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Routine trace element determination in silicate minerals and rocks by X-ray fluorescence

By

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With 3 figures and 3 tables

Zusammenfassung: 21 Spurenelemente (Nb, Zr, Y, Sr, U, Rb, Th, Pb, Ga, Zn, Cu, Ni, Co, Cr, Ce, Nd, Ba, V, La, Sc und S) werden mit Hilfe eines vollautomatischen Röntgen-Sequenzspektrometers in 70 min an einer Mineral- oder Gesteinspulvertablette gemessen. Die Messung beschränkt sich nur auf die $K\alpha$- oder $L\alpha$-Linien dieser Elemente. Auf die bisher üblichen zeitaufwendigen Untergrundmessungen kann verzichtet werden, da alle Untergrundmessungen mit Hilfe der Massenabsorption aus den Hauptelementkonzentrationen der Proben in einem Auswertungsprogramm (ZONKE) rechnerisch ermittelt werden. Im Programm werden zudem Drift, Interferenzen und Massenabsorption korrigiert.

Die Kalibrierung erfolgt mit den üblichen internationalen Gesteinsstandards. Die Nachweisbarkeitsgrenzen (N) dieser vollautomatischen Routinespurenelementanalyse liegen abhängig von den Anregungsbedingungen der Cr-Strahlung zwischen 3 und 10 ppm. Ausnahmen bilden Ce(N $\sim$ 25 ppm), Nd(N $\sim$ 15 ppm) und Schwefel (N $\sim$ 17 ppm). Unter Anwendung von Rhodium-, Molybdän-, Silber- oder Wolfram-Röhren könnten noch bessere Impulsausbeuten und damit tiefere Nachweisbarkeitsgrenzen erzielt werden. Die Reproduzierbarkeit dieser Methode ist abhängig von der Zählstatistik gut. Die Fehler betragen bei Konzentrationen von 10 bis 100 ppm ca. 2 bis 10%. Die Richtigkeit der Analyse kann mit folgenden max. rel. Fehlern angegeben werden: bei 1000 ppm Konzentration $\pm 5\%$, bei 100 ppm $\pm 10\%$, bei 10 ppm $\pm 20\%$ und bei 3 ppm $\pm 100\%$. Diese Richtigkeiten beziehen sich auf in sich konsistente Standardisierungen der US Geological Survey Gesteinsstandards AGV-1, BCR-1, G-2, GSP-1, W-1, DTS-1 und PCC-1 (Tab. 3).

Das Programm ZONKE (Fortran) kann auf Anfrage bei den Autoren bezogen werden.

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Abstract: Rapid and routine XRF determination of a large number of geologically interesting trace elements may be carried out using the synthetic background method proposed by FEATHER & WILLIS (1975), if major element concentrations are known. We discuss analytical methods and correction procedures for 21 trace elements (Nb, Zr, Y, Sr, U, Rb, Th, Pb, Ga, Zn, Cu, Ni, Co, Cr, Ce, Nd, Ba, V, La, Sc and S), and review the procedures for calculating background, interference mass absorption and errors. A Fortran program, ZONKE, is available on request.

The method is particularly useful for multi-element determination on a large number of samples, using fully automated XRF equipment.

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Introduction

In the past few years many earth science institutes have acquired automated or semi-automated XRF crystal spectromaters. Typically these instruments include automatic sample changers and/or automatic goniometers. With the introduction of automated instruments analytical techniques have been developed to permit efficient use of available machine time.

In this paper we review the problems involved in trace element determination in geological samples, and present an analytical method combined with a computer program which permits rapid and reasonably accurate analysis of 21 trace elements. This method is based mainly on the work of HOWER, (1959) and FEATHER & WILLIS (1975). Our intention is not so much to review the theory of trace element analysis: rather it is to describe how a routine system of analysis may be set up. The elements investigated are: Nb, Zr, Y, Sr, U, Rb, Th, Pb, Ga, Zn, Cu, Ni, Co, Cr, V, Ce, Nd, Ba, La, Sc and S. Table 1 gives analytical settings (see also NORRISH & CHAPPEL 1977, p. 256).

Several recent papers have discussed various aspects of trace element analysis in rocks: a good introduction to the techniques used is found in HOWER (1959), NORRISH & CHAPPEL (1977), STERN (1976) and FEATHER & WILLIS (1976). Books by JENKINS & DE VRIES (1970) and JENKINS (1974) provide detailed discussions of the theory of X-ray analysis.

Our analytical procedure assumes a prior knowledge of major element concentrations in the samples to be measured. However, for most trace elements the program could, if necessary, be modified to permit trace element determination without prior knowledge of major element chemistry, provided several additional background measurements were made.

Specimen requirements

Most silicate minerals and rocks consist of about 10 major oxides: SiO_2 (usually approx. 50%), MgO, CaO, Al_2O_3 and FeO and Fe_2O_3 being dominant. Other "major" oxides are TiO_2, MnO, K_2O, Na_2O, P_2O_5, H_2O and CO_2. Typically these oxides form approx. 99.5% of the rock. All other elements are treated as trace elements. In contrast to major element analysis, trace element analysis of rocks can make use of a series of simplifying assumptions.

The most important of these assumptions is that the trace elements make no significant contribution to the total mass absorption of the specimen for radiation at the trace element peak wavelength. This assumption (only true for $Z > 24$ in geological specimens) leads to the relation that for any particular element, z, measured at wavelength λ_z

$$\frac{C_{\text{unknown}}}{C_{\text{standard}}} = \frac{I_{\text{unknown}}}{I_{\text{standard}}} \cdot \frac{\Sigma_j W_j (\mu/\varrho)_{j\ \text{unknown}}}{\Sigma_j W_j (\mu/\varrho)_{j\ \text{standard}}} \qquad (1)$$

C = mass concentration of trace element in ppm
I = intensity of radiation measured in counts per second

Table 1. Instrumental settings on Philips sequential spectrometer PW 1450 using a Cr—X-ray tube: 80 kV and 30 mA for running all elements; scintillation counter with fine collimator for elements 1 to 12, flow counter with fine collimator for elements 13 to 22.

