

# Determination of Major and Trace Elements in Rocks Employing Optical Emission Spectroscopy and X-ray Fluorescence

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An optical emission spectrometric method for major element determination and an X-ray fluorescence method for the determination of trace elements are described.

The first method combines a tape machine with a direct reader and uses samples and synthetic standards which have been 'isoformed' by dilution (1 to 12) with Li tetraborate containing Sr tetraborate and Co oxide and fusion. The major element results obtained by this nearly matrix independent method are used in the correction for matrix effects in the trace element procedure where the samples and synthetic standards are diluted by mixing with Li tetraborate (2 to 1) before fusion. The synthetic standards are made from pure chemicals and processed in the same manner as the samples. Matrix effects are corrected for by means of absorption coefficients. Methods of correction based on the use of scattered background or incoherently scattered tube lines (Compton scatter) as intensity reference are also investigated and discussed.

The major elements determined are Si, Al, Fe, Ti, Mg, Ca, Na, K, and Mn. At present the trace element programme includes Zr, Y, Sr, Rb, Zn, Cu, Ni, Cr, and Ba; the programme can easily be extended to include other elements.

Results obtained for major and trace element abundances on some international reference samples and for trace elements in synthetic samples having major element composition quite different from that of the standards are presented.

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## 1. Introduction

From the 1920's and onwards the use of spectrochemical methods for the analysis of geologic material was for a long time concerned with, and confined to, determination of minor or trace constituents. Goldschmidt & Thomassen (1924) used X-ray spectrography for the determination of rare earths and other minor constituents of minerals, and later Goldschmidt and co-workers (Goldschmidt 1930 a, b; Goldschmidt & Peters 1931 a, b, 1932 a, b, c, d, 1933 a, b, c, 1934; Goldschmidt et al. 1933, 1934; Minami 1935; Strock 1936; Noll 1934; Engelhardt 1936) applied both X-ray and optical emission spectrography in the study of the distribution of many minor elements in the earth's crust and in meteorites. By using cathode layer, and very pure carbon electrodes purified by a method very similar to that later described by Gatterer (1941), Goldschmidt was able to detect very low concentrations of many elements by D.C. arc spectrography.

The determination of major constituents by spectrochemical methods was

regarded as less interesting because the high degree of accuracy generally required for such analyses was difficult to attain. Spectrochemical carbon arc methods for determining the major constituents of geologic material were, however, described by Jaycox (1947) and Kvalheim (1947) and further discussed and modified by Ahrens (1954).

The development of direct readers (spectrometers) for industrial metal analysis in the 1940's (Saunderson et al. 1945) was later followed by the introduction of such instruments in slag and rock analysis. Kvalheim & Vestre (1959) applied the ARL Production Control Quantometer to a carbon arc method for determining the major constituents of rocks, and Danielsson et al. (1959) developed the Tape machine for spark analysis of powdered samples of rocks etc., and combined it with a direct reader. This combination has been extensively used by C.R.P.G., Nancy (Govindaraju 1960, 1963, 1965; Roubault et al. 1960, 1964) especially for the analysis of granites, and by Danielsson (1967) for general use in geology and geochemistry. Scott et al. (1969) used the cathode layer carbon arc method in combination with a direct reader for the determination of low concentrations of different elements in soils, etc. Other examples of the use of direct readers in optical spectrochemical analysis of geologic material are given in a paper by Mitchell (1969).

A new era in X-ray analysis began in the late 1940's, mainly due to the work of Friedman & Birks (see Jenkins 1974) and the introduction of Geiger counters. The result was X-ray fluorescence spectrometers, frequently used nowadays for both major and trace element determinations. Because of the instrumental precision of present day direct readers (optical spectrometers and X-ray fluorescence spectrometers) the analyst can concentrate his attention on sample preparation, the selection of suitable spectral lines, the control of the processes occurring in the source of element-characteristic frequency emission (arc, spark, fluorescing sample), and mathematical corrections, in order to achieve maximum accuracy.

Danielsson et al. (1959) used the word 'isoformation' for sample preparations such as dilution and/or fusion which aim at the elimination or reduction of 'matrix effects' (inter-element effects). Unsatisfactory analytical results due to inter-element effects can also be corrected by the use of more or less complicated calculations (see e.g. Birks 1971). Access to a computer for such corrections is a necessity.

The analytical methods, systems or routines to be chosen or developed in different laboratories depend on the equipment available and the analytical tasks in question. At the Geological Survey of Norway the direct readers available are an ARL Production Control Quantometer combined with a Tape machine, and a Philips X-ray fluorescence spectrometer. The analytical problems include the determination of major, minor and trace constituents of minerals, rocks and similar materials, as well as ores. Accuracy is generally more important than speed, but a reasonable analytical speed is also important.

These requirements have led to a routine which is a combination of a quantometer method, in use for many years, with an X-ray fluorescence (XRF)



method. Since the major constituents are still easily determinable after considerable dilution, the samples and standards are diluted and fused with a borate flux and the major elements thereafter determined with the combined Tape machine/Quantometer. The trace constituents are determined by X-ray fluorescence. To avoid too much loss of radiation intensity the samples are, in this case, fused with only a small amount of Li tetraborate. Because of the slight dilution, matrix effects from the major elements can be significant. However, the contents of major constituents are known from the quantometric analysis, and accordingly the matrix effects can be corrected for by using calculations which take into account the influence of the major elements according to their concentrations and absorption coefficients.

