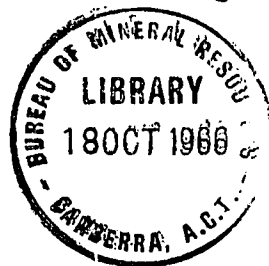


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TRACE ELEMENT ANALYSIS BY X-RAY SPECTROSCOPY WITH EMPHASIS ON THE
DETERMINATION OF BARIUM, LEAD, NICKEL AND ZINC.

by

J.M. Rhodes

The information contained in this report has been obtained by the Department of National Development, as part of the policy of the Commonwealth Government, to assist in the exploration and development of mineral resources. It may not be published in any form or used in a company prospectus without the permission in writing of the Director, Bureau of Mineral Resources, Geology and Geophysics.

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SUMMARY

A general method is given for the determination of trace elements in rocks, soils and minerals by X-ray spectroscopy, which can be applied to the determination of many elements.

Particular attention is paid to the calculation of correction factors to allow for inter-element effects, lack of linearity in the background, tube contamination, and matrix problems associated with the variation in bulk composition of the samples.

The general procedure is illustrated by specific methods for the determination of barium, lead, nickel, and zinc. The lower limits of detection for these elements are as follows: barium 20 ppm, lead 10 ppm, nickel 1 ppm, and zinc 1 ppm. The reproducibility is good; about 15-30% of the amount present at the detection limits of an element, falling to better than 2% of the amount present for concentration levels ten times that of the detection limit. The accuracy is satisfactory as shown in the text by comparison of the results obtained on several standard rocks with the recommended values and the values obtained by other analysts for these rocks.

Compared with other techniques these X-ray methods have a high standard of reproducibility and satisfactory accuracy, but they are relatively time consuming, and therefore are best applied to petrological problems, where it is required to distinguish small but systematic variations in trace element content in associated rock masses. They also provide, particularly in the case of lead and zinc, a supplementary method to other instrumental techniques.

INTRODUCTION

The purpose of this record is two-fold: to present a general method for the determination of trace elements in geological materials; and to describe and evaluate specific methods for the determination of barium, lead, nickel and zinc.

The methods described here are based on similar techniques used by Dr. K. Norrish and his co-workers in the Division of Soils, CSIRO, Adelaide. They have been adapted for use on the Phillips P.W. 1210 automatic X-ray spectrograph and for specific requirements of the BMR laboratory.

Throughout this record the following symbols will be used:

ppm	:	parts per million
cnts/sec	:	counts per second
P	=	peak intensity in counts per second
Bg	=	background intensity in counts per second
A	=	mass absorption coefficient
gm	=	gram

SAMPLE PREPARATION

The rock sample is crushed into small chips in a jaw crusher, and then crushed further to about 150-200 mesh in a Siebtechnik mill. The type of grinding vessel used depends on the elements to be determined. Tungsten carbide grinding vessels are unsuitable for the determination of tungsten, cobalt, and nickel. Probably the most satisfactory vessel for general purposes is one made of high carbon steel.

After grinding, 2 gms of samples are lightly pressed into pellets, backed by boric acid powder, and then compacted at a pressure of about 2 tons. The technique has been adequately described by Norrish and Hutton (1964). The pellets are quite sturdy and are suitable for the determination of most elements having characteristic K or L wavelengths of less than 3.0 angstroms and greater than 0.7 angstroms.

GENERAL METHOD

(a) Basic Procedure. The basic procedure for trace element determination is to count the X-radiation emitted by an element for an appropriate time interval at the peak position, and at two background positions on either side of the peak. A count length of 100 seconds for each position is adequate in most cases; when count rates are higher than about 1000 cnts/sec a shorter counting time of 40 seconds is sufficient.

During counting, both scintillation and flow counters are inoperative for about 3 microseconds following every pulse. This means that, in a given time, more X-rays are emitted from the sample than are recorded by the counter. This count loss or 'dead-time' becomes quite significant as the count rate increases. Thus, if 10^6 counts are recorded in 100 seconds the counter will have been inoperative for 3 of the 100 seconds and the count rate will be $\frac{10^6}{97} = 10,300$ cts/sec and not $\frac{10^6}{100} = 10,000$ cts/sec. Therefore in X-ray analysis the correct count rate for each position measured is obtained as follows:

$$\text{Correct count rate} = \frac{\text{No. of counts}}{\text{Time} - \text{No. of counts} \times 3 \times 10^{-6}} \dots\dots\dots(1)$$

The background is measured at equi-distant positions on either side of the peak, and the mean of the two values taken to obtain the average background. It is advisable to locate these positions as close to the peak as possible, preferably within 0.60° . Where two peaks are close together it may be impossible to obtain more than one position on which to measure the background.