No	Element	Z	Peak	Wavelength Å	Crystal	Angle (2θ)	Counting time (sec)	Interfering elements peaks
1	Nb	41	$K\alpha$	0.748	LiF 220	30.38	200	$YK\beta$
2	Zr	40	$K\alpha$	0.788	LiF 220 (or LiF 200)	32.04 (220)	100	$SrK\beta$
3	Y	39	$K\alpha$	0.831	LiF 220 (or LiF 200)	33.84 (220)	100	$RbK\beta$
4	Sr	38	$K\alpha$	0.877	LiF 220	35.80	100	
5	U	92	$L\alpha$	0.911	LiF 220	37.30	200	$RbK\alpha$
6	Rb	37	$K\alpha$	0.927	LiF 220	37.93	100	
7	Th	90	$L\alpha$	0.956	LiF 200	27.47	200	$PbL\beta_{1+3}$
8	Pb	82	$L\beta_{1+2}$	0.983	LiF 200	28.26	200	
9	Ga	31	$K\alpha$	1.341	LiF 200	38.88	100	
10	Zn*	30	$K\alpha$	1.437	LiF 200	41.70	100	
11	Cu*	29	$K\alpha$	1.542	LiF 200 + Filter	44.90	100	
12	Ni*	28	$K\alpha$	1.659	LiF 200	48.60	100	$CoK\beta$
13	Co*	27	$K\alpha$	1.791	LiF 220 or LiF 200	77.88 (220)	100	$FeK\beta$
14	Cr	24	$K\alpha$	2.291	LiF 200 + Filter	69.33	100	$VK\beta$
15	V	23	$K\alpha$	2.505	LiF 220	123.77	100	$TiK\beta$
16	Ce	58	$L\beta_1$	2.356	LiF 200 + Filter	71.62	400	$NdL\alpha$
17	Nd	60	$L\alpha$	2.370	LiF 200 + Filter	72.13	400	$CeL\beta$
18	Ba	56	$L\beta_2$	2.404	LiF 220	115.23	400	
19	Ba	56	$L\alpha$	2.776	LiF 200	87.17	400	$TiK\alpha$
20	La	57	$L\alpha$	2.665	LiF 220	138.78	200	
21	Sc	21	$K\alpha$	3.032	LiF 200	97.65	100	$CaK\beta_5$
22	S	16	$K\alpha$	5.373	PET	75.85	100	

* The combination of scintillation and flow counter may improve the count rate of these elements.

W_j = composition of samples or standards (major element oxides) in weight%
$(\mu/\varrho)_j$ = mass absorption coefficients of the major element oxides, calculated from data in tables by HEINRICH (1966) or REYNOLDS (1967)

Total mass absorption coefficient of rock matrix:

$$\mu' = \Sigma W_j \, (\mu/\varrho)_j \tag{2}$$

$$\frac{C_u}{C_s} = \frac{I_u}{I_s} \cdot \frac{\mu'_u}{\mu'_s} \qquad \text{(JENKINS \& DE VRIES 1970)} \tag{3}$$

In general, if intensities and matrix mass absorptions are known it is possible to determine the trace element concentration in an unknown sample by reference to a set of calibration standards. The calibration samples are best chosen from a variety of typical rock types, such that the range of concentrations of trace elements and the range of matrix mass absorption coefficients in the standards is equivalent to or greater than the ranges expected in the unknowns. Typically reference standards such as the U.S. Geological Survey suite of rock-standards (Table 3), or the South African National Institute of Mineralogy standards are used. For very accurate work carefully prepared spiked standards may be used, but for normal geochemical purposes this seems to be unnecessary. The use of a calibration suite of rock standards is very important, since it also reduces any non-linear effects not treated in the correction program.

Analytical procedure

Table 1 summarizes instrumental settings. The choice of X-ray tubes, filters, counters and collimators depends on the element being analysed. A Cr X-ray tube, the only tube available to us at the moment, has proved to be adequate, but ideally Rh, Ag, Mo or W tubes are preferable for the shorter wavelengths. Samples were normally run overnight in the automated Philips sequential X-ray spectrometer (PW 1450) to minimize drift. Long term drift corrections are made by running an external monitor standard. In general it was found that instrumental drift for short wavelength peaks using thermally stable crystals is not a significant factor in trace element analysis: this is in marked contrast to the important corrections in major element analysis. In normal operation calibration runs may be several weeks or even months apart, provided the spectrometer is operating continuously, day and night, to contribute to stability.

Correction procedure

Dead-time

Intensity measurements should be corrected for dead-time by the relation:

$$\text{I corrected} = \frac{\text{I measured}}{1 - I_m t_d + (I_m)^2 t_d^2/2! - \ldots} \qquad \text{(JENKINS 1974)} \tag{4}$$

where t_d is dead-time. For count rates (I in counts per second) less than 10^5 a first degree approximation is adequate.

Absorption

Most samples for our work had previously been determined for major elements. Thus the total mass absorption coefficient of a sample μ' (equation 2) could be calculated from HEINRICH's tables.

In practice it is not necessary to compute μ' for each peak wavelength being measured. HOWER (1959) noted that between major element absorption edges there is a linear relationship between the relative values of μ' of various samples which holds for all wavelengths between the absorption edges (Fig. 1). This relationship was further discussed by FEATHER & WILLIS (1975).

The trace elements were grouped into 8 classes (Table 2), depending on the major element absorption edges. For all elements of Z> about 37, Zr Kα mass absorption data may be used. In samples whose major element composition is not known, mass absorption may be empirically determined by measuring appropriate Compton Scatter peaks, or from selected background positions. Mo Compton Scatter is very useful for this, but was unfortunately not available to us. Selected background or Compton Scatter peak measurements can also be used to check the accuracy of calculated mass absorptions.