## 2. Major constituents

The constituents  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{MnO}$  are determined in a variety of geologic material with the ARL Quantometer combined with a tape machine. The method is very similar to the one used by Danielsson et al. (1961) for slags.  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{TiO}_2$  and  $\text{K}_2\text{O}$  are sometimes determined by X-ray fluorescence, using the same material as prepared for the quantometric determinations, i.e. 1 part of the sample is diluted with 12 parts of borate flux and fused. By this 'isofomation' matrix effects become negligible.

### 2.1 PREPARATION OF STANDARDS AND SAMPLES

One advantage of preparation by dilution and fusion is that the selection of suitable and reliable standards offers no real problem. Synthetic standards covering the concentration ranges of interest can be readily made from pure chemicals and treated in the same way as the samples.

The synthetic standards referred to in this paper are mixtures of 'specpure' oxides or carbonates. Carbonates are used for Na, K and Ca, oxides for Al, Fe, Mg, Ti and Mn. A powder of high purity natural quartz which has been leached with acids is used for Si. These substances are brought to stoichiometric composition by drying or ignition before being mixed. The hygroscopic oxides  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  are ignited for some hours at  $1100^\circ\text{C}$  to render them sufficiently stable.

The dilution and fusion procedure is as follows:

0.25 g of finely pulverized sample or standard is mixed with 3 g of borate flux containing 60% lithium tetraborate, 30% strontium tetraborate and 10% cobalt oxide. The mixture is transferred quantitatively to a non-wettable PtAu crucible, which is placed in a quartz dish and left for 5 minutes in a furnace at  $1000^\circ\text{C}$ . Usually 4 or more samples are fused simultaneously. After 5 minutes the crucibles are removed from the furnace and left to cool. The melt is loosened from the crucible and ground for one minute in a steel swing mill together with 0.5 g of Standard grade Whatman cellulose powder. The substance is now ready for the Tape machine, or X-ray analysis.

In certain cases agate or tungsten carbide swing mills are used to prevent contamination of the sample. In addition graphite crucibles can be substituted for platinum crucibles. A furnace for continuous fusion performance instead of batch operation, using graphite crucibles, has been described by Roubault et al. (1964) and Govindaraju (1965).

Sulphides tend to form a separate insoluble phase in the borate flux. Samples containing sulphur are therefore ignited, the ignition loss is recorded, and fusion is thereafter carried out in the normal way.

Carbon present in the sample as amorphous carbon, graphite or some other reducing compound may cause problems when heated in a platinum crucible, not only because of the well-known risk of platinum carbide formation, but also because of the possibility of reduction to the elemental form of elements which can readily alloy with platinum and thus escape determination. The alloying process seems to be reversible for many elements. These elements may be extracted again by other samples and thus cause erroneous analytical results.

This kind of loss or gain is in most cases negligible, but alternate heating and hydrochloric acid treatment of crucibles used for borate fusion, followed by analysis of the elements thus extracted, showed that the alloying possibility is real and should be considered when very accurate analyses are required.

## 2.2 QUANTOMETER ANALYSES

### 2.2.1 *Line programme*

Since the permanently installed line programme of the quantometer was intended for both arc and spark work, and with some emphasis on arc methods, our choice of suitable lines for spark work is limited to some extent. For tape machine determination of the major elements in rocks the following lines were chosen:

#### Reference lines:

Co	3518 Å
Li	4972 Å
Sr	4876 Å

#### Analysis lines:

Si	2881 × 2 Å	Mg	2795 Å	
Si	2514 Å	Ca	3179 Å	
Al	3944 Å	Ca	4454 Å	
Al	3092 Å	Na	3302 × 2 Å	
Fe	4404 Å	K	4044 Å	
Fe	2966 Å	K	7664 Å	(Interference filter and optical fibre)
Ti	3242 × 2 Å	Mn	2801 × 2 Å	
Mg	2779 × 2 Å	Mn	2593 Å	

The choice of reference elements and lines has been based on experience and statistical studies. Li 4972 is used as the reference line for Na 3302, K 4404

and K 7664, Sr 4876 for Ca 4454, and Co 3518 for Ca 3179 and the lines of the remaining elements. The two lines for each of the elements Si, Al, Fe, Ca and Mg usually give very similar, often identical, results. For K and Mn the lines K 7664 and Mn 2593 were found to be more reliable than K 4044 and Mn 2801.

### 2.2.2 Instrumentation

The equipment used for the quantitative determinations at NGU is:

ARL 7200 S Production Control Quantometer  
with digital voltmeter and printer.  
Primary slit: 38 microns.  
Secondary slits: 75 microns.

ARL Tape machine, somewhat modified.  
Tape: Edaplast spectrotape.  
Tape speed: 20 cm/second.

Source: ARL No. 4600.

Conditions: 15000 V, sparks per second.

Automatic termination by the Co-integration  
(i.e. Co-integrator reads 50 mV). The corresponding  
exposure time is approximately 25 seconds.

### 2.2.3 Calculations

Because of the extensive isoformation by dilution and fusion, the calculation or reading of concentrations from the intensity data recorded by the printer is a relatively simple process since matrix effects need not be considered. However, the data handling involved — conversion of the intensity data to intensity ratios, plotting and construction of a number of analytical calibration curves, and the reading of the percentages — is a time-consuming process which, with considerable advantage, can be left to a computer. At the Geological Survey this is done by basing the computer programme on an analytical evaluation function according to a simple equation of the second order. The intensity data of standards and samples to be analysed is punched on cards and fed to the computer.

