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Analytical procedures used in the Geochemical Laboratory of the Survey

by

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ANALYTICAL PROCEDURES USED IN THE GEOCHEMICAL LABORATORY OF THE SURVEY

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INTRODUCTION

This report describes the system of routine analysis of rocks and silicate minerals used in the chemical laboratories of Grønlands Geologiske Undersøgelse (GGU) in the last three years.

The first part is a short summary of the principles behind the methods used with references to original sources in the literature.

In the section on analytical accuracy a series of results are given some of which are treated statistically. These are meant as a guide to the accuracy of the methods used and as a basis for further, more developed statistical studies.

The last section of the report on procedures contains descriptions of the separate methods used in nummerical order and is used as a "recipe book" in the laboratory.

METHODS

The methods of rock and mineral analysis used by GGU during the last three years are based on principles developed from widely recognised original work. In order to adapt these methods to the special analytical system which we have found suitable the majority have been modified to a greater or lesser extent after a series of laboratory investigations on the effect of these modifications.

In choosing these methods and in adapting them to fit into an analytical system special emphasis has been given to obtaining an accuracy as good or better than that expected by "classical" methods (Fairbairn et al. 1951, Stevens et al. 1960); a speed considerably greater than the classical methods and a standard procedure in spite of the considerable variation in rock type. In this way the whole analysis can be carried out in a routine manner by laboratory staff following a fixed program. Our experience suggests that these three objectives can be reached using the combination of methods chosen, provided that a suitably planned laboratory set up is used.

The systematic rock analyses are carried out in three groups of separate determinations. In each of the first two groups (A and B) the determinations are made on aliquot portions of the dissolved sample whilst in the third group (C) a separate weighing out is necessary for each substance determined. As a control, total iron and titanium are determined in two different solutions prepared from the same specimen (Groups A and B).

The prepared specimen to be analysed is dried at 110°C for 2 hours and it is kept in a sealed airtight container during the whole analysis, thus all percentages refer to a substance which does not contain surface water.

Group A - SiO_2, TiO_2, Al_2O_3, Fe_2O_3 (total), CaO and MgO

The rock sample (0.5 g) is decomposed by sintering with sodium peroxide in a platium crucible as described by Rafter (1950). The sinter cake is treated with water and hydrochloric acid in a dish of clear fused quartz, the solution is evaporated and the residue dried on a waterbath. The major part of the silica is dehydrated and becomes insoluble in dilute hydrochloric acid. By treating the residue with warm 20% (by vol.) hydrochloric acid the soluble salts are brought into solution after which the crude silica is filtered out and determined conventionally by loss in weight after evaporation with hydrofluoric and sulphuric acids ("insoluble" silica).

The filtrate is diluted to 100 ml and is called solution A.

Impurities in the crude silica which consist mainly of titanium dioxide together with small amounts of iron- and aluminium-oxide are decomposed with potassium pyrosulphate, dissolved in water acidified with sulphuric acid and diluted to 100 ml. This is called solution A'.

SiO_2 An aliquot portion of solution A is used for spectrophotometric determination of that part of the total silica which escaped precipitation ("soluble" silica). "Soluble" silica usually forms between 0.2 and 0.5% of the rock.

The molybdenum blue method is used under conditions where iron and titanium, which are present in appreciable amounts, do not affect the results to any noticeable degree.

Total silica (="insoluble" silica + "soluble" silica) is thus determined by this combined gravimetric-photometric method.

CaO and MgO are determined volumetrically using a photometric indication of the endpoint (Patton and Reeder 1956, Riley 1958) out on a aliquot of solution A from which the majority of disturbing elements have been removed.

Fe_2O_3 (total), TiO_2 and Al_2O_3 are determined in aliquots of solutions A + A' (using equal volumes of the two solutions).

Iron and titanium are determined spectrophotometrically in the same solution by measuring the extinction of the dissolved ferri- and titanium complexes with tiron (Yoe and Jones 1944, Yoe and Armstrong 1947).

Aluminium is determined volumetrically using Watts' pH 10 method (Watts 1958). The hydroxyl ions released when potassium fluoride is added to a solution in which aluminium is combined as aluminate at pH 10 is titrated against hydrochloric acid. The titration is carried out potentiometrically and the titrant is turned off automatically at pH 10. Before titration the aluminium is separated from disturbing elements by a single precipitation together with other sesquioxides. The precipitation takes place without heating by adding ammonia + ammonium chloride to the aliquot portion until the pH has risen to 6.0 - 7.0. The precipitate can then be separated and washed quickly quantitatively by using a centrifuge. The precipitated hydroxides are dissolved in hydrochloric acid, the solution is diluted with water and adjusted to pH 10. Potassium fluoride is then added and the solution titrated against hydrochloric acid until the pH is again 10.0.

Group B - Na_2O, K_2O, Fe_2O_3 (total), TiO_2, MnO and P_2O_5

The sample (0.1 g) is decomposed by digestion with sulphuric and hydrofluoric acid, the fluorides are removed by evaporation and the residue taken up with water.

The solution is diluted to 50 ml (solution B) from which aliquot portions are taken for separate determinations.

Na_2O and K_2O are determined flame-photometrically with an E. E. L. flame photometer after iron and titanium have been removed by letting the solution pass through an anion exchanger in its citrate form as described by Riley (1958).

Fe_2O_3 is determined spectrophotometrically after reduction to ferrous iron with hydroxylamine. The extinction is measured at 560 mμ for a solution which contains the orange coloured tiron complex (Yoe and Armstrong 1947, Shapiro and Brannock 1956).

$\underline{TiO_2}$ is determined spectrophotometrically in the same way as described for solution A by measuring the extinction of its complex compound with tiron (Yoe and Armstrong 1947, Shapiro and Brannock 1956).

$\underline{MnO}$ is determined spectrophotometrically after oxidation to permanganate with potassium periodate (Shapiro and Brannock 1956, Willard and Greathouse 1917).

$\underline{P_2O_5}$ is determined spectrophotometrically by measuring the extinction of a solution which contains the yellow molybdo-divanado-phosphoric acid complex (Shapiro and Brannock 1956, Kitson and Mellon 1944).

Group C - FeO, H_2O^+, CO_2, (Fe_2O_3 total, F_2, Cl_2 and SO_3)

$\underline{FeO}$ is determined in a specially weighed 0.500 g portion of the sample by the conventional method of titration with potassium permanganate (Riley 1958, Shapiro and Brannock 1956, Kolthoff and Sandell 1952). If there are mineral grains present which are not decomposed by sulphuric and hydrofluoric acids, for example chromite, reference can be made to the methods described by Seil (1943) or Hey (1941).

$\underline{H_2O^+}$ Up to now we have determined H_2O^+ using Penfield's classical method as described by Kolthoff and Sandell (1952), or by loss on ignition and correction for FeO.

$\underline{CO_2}$ CO_2 is determined by measuring the volume of gas evolved when concentrated hydrochloric acid is added to a weighed portion of the specimen (van Tongeren 1937).

When the total iron content of the specimen exceeds 25-30% of the rock, specially weighed portions of the sample (0.5 g) are required for accurate determination of this oxide. The same is true of determinations of fluorine, chlorine, sulphur etc. These have only been carried out in special instances in our laboratory.

APPARATUS

All spectrophotometric measurements have been carried out with a Beckmann instrument, model DU, in the range 200-600 mμ. The large cuvette housing was used and a simple adapter was built to hold a "Struers flow-through cuvette" in a fixed position. The optical path of the cuvette is 1 cm.

The flame photometer employed for alkali determinations is an E. E. L. model using coal gas and air from a compressor.

Extraction is carried out using Quickfit extraction glass units. These are of the standard type for the extraction with heavy liquids and have a capacity of 60 ml. The condensed liquid distributor is modified so that the chloroform drips down towards the surface of the liquid from five different capillary tubes, the mouths of which are approximately 1 cm over the liquid surface. Electrothermal extraction heating units with a 500 ml capacity are used as a heat source.

Titration of calcium and magnesium is carried out using an "E. E. L. Quantitrator".

The centrifuge used must rotate at least 2500 r. p. m. We have found that the centrifuge gloss of the type designed for mineral oil analysis may be used with advantage. These are graduated to a volume of 50 ml.

The pH titrator for aluminium determinations used is a "Radiometer", type T. T. T. 1 with a magnetic controlled titrant flow.

Determination of silica is carried out in clear, fused quartz dishes (Vitrosil) with a capacity of 100 ml. The inner surface must be completely flawless.