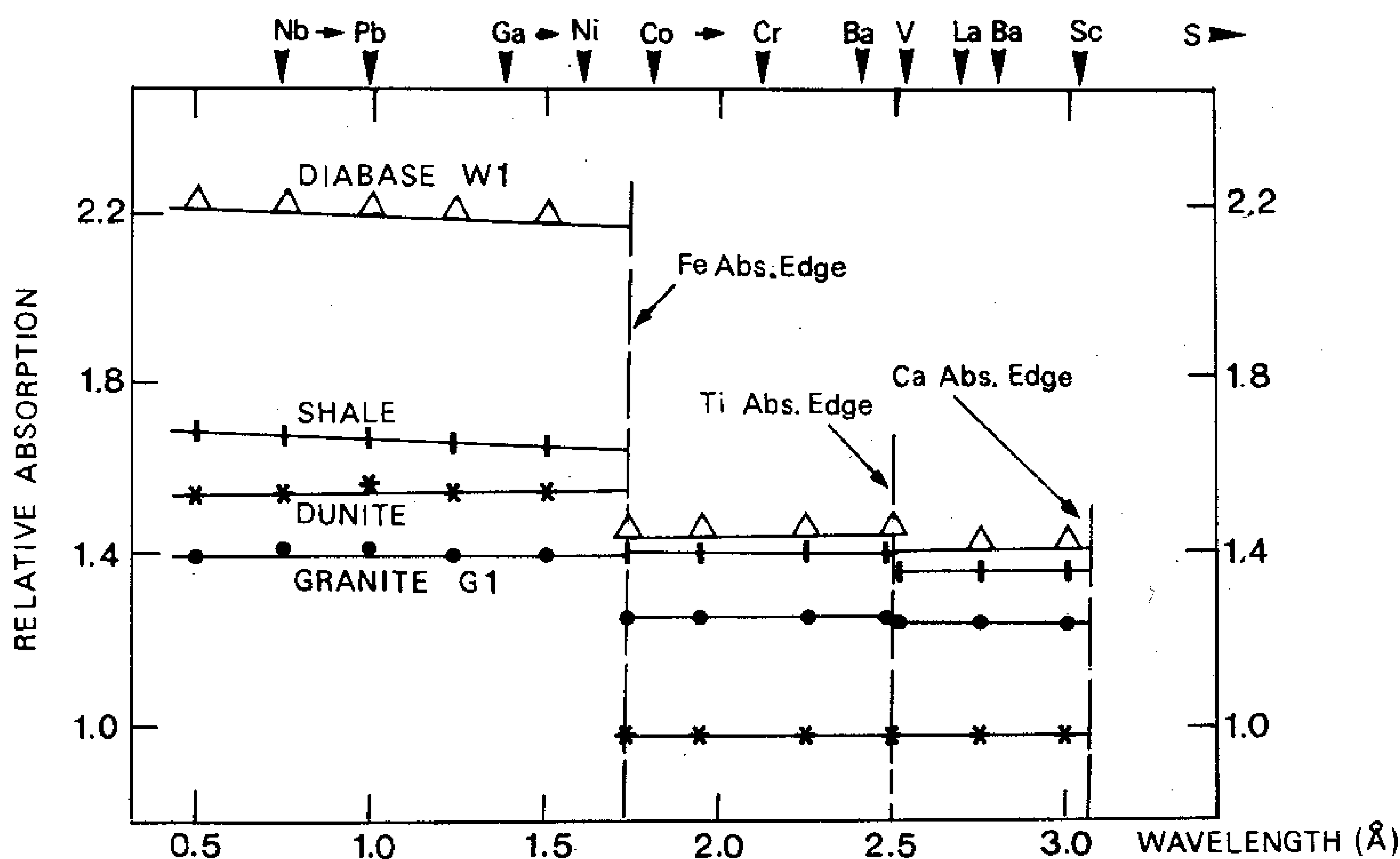


Fig. 1. Relative absorption versus wavelength for four different rock types (after HOWER 1959). The straight and almost horizontal lines indicate that the exciting radiation is absorbed (attenuated) by constant relative amounts in a rock for the trace elements with absorption edges in one of the three fields.

Table 2. Examples of performance for standards basalt BCR—1 and granodiorite GSP—1: Peak count rate (counts per second), background (counts per second, BKG), mass absorption (μ), absorption corrected counts per second (CCPS, after subtraction of interference and background $\times$ $1/\mu$), concentrations of elements in ppm, Zürich self consistent values chosen for calibration (CC), detection limits of elements in ppm (D.L.), concentration counting error in ppm = standard deviation ERR.

