A Contribution to the Analytical Chemistry of Silicate Rocks: A Scheme of Analysis for Eleven Main Constituents Based on Decomposition by Hydrofluoric Acid

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Acknowledgements.

Introductory notes.

The names of scientific journals are written in accordance with the Chemical Abstracts 1961 List of Periodicals.

In the separate references the details are given in the following order: name of author(s), name of journal, volume number, year of publication (in parenthesis) and page number.

The prename of authors is only given as initials.

The standard chemical nomenclature has been used. With the exception of the words sulfuric and sulfonic, sulphur and sulphur compounds have been written with ph.

Abbreviations.

In addition to the standard abbreviations, the following special abbreviations are used:

$$° = °C$$
$$h = hour(s)$$
$$min = minute(s)$$

I. The conventional, and modified conventional, schemes of silicate rock analysis.

A. Introduction.

For about two hundred years the principles followed in the chemical analysis of silicate rocks have been almost unchanged.[*] These principles are found in the selection of analytical methods for separation and determination known as the conventional or classical scheme of rock analysis.

In the progress of chemistry the conventional scheme has been modified and revised as new reagents and instruments were placed at the disposal of the analyst. However, the main features of the early schemes are still prevalent, and some of the methods of separation and determination are practically unchanged.

Among the chemists that have contributed to the development of rock analysis up to about 1850 are Bergman, Klaproth, Berzelius, and Thomson.[**] Important contributions were made later by Hillebrand, Dittrich[3], Jannasch[4] and Washington.

In 1894 Hillebrand[5] pointed out that earlier analyses had been incomplete in failing to report the presence of such important constituents as titanium and phosphorus, now known to be universally present in rocks.

Hillebrand[6] and Washington[7] critically revised the earlier schemes and devised and published through a number of years new and improved procedures for the major and minor constituents of rocks. For nearly

[*] The principles followed in an early scheme of rock analysis are exemplified in a paper by Bergman[1].

[**] For a survey of the development of analytical chemistry, including the principal contributors, in the period from 1750 to 1850, see e.g. Campbell and Mallen[2].

1. T. Bergman, Kgl. Svenska Vetenskapsakad. Handl., 40 (1779) 224.
2. W. A. Campbell and C. E. Mallen, Proc. Univ. Durham Phil. Soc., Ser. A, 13 (1959) 108.
3. M. Dittrich, Mitt. Badischen Geologischen Landesanstalt, 3 (1894) 75.
4. P. Jannasch, Praktischer Leitfaden der Gewichtsanalyse, von Veit & Comp., Leipzig, 1897.
5. W. F. Hillebrand, J. Am. Chem. Soc., 16 (1894) 90.
6. W. F. Hillebrand, U. S. Geol. Surv. Bull., No. 148 (1897) 15; No. 176 (1900); No. 305 (1907); No. 422 (1910) and No. 700 (1919).
7. H. S. Washington, Manual of the Chemical Analysis of Rocks. First edition, John Wiley & Sons, New York, 1904.

fifty years the authoritative textbook of rock analysis has been the one published in 1919 by Hillebrand (Bulletin No. 700 of the U. S. Geological Survey). This scheme is — in a more or less modified form — universally applied to-day. Modified conventional schemes are found in most textbooks of inorganic quantitative analysis. As an example of a typical modified conventional scheme, the following outline (reproduced from Stevens and Niles[8]) is given.

Outline of a conventional rock analysis

Main portion

Decompose sample by fusing with Na_2CO_3. Dissolve in dilute HCl. Evaporate to dryness. Redissolve in dilute HCl. Filter. Evaporate filtrate to dryness. Redissolve in dilute HCl. Filter.

Combined filtrates
Neutralize with NH_4OH to precipitate R_2O_3. Filter. Redissolve precipitate in dilute HCl. Reprecipitate with NH_4OH. Filter.