The average background value is subtracted from the peak value to give the correct count rate for the peak position. This value is a function of the amount of the element present in the sample.

The theoretical precision of any result is given by:

$$\sigma \% = \frac{100}{\sqrt{N}} \dots\dots\dots(2)$$

where σ % is the coefficient of variation, which is the standard deviation expressed as a percentage of N, the total number of counts measured.

Thus if 10,000 counts are accumulated on a sample one can be reasonably certain that 66% of all repeat runs will be within 1% of each other. Similarly, the theoretical precision at the 99% confidence level is given by:

$$\sigma \% = \frac{258}{\sqrt{N}} \dots\dots\dots(3)$$

For this, one can be confident that 99% of all repeat runs will be within 1% of each other if the total number of counts accumulated exceeds 67,000.

The basic procedure outlined is usually complicated by tail-effects of the peak being measured, or of neighbouring peaks, lack of linearity in the background, and contamination from the X-ray tube. The methods for overcoming these complications are discussed below.

(b) Tail Effects. These are due to the tails of a peak increasing the background slightly at the positions where it is measured. The increase in the background intensity above the value that would be obtained if the peak were absent is proportional to the intensity of the interfering peak.

By taking a series of synthetic standards containing 0, 1000, 5000 and 10,000 ppm of the element to be determined in a matrix of quartz, it is possible to find a factor for reducing the background to its correct value. This factor is usually expressed as a percentage of the peak intensity, and is determined as follows:

- (1) Determine the number of cnts/sec for the two background positions on a powdered quartz blank, and find the average background.
- (2) Determine the number of cnts.sec for the background and peak positions on the 10,000 ppm standard. Find the average background for this standard.
- (3) Subtract the average background obtained on the quartz blank from the average background obtained on the 10,000 ppm standard. Multiply this result by 100 and divide by the peak intensity of the standard to obtain the background correction factor expressed as a percentage of the peak intensity.

$$\text{Bg correction factor } \% = \frac{100 (\text{Average Bg}_{\text{standard}} - \text{Average Bg}_{\text{blank}})}{\text{peak counts}} \dots\dots(4)$$

Repeat this process several times for each of the synthetic standards to obtain an average background correction factor. This is then applied to the unknown sample as follows:

$$\text{Corrected average Bg} = \text{Average Bg} - (\text{Bg correction factor} \left(\frac{\text{Peak counts}}{100} \right)) \dots\dots(5)$$

If the interfering tail-effects are caused by a neighbouring peak close to the peak of the element being determined, then this interfering peak must also be measured so that the correction factor can be determined.

(c) Non-Linear Background and Tube Contamination. In most cases the background is sloping, and curved to varying degrees; consequently the average background obtained will be either too high or too low, depending on whether the background is concave or convex upwards. A further complication is that the target of the X-ray tube may be contaminated with the element being analysed. This results in more counts being obtained for a sample than is correct.

These problems are overcome by comparing the intensity of the average background of a pure blank, usually quartz, with the intensity obtained for the peak position on the blank. The correction factor is found as follows:

$$\text{Correction factor} = \frac{\text{Blank peak intensity}}{\text{Blank Bg intensity}} \dots\dots\dots(6)$$

If no background corrections are required the two intensities should be equal and the correction factor will be unity.

The process is repeated several times, and the average correction factor found. The determination of this correction factor is most critical, especially when low concentrations of an element are to be determined.

After the average background has been corrected for tail-effects, it is multiplied by the correction factor found above (e.g. (6)) to give the correct background figure. This is then subtracted from the peak value to give the correct peak intensity.

An example of the determination of hypothetical correction factors is given below, together with an example of the application of these factors to an unknown sample. All figures are expressed in cts/sec after correcting for 'dead-time' losses.