Pipettes. Normal glass pipettes are used for pipetting sample solutions. Most of the reagents are added automatically by pipettes mounted to reservoir bottles. Storage bottles containing alkaline reagents used for automatic pipetting are equipped with air inlet tubes containing a carbon dioxide absorbing substance, and reagent outlets made of polyethylene tubing.

EXPERIMENTAL INVESTIGATIONS

The sodium peroxide sintering method is rapid but needs careful preliminary treatment of the sample. The success of the method depends on the particle size of the prepared rock sample.

Our experience suggests that a grinding machine working on the pestle and mortar principle is most useful to obtain the fine division of the specimen required. However crushing should not be taken to extremes because of the danger that the iron present will become oxidised. We have investigated the effect of different crushing times on the FeO content of a specimen after drying at 110°C. For a rock with approximately 10% FeO, the FeO content fell approximately linearly by 0.5% after 4 hours crushing in an agate mortar open to the air and with a crushing pressure of 7 kg.

It is obvious that the sample and the peroxide should be mixed thoroughly before sintering.

Although in ideal conditions the decomposition with peroxide is extremely effective and universally applicable, certain technical difficulties exist which sometimes leaves a few mineral grains undissolved. As these are normaly decomposed by sodium pyrosulphate and therefore included in solution A' they have no effect on the determination of iron, titanium and aluminium. In the three years we have been using the method we have not noted undecomposed remains which were large enough or of such a composition that they could result in error in the determination of calcium, silica or magnesium.

The determination of separate substances in this system of rock analysis are based in principle on the methods cited and which, with the exception of silica- and aluminium-determinations, have been used in similar analytical systems.

Except for the alkalis the elements in group B are determined in a similar way to the methods used by Shapiro and Brannock. The combination of methods in group A has not been used in any other known analytical system for rock analyses. A series of preliminary experiments were therefore carried out before the present system was used. The following results may be mentioned:-

"Insoluble" silica, solution A

a) Both platinum and porcelain dishes are unsuitable for evaporation and dehydration with hydrochloric acid after the sample has been decomposed with sodium peroxide if silica is determined by the combined gravimetric-photometric method. Dishes of clear fused quartz are excellent. The dehydrated silica adhering to them is easily removed quantitatively while at the same time blind runs give very low silica results. Using quartz dishes the blind run gave a silica result of approximately 0.04% of a sample compared to 0.15-0.02% when good quality porcelain dishes are used.

b) Hydrogen peroxide derived from the sodium peroxide is removed quantitatively during the dehydration process thus having no effect on the separate determinations carried out with solution A.

c) Clear sample-solutions are obtained by using 20% by vol. hydrochloric acid to dissolve the soluble salts in the quartz dishes and by keeping solutions A and A' separate until use. (Using the method described here hydrolysis in the final sample solutions has not been noted even when TiO_2 and P_2O_5 respectively formed 8 and 0.5% of the rock).

The "soluble" silica dissolved in the 20% by vol. hydrochloric acid varies between 0.2% and 0.5% of the rock.

"Soluble" Silica

"Soluble" silica is determined by a slightly modified version of Jeffery's method which has resulted from a series of detailed investigations. According to Jeffery, iron, titanium and phosphorous have no effect on the extinction measurements at 650 mμ of the reduced molybdenum blue silicate complex, provided that they do not form more than 20, 8, and 10% of the specimen respectively.

The investigations in our laboratory showed that with iron in solution as a chloride this is only true within a very narrow pH range. The latter is difficult to maintain during routine analyses without the use of a special buffer.

If $FeCl_3$ equivalent to 5 mg Fe_2O_3 (20% of the sample) is present together with 125 mmg of silica in solution the pH range is between 0.75 and 0.85. Even within these narrow limits an error of -5% must be tolerated.

In the pH range (0.8 - 1.7) given by Jeffery in which the molybdenum blue complex is formed quantitatively (under specified reaction conditions) the error varies between 0 to -25% increasing with a rise in pH and with the precipitation of iron molybdate.

Our experience shows that apart from the influence of changes in pH the effect of a constant amount of iron (5 mg Fe_2O_3) is also controlled by traces of sulphate ions in the reacting solution. At pH 1.18 the error in determining 0.125 mmg SiO_2 in an aliquot portion is only -5% when in the presence of 2 mille-equivalents of sulphate ions. At the same pH without the presence of sulphate ions the error rose to -20%. Iron molybdate was only precipitated in the latter instance.

The addition of sulphate causes a weak electrolytic action which has the same effect on the reaction whether iron is present or not. Therefore the addition of 2 mille-equivalents of sulphate ions to aliquots of the sample and to the pure silica reference solutions does not introduce any errors. On the contrary it could be shown that errors arising from the presence of iron equivalent to 20% Fe_2O_3 in the rock sample were reduced to less than -5% in the pH range 0.85 - 1.35.

Because of the obvious advantages of using an increased pH range, sodium bisulphate is added during all determinations of soluble silica.

Separation of aluminium

When determining aluminium by the pH 10 method in rock samples containing magnesium, Watts first separated the two elements by a single precipitation of the sesquioxides with ammoniacal ammonium chloride solution before titration.

A series of other elements are wholly or partly removed at the same time and thus a more specific determination for aluminium is possible. When preliminary investigations were made in order to adapt the pH 10 method of aluminium determination to routine analysis emphasis was put onto finding a simple and rapid method of precipitation and separation. As the classical method of boiling and filtering takes considerable time, centrifuging was tried using pure aluminium standards and different rock types. The procedure used is the same as described later in this report.

The results of titrating 10 ml of a standard Al_2O_3 solution containing the equivalent of 10 mg Al_2O_3 with and without the above separation are given in table I. The largest deviation from the average value is given as percentage Al_2O_3 of the sample. In all cases within one series of experiments the reproducibility is better than ± 0.02 ml of the titrant. This also means that the average values of each series before and after separation are in agreement within the ± 0.02 ml margin of error. Following the same procedure, 1 ml of the titrant solution corresponds to approximately 2.5% Al_2O_3 in the sample, thus a ± 0.02 ml margin of error corresponds to ± 0.05% Al_2O_3 in the original sample.

TABLE I

	Non-centrifuged standard			Centrifuged standard		
Series	ml titrant	Mean	Largest deviation	ml titrant	Mean	Largest deviation
1	7.66	7.68	± 0.02 = 0.05 %	7.68	7.69	± 0.01 = 0.025 %
	7.66			7.68		
	7.67			7.70		
	7.70			7.69		
2	7.70	7.72	± 0.02 = 0.05 %	7.75	7.74	± 0.02 = 0.05 %
	7.70			7.76		
	7.71			7.72		
	7.74			7.73		
3	7.79	7.78	± 0.01 = 0.025 %	7.78	7.79	± 0.02 = 0.05 %
	7.77			7.81		
	7.79			7.80		
	7.78			7.79		

Table II shows the reproducibility of the precipitation separation determined by titrating 10 ml aliquots of solutions A + A' for 2 random samples. The results are the same as those of the pure standard solutions. The largest deviation from average in the amount of titrant used is given as % Al_2O_3 of the sample.

TABLE II

Sample	Aliquot	ml titrant	Average	Largest deviation
Biotite schist Anal. No. 47-63	1	5.80	5.80	± 0.01 = 0.025 %
	2	5.81		
	3	5.80		
	4	5.80		
Microcline-biotite-syenite Anal. No. 49-63	1	5.56	5.54	± 0.02 = 0.05 %
	2	5.54		
	3	5.56		
	4	5.52		

Table III shows the results of aluminium determinations of specimens of known composition. It can be seen that there is good agreement with aluminium determined by other methods.

It should be noted that the titration factor is determined by titrating 10 mg Al_2O_3 (10 ml non-separated aluminium standard) and it has been checked that this is valid at least in the range 0 - 10 mg, corresponding to 0 - 20% Al_2O_3 in the original sample.

TABLE III

Determination of aluminium in standard samples

	% Al_2O_3		
Sample	pH 10 method	Other method	Deviation
N.B.S. Soda-feldspar	19.00	19.06	- 0.06
"	19.05	"	- 0.01
"	19.05	"	- 0.01
G-1 Granite	14.22	14.21*	+ 0.01
	14.20	"	- 0.01
	14.20	"	- 0.01

*Goldich and Oslund (1956) in Stevens et al. 1960, pp. 36-37.