Combined precipitates
SiO_2 + residue (R_2O_3 + undissolved sample): Ignite and weigh. Add an excess of HF and a little H_2SO_4. Again ignite and weigh. Difference in weights is SiO_2. Add SiO_2 from R_2O_3 precipitate to get total SiO_2. Combine residue from SiO_2 with R_2O_3 precipitate.

Combined filtrates
Precipitate Ca as oxalate by adding excess of ammonium oxalate, $(NH_4)_2C_2O_4$. Filter. Redissolve CaC_2O_4 in dilute HCl. Neutralize with NH_4OH and reprecipitate CaC_2O_4. Filter.

Precipitate
R_2O_3 (Al_2O_3, Fe_2O_3, TiO_2, P_2O_5, and others), residual SiO_2, traces of MnO, undissolved residue: Determine all constituents other than Al_2O_3 and calculate Al_2O_3 by difference. See analysis of R_2O_3 below.

Combined filtrates
Add an excess of $(NH_4)_2HPO_4$ and NH_4OH. Redissolve precipitate in dilute HCl and reprecipitate.

Precipitate
CaC_2O_4. Ignite and weigh as CaO.

Filtrates
Discard. Contain alkali metals and elements not completely separated in foregoing precipitations.

Precipitate
Mg as magnesium ammonium phosphate with most of the MnO, BaO, and other constituents not completely removed by preceding precipitations: Ignite and weigh as $Mg_2P_2O_7$. Determine Mn and subtract as $Mn_2P_2O_7$. Calculate MgO.

8. R. E. Stevens and W. W. Niles, U. S. Geol. Surv. Bull., No. 1113 (1960) 3.

Analysis of R_2O_3 precipitate

Residual silica (SiO_2). — Dissolve R_2O_3, from above, by fusion with pyrosulfate and solution in dilute H_2SO_4, evaporate to fumes of SO_3, dilute with water, and digest to coagulate SiO_2. Filter, and ignite the precipitate and weigh. The ignited precipitate is SiO_2 + residue. Add HF, evaporate, ignite, and weigh residue. Difference in weights is residual SiO_2. Dissolve residue by fusion with a little pyrosulfate and combine with filtrate from residual SiO_2.

Total iron as Fe_2O_3. — May be determined on filtrate from SiO_2 in R_2O_3 or in a separate sample, by reduction to Fe^{+2} and measurement of the quantity of oxidant needed to oxidize to Fe^{+3}. Ti, V, Cr and others may interfere in some procedures. Reductants used: For sulfuric acid solution, zinc amalgam, H_2S, or SO_2; for hydrochloric acid solutions, $SnCl_2$, silver metal, or SO_2. Standard oxidant solutions used: For sulfuric acid solutions, $KMnO_4$ or $Ce(SO_4)_2$; for hydrochloric acid solutions, $KMnO_4$ (in the presence of excess Mn^{+2} and H_3PO_4), $K_2Cr_2O_7$, or $Ce(SO_4)_2$.

Titanium dioxide (TiO_2). — Usually determined either in filtrate from residual SiO_2 in R_2O_3 or in a separate sample by measuring the yellow color of peroxidized titanium in a sulfuric acid solution of the sample. Vanadium and iron may interfere.

Phosphorus pentoxide (P_2O_5). — Determined on a separate sample, dissolved in dilute HNO_3, by precipitating as the ammonium phosphomolybdate, and weighing as $Mg_2P_2O_7$ or determining colorimetrically.

Alumina (Al_2O_3). — Taken as R_2O_3 — (Fe as Fe_2O_3 + TiO_2 + SiO_2 in R_2O_3 + P_2O_5). Other constituents in the R_2O_3 (Cr_2O_3, V_2O_5 and others) are usually counted as Al_2O_3. Errors in determining other constituents in the R_2O_3 are reflected in errors in the figure for Al_2O_3.

Determinations made on separate samples

Ferrous and Ferric Oxides

Ferrous oxide (FeO). — Determined on a separate sample by dissolving in HF + H_2SO_4, diluting with dilute H_2SO_4 containing boric acid (to complex the fluoride ion), and titrating with a standard oxidant. Air-oxidation and failure to dissolve all FeO cause low results. Air-oxidation while sample is being dissolved is prevented by steam (simple method), or nonoxidizing gas (usually CO_2).