	Bg 1	Bg2	Average Bg	Peak intensity
10,000 ppm } standard }	450	350	400	10,000
quartz } blank }	400	300	350	325

The increase in the average background for the 10,000 ppm standard above the average background for the quartz blank is 50 cts/sec.

$$\text{Background correction factor} = \frac{50 \times 100}{10,000} = 0.5\%$$

For the quartz blank the peak intensity is less than the average background.

$$\text{Correction factor} = \frac{325}{350} = 0.93.$$

Consider a hypothetical sample giving the following counts:

	Bg1	Bg2	Average Bg	Peak intensity
Hypothetical sample	411	309	360	1130

(1) Correction for tail-effects:

$$\text{Background} = 360 - \frac{1130}{100} \times 0.52 = 354.3$$

(2) Linearity correction:

$$\text{Background} = 354.3 \times 0.93 = 329.5$$

$$\begin{aligned} \text{True Peak intensity (P)} &= \text{Peak intensity} - \text{corrected background} \\ &= 1130 - 329.5 \\ &= 800.5 \text{ cts/sec.} \end{aligned}$$

(d) Mass Absorption Co-efficients and Element Determination. The correct peak intensity obtained for an element in a sample is proportional to the amount of the element present, and to the mass absorption coefficient of the sample for the characteristic radiation of that element.

$$\text{ppm} = \frac{A \cdot P}{K} \dots\dots\dots(7)$$

Where ppm is the concentration of the element; A is the mass absorption coefficient for that element; P is the corrected peak intensity in cts/sec; K is a constant which is empirically determined from known standards. From this equation it is evident that mass absorption coefficients must be allowed for in trace element analysis in order to obtain accurate results. If the major element composition of the sample is known, the mass absorption coefficient for a particular trace element in a sample can be calculated as follows:

$$A_{\text{sample}} = \frac{\% \text{SiO}_2 \times A_{\text{SiO}_2}}{100} + \frac{\% \text{Al}_2\text{O}_3 \times A_{\text{Al}_2\text{O}_3}}{100} + \frac{\% \text{Fe}_2\text{O}_3 \times A_{\text{Fe}_2\text{O}_3}}{100} + \text{etc.,} \dots\dots(8)$$

Where A_{SiO_2} , $A_{\text{Al}_2\text{O}_3}$ etc., are the theoretical mass absorption coefficients of SiO_2 , Al_2O_3 , and the other major oxides for the characteristic radiation of the element being determined. The mass absorption coefficient of an oxide is determined as follows:

For rubidium $K\alpha$ radiation of wavelength 0.927\AA the mass absorption coefficients of silicon and oxygen are 14.6 and 2.64 respectively. The atomic weights of these elements are 28.06 for silicon and 16.00 for oxygen and the molecular weight of SiO_2 is 60.06. Consequently the mass absorption coefficient of SiO_2 for rubidium $K\alpha$ radiation is:

$$A_{\text{SiO}_2} = \left(\frac{28.06 \times 14.6}{60.06} \right) + \left(\frac{32.00 \times 2.64}{60.06} \right) = 8.23$$

In most cases a full silicate analysis is not available, and the mass absorption coefficient must be determined in some other way. The most accurate method, giving results with a theoretical accuracy of $\pm 1 - 2\%$ of the amount present, is to measure the mass absorption coefficient directly on the sample being analysed (Norrish and Sweatman, 1963). This method is time consuming, but most useful when high accuracy is required. An alternative, more rapid, method makes use of the fact that the background intensity close to the peak is approximately inversely proportional to the mass absorption coefficient. Thus the higher the mass absorption coefficient, the lower the background intensity. This method is less accurate than direct measurement since other factors such as diffraction and peak interference will also affect the background intensity. However it is believed to be equivalent in accuracy to the calculation of mass absorption coefficients from silicate analysis, having a theoretical accuracy of about $\pm 5\%$ of the amount present.

When the reciprocal of the background intensity is substituted for the mass absorption coefficient in equation (7), we have:

$$\text{ppm} = \frac{P}{B_g} \times \frac{1}{K} \dots\dots\dots(10)$$

Where B_g is the corrected background in cts/sec.