An additional advantage of a computer is that the analytical results can be produced on punched cards. These punched cards serve two purposes. They are used for the mathematical matrix corrections in the determinations of the trace constituents of the same sample (see later), and they are also convenient for various statistical studies.

### 2.2.4 Precision and accuracy

The precision measured under favourable conditions during a short period of time is often better than the precision experienced when the analytical results



Table 1. Precision of the quantometer/tape machine method obtained on 10 fusions of one sample (upper part of Table). Lower part shows precision of the instrument obtained on 10 determinations of one fused sample

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MnO
Mean (10)	47.50	13.68	16.61	1.94	7.23	7.99	2.41	2.31	0.264
s	0.39	0.12	0.13	0.028	0.058	0.042	0.048	0.077	0.0052
s <sub>r</sub> (%)	0.8	0.9	0.8	1.4	0.8	0.5	2.0	3.3	2.0
Mean (10)	47.43	13.74	16.73	1.98	7.30	8.15	2.44	2.34	0.263
s	0.66	0.05	0.13	0.027	0.11	0.020	0.049	0.073	0.0048
s <sub>r</sub> (%)	1.4	0.4	0.8	1.4	1.5	0.2	2.0	3.1	1.8

Table 2. Results obtained with the quantometer/tape machine method on USGS reference samples

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	
G-2	68.5	14.7	2.4	0.46	0.65	1.80	4.00	4.35	0.02	NGU
	69.11	15.40	2.65	0.50	0.76	1.94	4.07	4.51	0.03	Recom. val.
GSP-1	67.6	15.0	4.2	0.64	1.05	1.95	2.75	5.30	0.03	NGU
	67.38	15.25	4.33	0.66	0.96	2.02	2.80	5.53	0.04	Recom. val.
AGV-1	59.0	17.6	6.8	1.06	1.40	4.80	4.20	3.00	0.10	NGU
	59.00	17.25	6.76	1.04	1.53	4.90	4.26	2.89	0.10	Recom. val.
BCR-1	53.0	13.9	14.0	2.27	3.50	6.75	3.35	1.75	0.20	NGU
	54.50	13.61	13.40	2.20	3.46	6.92	3.27	1.70	0.18	Recom. val.

Table 3. Precision for the quantometer/tape machine method obtained under routine work conditions

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
Mean (10)	48.8	13.7	5.39	0.69	6.40	10.0	1.14	2.65
s	0.70	0.27	0.23	0.038	0.25	0.17	0.031	0.18
s <sub>r</sub> (%)	1.4	2.0	4.3	5.5	3.9	1.7	2.7	6.8

Table 4. Precision and accuracy for the quantometer/tape machine method obtained on Argillaceous Limestone 1A/1b

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
Mean (30)	5.20	4.12	1.58	0.164	2.16	41.16	0.33	0.77
s	0.13	0.14	0.19	0.033	0.11	0.43	0.041	0.12
s <sub>r</sub> (%)	2.5	3.4	12.0	20.6	5.1	1.0	12.4	15.6
Recom. val.	4.92	4.16	1.63	0.16	2.19	41.32	0.39	0.71

are collected from routine work over a long period of time. This observation is not uncommon in quantometry.

The precision to be expected under favourable conditions for the quantometric method of this paper is demonstrated in Table 1. The upper part of the Table shows the precision when 10 fusions of the same rock sample are

analysed by the quantometer within about a quarter of an hour. This precision may be regarded as the optimum precision of the quantometer/tape machine method. The lower part of the Table shows the corresponding precision for 10 runs of one fused sample which give the precision of the instrument. From the Table it can be concluded that under favourable conditions the spread of the results is due mainly to instrumental fluctuations. The accuracy obtainable under favourable conditions is shown in Table 2. The results for the four USGS standard samples were obtained from single runs of samples and synthetic standards, all within a short period of time.

Precision and accuracy of this quality cannot be expected for normal routines. For such routines Tables 3 and 4 must be regarded as more realistic. These Tables are based on the analysis of 3 check samples which were intermingled in an analytical routine programme run for a couple of months on a large number of samples ranging in composition from nearly pure limestone to silicate rock.

One silicate rock sample and the NBS Argillaceous limestone standards 1A and 1b were chosen as check samples. The 1b sample was used for  $\text{SiO}_2$  only, and 1A for the other components. The check samples (sometimes only one) were analysed about once a day as part of the routine programme. Since the NBS samples are also well known standards, Table 4 gives not only the precision but also a measure of the accuracy obtained.

### 2.3 DETERMINATION of Fe, Ti, Ca AND K BY X-RAY FLUORESCENCE

The powder prepared for the tape machine is also well suited for X-ray determination of the major elements Fe, Ti, Ca and K. The dilution with borate flux reduces the matrix effect considerably. Acceptable results can therefore be obtained even without the use of reference elements. Since Co is added to the flux this element can readily be used as reference for the Fe determination even though the concentration of Co is high compared with that of iron.