Valid figures for FeO cannot be obtained in the presence of appreciable organic matter, sulfides, or other materials that are easily oxidized.

Ferric oxide (Fe_2O_3). — Total iron as Fe_2O_3 — 1.1114 FeO.

Alkalies*

Collection of mixed chlorides of sodium and potassium. — Sample usually is decomposed by sintering with $CaCO_3$ and NH_4Cl (J. Lawrence Smith method), alkalies leached from the sintered product with water, purified, and weighed as (Na,K)Cl.

Potassium oxide (K_2O). — Usually is separated and weighed as K_2PtCl_6 and calculated to KCl. Sometimes it is separated and weighed as $KClO_4$.

Sodium oxide (Na_2O). — (Na,K)Cl—KCl, calculated to Na_2O.

Total Water

Usually volatilized by strong ignition with a flux, water collected and weighed in a cold glass tube (Penfield method) or collected on an absorbant and weighed. Sometimes taken as loss on ignition, which includes loss of CO_2 and gain by oxidation of FeO to Fe_2O_3. Valid figures for total water cannot be obtained in the presence of organic matter.

Uncombined water (H_2O^-). — This is usually taken as the loss in weight at 105° to 110° C. Varies with humidity and temperature of the atmosphere and exposure thereto.

Combined water (H_2O^+). — Total $H_2O—H_2O^-$. In order for the figure for H_2O^+ to be valid the figures for total H_2O and for H_2O^- must be correct.

Manganous Oxide (MnO)

Determined on a separate sample, dissolved in H_2SO_4 or HNO_3, by oxidation with bismuthate or periodate to the purple permanganate.

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Recent cooperative investigations — the results of which have been published in the U. S. Geological Survey Bulletin Nos. 980 (1951) and 1113 (1960) — have demonstrated that data of rock analyses from different analysts and laboratories may differ even to whole percentages

* Flame photometry is the universally adopted method today for the determination of the alkalies. (Footnote added by the present authors.)

for the main constituents. This fact has, of course, seriously disturbed both chemists and geologists and has initiated a thorough revision of the methods employed and a closer supervision of all details in the procedures of rock analysis. Many of the methods of the conventional schemes seem to be quite depenable if properly employed, while others are less satisfactory, e.g. because of the presence of systematic errors. These investigations have clearly demonstrated that rock analyses are not easily executed, and have been valuable in pointing out that the scatter of results is probably due, in part, to difference in care, knowledge and skill on the part of the analysts.

Thus, at present a state of doubt prevails as to the accuracy and precision of analytical results obtained by means of the modified conventional schemes of rock analysis, an unsatisfactory situation that stresses the need for further improvements in this field.

B. The disadvantages and common errors associated with the modified conventional schemes of rock analysis.

The present discussion is divided into two parts, one dealing with the general disadvantages of the modified conventional schemes as a whole, and another comprising the disadvantages and common errors associated with the separate methods of determination.

The general disadvantages of the modified conventional schemes are:

a. A large number of separate portions (usually seven) of the sample are needed for the determination of the usual 14 major constituents. This necessitates having a relatively large amount of the material to be analyzed, and the grinding and decomposition of the separate portions require considerable time.

b. The schemes are based upon a number of consecutive chemical separations, each of which must be properly executed in order to obtain reliable results. These separations are lengthy and require considerable experience and skill on the part of the analyst.

c. An assortment of expensive platinum equipment is necessary, which — in some rock-analyzing laboratories — may restrict the number of analyses that can be run simultaneously.

d. The sample is contaminated with platinum brought into solution during the decomposition of the sample, and for accurate results this amount must be removed during the course of the analysis.