Thus to obtain the concentration of the element in an unknown sample, the peak/background ratio for the sample is multiplied by a factor, the reciprocal of K . K is determined from the peak/background ratios obtained for synthetic standards containing 10,000, 5000, and 1000 ppm of the element be determined.

$$K = \frac{P}{B_g} \times \frac{1}{\text{ppm}} \dots\dots\dots(11)$$

These standards are each run several times and the average value of K is taken.

In some cases the calibration is non-linear above a certain concentration, and in this region the value for K will differ from the other standards. The departure from linearity can be checked by preparing other intermediate standards and plotting graphically the peak/background ratios of the standards against the concentration. If the concentration of an element in a sample is found to be greater than, or similar to, the limit of linearity for the elements, then it is necessary to dilute the sample with a blank reagent, preferably quartz, to a more convenient concentration level.

SPECIFIC EXAMPLES

The general procedures given in the proceeding section can be adopted for the determination of a large number of trace elements. Using similar techniques, but measuring mass absorption coefficients, Dr. Norrish and his co-workers at the CSIRO, Adelaide, have developed methods for the determination of about twenty trace elements in soils and rocks. These include, Ba, Cl, Co, Cr, Cu, Ga, La, Mn, Nd, Ni, Pb, Rb, Sr, Th, U, V, Y, Zn, Zr.

So far methods for the determination of four of these elements Ba, Pb, Ni, Zn have been developed in the BMR laboratory for the Phillips 1210 X-ray spectrograph. Operating conditions are summarised in Table 1, and the methods are described in detail below. It should be emphasised that the correction and calibration factors given below will not apply once the spectrograph has been re-aligned or adjusted in any way. It is advisable to determine new factors prior to commencing a major analytical programme.

(a) Barium

The Barium $L\beta_2$ line is used for the determination barium, since titanium interferes with $L\beta_1$ line. The background is sloping and strongly curved due to the close proximity of the $K\beta$ line of the chromium tube. The pelleted sample is counted for 100 seconds on the Ba $L\beta_2$ position, and for the same time length on two background positions one degree on either side of the peak. At these positions 'tail-effects' are fairly large, and 4.42% of the peak value has to be subtracted from the average background to correct for them. Because the background is strongly curved the average background so obtained is too high and has to be reduced to the correct value by multiplying by a factor of 0.786. The corrected background is subtracted from the peak value to give the correct count rate for barium. This is then divided by the background to give the peak/background ratio, which is directly proportional to the concentration of barium in the sample. The peak/background ratio is multiplied by a factor ($\frac{1}{K} = 871.99$) to obtain the number of ppm barium in the sample.

TABLE 1

OPERATING CONDITIONS FOR TRACE ELEMENTS DETERMINATION

ELEMENT	BARIUM	LEAD	NICKEL	ZINC
Line	$L\beta_2$	$L\beta_1$	$K\alpha$	$K\alpha$
Crystal	LiF	LiF	LiF	LiF
Angle	73.50°	28.26°	48.70°	41.82°
Background	74.50° 72.50°	30.01 -	47.10° (50.30°)	41.32° 42.32°
Collimator	Coarse	Fine	Fine	Fine
Vacuum	Yes	Yes	Yes	Yes
Tube	Cr	Mo	W	W
Kv	60	80	45	45
Ma	26	25	43	43
Counter	Flow	Scintillation	Flow	Scintillation
E.H.T.	630	320	630	310
Pulse Height Analysis	Manual	Automatic	Manual	Manual
Lower Level	270	475	240	90
Window	200 x 1	500 x Ext	220 x 1	250 x 1
Cnts/sec 1000 ppm standard	1160	7700	3600	1600

The calibration is linear up to 1.0% barium and the limit of detection is of the order of 20 ppm. Reproducibility is good, being about $\pm 1-2\%$ of the amount present. The mean deviation for 14 samples ranging from 200-17000 ppm Ba was found to be 0.5% of the amount present.

Results obtained on a number of standard rocks are given in Table 2, together with the recommended values, results obtained by other analysts, and the range of results for the standards quoted in the literature. Tests on synthetic standards containing different amounts of barium in different matrices suggest that the method is accurate to within $\pm 5\%$ of the amount present.