Analytical calibration curves were based on the same synthetic standards as used for the quantometer procedure, and the net intensities of the  $\text{K}\alpha$  lines were measured. The results obtained on G-2, GSP-1, AGV-1 and BCR-1 are given in Table 5. All determinations are made with a W tube. A LIF (200) crystal was used for Fe and Ti, and an EDT crystal for Ca and K. For Fe a scintillation counter was used and a flow counter for the other elements.

### 3. Trace constituents

In the procedure described here trace constituents are determined by X-ray fluorescence analysis of samples fused with a relatively small amount of borate flux. Because of the slight dilution, matrix effects are present and must be corrected for. This correction makes use of absorption coefficients and the analytical results from the quantometric determination of the major elements.

The trace elements dealt with in this paper are Zr, Y, Sr, Rb, Zn, Cu, Ni,

Table 5. Results obtained by X-ray fluorescence analyses (NGU) of powders prepared for the tape machine. Recommended values by Flanagan (1973)

Sample	Fe <sub>2</sub> O <sub>3</sub> %	TiO <sub>2</sub> %	CaO %	K <sub>2</sub> O %	
Granite	2.77	0.47	1.84	4.40	NGU
USGS G-2	2.65	0.50	1.94	4.51	Recom. val.
Granodiorite	4.35	0.65	2.11	5.40	NGU
USGS GSP-1	4.33	0.66	2.02	5.53	Recom. val.
Andesite	6.80	1.06	5.08	2.91	NGU
USGS AGV-1	6.76	1.04	4.90	2.89	Recom. val.
Basalt	13.15	2.24	7.04	1.80	NGU
USGS BCR-1	13.40	2.20	6.92	1.70	Recom. val.

Cr and Ba. These were the elements included in an analytical routine procedure originally worked out for the study of basic rocks. Extension of the analytical programme, however, causes no great problems and, as will be seen later, the method is also readily applicable to samples with compositions differing very much from that of basic rocks.

### 3.1 PREPARATION OF STANDARDS

The reasons for the choice of synthetic standards rather than natural standards for the major elements are equally valid for the trace elements. The standards were therefore made up from specpure chemicals, the purity of which was checked by optical emission spectrography and XRF. Since the original analytical task was the study of basic rocks the composition of the synthetic base mixture was chosen to approximate that of a greenstone (metabasalt).

The base mixture was made by mixing 55% quartz, 15% Al<sub>2</sub>O<sub>3</sub>, 10% Fe<sub>2</sub>O<sub>3</sub>, 10% CaCO<sub>3</sub>, 5% MgO and 5% Na<sub>2</sub>CO<sub>3</sub>. By admixture of 1% of each of the minor elements (in form of oxides) to this base and successive dilution, a synthetic standard series ranging down to 10 ppm was prepared. These standards are referred to hereafter as 'greenstone standards'.

### 3.2 PREPARATION OF TEST SAMPLES

The analytical curves or functions used in this work are based on intensity measurements obtained for the greenstone standards. In order to test the effectiveness of the matrix correction method used for matrices differing more or less from the greenstone matrix, 8 synthetic test samples were prepared. These were samples containing 1000 ppm and 100 ppm of each of the trace elements in the following very different matrices:

a) a synthetic granite matrix; b) a quartz matrix; c) an Al<sub>2</sub>O<sub>3</sub> matrix; and d) a Fe<sub>2</sub>O<sub>3</sub> matrix.

The granite matrix had the following composition: 75% quartz, 13% Al<sub>2</sub>O<sub>3</sub>, 2% Fe<sub>2</sub>O<sub>3</sub>, 5% K<sub>2</sub>CO<sub>3</sub> and 5% Na<sub>2</sub>CO<sub>3</sub>.

The 8 test samples are referred to as Gr 1000 and Gr 100, Si 1000 and Si 100, Al 1000 and Al 100, Fe 1000 and Fe 100.



## 3.3 FUSION OF STANDARDS AND SAMPLES

In order not to lose too much of the X-ray intensity the fusion process uses only a minimum amount of flux, the main purpose being to obtain a degree of isoformation of standards and samples by decomposition of the mineral constituents.

The fusion procedure chosen is as follows:

4 g of finely powdered sample or standard is mixed with 2 g  $\text{Li}_2\text{B}_4\text{O}_7$  for 1 minute in a Spex mixer. The mixture is transferred to a non-wettable PtAu crucible and heated to melting over a burner. The crucible is then left in a furnace at  $1000^\circ\text{C}$  for 5 minutes. If the melt does not loosen easily from the crucible after cooling, the crucible is reheated and quenched in cold water. After cooling the melt is ground in an agate swing mill for 1 minute. The resultant powder is placed in sample cups and after manual pressing is ready for analysis. This method of fusion, by which most rock samples are effectively decomposed, is rapid and well suited for routine analyses of the minor constituents. The test samples of quartz,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  seemed, however, not to be completely decomposed.

## 3.4 X-RAY LINE PROGRAMME

The X-ray analysis is carried out without the use of reference elements. The lines used and their interference and background characteristics are listed below.