Element	Z	Mass Absorption Family	Basalt BCR—1 Peak	BKG	$1/\mu$	CCPS	CC ppm	D.L. ppm	ERR* ppm	Granodiorite GSP—1 Peak	BKG	$1/\mu$	CCPS	CC ppm	D.L. ppm	ERR** ppm
Nb	41	Zr	1046.8	980.6	.0926	687	15	3.3	.2	1492.2	1336.6	.1301	1175	30	2.8	.1
Zr	40	Zr	1755.8	823.5	.0926	8825	192	4.1	<.1	4429.7	1117.0	.1301	24561	524	3.3	<.1
Y	39	Zr	866.2	679.5	.0926	1584	38	4.1	.1	1347.8	917.4	.1301	1158	30	3.5	.1
Sr	38	Zr	1735.8	555.0	.0926	12753	33	4.0	<.1	1938.0	743.6	.1301	9177	238	3.3	<.1
U	92	Zr	494.0	474.3	.0926	100	1.80	2.6	1.3	659.1	632.1	.1301	46	2.90	2.1	2.9
Rb	37	Zr	618.5	453.9	.0926	1778	49	3.9	.1	1754.8	602.7	.1301	8853	252	3.2	<.1
Th	90	Zr	986.3	946.2	.0926	271	5.3	6.1	1.8	1629.7	1264.6	.1301	2595	102	4.5	<.1
Pb	82	Zr	900.4	862.3	.0926	412	19	6.3	.6	1323.5	1143.6	.1301	1382	56	.6	4.1
Ga	31	Zn	291.8	192.3	.0177	5626	23	1.9	.1	381.5	269.1	.0246	4567	22	1.8	<.1
Zn	30	Zn	384.7	173.7	.0177	11928	125	4.7	.1	468.0	222.3	.0246	9981	105	3.8	<.1
Cu	29	Cu	76.6	67.0	.0147	490	16	7.2	3.4	109.8	87.7	.0215	725	32	5.6	1.3
Ni	28	Cu	115.6	96.3	.0147	1298	22	7.0	.9	153.9	126.0	.0215	1294	20	5.5	.4
Co	27	Co	98.2	27.0	.0154	1767	39	4.5	.5	49.5	28.2	.0161	70	4	4.4	9.6
Cr	24	Cr	11.1	6.0	.0078	357	19	9.7	9.1	7.6	6.0	.0081	168	17	9.4	17.4
V	23	V	888.7	27.0	.0065	50629	39	3.6	.1	219.3	26.8	.0064	5139	55	3.6	.3
Ce	58	Cr	7.2	4.0	.0078	194	53	20.9	large	15.4	4.0	.0081	1154	392	24.6	18.3
Nd	60	Cr	6.9	4.0	.0078	184	26	10.7	large	13.2	4.0	.0081	886	184	15.3	13.9
BaLβ_2	56	Cr	287.7	84.7	.0078	25659	674	10.1	.3	448.9	87.8	.0081	44266	1284	10.1	.2
BaLα	56	Sc	1787.1	16.1	.0038	397378	673	.4	<.1	2668.0	15.4	.0038	679516	1290	.6	<.1
La	57	Sc	63.0	23.0	.0038	4491	24	2.4	.5	73.8	23.0	.0038	7379	195	14.2	2.1
Sc	21	Sc	178.0	15.0	.0038	42746	33	.4	<.1	54.8	14.9	.0038	10532	7	.4	<.1
S	16	S	189.1	69.4	.0010	106788	420	20.0	.6	121.4	66.9	.0010	43055	162	20.0	1.3

* using basaltic calibration, ** using granitic-granodioritic calibration.

Background correction

The usual method of background correction is, as with major elements, the measurement of intensity at a wavelength or wavelengths slightly offset from the peak being studied; the offset being carefully chosen to avoid interfering peaks. For some trace elements this is possible, but in many cases the background is strongly curved and it is better to fit a curve or an "envelope" of lines to a set of measurements (e.g. for Nb, Zr, Y, Sr, Rb).

Various authors (Hower 1959, Feather & Willis 1975) have noted the relationship between background and μ', and Feather & Willis proposed a simple method of background correction which avoids the difficulty of finding interference-free positions. Background originates from a mixture of coherent and incoherent scattering of primary radiation, and from general instrument noise. Since scattering is inversely proportional to sample mass absorption at that wavelength they suggested that backgrounds could be calculated from a known calibration curve of sample "blank" background intensities vs. $1/\mu'$ (Fig. 2). Once the calibration curve has been established no further background measurements are needed if μ' is known in the specimen to be measured. The method is thus very efficient in usage of machine time if large numbers of unknown samples are to be analysed.