From the figures given in the last three tables it can be seen that the method used in separating aluminium gives a quantitative result which is within the margin of error of the titration. It has also been shown that basic rocks with 11% CaO and 7% MgO do not give too high a result which means that the method is exceptionally applicable to most silicate rock types. (If the calcium content is very high sodium oxalate can be added in addition before titration as described in Watts' original work (Watts 1958).

ANALYTICAL ACCURACY

Errors in measurement

When discussing the question of accuracy it is necessary to know the reproducibility of the measurements themselves and what effect variations in these measurements have on the final figures for each element.

These errors in measurement which do not include errors in weighing, pipetting, or separation, may be considered as absolute quantities within the range of measurements used. They must be treated as the minium error to be expected even if the method itself is acceptable and free from other possible sources of error. They are determined by making repeated measurements of weight, volume, extinction or emission of the same quantities of material or equal parts of the same solution to be measured and noting the largest deviation from the average value. (The errors of measurement include errors in taking aliquots of the solution measured).

A summary of the approximate absolute size of the errors and the highest relative percent error within the range of measurements used is given in table IV.

TABLE IV

Summary of the size of errors of measurement in different weight percent ranges.

Absolute error in measurement ±	% measurement error in the systematic weight percent ranges				
	<1%	<5%	<10%	<100%	
SiO_2, weight-extinction = 0.05%	100	5	1	0.5	0.05
Al_2O_3, vol. = 0.02 ml = 0.05%	50	5	1	0.5	0.05
CaO, vol. = 0.1 ml = 0.05%	50	5	1	0.5	0.2*
MgO+CaO, vol. = 0.1 ml = 0.03% (MgO)	50	3	0.6	0.3	0.2*
Fe_2O_3/FeO, vol. = 0.05 ml - 0.02%	100	2	0.4	0.2	0.02
Fe_2O_{3A}, ext. = 0.002 = 0.03%	18	3	0.6	0.3	0.03
Fe_2O_{3B}, ext. = 0.002 = 0.05%	14	5	1.0	0.5	0.05
Na_2O, K_2O, emission = 0.5% of scale = 0.06%	12	6	1.2	0.6	0.06
TiO_{2A}, ext. = 0.002 = 0.010%	4	1	0.2	0.1	0.01
TiO_{2B}, ext. = 0.002 = 0.015%		6	0.3	0.15	0.02
MnO, ext. = 0.002 = 0.015%		4	0.3	0.15	0.02
P_2O_5, ext. = 0.002 = 0.020%		2	0.4	0.20	0.02
H_2O+, weight = 0.0002g = 0.04%	Measurement error negligable in comparison to those due to the method used.				

* The lower limit of error at the 100% level can be reduced to approx. 0.05% by adding a CaO standard, thereby raising the total titrant used. This is because a certain minium of titrant solution must be added in order to determine the amount of titrant used from the titration curve with the errors of measurement given. The percentage figures for MgO + CaO give the total equivalent amount of MgO.

Precision

During the last three years we have paid special attention to checking reproducibility of our silica, aluminium and alkali determinations. A series of figures resulting from this work are included in order to give an impression of what precision can be expected from routine analyses of various rock types.

The figures are used to express the standard deviation (= std. dev.) from the average value for the elements listed.

For a uniform set of separate determinations the standard deviation is given by the formula:

$$\text{std. dev.} = \sqrt{\frac{\Sigma(x - \bar{x})^2}{N - 1}}$$

where $(x - \bar{x})^2$ is the square of the deviation from the average value of a single determination and N - 1 is the number of degrees of freedom for N single determinations.

When the standard deviation is calculated from duplicate determinations the formula

$$\text{std. dev.} = \sqrt{\frac{\Sigma d^2}{2n}}$$

where d is the difference between the duplicates and n is the number of duplicates.

TABLE V

Precision of SiO_2 values from different sets of analyses (separated by horizontal lines).

Analyst	Sample			
	69-63 Gabbro	24-64	70-63 Granite	N.B.S.99 Soda-feldspar
	%	%	%	%
I.W.	46.14	45.45	76.15	
	46.15		76.40	
	46.17		76.39	
	46.20		76.28	
B.I.B.	46.22		76.40	68.50
	46.32		76.20	68.43
	46.35			
	46.32			
A.M.D.	46.47	45.39		68.33
	46.33	45.46		68.51
	46.45	45.63		68.23
	46.15			68.40
A.M.D.		45.64		
		45.50		
A.M.D.		45.50		
A.M.D.		45.40		
		45.40		
Average	46.27	45.48	76.30	68.40
Degrees of freedom	11	8	5	5
Sum of squares	0.1504	0.0707	0.0616	0.0565

$$\text{std. dev.} = \sqrt{\frac{0.3392}{29}} = 0.11 \ \%\ SiO_2$$

TABLE VI

Precision of duplicate Al_2O_3 values determined in different series of analyses with a time interval between them of at least 24 hours.

Analysis no.	Sample	% Al_2O_3		d
70-63	Granite	12.00	12.00	0.00
4-61	"	12.70	12.80	0.10
50-63	"	14.18	14.15	0.03
G-1	"	14.22	14.20	0.02
48-63	"	14.24	14.42	0.18
83-63	Gabbro	14.33	14.36	0.03
49-63	Biotite-syenite	14.46	14.30	0.16
47-63	Biotite-schist	15.39	15.21	0.18
5-61	Syenite	15.90	16.00	0.10
69b-63	Basalt	17.21	17.31	0.10

Sum of squares (d^2) = 0.1226
Number of duplicates = 10

std. dev. = $\sqrt{0.0061}$ = 0.08 % Al_2O_3

TABLE VII

Precision of Al_2O_3 values within one set of analyses.

Set	1	2	3	4
Analysis no.	49-	69b-	69a-	70-63
	%	%	%	%
	14.15	17.22	17.21	12.00
	14.14	17.31	17.21	12.00
	14.02	17.42	17.23	12.00
		17.30	17.10	11.97
Average	14.10	17.31	17.19	11.99
Degrees of freedom	2	3	3	3
Sum of squares	0.0105	0.0203	0.0105	0.0007

$$\text{std. dev.} = \sqrt{\frac{0.0420}{11}} = 0.06\ \%\ Al_2O_3$$

Precision of Al_2O_3 values in aliquots (10 ml) of a single sample solution in the same set of analyses.

Set	1	2	3	4
Analysis no.		Standard solution		47-63
	ml	ml	ml	ml
	7.75	7.78	7.68	5.80
	7.76	7.81	7.68	5.81
	7.72	7.80	7.70	5.80
	7.73	7.79	7.69	5.80
Average	7.74	7.79	7.69	5.80
Degrees of freedom	3	3	3	3
Sum of squares	0.0010	0.0006	0.0003	0.0001

$$\text{std. dev.} = \sqrt{\frac{0.0020}{12}} = 0.013\ \text{ml} = 0.03\ \%\ Al_2O_3{}^{*}$$

* Titration factor f = 2.58 (this can vary slightly from one set of analyses to another).

TABLE VIII

a) Precision of Na_2O and K_2O values within the same set of analyses

Set	1	2	3	4	5	6	7
	69-63 Gabbro		G-1 Granite	70-63 Granite	80-63 Diorite	N.B.S. 99 Soda-feldspar	
% Na_2O	3.50	3.50	3.18	4.95	4.25	10.87	10.79
	3.45	3.52	3.27	5.00	4.36	10.87	10.79
	3.45	3.48	3.27	4.95	4.25	10.87	10.77
	3.45	3.50	3.32	4.90	4.10	10.76	10.79
Average	3.46	3.50	3.26	4.95	4.24	10.84	10.78
Degrees of freedom	3	3	3	3	3	3	3
Sum of squares	0.0009	0.0008	0.0102	0.0050	0.0342	0.0091	0.0001
Std. dev.	0.053		0.057	0.041	0.107	0.039	
% K_2O	0.50	0.50	5.57	4.10	2.25	0.38	0.42
	0.50	0.50	5.43	4.20	2.36	0.42	0.38
	0.50	0.50	5.57	4.20	2.30	0.42	0.38
	0.50	0.50	5.61	4.10	2.25	0.38	0.38
Average	0.50	0.50	5.55	4.15	2.29	0.40	0.39
Degrees of freedom	3	3	3	3	3	3	3
Sum of squares	0.0000	0.0000	0.0188	0.0100	0.0082	0.0016	0.0012
Std. dev.	0.000		0.079	0.058	0.052	0.023	

Std. dev. for Na_2O at 3-5% level (set 1-5): $\sqrt{\frac{0.0511}{15}} = 0.06\ \%$ (= 1.9 - 1.2 rel. %)