(b) Lead

The lead $L\beta_1$ line is used for the determination of lead, since the arsenic $K\alpha$ line interferes with the lead $L\beta_1$ line. The pelleted sample is counted for 100 seconds on the peak position at 28.26° , and on

a background position at 30.01° . Only one background position can be measured because of the close proximity of the thorium $L\alpha$, and rubidium $K\alpha$ peaks on the low angle side of the peak. The background is measured at some distance from the peak to avoid 'tail-effect' corrections, and because of small $L\beta$ lead lines clustering around the base of the $L\beta$ peak. In samples containing abundant arsenic, 'tail-effects' from the nearby arsenic $K\alpha$ line may increase the background slightly. Arsenic is rare in most rocks (0-7 ppm), but if the sample is mineralised, arsenic may be present and the method would require revision.

The background is straight, but sloping, and tail-effects are absent; consequently the average background is multiplied by a factor of 1.1921 to obtain the correct value. The corrected background is subtracted from the peak value to obtain the correct count rate for lead. This is then divided by the corrected background to obtain the peak/background ratio, which is then multiplied by a factor ($\frac{1}{K} = 490.72$) to obtain the ppm lead in the sample.

The calibration is linear up to 0.5% Pb. Samples containing more lead than this must be appropriately diluted with quartz prior to analysis. The limit of detection is of the order of 10 ppm. Reproducibility varies with concentration, with a range of about $\pm 15\%$ of the amount present for 10 ppm, about $\pm 2\%$ of the amount present for 100 ppm, and less than $\pm 1.0\%$ of the amount present for 1000 ppm. Results obtained on several standard rocks are given in Table 2, together with the results of other analysts for comparison.

(c) Nickel

The pelleted sample is counted for 100 seconds on the nickel $K\alpha$ peak at 48.70° , and on a background position at 47.10° . A second background position can be measured at 50.30° providing the sample is low in iron. If the iron content is high, the 'tail' of the iron $K\beta$ line increases the background intensity giving erroneous results. A remedy for this is to measure the background closer to the nickel peak, at 48.00° and 49.46° . In this case the nickel 'tail-effects' are larger and it is impossible to analysis samples crushed in a tungsten carbide mill, since the 49.46° position lies close to the tungsten LL line.* The background is fairly flat, but is complicated by the presence

* Since this work was completed, it has become apparent that the scintillation counter with a long collimator could be used for nickel. In this case the peaks would be sufficiently separated to cut out the interference of the iron $K\beta$ line.

of a small 'hump' due to nickel contamination of the tube and the presence of the tungsten LL line. The tube contamination is reduced to a certain extent by fitting a lead shield, with an hole of 8mm diameter aperture, over the tube window.

About 0.14% of the peak value is subtracted from the background value to allow for 'tail-effects', and the modified background is multiplied by a factor of 1.4349 to obtain the corrected background position. This is subtracted from the peak value to obtain the correct count rate for nickel. This is then divided by the corrected background to obtain the peak/background ratio, which in turn is multiplied by a factor ($\frac{1}{K} = 69.108$) to obtain the number of ppm in the sample.

The calibration is linear up to 1.0% Ni and the detection limit is about 1 ppm. Reproducibility varies with composition, with a range of $\pm 30\%$ of the amount present for 1 ppm, $\pm 3\%$ of the amount present for 10 ppm, and less than $\pm 2\%$ of the amount present for 100 ppm and over. Results obtained on several standard rocks are given in Table 2, together with the results of other analysts for comparison.

(d) Zinc

The pelleted sample is measured for 100 seconds on the zinc K_{α} line at 41.83° , and on two background positions at 41.33° and 42.33° . The background is flat and fairly smooth, and 'tail-effects' are slight. The only line likely to interfere is the second order zirconium K_{β} line. This is successfully removed by pulse height analysis (settings given in Table 1). The average background is reduced by about 0.23% of the peak value, and then multiplied by a factor of 1.0694 to obtain the corrected background. This is subtracted from the peak value, and the zinc counts are then divided by the background to give the peak/background ratio. This is multiplied by a factor ($\frac{1}{K} = 46.744$) to obtain the number of ppm zinc in the sample.

The calibration is linear up to 1.0% Zn, and the detection limit is about 1 ppm. Reproducibility for samples containing more than 30 ppm. Zn is of the order of $\pm 2\%$ of the amount present.