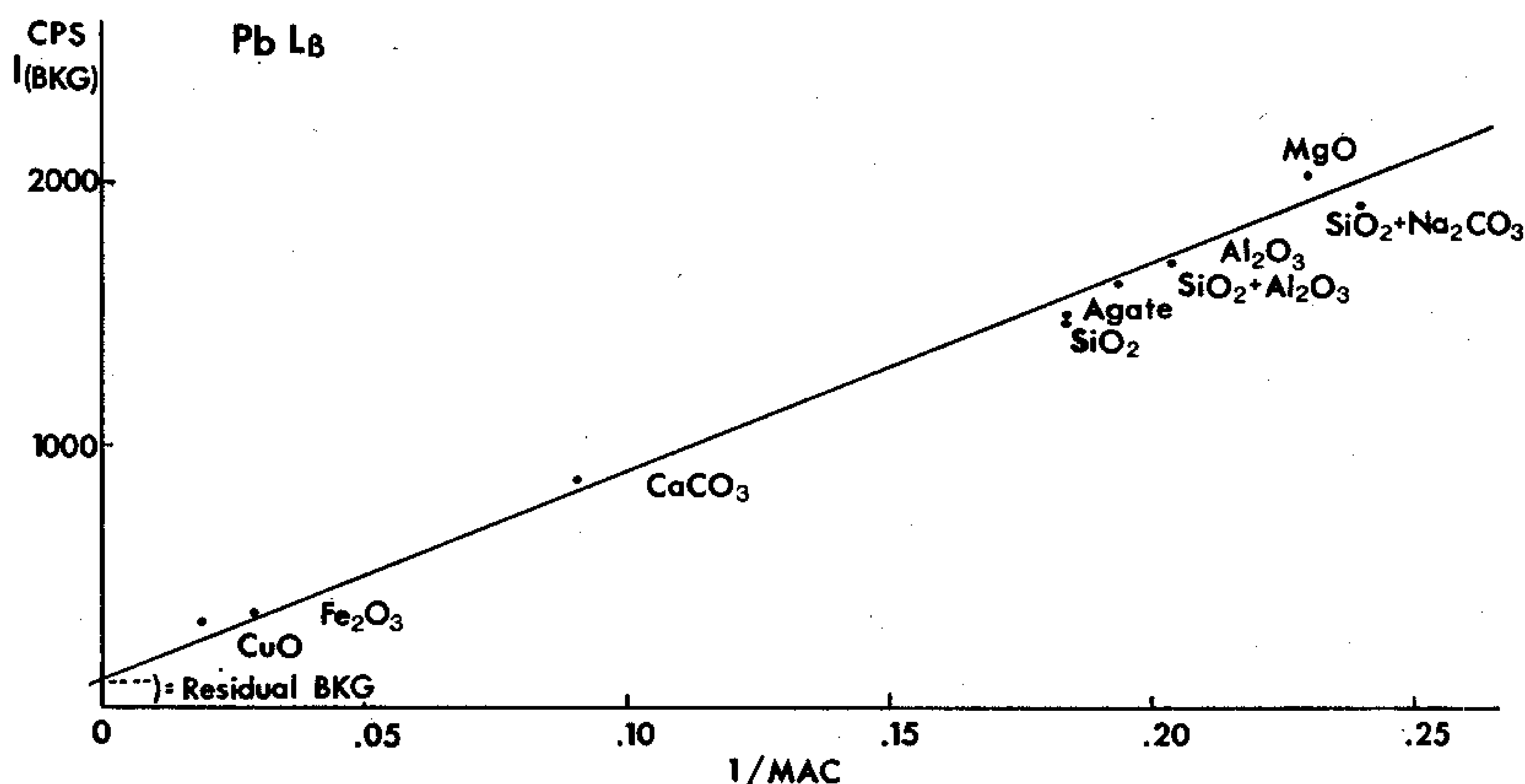


Fig. 2. Example of a "blank" background calibration at the PbLβ peak position using several different blank-standards. Plot of background intensity $I_{(BKG)}$ in CPS versus 1/MAC (mass absorption coefficient). This line is later (in programm ZONKE) used to calculate the "synthetic" backgrounds of the PbLβ peak for the rock-standards and unknown samples.

Interference corrections

Many elements have subsidiary lines which interfere with lines being measured (Table 1). Peaks are generally chosen so as to avoid interference, but in some cases it is unavoidable. Fig. 3 illustrates the Ti—V—Cr problem.

TiK_β (2.514 Å) interferes with VK_α (2.505 Å), and VK_β (2.285 Å) interferes with CrK_α (2.291). In most cases, both the interfering element and the element being interfered with are of geochemical interest and are being analysed.

a) If this is so, the normal method of correction for interference is by making interference standards (SNETSINGER et al. 1968). These consist of blank material (e.g. SiO_2) homogeneously mixed with a small amount (e.g. roughly 2000—3000 ppm) of the interfering element. These samples are then measured at the various peaks concerned, corrected for mass absorption and background and interference factors calculated. Typically several interference standards are measured and the results averaged. Attention should be paid particularly to the Vanadium interference on Chromium. The calculation of an accurate interference factor requires an accurate determination of the Chromium background. The interference factors obtained are then used for correction of calibration standard and unknown counts in a simple ratio calculation.

Example: Interference of Rb on Y (Interference factor RBY measured on the Rb-interference standard at the YK_α and RbK_α positions)

$$\mathrm{RBY} = \frac{\mathrm{CPS}\ (\mathrm{YK}_\alpha)}{\mathrm{CPS}\ (\mathrm{RbK}_\alpha)} \tag{5}$$

Correction for all other unknown samples:

$$\mathrm{CPS}\ (\mathrm{YK}_\alpha) = \mathrm{CPS}\ (\mathrm{YK}_\alpha) - \mathrm{CPS}\ (\mathrm{RbK}_\alpha) \times \mathrm{RBY} \tag{6}$$

b) In some cases major elements not being measured interfere with trace elements (Table 1 and Fig. 3). This is particularly severe in the case of Ti on V interference, Ti on BaL_α, Fe on Co, and the $CaK\beta_5I$ on Sc.

Interference standards can be made up containing an accurately known content of pure TiO_2, Fe_2O_3 and $CaCO_3$ in a matrix totally free from the trace element being measured. Interference factors may then be calculated as before:

Example: Ti on V interference

Interference factor VTI measured on the Ti-interference standard at VK_α position:

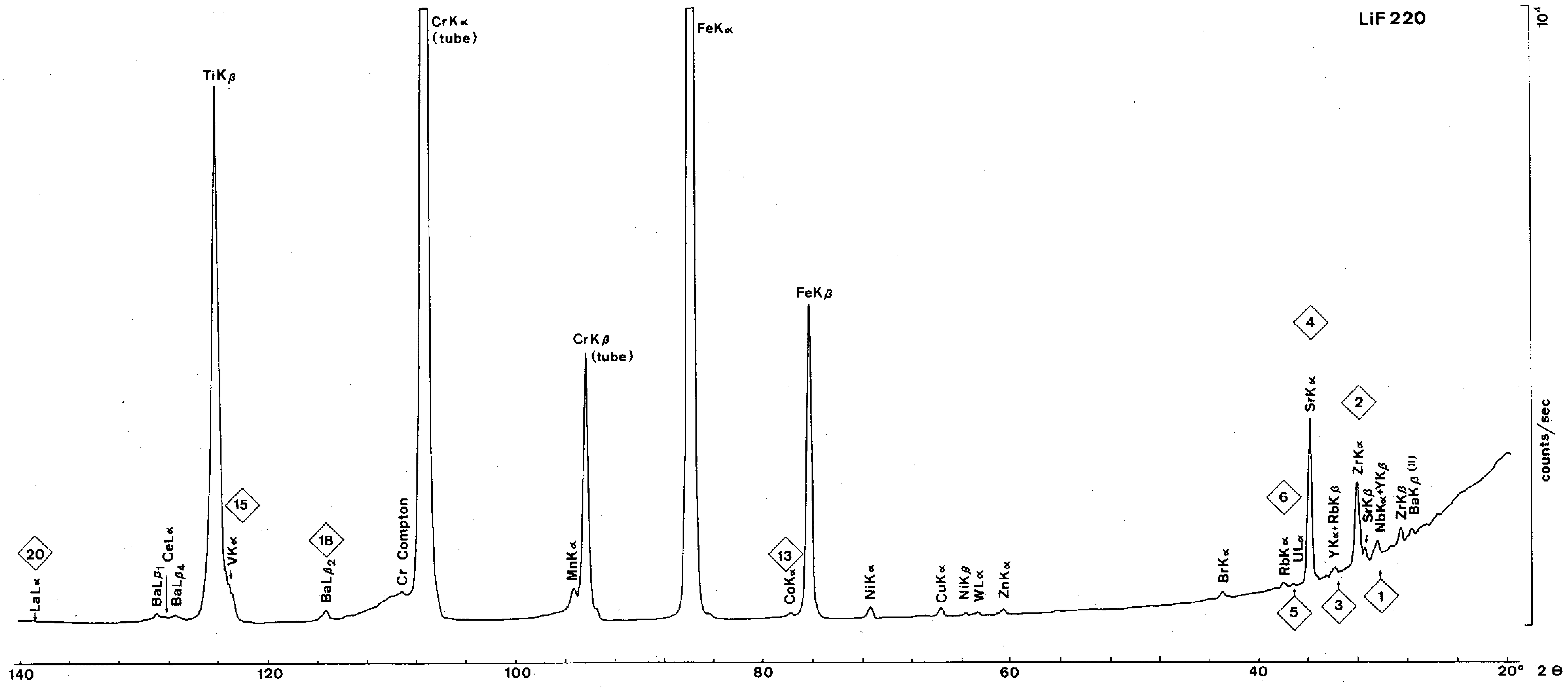
$$\mathrm{VTI} = \frac{\mathrm{CPS}\ (\mathrm{VK}_\alpha)_{\mathrm{standard}}}{\mathrm{TiO_2}(\mathrm{Wt}\%)_{\mathrm{standard}}} \tag{7}$$

