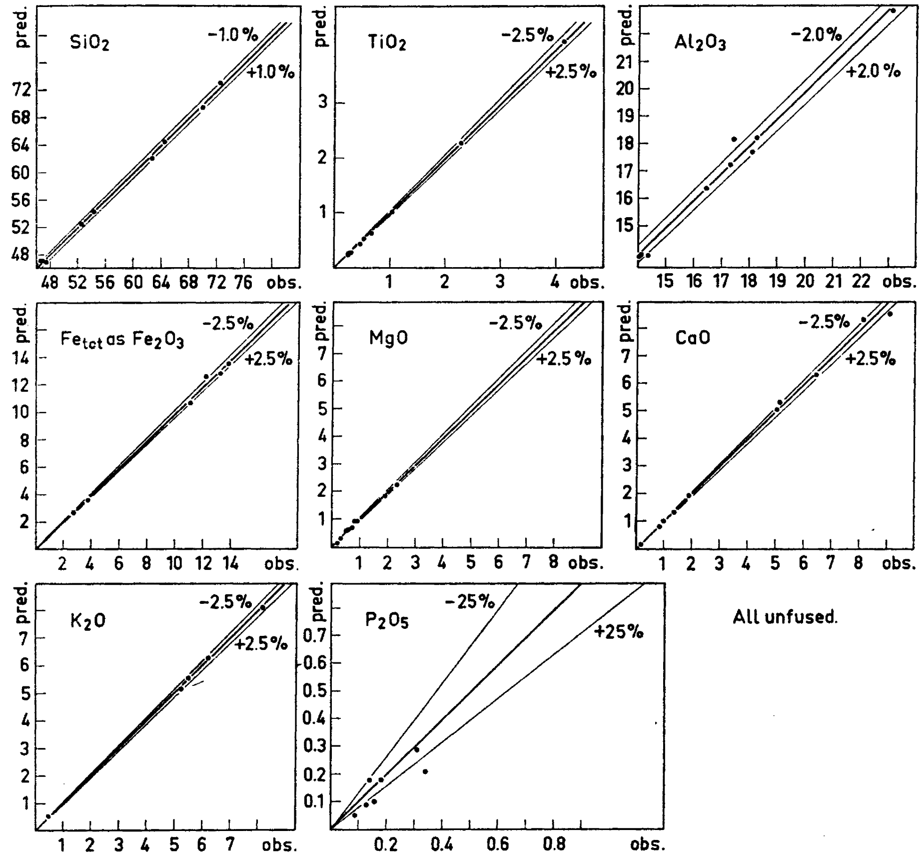

Fig. 3. Observed and predicted values of unfused samples.

Table 7. Observed and predicted values for Al_2O_3.

Unfused rock specimens. Corrected according to eqn. (7).			
	obs.	pred.	diff.
NS-2	23.10	22.93	0.17
GA-100	18.23	18.24	—0.01
A-100	18.10	17.72	0.38
AGV-1	17.40	18.24	—0.84
N-100	17.28	17.15	0.13
T-1	16.46	16.40	0.06
DI-100	14.30	13.94	0.36
G-100	14.00	13.89	0.11
G-1	14.08	13.97	0.11

Table 7. Continued.

Fused rock specimens. Corrected according to eqn. (7).	obs.	pred.	diff.
T-1	16.46	16.39	0.07
N-100	17.28	17.19	0.09
W-1	14.94	14.73	0.21
G-100	14.00	14.19	−0.19
G-1	14.08	13.82	0.26
GR	14.54	14.90	−0.36
NBS 70	18.03	18.02	0.01
NS-1	21.70	21.95	−0.25
NS-2	23.10	22.90	0.20
Milford	10.00	9.85	0.15
Sy-1a	9.01	9.10	−0.09
AGV-1	17.50	17.30	0.20
Antocord	8.90	9.07	−0.17
A-100	18.10	17.84	0.26
DI-100	14.30	14.17	0.13
GA-100	18.23	18.53	−0.30

For the 215 Grimstad granite rock analyses the standard deviation of $\sum_{\text{pred}} - \sum_{\text{obs}}$ is 0.9918 (Table 8). This indicates that the matrix problem of X-ray fluorescence analysis of silicate rocks may be satisfactorily solved by the above outlined calibration methods when applied to statistical treatment of large numbers of analyses of rocks ranging from amphibolites to granites.

The efficacy of the outlined method depends on the mineral content of the rocks. When special rock types, like pyroxenites or limestones, are analyzed, the μ values may turn out to be different. This is true for mineral analyses as well where additional calibration may also be necessary for elements obeying eqn. (1) in rocks.