CONCLUSIONS

The general procedures given here, illustrated by application to the determination of barium, lead, nickel, and zinc, can be applied to the determination of many elements in rocks and soils.

The methods described for the determination of these four elements can be used in the following concentration ranges:

barium	-	20 ppm to 1.0%
lead	-	10 ppm to 0.5%
nickel	-	1 ppm to 1.0%
zinc	-	1 ppm to 1.0%

Samples containing greater amounts of these elements should be diluted with quartz to the appropriate concentration range prior to analysis. In this way it is possible to analyse for any concentration level above the detection limit for a particular element.

The reproducibility of the methods described varies with the concentration of the element in the sample, but is of the order of $\pm 2\%$ of the amount present in most cases. This is good in comparison with other methods of element analysis.

It is more difficult to assess the overall accuracy of the methods, since agreement between analysts on the trace element content of standards is not good (see range of published values given in Table 2), particularly for barium, lead, and zinc - three of the elements considered here. Where there is some agreement, as in the case of nickel in G1, T1, S1; zinc in G1 and W1; and barium in S1, the X-ray results are very close to the recommended values.

The time taken to analyse a sample in duplicate is about twelve minutes, and providing the samples are prepared previously, about thirty samples can be analysed in a day.

The X-ray spectrographic methods described are relatively time-consuming compared with other methods, but are highly reproducible with reasonable accuracy. Thus they are ideally suited to petrological problems, where it is required to distinguish small but systematic variations in trace element content in a relatively small number of samples. X-ray determinations also provide a supplementary method to other, more productive, instruments for checking results on critical samples. This is particularly important in the case of lead and zinc, since these two elements can only be determined in a restricted range by other methods.

RECOMMENDATIONS

1. The methods described can easily be adapted for automatic operation, each peak and background position requiring one of the instrument's 15 available channels.

If this procedure were to be adopted, it would be convenient to analyse a suite of neighbouring elements on the same sample. This could be done by measuring alternate peak and background positions and then applying empirically determined inter-element correction factors.

Two suitable series are:

<u>Tungsten tube</u>		<u>Molybdenum tube</u>	
Zn	K_{∞}	Zr	K_{∞}
Cu	K_{∞}	Y	K_{∞}
Ni	K_{∞}	Sr	K_{∞}
Cr	K_{∞}	U	L_{∞}
		Rb	K_{∞}
		Th	L_{∞}
		Pb	L_{β}

2. A gold tube would improve the determination of nickel, zinc, and copper, since the target of the tungsten tube contains these elements as impurities.

3. A recently produced Lithium Fluoride crystal, cut parallel to the (220) reflection plane, with a d-spacing of about 2.848 Å, would give greater resolution, thus reducing inter-element interference and removing the need for 'tail effect' calculations.

4. It would be possible to use the 1540 manual X-ray spectrograph for the direct determination of mass absorption coefficients, providing the scintillation counter were connected to the counting circuitry of the 1210 automatic X-ray spectrograph. In this way trace elements could be determined with even greater accuracy.

REFERENCES

- BALL, T.K., and FILBY, R.H., 1965 - The zinc contents of some geochemical standards by neutron activation and X-ray fluorescence analysis. Geochim. et Cosmochim. Acta, 18, 737-740.
- FILBY, R.H., 1964 - The content of several trace elements in some standard rock samples. Geochim. et Cosmochim. Acta, 28, 265-269.
- FLEISCHER, M., 1965 - Summary of new data on rock samples G-1 and W-1, 1962-1965. Geochim. et Cosmochim. Acta, 29, 1263-1283.
- KAYE, M.J., 1962 - X-ray fluorescent determination of several trace elements in some standard geochemical samples. Geochim. et Cosmochim. Acta, 29, 139-143.
- NORRISH, K., and HUTTON, J.T., 1964 - Preparation of samples for analysis by X-ray fluorescent spectrography CSIRO Div. Rep., 3/64.
- NORRISH, K., and SWEATMEN, T.R., 1963 - The application of X-ray fluorescent to the analysis of natural materials. Australian Academy of Science, paper presented to the 4th Australia Spectroscopy Conference, Canberra.
- TAYLOR, S.R., and KLOBE, P., 1964 - Geochemical standards. Geochim. et Cosmochim. Acta, 28, 447-454.
- THOMAS, W.K.L., and KEMPE D.R.C., 1963 - Standard geochemical sample T-1 supplement No.1. Government Printer, Dar Es Salaam.
- WEBBER, G.R., 1965 - Second report on analytical data for C.A.A.S. syenite and sulphide standards. Geochim. et Cosmochim. Acta, 29, 229-248.