Correction procedure for all other unknown samples:

$$\mathrm{CPS}\ (\mathrm{VK}_\alpha) = \mathrm{CPS}\ (\mathrm{VK}_\alpha) - \mathrm{TiO_2}\ (\mathrm{Wt}\%\ \text{unknown sample}) \times \mathrm{VTI} \tag{8}$$

Ca-rich rocks (CaO $> 10\%$) require an additional empirical correction for LaL_α, VK_α, BaL_{β_2} and BaL_α. This correction is treated with the interrefence correction.

For trace elements whose absorption edge is at longer wavelength than that of Fe a further correction may be applied to allow for enhancement



LiF 220
10⁴
counts/sec
2θ
140
120
100
80
60
40
20°
LaLα
BaLβ1
CeLα
BaLβ4
TiKβ
VKα
BaLβ2
Cr Compton
CrKα (tube)
MnKα
CrKβ (tube)
FeKα
CoKα
FeKβ
NiKα
CuKα
NiKβ
WLα
ZnKα
BrKα
RbKα
ULα
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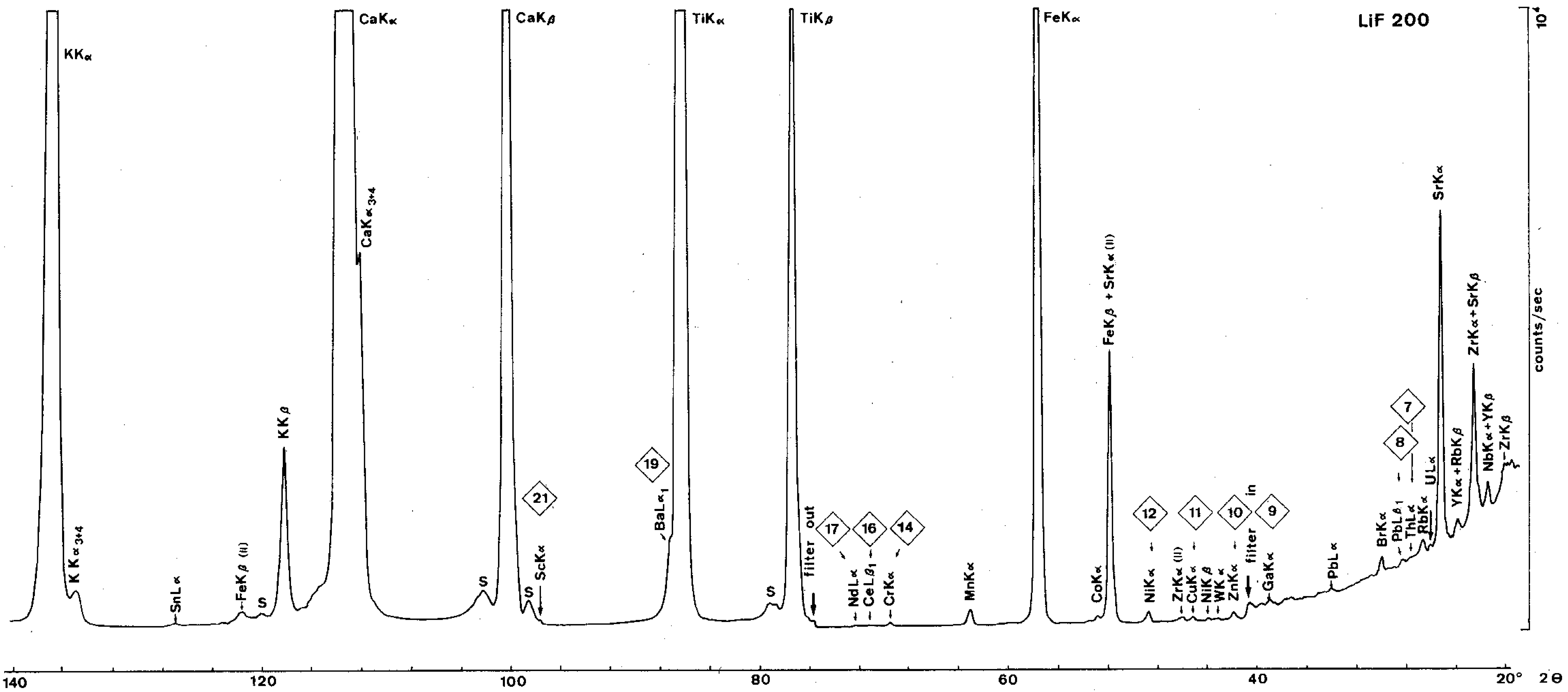

Fig. 3. Typical spectra for Knippa Basalt obtained with a chromium target X-ray tube and the LiF (200) and LiF (220) analysing crystals. The numbers 1—21 mark the peaks being used in our method (see also Table 1). S = Satellite-peaks (Bertin 1978, Schoun 1972, Scientific Equipment Department Philips 1965). The trace element concentrations of Knippa Basalt are given in Table 3.

effects. The L-peaks of Ce, Nd, Cr, Ba, La, V and to a lesser extent, Sc and S are affected by this. Similarly Ti and Ca enhancement effects may be significant with Sc and S.