Std. dev. for K_2O at 2-6% level (set 3-5) : $\sqrt{\frac{0.0370}{9}} = 0.06\ \%$ (= 3.2 - 1.1 rel. %)

b) Precision of Na_2O and K_2O values determined in different analysis series and at different times

Date	% Na_2O	% K_2O
14/10-63	10.95	0.42
6/1 -64	10.84	0.40
9/1 -64	10.78	0.39
15/4 -64	10.83	0.39
16/4 -64	10.90	0.53
4/5 -64	10.77	0.39
Average	10.85	0.42
Degrees of freedom	5	5
Sum of squares	0.0243	0.0152
Std. dev.	0.07	0.05

TABLE IX

Precision of the analysis of GGU sample no. 26272, astrophyllite-granite

Analyst	I. W.			
Analysis no.	70a-	70b-	70c-	70d-63
SiO_2	76.15	76.40	76.39	76.28
TiO_2	0.12	0.12	0.12	0.12
Al_2O_3	12.00	12.00	12.00	11.97
Fe_2O_3	0.81	0.81	0.81	0.77
FeO	0.90	0.90	0.90	0.91
MnO	0.03	0.02	0.03	0.03
MgO	0.0	0.0	0.0	0.0
CaO	0.0	0.0	0.0	0.0
Na_2O	4.95	5.00	4.95	4.90
K_2O	4.10	4.20	4.20	4.10
P_2O_5	0.04	0.04	0.05	0.04
H_2O+	0.04	0.08	0.04	0.06
Total	99.14	99.57	99.49	99.18
Fe_2O_3 (A+A')	1.81	1.81	1.81	1.78
Fe_2O_3 (B)	1.72	1.72	1.81	1.77

TABLE X

Precision in the analysis of GGU sample no. 39941, basalt

Analyst	B.I.B.				I.W.			
Analysis no.	69a-	69b-	69a-	69a-63	69b-	69b-	69b-	69b-63
SiO_2	46.22	46.32	46.35	46.32	46.14	46.09	46.17	46.20
TiO_2	2.60	2.60	2.63	2.63	2.58	2.58	2.58	2.58
Al_2O_3	17.21	17.21	17.23	17.10	17.22	17.31	17.42	17.30
Fe_2O_3	10.79	10.74	10.79	10.79	10.78	10.78	10.73	10.79
FeO	2.28	2.26	2.26	2.29	2.28	2.28	2.29	2.26
MnO	0.12	0.12	0.12	0.11	0.13	0.13	0.13	0.12
MgO	4.92	4.82	4.85	4.88	4.94	4.88	4.88	4.88
CaO	8.64	8.73	8.64	8.73	8.60	8.64	8.73	8.82
Na_2O	3.50	3.45	3.45	3.45	3.50	3.50	3.50	3.50
K_2O	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
P_2O_5	0.60	0.60	0.60	0.60	0.60	0.61	0.61	0.59
H_2O+	2.13				2.13			
Total	99.51	99.48	99.60	99.58	99.40	99.44	99.67	99.67
Fe_2O_3 (A+A')	13.17	13.22	13.24	13.22	13.30	13.29	13.22	13.30
Fe_2O_3 (B)	13.30	13.25	13.30	13.30	13.24	13.24	13.24	13.21

Note

Water has been determined only once by correcting the loss on ignition. A single determination using Penfield's method gave 1.48 %.

Accuracy

Deviation from classical analyses:-

TABLE XI

Method	As described/classic		As described/classic		As described/classic	
Analyst	I. W.	B. I. B.	B. I. B.	B. I. B.	A. M. D.	M. M.
Sample	70-63 astrophyllite-granite		69-63 basalt		58-64 basalt	
SiO_2	76.31	76.33	46.32	46.42	47.95	48.38
TiO_2	0.12	0.14	2.62	2.56	2.72	2.72
Al_2O_3	12.00	12.54	17.20	17.49	12.48	12.36
Fe_2O_3	0.80	0.73	10.78	10.96	4.75	5.10
FeO	0.90	0.89	2.27	2.38	9.70	10.33
MnO	0.03	0.02	0.12	0.13	0.22	0.14
MgO	0.0	0.0	4.86	4.82	5.53	5.97
CaO	0.0	0.0	8.69	8.67	10.37	10.47
Na_2O	4.95	4.92	3.46	3.59	2.67	
K_2O	4.15	4.06	0.50	0.41	0.47	
P_2O_5	0.04	trace	0.60	0.61	0.41	0.36
H_2O+	0.06	0.11	2.13*)	2.13*)	2.16*)	
Total	99.36	99.74	99.55	100.17	99.43	

Note

*) H_2O determined using the loss on ignition method.

The classical method described is that described by Kolthoff and Sandell (1952)

The analyses using the method described in this paper are averages of a set of four separate determinations.

Differences between analyses carried out in our laboratory using the methods descibed in this report and analyses of the same rocks carried out in another laboratory using Riley's macro method (Riley 1958).

The analyses quoted here were carried out as random routine work at both laboratories and are given as an example of possible (and in fact apparent) differences which occur when two laboratories use different analytical systems. Water has been determined in our laboratory by means of Penfield's method without flux.

TABLE XII

Method	As described	Riley	As described	Riley	As described	Riley
Sample	77-63 Nepheline-syenite		78-63 Nepheline-syenite		79-63 Nepheline-syenite	
SiO_2	54.35	54.55	52.60	53.04	53.87	54.39
TiO_2	0.41	0.38	0.30	0.24	0.42	0.42
Al_2O_3	11.29	11.80	14.58	15.68	12.04	12.65
Fe_2O_3	5.90	6.53	5.23	5.44	4.02	4.80
FeO	7.45	7.44	5.44	5.13	9.11	9.12
MnO	0.60	0.58	0.49	0.52	0.59	0.58
MgO	0.09	0.36	0.03	0.32	0.06	0.36
CaO	0.71	0.53	0.93	0.58	0.80	0.45
Na_2O	7.60	7.18	10.10	9.30	6.70	6.46
K_2O	6.43	6.12	4.71	4.43	7.40	7.23
P_2O_5	0.69	0.56	0.54	0.49	0.42	0.33
CO_2	0.00	0.00	0.00	0.00	0.00	0.00
H_2O+	2.38	2.75	3.54	3.86	2.46	3.08
Total	97.90	98.78	98.49	99.03	97.89	99.87

Semi-quantitative X-ray analysis

ZrO_2	0.1		0.4		0.05	
CeO_2	0.6		0.4		0.4	
ZnS	1.0		0.4		1.0	

TABLE XIII

Duplicate analyses of standard samples carried out in this laboratory

	Method as described		Other method
	%	%	%
Sample: G-1, Granite			
SiO_2	72.3	72.4	72.51*
TiO_2	0.28	0.26	0.26
Al_2O_3	14.22	14.20	14.21
CaO	1.41	1.41	1.35
MgO	0.41	0.41	0.37
MnO	0.03	0.03	0.03
Na_2O	3.23	3.30	3.29
K_2O	5.50	5.58	5.52
P_2O_5	0.09	0.09	0.08
Fe_2O_3 (A+A')	1.94	1.94	1.86
Fe_2O_3 (B)	1.91	1.87	
Sample: W-1, Diabase			
SiO_2	52.7	52.5	52.62*
TiO_2	1.07	1.07	1.08
Al_2O_3	14.79	14.77	15.00
CaO	10.80	10.85	11.00
MgO	6.46	6.46	6.60
Fe_2O_3 (A+A')	10.92	10.98	11.11
Sample: N.B.S. 99, Soda-feldspar			
SiO_2	68.40	68.51	68.66†
TiO_2	0.03	0.03	0.02
Al_2O_3	19.00	19.05	19.06
CaO	0.53		0.36
MgO	0.03		0.05
Na_2O	10.78	10.84	10.73
K_2O	0.40	0.40	0.41
Fe_2O_3 (A+A')	0.14	0.14	0.07

No corrections have been made for the chemicals used to bring the sample into solution.

* Goldich and Oslund (1956) in Stevens et al. 1960

† Average of 6 analyses reported by N.B.S.

EVALUATION OF THE ANALYTICAL RESULTS

The analyses can be divided between two assistants who both work on a set of 4-6 specimens at once. Each assistant in our laboratory notes her results on a specially printed filing card, one designed for the elements in Group A the other for elements in Groups B and C. Apart from these results the following details are noted under the symbols C, U, F and S for each sample.

C Whether or not gas is given off when hydrochloric acid is added to the peroxide sintercake after it has been leached with water, or when sulphuric acid is added while making solution B and during the determination of FeO (Groups B and C).