Mica-schists, phyllites, and greywackes have not been included in the present study, and again other μ values may be found for these rock types.

During the printing of this paper, the paper by Holland and Brindle[7] came to our knowledge. Their approach is based upon the same equation as our eqn. (3). They claim that the use of other methods "have demonstrable weakness". The data of Table 8 show that this statement is not always true. Eqn. (3), though very general, fails to work over the whole range of SiO_2 concentrations unless an additional term is added.

Likewise, the paper by Kodama, Brydon and Stone[8] appeared after the present paper was completed. They use a matrix correction equation which is less specific than our eqn. (2), it contains a constant that will include existing errors in the numerical material. However, they conclude: "Regardless of what the "true" values are, the present X-ray method gives values which are within acceptable limits of the published mean compositions", and this is certainly true.

Table 8. Difference (Δ) of $\sum$ predicted and $\sum$ observed for 215 chemical analyses from the Grimstad granite (Christie *et al.*[6]). Standard deviation of difference: 0.9918. Extreme difference values at extreme SiO_2 concentrations are due to eqns. (3) and (4) not running from zero at $I_{Si\ 0}$ asymptotically to the value $I_{Si\ 100}$ at $SiO_2 = 1.00$.

Sample	SiO_2	Σ calc.	Σ obs.	Δ
H 9	71.82	98.6933	98.59	-.1033
H 10	72.40	98.7150	98.10	-.6150
H 10 1	72.66	98.7248	98.30	-.4248
H 12	72.94	98.7353	98.34	-.3953
H 13	73.24	98.7465	98.31	-.4365
H 14	73.85	98.7694	98.45	-.3194
I 7 64	70.98	98.6618	101.72	3.0582
I 7 65	74.31	98.7866	100.10	1.3134
I 8	68.01	98.5504	97.63	-.9204
I 9	71.93	98.6974	99.64	..9426
I 10	70.31	98.6366	99.31	.6734
I 11	70.25	98.6344	99.81	1.1756
I 12	71.45	98.6794	98.98	.3006
I 13 B	69.68	98.6130	99.03	.4170
I 15	70.98	98.6618	98.11	-.5518
I 16	67.57	98.5339	97.66	-.8739
I 17	69.32	98.5995	98.13	-.4695
I 18	70.96	98.6610	99.19	.5290
I 18 2	63.29	98.3734	97.42	-.9534
I 18 3	70.90	98.6588	99.35	.6912
K 7	68.40	98.5650	99.57	1.0050
K 8	70.38	98.6393	99.01	.3707
K 9	70.15	98.6306	99.13	.4994
K 10	70.20	98.6325	99.19	.5575
K 11	68.29	98.5609	99.59	1.0291
K 12	70.99	98.6621	98.81	.1479
K 14 1	57.80	98.1675	96.o6	-2.1075
K 16	70.67	98.6501	98.90	.2499
K 17	71.27	98.6726	99.06	.3874
K 18	71.40	98.6775	98.35	-.3275
K 21	74.74	98.8028	98.77	-.0328
L 7	72.01	98.7004	99.02	.3196
L 8 A	70.60	98.6475	98.21	-.4375
L 10	66.84	98.5065	97.57	-.9365
L 11	71.39	98.6771	98.98	.3029
L 12	71.23	98.6711	99.03	.3589
L 14	72.50	98.7187	98.83	.1112
L 15	67.76	98.5410	95.23	-3.3110
L 16	71.30	98.6738	98.80	.1262
L 17	71.80	98.6925	99.10	.4075
L 18 1	69.39	98.3771	98.18	-.1971
L 19	70.57	98.6464	98.90	.2536
L 20	71.01	98.6629	97.41	-1.2529
L 22	70.70	98.6513	99.05	.3987
M 8 A	69.63	98.6111	97.87	-.7411
M 9	69.10	98.5913	98.38	-.2113
M 10	70.21	98.6329	98.61	-.0229
M 11	69.81	98.6179	97.64	-.9779
M 13	71.72	98.6895	98.01	-.6795
M 14	71.97	98.6989	98.96	.2611
M 15	70.62	98.6483	98.12	-.5283
M 16	71.00	98.6625	98.93	.2675
M 17	69.24	98.5965	97.71	-.8865
M 19	69.76	98.6160	97.89	-.7260
M 2o	70.96	98.6610	99.07	.4090
M 21	68.95	98.5856	99.16	.5744