One semi-quantitative method of correction is by using enhancement standards made of known amounts of the enhancing and enhanced elements. In our experience these effects may probably be neglected provided a calibration standard set is used whose compositional range in Fe, Ti and Ca is similar to that of the unknowns. However, in unknown rocks such as ironstones and limestones where Fe, Ti or Ca dominate the rock matrix the enhancement effects will be significant.

Detection limits and errors

The lower limit of detection may be roughly calculated from NORRISH & CHAPPEL (1977)

$$LLD = \frac{6}{m}\sqrt{\frac{Cb}{T}}, \text{ where} \tag{9}$$

m = Number of counts per second per unit concentration in the sample
Cb = number of background counts per second
T = analytical time

Counting error is given by standard deviation

$$ERR = \frac{\sqrt{Np + Nb}}{Np - Nb}, \tag{10}$$

where Np = peak counts, Nb = background counts.

The counting error merely evaluates count statistics. Examples of LLD and ERR for two US Geological Survey standard rocks BCR—1 are given in Table 2.

Sample preparation

Geological samples may be easily prepared for trace element analysis since no flux is needed (in contrast to the requirements of major element analysis). Rocks are first ground to the finest powder possible in an agate or tungsten carbide swing mill (note: WC tends to contaminate samples in elements such as W, Co and Ta). Cleanliness is essential and for important samples pre-contamination with waste rock of the same sample is a good procedure. Samples are then pressed into powder pellets at pressures around (200 kp/cm² or 31 tons / sq. inch). Two common preparation techniques may be used:

a) backing the sample with boric acid (see NORRISH & CHAPPELL 1967)
b) addition of a binder to the rock powder (FEATHER & WILLIS 1976).

In our experience a few drops of 2% polyvinyl alcohol solution (e.g. Hoechst Mowiol) may be added to the rock powder, which is then well mixed in a mortar before pressing. On pressing to circa 150 kp/cm² or 23 tons/sq.

inch) and drying in an oven for 1—2 hours at about 105°C a pellet is produced which is strong enough to withstand rotation and vacuum in an X-ray spectrometer. The advantage of this technique is that the pellet is double-sided and may thus be analysed in duplicate. Alternatively the pellet may be bound by milling it with a resin or with Mowiol, but in this case approx. 10% binder is needed.

The size of the pellets depends on the X-ray spectrometer being used, but typically they are 40 mm diameter. The critical depth of penetration may be calculated from

$$I = I_0 \, e^{-(\mu/\varrho)\varrho \, d \, \sin\psi} \qquad (11)$$

or

$$I = I_0 \, e^{-\mu'\varrho \, d \, \sin\psi} \qquad (12)$$

where $\mu' = \Sigma W_j(\mu/\varrho)_j$, ψ is about 45° for many machines, ϱ = density of sample. If $I/I_0 = 1/100$ (for 99% of the radiation), $4.6 = \mu'\varrho \, d \sin\psi$.

For the shortest wavelength radiation used (Nb K_α) μ' is usually 10—20 for basalts, or down to 5 for granites (Table 2), giving critical depths of a few mm for most rock types. Typically 8—10g of sample is adequate for a 40 mm diameter pellet. Feather & Willis (1975) quote a similar figure from an empirical determination for MoK_α radiation (0.711 Å). In contrast, for long wavelengths (e.g. S), penetration is very shallow (0.04 mm) and samples must be kept smooth and clean.

The following suite of samples is prepared:

1) A series of blank background-calibration standards. This series must contain pellets whose μ' values cover the range expected in the unknown and standard rock samples. Blank pellets must be prepared from either "specpure" material, or, in the case of SiO_2, from very pure natural material (since "specpure" SiO_2 cannot be pressed easily into a pellet). Typical blanks are SiO_2, $CaCO_3$, Fe_2O_3, CuO, Al_2O_3 MgO, 50% SiO_2 + 50% Na_2CO_3 etc.

2) A series of interference correction standards, usually 1000—3000 ppm (not accurately known) of the interfering element in a matrix of SiO_2 (agate) or dunite, depending on the element being studied. If the interference of a major element with a trace element is being measured the concentration of the major element in the interference standard must be most accurately known and the pellet well homogenized (e.g. 1% TiO_2 in a SiO_2 matrix).

3) A series of calibration standards, such as USGS reference standards. Standards may also be made by "standard addition" techniques.

4) Unknowns. It is most important that all standards be prepared under similar conditions with as little cross-contamination as possible. For accurate analysis of elements such as S the surface of the samples should be disturbed as little as possible.

Calculation of results

A computer program "ZONKE" has been written by E.G.N. to carry out correction procedures discussed above for 21 elements (easily extendible to other elements). This program is available on request from any of the authors. It is available in forms designed to run on either CDC or IBM computers.

a) Input

Data input consists of a series of blocks:

A) Heading card, mass absorption check switch and analytical counting times.
B) Titles, major element oxides, exclusion controls for line fits and counts of mass. Absorption standards (blanks).
C) "Flip" title
D) Titles, major element oxides, and counts of interference standards (and enhancement standards if necessary).
E) "Flip" title
F) Title, major element oxides, exclusion controls for line fits, concentrations and counts of calibration standards.
G) "Flip" title.
H) Titles, major element oxides, and counts of unknowns.
I) Terminator.

b) Logic

The program contains a series of logical blocks:

1) Dimensioning, initialization of variables etc.
2) Data blocks for calculation of mass absorption coefficients. Eight separate sets of data are used, all calculated for major element oxides from HEINRICH's coefficients (1966). Table 2 lists the grouping of elements into M.A.C. sets. For any new elements with a wavelength greater than 0.75 Å Zr mass absorption coefficients can be used.
3) Read in Heading Card and switches for mass absorption checks (see below no. 12).
4) Read in and write analytical times.
5) Read and write sample name. A "Flip" (e.g. 99999) card is used at the end of each block of input to direct the program.
6) Read and write major element oxides in order.
7) Read and write exclusion cards for blanks and calibration standards (see below no. 11, 13).
8) Read and write peak counts for 22 element peaks, a Compton Scatter peak and (a) selected background position (s). Correct for dead-time if necessary. Adjust counts for drift of the internal standard.
9) Calculate counts/second.
10) Calculate mass absorption coefficients for sample (using major element oxide compositions) for all 22 trace element wavelengths. Calculate "infinite" thickness of sample. Write M.A.C. and thickness. Return to no. 5 if in "blank" data block.
11) On reaching the first "Flip" card fit regression of "Peaks" vs "1/mass absorption" for 22 element peaks, omitting those sample-peaks excluded (no. 6) because of contamination or interference. Lines are separately regressed against X and Y axes and geometrically averaged. These lines are later used to calculate "synthetic" backgrounds. They usually do not pass through the origin. Write slopes and intercepts. Return to no. 5.
12) Read interference (and enhancement) standards. For each sample calculate synthetic backgrounds and subtract from peaks. If necessary check relative mass absorption levels by using Compton Scatter and measured background position (no. 8) and adjust levels accordingly. Multiply peaks by mass absorption coeffi-

Table 3. USGS Reference standards and Knippa Basalt.

		Andesite AGV—1		*Basalt* BCR—1		*Dunite* DTS—1		*Granite* G—2		*Granodiorite* GSP—1		*Peridotite* PCC—1		*Diabase* W—1		*Knippa Basalt*	
		R.V.*	ZH	R.V.*	ZH	R.V.*	ZH	R.V.*	ZH	R.V.*	ZH	R.V.*	ZH	R.V.*	ZH	R.V.**	ZH
1	Nb	15	13	14	15	<3	R	14	7	29	30	<2	R	10	12	~82	89
2	Zr	225	230	190	192	3	R	300	306	540	524	7	R	105	101	~290	285
3	Y	21	20	37	38	0.05	R	12	10	30	30	<5	R	25	25	~25	30
4	Sr	657	659	330	331	0.35	R	479	479	233	238	0.4	R	190	194	~1010	990
5	U	2	1.55	1.74	1.8	0.004	R	2	R	2.56	2.9	<1	R	0.6	R	?	~3
6	Rb	67	67	46	49	0.053	R	168	165	254	252	0.1	R	21	27	28	33
7	Th	6	4.1	6	5.3	0.01	R	24	22	104	102	<1	R	2.4	2.4	?	<6
8	Pb	35	34	18	19	14	11	31	29	51	56	13	R	8	R	?	11
9	Ga	21	20	20	23	0.2	R	23	19	22	22	0.4	R	16	19	20	21
10	Zn	84	84	120	125	45	46	85	85	98	105	36	40	86	87	125	112
11	Cu	60	60	18	16	7	9	12	R	33	32	11	13	110	114	~65	71
12	Ni	19	21	16	22	2269	2330	5	8	13	20	2339	2315	76	77	~345	332
13	Co	14	14	38	39	133	133	6	R	6	4	112	111	47	46	77	74
14	Cr	12	R	17	19	4000	3999	7	R	13	17	2730	2730	114	120	~450	490
15	V	125	124	399	391	10	R	35	36	53	55	30	R	254	259	?	195
16	Ce	63	60	54	53	0.06	R	150	159	394	392	0.1	R	23	24	111	112
17	Nd	39	25	29	26	<0.02	R	60	45	188	188	<1	R	15	10	54	54
18/19	Ba	1208	1207	675	674	2.4	R	1870	1866	1300	1295	1	R	160	165	~660	645
20	La	35	35	26	24	0.04	R	96	105	191	195	0.2	R	10	R	55	55
21	Sc	13	15	33	33	3.6	3.6	4	5	7	7	7	7	35	35	?	20
22	S	<10	R	392	420	<10	R	24	26	162	159	<10	R	123	105	?	310

R = Restrictions in calibration due to low concentrations
R.V. = Recommended values, ZH = self consistent values obtained in Zürich
* = Flanagan (1972 and 1976)
** = Ganapathy et al. (1970), Gast et al. (1970) and Tera et al. (1970)

cients and calculate interference factors and enhancement factors. Generally two or more interference standards are used for each interference problem. Return to no. 5. On reaching next "Flip" card average the interference factors for each peak. Write factors. Return to no. 5.

13) Read Calibration standards. For each standard calculate and write mass absorption coefficients (reset if necessary by Compton Scatter and background test); calculate, write and subtract backgrounds; multiply by mass absorption coefficient; subtract interference and enhancement factors. Store and write. Return to no. 5. On reaching "Flip" card fit calibration lines, which should pass through the origin. Lines are regressed separately on X and Y axes and then averaged geometrically. From memory calculate standards as "unknowns" to give an indication of the quality of fit. Write. Return to no. 5. Note that it is not necessary to store standard peak data; for running on small machinelinked computers this may be deleted.
14) Read unknowns. For each unknown calculate and write mass absorptions; backgrounds; corrected counts after multiplication by mass absorption and allowing for interference and enhancement. Calculate concentrations from average, X-regression and Y-regression calibration lines. Calculate counting errors and detection limits. Return to no. 5 until terminator is reached.

It should be noted that various error calculations only allow for regression errors in the calibration and for statistical errors in counting. A major source of error is in calculating mass absorption coefficients (M.A.C.): there is no simple way of estimating errors resulting from background or M.A.C.-calculations. However, for routine purposes the results are quite adequate.

The program is strictly sequential, and it is only necessary to store count data from one sample at a time, plus the internal standardization, although in normal use all standards are stored to run as "unknowns". Thus, if necessary, the memory needed, may be written down to a very low level. No variable need to be two-dimensional. Table 3 gives an example for the trace element concentrations of the USGS-rock reference standards and Knippa Basalt obtained with the described method.

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