	Interferences	Background
Zr $\text{K}\alpha$	Sr $\text{K}\beta_1$	Sloping
Y »	Rb $\text{K}\beta_1$	»
Sr »	none	»
Rb »	»	»
Zn »	»	Flat
Cu »	Tube line (W $\text{L}\alpha_1 - 1$ )	»
	Tube line (contamination)	
Ni »	Tube line (contamination)	»
	Rb $\text{K}\beta_1$ 2nd order	
	Y $\text{K}\alpha$ 2nd order	
Cr »	Tube line (contamination)	»
	V $\text{K}\beta_1$	
Ba $\text{L}\beta_2$	Tube line (Cr $\text{K}\alpha - 1$ )	»

$\text{K}\alpha$  lines are used for all elements except Ba. Ba $\text{K}\alpha$  cannot be used because of its short wavelength, and the  $\text{L}\alpha_1$ -line is disturbed by Ti $\text{K}\alpha$ , especially in the case of basic rocks due to their relatively high Ti content. Ba $\text{L}\beta_1$  suffers interference from Ce $\text{L}\alpha_1$ , and thus the best choice is Ba $\text{L}\beta_2$ . For the Ba determination a Cr tube is used. With this tube Ba $\text{L}\beta_2$  is also stronger than Ba $\text{L}\beta_1$ .

since only the  $\beta_2$  line is excited by  $\text{CrK}\alpha$ . A disadvantage is that the  $\text{CrK}\alpha$  tube line also, to some extent, interferes with  $\text{BaL}\beta_2$ . In some cases a W tube was used for the Ba determination, although the intensity was observed to be only about one third that obtained with a Cr tube. In a great many rock-types, however, the Ba content is also large enough to allow a good determination with a W tube.

Interferences from lines belonging to elements present in the sample (see list) are corrected for by means of correction factors. For each analytical line with interferences this factor is calculated from measurements on standards containing only the interfering element in an otherwise pure greenstone base. The factor to be used for the calculation of the correction is the ratio of the net reading at the position of the analytical line and the net reading of the analysis line of the interfering element. The interference on  $\text{NiK}\alpha$  from the second order lines of  $\text{YK}\alpha$  and  $\text{RbK}\beta$  can be removed by the use of a discriminator.

Tube lines originating from the tube material (W and Cr) or its contents of impurities (Cu, Ni, Cr) represent another type of interference. A correction factor for such interference was derived from measurements at the line position and its background position for a blank represented by a fused pure greenstone base. Similar measurements on the fused bases used for the different test samples confirmed that this correction factor is nearly matrix independent.

Since the analytical method is based on net intensities, background measurements and corrections are necessary. For lines having sloping background, i.e. those of Zr, Y, Sr and Rb, measurements were made on both sides of the line and the average taken as the true background. Measuring only one background is less reliable because the change of background with wavelength is matrix dependent. Background disturbances by elements like Th, U and Pb, which have lines in the wavelength region used, might cause trouble if present, and should be checked for.

The interference from  $\text{VK}\beta_1$  on  $\text{CrK}\alpha$  is serious when the V-content is high, but is difficult to correct for because  $\text{TiK}\beta_1$  interferes with  $\text{VK}\alpha$ . In this case V was checked for by emission spectrography.

### 3.5 INSTRUMENTATION

All measurements were carried out on a Philips PW 1540 X-ray spectrometer operated at 40 kV and 18 mA. For Ba a Cr tube and flow counter were used, and a W-tube and scintillation counter were used for all the other elements. The analysing crystal was LiF (200). The counting time was 100 seconds for all measurements.

### 3.6 MATHEMATICAL CORRECTION FOR MATRIX EFFECTS USING ABSORPTION COEFFICIENTS

The analytical curves of the procedure described are constructed for the greenstone matrix only and are straight lines according to the analytical function

$$c_{\text{X (greenstone)}} = k_{\text{X (greenst.)}} \cdot I_{\text{X (greenst.)}} + b_{\text{X (greenst.)}}$$



where  $c_X$  is the concentration of element X,  $I_X$  the net measurement of the intensity of the analysis line of element X, and  $k_X$  and  $b_X$  are constants.  $b$  is in most cases zero, and  $I/k = \frac{dI}{dc}$  is the sensitivity of the procedure.

Because of difference in absorption, the readings  $I_X$  of element X in other matrices must be converted to corrected readings which allow use of the greenstone analytical functions.

The absorption of the primary radiation is normally of minor importance and can be neglected. The element-characteristic fluorescent radiation, on the other hand, undergoes significant matrix dependent absorption on its way out of the sample. The magnitude of this absorption expressed by the total mass absorption coefficient of the matrix in question, relative to that of the greenstone matrix, is the factor used in this paper for the above-mentioned conversion of readings. A thorough treatment of this subject has been given by Hower (1959), Müller (1964) and others. The total mass absorption coefficient can be calculated by use of available Tables of absorption coefficients. It is the sum of the products of mass absorption coefficient and weight fraction of each element making up the matrix, as shown in Table 7 for the greenstone matrix.

Manual correction calculation of this kind is time-consuming. The calculation is, however, well suited for electronic data processing, and a computer programme was therefore written for this purpose. The computer is simply fed with the net X-ray intensity readings for the trace elements and the analytical results for the major elements. All other information, mass absorption coefficients, weight ratio of sample to flux and the constants  $k$  and  $b$  of the analytical functions are built-in parameters in the computer programme.

Different Tables of mass absorption coefficients are available (Heinrich 1966; Jenkins & De Vries 1970; Liebafsky 1971). For this work the Tables by Heinrich were chosen. One advantage of these Tables is that they give directly the coefficients for the most frequently used lines.  $Ba L\beta_2$  is not covered by the Tables and the required interpolation for this wavelength was made on the basis of wavelength raised to the 2.8 power. The constancy of the ratio of the coefficients of two neighbouring fluorescence lines (Fairbairn & Hurley 1971) was taken as a measure of the quality of the mass absorption coefficients. This ratio is, for Rb and Sr, shown in Table 6, which also lists all the mass absorption coefficients used in the present work.