N 7	68.95	98.5856	98.55	-.0356
N 8	70.31	98.6366	97.59	-1.0466
N 10	71.00	98.6625	99.20	.5375
N 12	71.01	98.6629	97.08	-1.5829
N 13	69.68	98.6130	97.82	-.7930
N 14	66.55	98.4956	98.61	.1144
N 15	70.20	98.6225	99.22	.5875
N 16	69.37	98.6014	98.57	-.0314
N 17	69.58	98.6092	97.93	-.6793
N 18	69.92	98.6220	97.37	-1.2520
N 19	71.25	98.6906	97.71	-.9806
O 7	71.25	98.6719	98.73	.0581
O 9 1	68.89	98.5834	97.56	-1.0234
O 13	69.14	98.5928	98.81	.2172
O 14	68.40	98.5650	98.99	.4250
O 15	70.21	98.6329	98.34	-.2929
O 16 A	68.87	98.5826	98.03	-.5526
O 18	70.31	98.6366	98.65	.0134
O 25 1	70.18	98.6317	98.95	.3182
P 7	72.54	98.7202	99.23	.5097
P 8	70.79	98.6546	99.35	.6954
P 9	70.50	98.6437	98.87	.2262
P 10	69.98	98.6243	98.70	.0757
P 11	70.63	98.6486	97.64	-1.0086
P 12	71.10	98.6663	98.40	-.2663
P 13	69.23	98.5961	98.97	.3739
P 14	70.62	98.6483	98.34	-.3083
P 15	70.35	98.6381	98.06	-.5781
P 16	70.25	98.6344	98.18	-.4544
P 17	69.78	98.6168	98.90	.2832
P 18 2	57.55	98.1581	99.82	1.6619
P 24 2	69.61	98.6104	98.11	-.5004
Q 8	68.94	98.5853	98.78	.1947
Q 9	70.48	98.6430	99.40	.7570
Q 11	70.30	98.6363	98.25	-.3863
Q 12	71.12	98.6670	98.73	.0630
Q 13	77.30	98.8988	99.35	.4512
Q 14	71.30	98.6738	98.37	-.3038
Q 15	69.65	98.6119	99.17	.5581
Q 16	70.14	98.6302	99.59	.9579
Q 17	69.55	98.6081	99.02	.4119
R 8	71.75	98.6906	99.08	.3894
R 11	70.77	98.6539	99.47	.8161
R 12	60.70	98.2763	101.44	3.1637
R 13	53.78	98.0168	99.69	1.6732
R 14 A	72.70	98.7263	99.62	.8937
R 15	70.03	98.6261	98.48	-.1461
R 16	69.74	98.6153	99.00	.3847
R 19 A	68.10	98.5537	98.71	.1562
R 24 1	68.57	98.5714	98.04	-.5314
S 9	68.10	98.5537	98.69	.1362
S 10	69.63	98.6111	98.07	-.5411
S 11	71.00	98.6625	97.71	-.9525
S 12	72.24	98.7090	99.14	.4310
S 13	68.25	98.5594	97.95	-.6094
S 14 10	57.20	98.1450	98.30	.1550
T 10	71.30	98.6738	99.12	.4462
T 11	69.23	98.5961	97.04	-1.5561
T 12	69.91	98.6216	97.71	-.9116
T 13	71.16	98.6685	97.81	-.8585
T 14	71.15	98.6681	97.91	-.7581
T 18	69.68	98.6130	97.67	-.9430
T 19	70.21	98.6329	98.13	-.5029
U 10 1	68.99	98.5871	97.21	-1.3771
U 11	69.05	98.5894	97.30	-1.2894
U 12	69.71	98.6141	97.93	-.6841
U 13	75.37	98.8264	98.12	-.7064
U 15	71.84	98.6940	98.08	-.6140
U 17	70.30	98.6363	98.95	.3137
U 18	69.07	98.5901	97.86	-.7301
V 8 1	76.00	98.8500	97.81	-1.0400
V 10 1E	70.95	98.6606	97.65	-1.0106
V 11	74.45	98.7919	98.30	-.4919
V 13	68.42	98.5657	97.20	-1.3658
V 15	69.63	98.6111	97.58	-1.0311
V 17	70.00	98.6250	97.39	-1.2350
V 18	72.70	98.7263	98.91	.1837
W 11 1	74.12	98.7795	98.60	-.1795
W 14	73.44	98.7540	98.48	-.2740
W 15	73.68	98.7630	98.94	.1770
W 17	68.67	98.5751	97.35	-1.2251
C 21 1	46.74	97.7528	98.90	1.1472
D 20 1	56.22	98.1083	97.06	-1.0483
F 8	74.06	98.7773	98.56	-.2173
F 9	46.39	97.7396	96.73	-1.0096
F 10	74.24	98.7840	99.22	.4360
F 11	74.98	98.8118	99.38	.5682
F 11 1	74.08	98.7780	98.66	-.1180
F 12	52.23	97.9586	96.93	-1.0286
F 19 1	54.44	98.0415	95.96	-2.0815
G 18 1	49.00	97.8375	98.53	.6925
H 14 1A	76.80	98.8800	100.31	1.4300
H 14 1B	79.56	98.9835	100.32	1.3365
H 14 1C	78.71	98.9516	100.02	1.0684
H 14 1D	85.98	99.2243	102.57	3.3457
H 14 1E	76.70	98.8763	100.06	1.1837
H 15	49.97	97.8739	99.46	1.5861
H 18 1	52.52	97.9695	95.49	-2.4795
I 7 1	69.50	98.6063	98.50	-.1063