U Material undissolved when the sample is first brought into solution.

F Precipitation (if any) in the working solutions which occur during the analysis.

S Presence of H_2S as shown by the reaction on lead acetate paper when sulphuric acid is added to the moistened sample.

These notes are of obvious use to the analyst who is leading the work and who must judge the results. For example the presence of graphite is indicated by evolution of gas when sulphuric acid is added to the leached sinter cake while none is evolved when sulphuric acid is added to groups B and C. If gas is given off in both cases this suggests that carbonate is present which will require a carbonic acid determination.

$\underline{SiO_2}$. As may be seen from the tables given earlier the accuracy with which SiO_2 can be determined is comparable to the results obtained by classical methods (Fairbairn et al. 1951, Stevens et al. 1960). In both cases there is a slight tendency for low results which may be seen by the statistical grouping of results about the average value M shown in the sketches fig. 1, a and b.

The most likely explanation of this type of error distribution is that under some conditions more SiO_2 sticks onto the surface of the dishes than in other conditions.

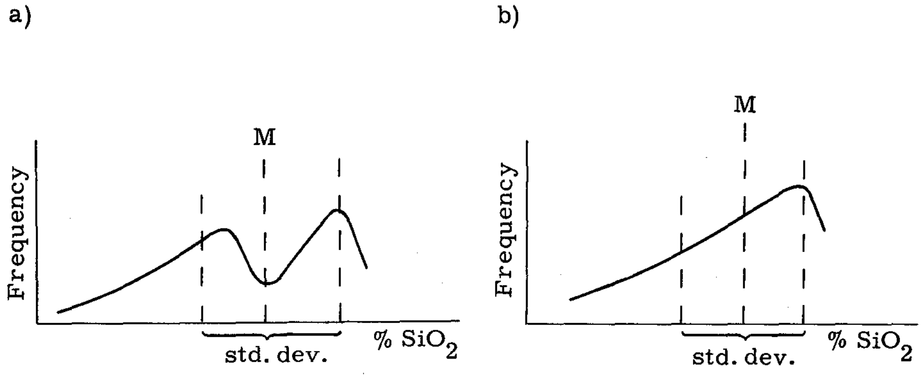

Fig. 1.

Aluminium. It can be seen that the aluminium determinations using the methods described are slightly lower than those obtained by classical methods. This is in good agreement with Watts' original work (Watts 1958).

Water. It should be noted that although it is possible to reproduce the figure for water this may not agree with the true water content present. The values obtained depend to a large extent on the method used (Fairbairn et al. 1951). Penfield's method without the addition of flux generally gives the lowest value while the loss on ignition method (with FeO correction) gives the highest. The correct value is somewhere between the two which may differ by as much as 100 %. (It should be remembered that the loss on ignition is not a measure of water content alone as sulphur, organic and other volatile material are given off and may be calculated wholly or partly as water.

A total much below 100 % may suggest that the water determination is too low. If this is still the case using the loss on ignition method it is worth looking for and determining more unusual elements. At GGU the elements Ba, Zr, Sr, Cr, rare earths etc., are usually determined using X-ray fluorescence which is sufficiently accurate provided a few standards are available.

Major errors in analysis and calculations can be seen if the total differs more than normal from 100 %. It is therefore a useful check on the accuracy of the analysis to note whether the total is close to 100 %.

As the figures for Fe_2O_3 and MgO are found by subtraction they are dependent on two variables and there is the possibility that their sum, and therefore the total, will appear normal although one of the variables is incorrect.

$$1)\ \%\,(Fe_2O_3) = \%\,(Fe_2O_3 + FeO.\,f) - \%\,(FeO.\,f)$$
$$2)\ \%\,(MgO) = \%\,(MgO + CaO.\,f) - \%\,(CaO.\,f)$$

As the molecular weight of Fe_2O_3 is larger than FeO and the molecular weight of MgO is smaller than CaO, a value of FeO which is much too low or a value of CaO which is much too high may lead to an analysis total exceeding 100 %.

If the latter is the case it may be worth checking FeO and CaO. For example a CaO value which is much too high (and a corresponding low MgO value) may be caused by the addition of the incorrect buffer during titration. Otherwise major errors in the calculation of FeO and CaO are necessary before the mistake can be seen in the final total.

PROCEDURES

Group A - SiO_2, TiO_2, Al_2O_3, Fe_2O_3 total, CaO and MgO

Preparation of solution A ("insoluble" SiO_2, "soluble" SiO_2, CaO and MgO)

Reagents

1) Sodium peroxide, E. Merck, p.a. 2.0 g portions are weighed out into 10 ml specimen tubes which are immediately sealed with an airtight stopper and kept in a desicator.
2) 20 % by vol. hydrochloric acid.

Procedure

1) Weigh out 0.5000 g of the sample and transfer to a platinum crucible.
2) 2.0 g sodium peroxide is mixed with the sample by stirring with a platinum rod. Any particles which stick to the rod are rubbed off onto a little sodium peroxide on a piece of paper which is then added to the main portion.
3) The covered crucible is placed in a muffle-oven which has already been adjusted to keep a constant temperature of $480^\circ \pm 10^\circ C$. Care is taken to see that this temperature is not exceeded. After 15 minutes the crucible is removed from the oven and placed to cool on a steel plate.
4) The sinter cake is transferred to a 100 ml clear, flawless quartz dish.
5) Cover the dish with a watch glass and pour approximately 20 ml cold distilled water in via the lip. A strong reaction takes place which stops after a few seconds. Rinse the watch glass, stir with a glass rod and then add 10 ml conc. hydrochloric acid. Any evolution of gas at this point is noted (CO_2).
6) The residue of material in the crucible is extracted by filling up the crucible with distilled water once followed by filling it twice with 1:1 hydrochloric acid (the last time warm on a hot plate). Each time the contents of the crucible are rinsed over into the dish with distilled water. Finally fragments which have spattered on the inner walls of the dish are rinsed down and the glass rod is rinsed and put to one side.
7) The dish is placed on a boiling water bath. It must remain there for at least 2 hours after all the visible liquid has been evaporated.
8) Add 25 ml 20 % by vol. hydrochloric acid, stir with a glass rod and cover with a watch glass. After 10 minutes remove from the water bath, rinse the watch glass and stir with the glass rod.

9) After another 5 minutes filter the solution through a 9 cm filter (type: "weissband") into a 100 ml volumetric pyrex flask. Wash the filter with warm distilled water until the flask is nearly full.
10)After cooling to room temperature fill up to the 100 ml mark with distilled water and mix well. This is Solution A.

"Insoluble" silica

1) Place the filter containing the "insoluble" silica in a 30 ml platinum crucible and dry for half an hour at 110°C.
2) Burn off the filter.
3) Ignite the crucible (with the lid partially closed) in an electric furnace at 1150°C for 15 minutes.
4) Place in a desicator and weigh after 3/4 of an hour. Note the weight 1.
5) Moisten the ignited silica in the crucible with a few drops of distilled water and 5-6 drops 1:1 sulphuric acid. Add 5 ml hydrofluoric acid and place on a hot plate. When the hydrofluoric acid has evaporated raise the heat - for example by using a quartz surface evaporater, and continue heating until there are no more SO_3 fumes.
6) Heat in an electric furnace at 1150° for 5 minutes (or over a good burner). Set in a desicator, weigh again after 3/4 of an hour. Note weight 2.
7) Calculation.

   % "Insoluble" silica = (weight 1 - weight 2) x 200.

"Soluble" silica

Reagents

1) Ammonium molybdate solution. 10 g of ammonium molybdate are weighed out accurately and transferred to a polyethylene bottle with a mark at the 100 ml level. It is then dissolved in 50 ml 2N ammonia and is diluted up to 100 ml with distilled water.
2) 10 % oxalic acid. 50 g is dissolved in 450 ml distilled water. The solution is kept in a polyethylene bottle.
3) Reducing solution. Dissolve 0.15 g 1-amino-2 naphthol-4-sulphonic acid and 0.7 g anhydrous sodium sulphite in 100 ml of distilled water. Add 9.0 g of sodium-meta-bisulphite and stir until the solution is clear. Keep in a polyethylene bottle. The solution will keep for a maximum of 2 months.
4) 0.1 M sodium bisulphate solution in a polyethylene bottle.