Fusion of synthetic samples containing different carbonates and in different amounts showed that  $CO_2$  was completely removed from the samples. From Table 7 it is seen that loss of volatiles from the sample during fusion is not taken into consideration, nor is the increase in concentration of the major elements caused by such losses or change in the weight ratio sample to flux. Calculations show that this way of calculation gives the same final result as if the calculation had used major element concentrations based on ignited sample, and which also takes into consideration the change in weight ratio sample to flux. By the latter method of calculation the concentrations of trace elements must be reduced to the basis of original sample weight. Typical trace

Table 6. Mass absorption coefficients (Heinrich)

$\lambda$	ZrK $\alpha$	YK $\alpha$	SrK $\alpha$	RbK $\alpha$	ZnK $\alpha$	CuK $\alpha$	NiK $\alpha$	CrK $\alpha$	BaL $\beta_2$	Ratio
Z	0.787	0.830	0.876	0.927	1.436	1.542	1.659	2.291	2.404	$\mu_{\text{Rb}}/\mu_{\text{Sr}}$
Si	9.5	11.0	12.8	15.0	50.4	61.4	75.2	183.8	211.1	1.172
Al	7.6	8.9	10.3	12.0	40.7	49.6	60.7	149.0	171.2	1.165
Fe	49.9	57.7	66.8	78.0	256.3	311.1	379.6	113.0	129.4	1.168
Ti	32.3	37.3	43.3	50.5	166.8	202.6	247.3	597.0	681.6	1.166
Mg	6.0	7.0	8.1	9.5	32.4	39.5	48.4	119.1	136.9	1.173
Ca	25.1	29.0	33.7	39.3	130.5	158.6	193.7	469.2	537.8	1.166
Na	4.6	5.4	6.3	7.3	24.8	30.3	37.2	91.4	105.1	1.159
K	22.0	25.5	29.5	34.5	115.0	139.8	171.0	415.4	476.4	1.169
Mn	45.2	52.2	60.5	70.5	232.0	281.6	343.6	100.5	115.1	1.165
O	1.9	2.2	2.6	3.1	10.5	12.9	15.8	39.4	45.3	1.192
C	0.7	0.8	0.9	1.1	3.8	4.6	5.7	14.2	16.4	1.222
Li	0.1	0.1	0.1	0.1	0.4	0.5	0.6	1.5	1.7	1.000
B	0.4	0.4	0.5	0.6	2.1	2.5	3.1	7.9	9.1	1.200

Table 7. Computation of mass absorption coefficients for fused greenstone standards

4 g standard (greenstone): 55% SiO<sub>2</sub>, 15% Al<sub>2</sub>O<sub>3</sub>, 10% Fe<sub>2</sub>O<sub>3</sub>, 5.60% CaO, 5% MgO, 2.92% Na<sub>2</sub>O + (6.48% CC, 2 g flux: 100% Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>)

Absorbing element	Percentage	ZrK $\alpha$	YK $\alpha$	SrK $\alpha$	RbK $\alpha$	ZnK $\alpha$	CuK $\alpha$	NiK $\alpha$	CrK $\alpha$	BaL $\beta_2$
Si	25.70	2.442	2.827	3.290	3.855	12.953	15.780	19.326	47.237	54.253
Al	7.94	0.603	0.707	0.818	0.953	3.232	3.938	4.820	11.831	13.593
Fe	6.99	3.488	4.033	4.669	5.452	17.915	21.746	26.534	7.899	9.045
Ca	4.00	1.004	1.160	1.348	1.572	5.220	6.344	7.748	18.768	21.512
Mg	3.02	0.181	0.211	0.245	0.287	0.978	1.193	1.462	3.597	4.134
Na	2.17	0.100	0.117	0.137	0.158	0.538	0.658	0.807	1.983	2.281
O	43.70	0.830	0.961	1.136	1.355	4.589	5.637	6.905	17.218	19.796
	93.52	8.648	10.016	11.643	13.632	45.425	55.296	67.602	108.533	124.614
Li	8.20	0.008	0.008	0.008	0.008	0.033	0.041	0.049	0.123	0.139
B	25.20	0.102	0.102	0.128	0.154	0.537	0.640	0.793	2.022	2.329
O	66.21	1.258	1.457	1.721	2.053	6.952	8.541	10.461	26.087	29.993
	100.0	1.368	1.567	1.857	2.215	7.522	9.222	11.303	28.232	32.461
4/6 base:		5.765	6.677	7.762	9.088	30.283	36.864	45.068	72.355	83.076
2/6 flux:		0.456	0.522	0.619	0.738	2.507	3.074	3.768	9.411	10.820
		6.221	7.199	8.381	9.826	32.790	39.938	48.836	81.766	93.896

elements do not contribute appreciably to the absorption, and in the calculations referred to trace elements have been treated as non-absorbing.