Table 8. Continued.

Sample	SiO$_2$	Σ calc.	Σ obs.	Δ
I 7 1B	68.39	98.5646	98.40	-.1646
I 17 1	49.79	97.8671	96.79	-1.0771
I 19	75.25	98.8219	100.01	1.1881
K 6	81.31	99.0491	101.59	2.5409
K 6 1	69.33	98.5999	97.17	-1.4299
K 6 2	67.59	98.5346	98.48	-.0546
K 12 1B	52.60	97.9725	97.20	-.7725
L 4 1	69.03	98.5886	99.65	1.0614
L 8 B	71.40	98.6775	99.95	1.2725
M 8 B	69.70	98.6138	99.17	.5562
N 6	74.60	98.7975	98.98	.1825
O 16 B	66.75	98.5031	98.94	.4369
O 25 2	78.50	98.9438	99.32	.3762
P 24 1	68.07	98.5526	98.40	-.1526
P 24 5	71.41	98.6779	97.30	-.7479
Q 7	75.18	98.8192	99.72	.9007
R 7	55.75	98.0906	99.78	1.6894
R 9 1A	56.38	98.1142	99.90	1.7857
R 9 1B	69.91	98.6216	99.38	.7584
R 10 1 A	55.41	98.0779	98.54	.4621
R 10 1 B	59.20	98.2200	96.36	-1.8600
R 14 B	71.10	98.6663	99.60	.9337
R 19 1 B	67.80	98.5425	98.03	-.5125
S 7	74.08	98.7780	99.19	.4120
S 8 1	60.01	98.2504	98.77	.5196
S 13 29	53.80	98.0175	96.90	-1.1175
S 14 3	56.00	98.1000	97.20	-.9000
S 14 5	61.50	98.3063	97.64	-.6663
S 14 7	60.70	98.2763	96.97	-1.3063
S 14 14	62.60	98.3475	97.58	-.7675
S 14 23	52.20	97.9575	98.00	.0425
S 15 32B	65.50	98.4562	98.15	-.3063
S 15 32C	66.20	98.4825	98.09	-.3925
T 7	74.10	98.7788	98.64	-.1388
T 8 1	72.30	98.7113	99.51	.7987
T 8 1A	56.60	98.1225	98.20	.0775
T 8 2	76.10	98.8538	100.01	1.1562
T 8 2A	58.40	98.1900	98.90	.7100
T 8 3	56.70	98.1263	99.00	.8737
T 8 4	57.20	98.1450	98.00	-.1450
T 8 5	57.30	98.1488	98.80	.6512
T 8 6	63.50	98.3813	99.40	1.0187
T 8 7	57.60	98.1600	101.10	2.9400
T 8 8	58.40	98.1900	99.00	.8100
T 8 A	69.68	98.6130	100.99	2.3770
T 8 B	60.15	98.2556	95.86	-2.3956
T 14 8	56.60	98.1225	97.46	-.6625
U 9 2	71.30	98.6738	96.85	-1.8238
V 10 1 A	71.82	98.6933	98.17	-.5233
V 10 1 B	69.57	98.6089	97.78	-.8289
V 10 1 C	68.67	98.5751	97.21	-1.3651
V 10 1 D	71.43	98.6786	98.36	-.3186
V 10 1 F	69.72	98.6145	97.30	-1.3145
V 10 1 G	69.53	98.6074	96.64	-1.9674
V 13 4	52.00	97.9500	98.10	.1500
W 11 2	72.23	98.7086	98.25	-.4586

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