5) 5 % by vol. hydrochloric acid in a polyethylene bottle.
6) SiO_2 standard. Weigh out accurately 0.1183 g sodium metasilicate ($Na_2SiO_3 . 9H_2O$) and dissolve it in approximately 500 ml distilled water. Add 50 ml concentrated hydrochloric acid and dilute to 1 litre. Keep in a polyethylene bottle. This standard has a concentration of silica corresponding to a solution A containing 2.5 mg "soluble" silica or 0.5 % of the sample.

Directions

1) Pipette 2.5 ml standard, 2.5 ml solution A and 2.5 ml 5 % by vol. hydrochloric acid into different 50 ml volumetric flasks.
2) Add 5 ml 0.1 M sodium bisulphate.
3) Add 0.5 ml of the molybdate solution. Mix well and allow to stand for 10 minutes. The pH at this point should be between 0.85 and 1.35.
4) After exactly 10 minutes add 2.5 ml oxalic acid, immediately followed by 1 ml reducing solution. Mix well.
5) Dilute to the 50 ml mark with distilled water and put aside for at least an hour.
6) Measure the extinction in a 1 cm cell at 650 mμ (the solution of 5 % by vol. hydrochloric acid is used as a zero reference).
7) Calculation

$$\% \text{ "soluble" silica} = 0.5 \frac{\text{extinction sample}}{\text{extinction standard}}$$

Calcium and magnesium

Reagents

1) 8-hydroxyquinoline. Dissolve 20 g in acetone and dilute to 100 ml.
2) 2M sodium acetate, made by dissolving the salt in distilled water. Keep in a polyethylene bottle.
3) Chloroform p.a.
4) Titrant: Titriplex III-solution (disodium salt of ethylene-diaminetetraacetic acid). 3.00 g Titriplex III (E. Merck) is dissolved in distilled water and diluted up to 5 litres in a volumetric flask. Keep in a polyethylene bottle.
5) Buffer pH 12. 100 g sodium hydroxide are dissolved in distilled water and diluted up to 1 litre. Keep in a polyethylene bottle.

6) Buffer pH 10. 70 g ammonium chloride are dissolved in 600 ml ammonia and diluted up to 1 litre with distilled water. Keep in a polyethyle bottle.
7) Erio-T-indicator. 0.2 g Eriochrome Black T is mixed with 50 g potassium chloride in an agate mortar. The potassium chloride crystals are crushed to a fine powder at the same time. The powder is then mixed thoroughly with 5 g ascorbic acid, 1.0 g magnesium-titriplex (the magnesium disodium salt of ethylene-diaminetetra-acetic acid), and 25.0 mg Titriplex III.
8) Cal-red-indicator. 0.6 g cal-red (Patton and Reeder 1956) is mixed with 50 g potassium chloride in an agate mortar at the same time that the latter is crushed to a fine powder. Both are then mixed with 10 g of ascorbic acid.
9) Standard $CaCl_2$ solution. Weigh out 1.7850 g $CaCO_3$ (E. Merck p.a. dried at 110°C for 1 hour) in a 400 ml beaker, add 50 ml distilled water and then dilute hydrochloric acid gradually until all the carbonate has dissolved. Add 70 ml concentrated hydrochloric acid, transfer to a two litre volumetric flask and dilute up to the mark with distilled water. Keep in a polyethylene bottle. The solution contains the equivalent of 0.500 mg CaO/ml.
10) Standard $MgC1_2$ solution. Dissolve 0.3015 g of "specpure" magnesium in a few millilitres of dilute hydrochloric acid. Add 70 ml concentrated hydrochloric acid and dilute up to 2 litres with distilled water in a volumetric flask. Keep in a polyethylene bottle. The solution contains the equivalent of 0.250 mg MgO/ml.
11) Sea sand, purified with acid and ignited (E. Merck).

Extraction of disturbing elements

A 500 ml extraction flask is filled with 250 ml chloroform, 100 ml 30 % by vol. sulphuric acid and approximately 0.25 g sand. 50 ml of chloroform are poured into the bottom of the extractor. The apparatus is then ready for at least 10 extractions which are carried out in the following way:

1) Pipette 20 ml of solution A into the extractor.
2) Add 25 ml 2M sodium acetate solution and mix by carefully swirling the extractor. (The pH should be between 4.9 - 5.1).
3) Add 5 ml 8-hydroxyquinoline and mix again.
4) Put the apparatus together and connect up the supply of cooling water.
5) Put the heating element full on. When distilled chloroform begins to run back set the element so that it gives a suitable boiling temperature. Continue the extraction for half an hour. The water rich fraction should be clear

and colourless. (It does not matter that a few dark coloured drops stick onto the glass walls as these are easily removed during filtering).

6) Let the apparatus cool down (approximately 1/2 an hour).
7) Pour the contents of the extractor into a 100 ml separation funnel and rinse out well with distilled water.
8) Tap off the chloroform rich fraction and pour it back into the extractor.
9) Filter the water rich fraction into a 250 ml volumetric flask through a moistened 12.5 cm filter (type "Schwartzband").
10) Rinse the separation funnel a couple of times with distilled water, filter the rinsing water and finally wash the filter.
11) Dilute the filtrate with distilled water up to the 250 ml mark and mix.
12) The same operation is carried out using standard solutions instead of the sample solution.

Titration

Both magnesium and calcium are titrated with Titriplex III on the photoelectric titrator, using an orange filter (Ilford No. 607). The end point is determined by drawing a graph of the critical range.

Aliquots of the extracted solutions are used to determine two different titrant volumes;

a) V_{ET} = volume of titrant used when titrated against 50 ml of the extracted solution using the pH 10 buffer and Erio T-indicator (MgO titration).

b) V_{CR} = volume of titrant used when titrated against 50 ml of the extracted solution using the pH 12 buffer and Cal-red-indicator (CaO titration).

Procedure

1) Pipette 50 ml of the extracted solution A into a 250 ml titration beaker and dilute to approximately 150 ml with distilled water.
2) Add 10 ml buffer.
3) Start stirring and add 0.10 g of indicator.
4) Add the titrant from the burrette until the colour of the solution shows that the end point is close. Continue titration until the nearest whole number of millilitres has been added and note the burrette reading.
5) Set the galvanometer on 0 (absorption scale) by using the potentiometer and fill the burrette to the 0 point.

6) Continue adding titrant 0.5 ml at a time and read the galvanometer after each addition of titrant. Note all readings.

   When the difference between three consecutive galvanometer readings is constant (normally = 0) the titration is finished.

7) Plot on graph paper with the amount of titrant on the abscissa, the turning point of the curve gives the titrations end point. Read and note the ml of titrant used at the end point.

8) Add the amount of titrant used (4 and 7 above) and note these as V_{ET} and V_{CR} respectively.

Standardisation of the titrant and calculation of % CaO and % MgO

1) Titrate 50 ml of the extracted CaO standard in the same way as described above and determine the titrant volumes V_{ET} and V_{CR}. These should be equal provided the correct indicator is used. If not, the factor f is calculated, where $f = V_{ET}/V_{CR}$ and this is used later as a conversion factor for V_{CR} when the % of MgO is calculated. Note the factor $f_{Ca} = 10/V_{CR}$.

2) Titrate 50 ml of the extracted MgO standard as described above and determine V_{ET}.

Note the factor $f_{Mg} = 5/V_{ET}$.

3) Calculation: When V_{ET} and V_{CR} are determined for 50 ml of the extracted solution A, the calculation is as follows:

$$\% \text{ CaO} = V_{CR} \cdot f_{Ca}$$

$$\% \text{ MgO} = (V_{ET} - V_{CR} - 2.0 \cdot \% \text{MnO}) \cdot f_{Mg}$$

Note

1) (2.0 . %MnO) is the correction used when small amounts of manganese are present. If more than 0.3 % MnO is present it is removed from the extracted solution by precipitation and filtering. This can be done rapidly following the method described by Riley (1959). The correction in the formula above is then unnecessary.

2) The amount of Titriplex III additive necessary in the Erio T-indicator probably varies when chemicals from different firms are used.

Preparation of solution A' (Fe_2O_3, TiO_2 and Al_2O_3 in solutions A + A')

Reagents

Potassium pyrosulphate is weighed out in 2.0 g portions and stored in 10 ml specimen tubes which are ready for use.

Procedure

1) After the determination of "insoluble" silica by defuming with hydrofluoric acid and ignition, the crucible still contains small amounts of oxides which contaminated the crude silica. Add 2.0 g potassium pyrosulphate, cover the crucible and place for half an hour in a muffle-oven at 575 $\pm 10^{\circ}C$.
2) Let the crucible cool down, add 1.0 ml 1:1 sulphuric acid and 3/4 fill with distilled water.
3) Heat gently on a hot plate until everything is dissolved. Allow to cool and transfer contents to a 100 ml pyrex volumetric flask. Fill up to the mark with distilled water and mix.