### 3.7 CORRECTION OF MATRIX EFFECTS BY USING SCATTERED PRIMARY RADIATION AS A REFERENCE

Scattering of the primary tube spectrum consists of coherent and incoherent scattering. The power of the scattering is strongly dependent on matrix and wavelength. Based on this dependency different methods have been proposed and used for the correction of matrix effects (see e.g. Andermann & Kemp 1958; Cullen 1962; Kalman 1962; Taylor & Andermann 1971; Clark & Mitchell 1973). A certain wavelength has to be selected as intensity reference,



Table 8. Precision of the X-ray method (upper part of Table). Precision of the instrument (lower part of Table)

	Zr	Y	Sr	Rb	Zn	Cu	Ni	Cr	Ba
Mean (ppm)	128.3	37.7	303.8	69.8	93.4	35.3	59.8	183.6	234.3
s (ppm)	2.45	1.49	2.57	2.62	2.59	3.43	3.26	3.31	25.8
s <sub>r</sub> (%)	1.9	4.0	0.8	3.8	2.8	9.7	5.5	1.8	11.0
Mean (ppm)	124.8	38.4	309.1	71.2	94.5	35.4	59.7	183.2	234.1
s (ppm)	1.40	1.58	3.35	2.30	2.12	4.55	2.06	2.30	16.2
s <sub>r</sub> (%)	1.1	4.1	1.1	3.2	2.2	12.9	3.5	1.3	6.9

but the choice of wavelength has been much discussed in the literature. The use of coherently scattered tube lines were advised against by Reynolds (1963), whereas incoherently scattered lines (Compton peaks) have generally been recommended as more suitable. The results shown in Table 10 were obtained by use of the incoherently scattered MoK $\alpha$  tube line as reference line for Rb and Sr. The results appear to be fairly promising.

When a W tube is used, however, there are no suitable incoherently scattered tube lines available. In this case it was therefore decided to make use of a background wavelength and, since at short wavelengths incoherently scattered radiation is supposed to be strong compared to coherently scattered radiation, the background at  $2\theta = 17^\circ$ , corresponding to a wavelength of  $0.59 \text{ \AA}$ , was chosen. This background was used as intensity reference for all the trace elements of this work, and the results are listed along with those based on other calculation procedures in Table 9.

### 3.8 PRECISION

The precision of the method was investigated by analysing 10 fusions of one greenstone sample. The precision of the instrument was tested by analysing one fused sample 10 times. The results of the measurements are shown in Table 8. There seems to be no significant difference between the precision of the method and that of the instrument.

### 3.9 DETECTION LIMITS

If the limit of detection,  $C_L$ , is taken as the concentration corresponding to a measurement  $x_L = \bar{x}_b + 3s_b$ , where  $\bar{x}_b$  is the mean and  $s_b$  the standard deviation of the background reading, then

$$C_L = \frac{3}{S} \cdot \sqrt{\frac{R_b}{T_b}}$$

where  $S$  is the slope of the analytical calibration curve in  $\frac{\text{counts per second}}{\text{ppm}}$  (= sensitivity).

$R_b$  = True background counting rate

$T_b$  = Counting time on the background

The calculation gives the following limits of detection in a greenstone matrix.

Table 9. Summary of results on trace elements

	Zr ppm	Y ppm	Sr ppm	Rb ppm	Zn ppm	Cu ppm	Ni ppm	Cr ppm	Ba ppm	
Granite USGS G-2	397	7	624	201	122	32	5	0	1585	Unfused, uncorrected
	407	5	609	203	98	37	5	0	1813	Fused, uncorrected
	316	6	499	160	99	18	0	0	1715	Unfused, corrected
	335	4	501	168	81	31	4	0	1976	Fused, corrected
	384	5	573	192	92	35	5	0	1708	Scattered b.g. at 17.0 as reference
	300	12	479	168	85	11.7	5.1	7	1870	Recommended values
Granodiorite USGS GSP-1	610	29	283	267	134	58	14	3	1064	Unfused, uncorrected
	698	25	271	271	108	36	7	0	1210	Fused, uncorrected
	534	25	248	234	118	33	9	4	1222	Unfused, corrected
	624	23	242	243	97	32	6	0	1350	Fused, corrected
	701	26	272	273	108	36	7	0	1216	Scattered b.g. at 17.0 as reference
	500	30.4	233	254	98	33.3	12.5	12.5	1300	Recommended values
Andesite USGS AGV-1	254	17	724	64	93	101	17	6	942	Unfused, uncorrected
	234	13	715	70	88	64	15	6	1089	Fused, uncorrected
	244	16	695	61	89	71	15	8	1035	Unfused, corrected
	228	13	696	68	86	62	15	7	1206	Fused, corrected
	243	14	740	72	91	66	16	7	1127	Scattered b.g. at 17.0 as reference
	225	21.3	657	67	84	59.7	18.5	12.2	1208	Recommended values
Basalt USGS BCR-1	164	27	280	33	114	14	7	15	535	Unfused, uncorrected
	158	28	280	35	105	12	7	21	570	Fused, uncorrected
	202	33	345	40	138	9	16	19	593	Unfused, corrected
	195	34	344	44	128	14	9	24	658	Fused, corrected
	196	34	345	44	129	14	9	26	703	Scattered b.g. at 17.0 as reference
	190	37.1	330	46.6	120	18.4	15.8	17.6	675	Recommended values
Biotite CRPG Mica-Fe	526	26	0	1240	968	0	10	65	58	Unfused, uncorrected
	579	3	0	1374	847	0	13	56	83	Fused, uncorrected
	871	43	0	2040	1581	0	36	74	64	Unfused, corrected
	940	5	0	2222	1360	0	21	63	94	Fused, corrected
	882	5	0	2093	1289	0	20	85	127	Scattered b.g. at 17.0 as reference
	-	-	6	2300	1350	4	35	90	140	Recommended values
Granite CRPG CRGR	214	19	729	201	78	586	55	63	873	Unfused, uncorrected
	267	9	691	205	70	358	64	77	924	Fused, uncorrected
	183	16	622	172	67	328	43	69	950	Unfused, corrected
	232	8	604	179	61	314	56	84	1014	Fused, corrected
	254	9	659	195	66	341	61	73	881	Scattered b.g. at 17.0 as reference
	180	19	550	175	60	345	55	110	1050	Recommended values
Larvikite ASK-1	607	40	868	100	74	17	137	29	917	Unfused, uncorrected
	737	39	797	99	101	14	113	22	978	Fused, uncorrected
	546	36	782	90	67	13	121	34	1028	Unfused, corrected
	676	36	732	92	93	13	104	25	1107	Fused, corrected
	732	39	792	100	100	14	112	22	972	Scattered b.g. at 17.0 as reference
	(400)	-	(680)	(85)	(105)	(7)	(110)	(40)	(1130)	Recommended values