TABLE 2

RESULTS OBTAINED ON STANDARD SAMPLES IN THE BMR LABORATORY
BY X-RAY SPECTROSCOPY COMPARED WITH THOSE OF OTHER
ANALYSTS

Standard	Ba X-ray	Ba other analysts	Pb X-ray	Pb other analysts	Ni X-ray	Ni other analysts	Zn X-ray	Zn other analysts				
G1	1025	938-1400 1220 1030 1250	(a) (b) (e) (h)	56	22-90 49 38 50 52 40	(a) (b) (e) (h) (i) (k)	3	1-14 1-2 1.5 <3	(a) (b) (e) (k)	47	17-70 15 47 34 45.7 50	(a) (b) (e) (f) (g) (k)
W1	187	130-257 180 187 170	(a) (b) (e) (h)	Not done			65	60-85 78 67 64 75 63 70	(a) (b) (e) (f) (h) (i) (k)	86	66-110 82 82 77 82.8 80	(a) (b) (e) (f) (g) (k)
S1	335	63-400 300 360 330	(a) (c) (e) (h)	404	400-870 495 427 400 365	(a) (c) (e) (h) (k)	36	20-82 37 32 40 55	(a) (c) (e) (h) (k)	220	70-350 193 231 259 230	(a) (c) (e) (g) (k)
T1	600	560-800 680 588	(a) (d) (e)	42	14-50 37 34	(a) (d) (e)	12	5-32 13 11 12	(a) (d) (e) (f)	197	160-227 190 170 198	(a) (d) (e) (f)
GR.	1120	950-2450 1005	(a) (e)	38	34 n.d.	(e) (k)	42	35-80 43 46	(a) (e) (k)	61	64 73	(e) (k)
N.B.S. 91 opal glass	61	70	(h)	856 or 941	900	(j)	2	<10 n.d.	(f) (h)	742	708 640	(f) (j)
N.B.S. 99 soda feldspar	120	115	(h)	80	62	(i)	9	8	(h)	18	14.6	(g)
G2	1860	No information		36	No information		3	No information		98	No information	
G.S.P. 1	1280	" "		71	" "		7	" "		120	" "	
A.G.V. 1	1240	" "		42	" "		16	" "		94	" "	
B.C.R. 1	765	" "		23	" "		10	" "		119	" "	
D.T.S. 1	40	" "		13	" "		3550	" "		50	" "	
P.C.C. 1	45	" "		14	" "		3580	" "		52	" "	
B.M.R. Mt. Isa A	Not done	" "		5690	" "		210	" "		27,500	" "	
B.M.R. Mt. Isa B	Not done	" "		11,800	" "		34	" "		99,000	" "	
B.M.R. A55 Low	Not done	" "		41	" "		112	" "		39	" "	
B.M.R. A55 High	Not done	" "		8740	8000	(k)	535	400	(k)	502	460	(k)
B.M.R. B 113 Cullen Granite	Not done	" "		43	No information		6	No information		26	No information	
B.M.R. M.A.H. 2 Carbonate	Not done	" "		12	" "		7	" "		31	" "	
B.M.R. Shale base	Not done	" "		11	" "		15	" "		35	" "	

n.d. not detected

- (a) range of published values
 (b) recommended values for G1 and W1 (Fleischer 1965)
 (c) recommended values for S1 (Webber 1964)
 (d) recommended values for T1 (Thomas and Kempe 1963)
 (e) unpublished X-ray results obtained by Dr. K. Norrish,
 CSIRO

- (f) X-ray results (Kaye, 1965)
 (g) X-ray and neutron activation results (Bail and
 Filby, 1965)
 (h) optical spectrographic results (Taylor and
 Kolbe, 1964)
 (i) optical spectrograph results (Filby 1964)
 (j) chemical value from N.B.S. circular 552 (1954)
 (k) unpublished atomic absorption spectroscopy
 results obtained by S. Baker in the BMR
 laboratory