Determination of Fe_2O_3 and TiO_2

Reagents

1) Tiron-solution. 4.0 g Tiron (Brenzcatechin-3.5-disulphonic acid) is dissolved in 100 ml distilled water.

2) Acetate-buffer. 420 g hydrous sodium acetate (reagent grade with $3H_2O$) and 100 ml acetic acid are dissolved in distilled water, diluted to 5 litres and mixed.

3) Sodium dithionite, p.a. ($Na_2\ S_2O_4$).

4) Fe_2O_3 standard. 0.500 g Ferrum oxydatum E. Merck, p.a. (dried at 110°C) is weighed out and transferred to a 250 ml beaker. 50 ml concentrated hydrochloric acid and 50 ml distilled water are added and the beaker is placed on a boiling water bath.

After approximately 1 hour any undissolved material is filtered off and washed. The filtrate is collected in a 1 litre volumetric flask. The filter is burnt off, ignited (in a quartz crucible) and the remaining oxides are taken up with 1 g potassium pyrosulphate. The melted mass is dissloved in distilled water and is transferred to the filtrate in the volumetric flask. Dilute the solution to 1 litre and mix. The concentration of iron in this standard solution corresponds to a solution A made by completely dissolving a specimen containing 10 % Fe_2O_3.

5) TiO_2 standard.

Weigh out 0.0500 g TiO_2, N.B.S. standard sample no. 154a (dried at 110°C). Take up with 10 g potassium pyrosulphate in a clear quartz crucible. The cooled mass is transferred to a beaker and dissolved in 10 ml 1:1 sulphuric acid + approximately 50 ml distilled water. Transfer the solution to a 1 litre pyrex volumetric flask, dilute to the mark and mix. This standard corresponds to a solution A' which contains the total amount of titanium from a sample with 1 % TiO_2.

6) 5 vol % hydrochloric acid (as used for the determination of "soluble" silica).

Procedure

1) Pipette 2.5 ml 5 vol % by vol. hydrochloric acid into a 100 ml volumetric flask (0 - reference). Pipette 2.5 ml solution A into another 100 ml flask and 2.5 ml Fe_2O_3 standard into a third flask.
2) Add 5 ml tiron reagent to each of the flasks and rinse the sides of the flasks with distilled water.
3) Pipette nothing into the first bottle,
   2.5 ml solution A' into the second, and
   2.5 ml TiO_2 standard into the third.
   (Let the pipette drain onto the walls of the measuring flasks). Rinse the sides of the flasks with distilled water.
4) After approximately 2 minutes add 50 ml buffer. Fill up to the mark with distilled water and mix. (The pH should now be 4.7).
5) Measure the extinction of the standard and sample at 560 mμ.

Calculation

$$\% \ Fe_2O_3 = 10 \times \frac{\text{extinction sample}}{\text{extinction standard}}$$

6) 15-20 g sodium dithionite is added to the remaining solution and the flask is swirled gently until the reaction is complete (the liquid must not be shaken).
7) Measure the extinction of the standard and specimen at 410 mμ before 10 minutes have passed.

Calculation

$$\% \ TiO_2 = 1 \times \frac{\text{extinction sample}}{\text{extinction standard}}$$

Determination of Al_2O_3

Reagents

1) Precipitation reagent. 70 ml ammonia, 60 g ammonium chloride and 0.1 g methyl red are dissolved in distilled water and diluted up to one litre. Keep in a pyrex glass bottle.
2) Washing solution. 2 % sodium chloride solution in distilled water.

3) Sodium hydroxide, 25 %, in a polythene bottle.

4) Potassium fluoride solution, 25 % made of 2 kg pure potassium fluoride (E. Merck), 6 litres distilled water, and 7.5 ml 25 % potassium hydroxide. The pH is corrected if necessary by adding potassium hydroxide until between 10.8-11.2. Keep in a polyethylene bottle.

5) 0.1 N hydrochloric acid.

6) Aluminium standard. Dissolve 0.5291 g pure aluminium wire in 50 ml concentrated hydrochloric acid and 100 ml distilled water. Dilute up to 1 litre in a measuring flask. This solution contains the equivalent of 1.0 mg Al_2O_3/ml, corresponding to a Solution A which contains the total aluminium from a sample with 20 % Al_2O_3.

Note: Alkaline solutions must be kept so that carbon dioxide from the air does not get in. All reagents including distilled water must be measured out accurately.

Procedure (separation and titration)

1) Pipette 10 ml solution A and 10 ml solution A' into a centrifuge glass.
2) Add the precipitating reagent until the point at which the indicator changes from orange to yellow. Make sure that the solution in the lower narrow part of the glass is mixed with the rest of the solution by stirring with a glass rod. Rinse the glass rod and fill the glass up to the 50 ml mark with distilled water.
3) Centrifuge for 5 minutes.
4) Decant the clear yellow solution away.
5) Add 25 ml 2 % sodium chloride and stir with the glass rod. Rinse the glass rod and fill up to 50 ml with distilled water.
6) Centrifuge for 5 minutes.
7) Decant again.
8) Dissolve the precipitate in the centrifuge glass with 2 ml 1:1 hydrochloric acid.
9) Transfer the solution into a 600 ml glass beaker by filling the centrifuge glass to the 50 ml mark 5 times and pouring the contents each time into the beaker so that the total volume solution is approximately 250 ml.
10) Put the electrodes of the pH measuring instrument into the solution, switch on and add 25 % sodium hydroxide until the pH is 11.5-12.0.

11) Add 1:1 hydrochloric acid carefully from a burette until the pH has fallen to 11.0.

12) Rinse the beaker and the electrodes with 50 ml distilled water (from a pipette).

13) Titrate with 0.1 N hydrochloric acid until the pH is 10.0 without noting the amount used.

14) Add 50 ml potassium fluoride solution from a pipette.

15) Titrate again with 0.1 N hydrochloric acid until pH 10.0 and note the amount used a.

16) Repeat stages 10-15 using 1 ml 1:1 hydrochloric acid in 250 ml distilled water instead of the dissolved precipitate. Note the amount used b.

17) Repeat stages 10-15 again using 10 ml standard in 240 ml distilled water. Note the amount used a'.

Calculation

From a' and b the factor f may be calculated,

$$f = \frac{20}{a'-b}$$

$$\% \, Al_2O_3 = f(a - b)$$

Group B - Na_2O, K_2O, Fe_2O_3 total, MnO and P_2O_5

Preparation of solution B

1) Weigh out 0.1000 g of the sample and transfer to a 50 ml platinum crucible.
2) Moisten the powder with distilled water and add 1.5 ml 1:1 sulphuric acid.
3) Add 5 ml hydrofluoric acid.
4) Cover the crucible with a tight fitting lid and digest overnight on a boiling water bath.
5) Remove the cover and evaporate the hydrofluoric acid.
6) Add 15-20 drops (approximately 0.5 ml) nitric acid and let the crucible stand for 10 minutes on a hot plate. (Beware of splashes.). Then use the quartz-surface evaporator as an additional heat source until strong fumes of sulphur trioxide evolve.
7) Let the crucible cool down.
8) Fill the crucible 3/4 full with distilled water cover and let it stand on a low hot plate until solution clear.
9) Let the crucible cool down, transfer the solution to a 50 ml Pyrex volumetric flask, fill up to the mark and mix. This is solution B.

10)Make a "blind" solution B by the same method.

Note

Aliquots for the determination of the alkali metals in solution B must be taken the same day that the solutions are put into the flasks.

Determination of Na_2O and K_2O

Reagents

1) Amberlite IRA-400 (analytical grade) in citrate form. Directions for preparation and regeneration are given by Riley (1958).
2) Ammonium sulphate solution. 100 g/l.
3) Sodium standard. Make a stock solution which contains 0.2291 g anhydrous sodium sulphate per litre, equivalent to 100 mg Na_2O/l. From this solution working standards with 0, 1, 2, 3, 4 and 5 ppm Na_2O containing 4 ml 10% ammonium sulphate per 100 ml are made up.
4) Potassium standard. Make a stock solution which contains 0.1850 g anhydrous potassium sulphate per litre, equivalent to 100 mg K_2O/l. From this solution working standards are made in the same way as described above for sodium.

Note

All the reagents used for alkali determinations must be kept in polyethylene bottles.