(Continued opposite)





W-tube:

Element	S	R <sub>i</sub>	C <sub>L</sub> (ppm)
Zr	2.2	1079	4.5 ppm
Y	2.3	1020	4.2 »
Sr	2.2	875	4.0 »
Rb	2.1	781	4.0 »
Zn	1.9	405	3.2 »
Cu	1.3	477	5.0 »
Ni	1.5	312	3.5 »
Cr	0.8	55	2.8 »
Ba	0.03	34	58 »

Cr-tube:

Ba	0.08	84	34 »
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## 3.10 RESULTS AND DISCUSSION

The results obtained on the international reference samples as well as on the synthetic test samples are given in Table 9. The samples named Larvikite ASK-1 and Schist ASK-2 are internordic geological reference samples. The recommended values for these are based on very few determinations and are therefore put in parentheses. Values near the detection limit should not be considered when evaluating which method is to be preferred.

The Table shows the necessity of some form of matrix effect correction. Mathematical matrix correction on fused samples seems to be superior to the other methods; furthermore, the importance of fusion seems to increase with increasing wavelength.

As regards Zr there are disagreements for GSP-1 and CRGR. By comparison with the values obtained by a number of analysts (Flanagan 1973) on this material, however, our values fall well within the range of values obtained in other laboratories. For synthetic test samples the mathematical correction method gives good results for Zr, Sr and Rb in all matrices, and for Zn, Cu and Ni in all matrices except Fe<sub>2</sub>O<sub>3</sub> where the results are about 20–25% too high (exception: Cu in Fe 100). It should be remembered, however, that Fe<sub>2</sub>O<sub>3</sub> is an exceptional matrix compared to greenstone, thus having a very large correction factor. As far as Cr and Ba in the Fe<sub>2</sub>O<sub>3</sub> matrix are concerned, it is difficult to explain why the Ba values are higher than the Cr values. Enhancement from Fe on Cr and Ba would be expected to influence Cr more than Ba.

The method of scattered background cannot be used when an absorption edge for a matrix element lies between the analytical line and the measured scattered background position. This is clearly demonstrated for Cr and Ba in Fe 100 and Fe 1000. Otherwise, scattered background seems to give acceptable results.

Results obtained by use of the MoK $\alpha$  Compton peak for Sr and Rb determinations are shown in Table 10. Good results are obtained on unfused as well as



Table 10. Results obtained by using the MoK $\alpha$  Compton peak as matrix correction

Sample	Rb (ppm)			Sr (ppm)		
	Fused sample	Unfused sample	Recom. values, respectively correct values	Fused sample	Unfused sample	Recom. values, respectively correct values
G-2	160	166	168	482	505	479
GSP-1	235	248	254	233	245	233
AGV-1	62	60	67	658	693	657
BCR-1	41	42	46.6	322	347	330
Mica-Fe	2091	2130	2300	—	—	6
CRGR	170	176	175	584	623	550
Larvikite	87	93	(85)	686	736	(680)
Schist	187	181	(175)	115	108	(100)
GR 100	94		100	96		100
GR 1000	986		1000	998		1000
Al 100	99		100	101		100
Al 1000	1007		1000	1018		1000
Si 100	95		100	98		100
Si 1000	996		1000	989		1000
Fe 100	87		100	92		100
Fe 1000	939		1000	952		1000

fused samples. The Compton peak correction factor established for Sr and Rb can be used also for the elements Zr, Y, Zn, Cu and Ni since the factor is nearly identical for all these elements.

The elements Y, Sr and Rb have good sensitivity ( $\frac{dI}{dc}$ ) with a Mo-tube, which has a suitable K $\alpha$  Compton peak to be used for matrix correction. Zr, Zn, Cu and Ni, however, have better sensitivity with a W-tube, but this tube gives no suitable Compton peak. A combination of two tubes could therefore be used, a W-tube for measuring analytical lines and backgrounds, and a Mo-tube for establishing the correction factor. The elements Cr and Ba can in many cases be analysed even without matrix corrections, since their correction factors vary only slightly with the matrix.

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