e. As shown by Shell[9] iron may be lost during the initial sodium carbonate fusion. The majority of fusions are made with a gas burner as the source of heat. During most decompositions a reducing atmosphere is maintained around the crucible, this resulting in a partial reduction of iron to the metallic state. Reduced iron is picked up and strongly held by the platinum crucible. As pointed out by Shell[9], appreciable amounts of iron may be lost in this way. In most analyses this source of error is ignored.

f. The schemes are unsuitable for the analysis of rocks containing more than a few tenths of a percent of fluorine and boron. Consequently, all samples should be tested for fluorine and boron before the analysis is started. Such preliminary qualitative tests are not always made. In the presence of fluorine, silicon is lost by volatilization during the dehydration of silicic acid, and correct results for the latter constituent cannot be obtained. Boron is likely to accompany silicon, and both constituents are volatilized by the hydrofluoric acid-sulfuric acid treatment, high results for silicon being obtained.

g. Large amounts of salts are introduced from the flux* used and from the consecutive chemical separations. In the presence of large concentrations of salts some precipitates, e.g. magnesium ammonium phosphate, may be obtained in an impure state or with a wrong composition**.

The disadvantages and common errors associated with the separate methods of a typical modified conventional scheme will now be discussed, special emphasis being laid upon the accuracy and precision obtainable with these methods.

a. Silicon

The gravimetric method for this important constituent is less satisfactory. It is not possible to collect all of the silicon by two dehydrations, although most of the silicon that goes into solution may be reco-

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* It is customary to use an amount of flux varying from 3 to 5 times the weight of the sample. A ratio of flux to sample of about 1 : 1 was suggested by Finn and Klekotka[10].

** It is customary in many laboratories to remove ammonium salts by evaporation with nitric acid before precipitating magnesium.

9. H. R. Shell, Anal. Chem., 26 (1954) 591.

10. A. N. Finn and J. F. Klekotka, J. Res. Nat. Bur. Stand., 4 (1930) 809.

vered in connection with the determination of the mixed oxides; as pointed out by Hillebrand[11], some silicon seems to escape recovery altogether. The presence of this systematic negative error has been discussed recently by Fairbairn[12], Fairbairn and Schairer[13] and Jeffery[14], and studies of the losses of silicon at the different stages of the conventional gravimetric determination have been carried out by Stevens and Chodos[15] and by Andersson[16]. Thus, in addition to being tedious and time-consuming, the method for silicon is also beset with a serious systematic negative error which may amount to 0.2—0.4 per cent (absolute) of silicon dioxide.

b. Aluminium

Because it is based on determination by difference, the method for aluminium is in principle less satisfactory. All errors made during the determinations of the other members of the mixed oxide group (in most modified conventional schemes this group is assumed to consist only of aluminium, titanium, phosphorus and iron) and the failure to report the amount of silicon and manganese collected with the mixed oxide group*, as well as the presence of uncommon constituents** precipitable in the mixed oxide group, introduce errors into the result for aluminium. As would be expected, the presence of a systematic positive error for aluminium was confirmed by Fairbairn[12] and Fairbairn and Schairer[13].

c. The total content of iron, titanium and phosphorus

For the determination of these constituents various titrimetric and photometric methods are employed. The total content of iron and titanium are frequently determined in the solution of the mixed oxides, but they may also be determined on separate portions of the sample, as is

* The figure for aluminium is not affected by silicon if the latter component is determined in or removed from the mixed oxides.

** Trace amounts of elements such as chromium, vanadium, zirconium, thorium and other components are usually present in rocks.