Details of the ion exchange column's shape and filling are given by Riley (1958). It should be noted that we have found it safest to use capillary tubing on the ion exchange column outlet to obtain quantitative results.

Procedure

1) Pipette 2 ml 10 % ammonium sulphate solution into a 50 ml volumetric flask and place under the outlet of the ion exchanger.
2) Pipette 1 ml solution B into the top of the column.
3) Let the solution soak in the exchanger and wash it down with small amounts of distilled water until the flask is approximately 3/4 full.
4) Remove the flask, fill up to the mark and mix well.
5) When the "blind" value is wanted repeat using the "blind" solution B.

Calibration of instrument

1) Adjust the air pressure to 10 lb/sq.in. and the gas supply as written in the instrument's directions for use.

2) Adjust the galvonometer needle so it gives exactly 100 at 5 ppm Na_2O (see that the correct filter is used) and 0 using distilled water. Run all the Na_2O standards from 0 to 5 ppm, and check 0 and 100 adjustment between each reading. Repeat everything and note the average value for each concentration so that a graph may be drawn.
3) Repeat 2) using the K_2O standards from 0-5 ppm.
4) Draw up a curve for each of the alkali metals with % metal oxide on the abscissa.

Photometric measurements of the sample and "blind" solutions

1) Check 100 and 0 points with 5 ppm Na_2O and distilled water. Measure the solutions. Check 100 and 0 points and measure the solutions in the opposite order. (This applies to a series of 4 samples).
2) Repeat 1) using K_2O standard (remember to change the filter).
3) Read off the % of the alkali oxides from the curves. The % alkalis given from the curves minus the % given by the "blind" solution B gives the % metalic oxides in the specimen.

Determination of Fe_2O_3 (total)

Reagents

1) Hydroxylamine-hydrochloride, 10 % solution.
2) Sodium citrate-dihydrate, 10 % solution.
3) Orthophenanthroline, 0.1 % solution.
4) Fe_2O_3 standard. Weigh out 0.491 g Mohr's salt (E. Merck). Dissolve in a beaker in 10 ml 1:1 sulphuric acid and approximately 300 ml distilled water while stirring and warming to boiling point.

When completely dissolved allow to cool, transfer to a 500 ml volumetric flask, dilute to the mark and mix. This solution contains the equivalent of 0.2 mg Fe_2O_3/ml corresponding to a solution B made from a sample with 10.00 % Fe_2O_3.

Procedure

1) Set out 3 100 ml volumetric flasks and pipette nothing into the first (0-reference),

   5 ml solution B into the second,

   5 ml standard into the third.
2) Add 5 ml hydroxylamine-hydrochloride solution to each of the flasks and allow them to stand for 10 minutes.

3) Add 10 ml orthophenanthroline solution to each flask.
4) Add 10 ml sodium citrate solution to each flask.
5) Dilute up to 100 ml mark with distilled water and mix.
6) After an hour measure the extinction at 560 mμ.

Calculation

$$\% \ Fe_2O_3 \text{ total} = 10 \times \frac{\text{extinction sample}}{\text{extinction standard}}$$

Determination of MnO

Reagents

1) Potassium periodate.
2) Acid mixture. 1300 ml distilled water, 200 ml phosphoric acid and 500 ml sulphuric acid are mixed together.
3) Standard MnO. Weigh out 0.0535 g N.B.S. standard sample no. 25b (manganese ore) and transfer to a 250 ml beaker. Add 25 ml 1:1 nitric acid and 2-3 ml 3 % hydrogen peroxide. Place on a boiling water bath until there are no dark remains left. Allow to cool and add 50 ml concentrated sulphuric acid. Heat to evaporate and continue heating until sulphur trioxide fumes are given off. Allow to cool and dilute to approximately 200 ml after which all the material should have dissolved.

Allow to cool to room temperature and transfer to a 2 litre volumetric flask, fill up to the mark with distilled water and mix. Keep in a glass bottle with a glass stopper. This solution contains the equivalent of 0.02 mg MnO/ml, which corresponds to a solution B made from a sample containing 1.00 % MnO.

Procedure

1) Pipette 10 ml distilled water (for 0-reference), 10 ml standard solution and 10 ml solution B into separate 100 ml beakers.
2) Add 25 ml of the acid mixture to each beaker.
3) Add approximately 0.2 g potassium periodate.
4) Cover the beakers with watch glasses and place on a hot plate. Keep on the hot plate for 10 minutes after boiling point is reached.
5) When the solutions have cooled slightly transfer contents to 50 ml measuring flasks. Fill nearly to the 50 ml mark with distilled water and let the bottles cool down to room temperature. (Place on a large metal plate or under running water).

6) After cooling fill up to the mark and mix.
7) Measure the extinction at 525 mμ.

Calculation

$$\% \text{ MnO} = 1 \times \frac{\text{extinction sample}}{\text{extinction standard}}$$

Note

To save solution B when pipetting use a water repelling pipette. (It is then unecessary to rinse the pipette with the solution before taking aliquots).

Determination of P_2O_5

Reagents

1) Molybdivanadate solution. a) Weigh out 1.25 g ammonium-metavanadate and dissolve in 400 ml 1:1 notric acid. b) Weigh out 50 g ammonium molybdate and dissolve in 400 ml distilled water. Pour "a" into "b" while stirring and fill up to 1 litre with distilled water.

2) P_2O_5 standard. Weigh out 0.2876 g KH_2PO_4, (dried for an hour at 110°C), dissolve in distilled water, dilute to 100 ml in a volumetric flask and mix.

Pipette 10 ml of this solution into a 1 litre volumetric flask, add 10 ml 1:1 nitric acid, dilute up to the mark and mix. Keep in a glass bottle with a glass stopper. This standard solution contains the equivalent of 15.0 mg P_2O_5/litre corresponding to a solution B made from a sample with 0.75 % P_2O_5.

Procedure

1) Pipette 15 ml distilled water (for 0-reference), 15 ml solution B and 15 ml standard solution into different 50 ml volumetric flasks.
2) Add 10 ml molybdivanadate solution into each flask and mix.
3) Fill to the mark with distilled water, mix and allow to stand at least 5 minutes before taking a photometric measurement.
4) Measure the extinction of the specimen and the standard at 430 mμ.

Calculation

$$\% \text{ } P_2O_5 = 0.75 \times \frac{\text{extinction sample}}{\text{extinction standard}}$$

Note

To save solution B when pipetting use a water repelling pipette.

Group C - FeO, H_2O^+ and CO_2

Determination of FeO

Reagents

1) Acid-indicator mixture. Mix carefully 250 ml sulphuric acid, 250 ml phosphoric acid and 250 ml distilled water. When the mixture has cooled add 25 ml 0.2 % barium-diphenylamine sulphonate and distilled water to a total volume of 1 litre. Mix well.
2) Boric acid solution, 5 % (saturated).
3) Standard potassium dichromate. Weigh out 2.728 g $K_2Cr_2O_7$ p.a. (dried for an hour at 110°C). Dissolve it in distilled water and dilute to 2 litres in a volumetric flask. This standard solution contains the equivalent of 2.00 mg FeO/ml.

Procedure

1) Weigh out 0.500 g of the sample in a 40 ml platinum crucible.
2) Moisten the powder with approximately 1 ml distilled water and add 10 ml 1:1 sulphuric acid. If gas is given off at this point it should be noted. Likewise the presence of H_2S should be noted.
3) Cover the crucible and heat until nearly boiling on an electric heater.
4) Remove the cover slightly to one side and add 5 ml hydrofluoric acid. Replace the cover immediately.
5) Heat continuously until boiling and then allow to boil for 10 minutes.
6) While the solution is boiling a 600 ml beaker is filled half full with distilled water after which 25 ml boric acid solution is added.
7) After 10 minutes boiling the covered crucible is put into the beaker using tweezers. Add 20 ml acid-indicator mixture, stir and titrate immediately until the colour changes from grey to strong blue-violet. Note the amount of titrant used.
8) Check to see that there are no dark particles remaining at the bottom of the beaker.

Calculation

$$\text{ml titrant} \times 0.4 = \%\ \text{FeO}$$

Determination of H_2O^+ and CO_2

We follow the classic directions given in Kolthoff and Sandell's textbook (1952) to determine water by Penfield's method (see summary). Carbon dioxide is only determined if there is a positive qualitative reaction with H_2SO_4. We have used the loss on ignition after correction for FeO as an approximate check on the sum of $CO_2 + H_2O^+$.

The detailed instructions for these determinations will not be repeated here.

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