11. W. F. Hillebrand, J. Am. Chem. Soc., 24 (1902) 369.
12. H. W. Fairbairn, Geochim. Cosmochim. Acta, 4 (1953) 143.
13. H. W. Fairbairn and J. F. Schairer, Am. Mineralogist, 37 (1952) 744.
14. P. G. Jeffery, Geochim. Cosmochim. Acta, 19 (1960) 127.
15. R. E. Stevens and A. A. Chodos, U. S. Geol. Surv. Bull., No. 1113 (1960) 45.
16. L. H. Andersson, Arkiv Kemi, 19 (1963) 249.

always the case for phosphorus. Some of the procedures used for the determination of these constituents suffer from interference from other major and minor components. In a discussion of the results of chemical analyses of the standard rocks G 1 (a granite) and W 1 (a diabase)* Stevens and Niles[17] have pointed out that methods for the total content of iron based on reduction to iron(II) and subsequent titration with an oxidizing agent tend to give high results and (presupposing the absence of a systematic error in the method for iron(II)) consequently also for iron(III). They have further pointed out that the different methods used for the determination of titanium and phosphorus did not seem to exhibit any significant systematic errors.

d. Calcium and magnesium

If properly carried out, and in the absence of more than a trace of barium and strontium, the results for calcium and magnesium can be regarded as dependable. The problem arising out of the presence of manganese has to be mentioned at this point. In the conventional and modified conventional schemes it is not customary to try to precipitate manganese together with the mixed oxides. As pointed out by Hillebrand[18] and by Washington[19] the content of manganese then distributes itself between the mixed oxides, calcium oxide and magnesium pyrophosphate. Jeffery and Wilson[20] have shown that, for rocks low in magnesium, some manganese is also found in the final filtrate. Strict accuracy would require that the amounts of manganese which contaminate these 3 precipitates be determined. This is, however, usually recommended only for the magnesium pyrophosphate and consequently positive systematic errors are to be expected in the results for aluminium and calcium. The small amount of manganese normally present in rocks (usually below 0.20 % as manganous oxide) and the distribution of this amount between the different precipitates, however, will cause errors which are usually considered to be negligible.

* In the present investigation these rocks will be referred to as standard rocks, although the U. S. Geological Survey prefers to call them reference samples.

17. R. E. Stevens and W. W. Niles, U. S. Geol. Surv. Bull., No. 1113 (1960) 21.
18. W. F. Hillebrand, U. S. Geol. Surv. Bull., No. 700 (1919) 134.
19. H. S. Washington, Manual of the Chemical Analysis of Rocks. First edition, John Wiley & Sons, New York, 1904, p. 15.
20. P. G. Jeffery and A. D. Wilson, Analyst, 84 (1959) 663.

There is a tendency now to replace the conventional gravimetric methods for calcium and magnesium by titrimetric methods based on complex formation, e.g. with ethylenediaminetetraacetic acid or its disodium salt (EDTA). These methods are more rapid and can be expected to give dependable results*.

e. Sodium and potassium

Flame photometry is the method almost universally adopted now for the determination of these constituents. The introduction of the flame photometer into rock analysis represents a major improvement. These elements are now determined directly and rapidly, and with an accuracy and precision generally superior to those obtainable by the methods previously employed.

f. Hygroscopic water (H_2O^-) and the total content of water

Correct analytical results for these constituents can only be obtained if the preliminary operations of crushing and grinding are properly executed.

Hillebrand[21] has pointed out that water is taken up during grinding and that the finer the state of subdivision, the higher the results that will be found for water. He also called attention to the important fact that the water taken up during grinding is not completely expelled by heating at 105—110°.

The method for determining hygroscopic water is in principle extremely simple and few, if any, errors would be expected in this determination. Nevertheless, in discussing the results of recent cooperative analyses of a silicate rock Jeffery[22] concluded that the low results for hygroscopic water obtained by some analysts were probably caused by incomplete drying. The laboratories participating in these analyses were geographically separated, and the differing results discussed by Jeffery

* In the EDTA titration of calcium at pH 12.0—14.0, and in the presence of a suitable reducing agent, manganese(II) is quantitatively precipitated as the hydroxide and does not interfere. However, manganese(II) ions do interfere in the EDTA titration of the sum of calcium and magnesium which is made at pH 10.0—11.0.

21. W. F. Hillebrand, J. Am. Chem. Soc., 30 (1908) 1120.
22. P. G. Jeffery, Research Report Project No. PCS 43, Department of Scientific and Industrial Research, Warren Spring Laboratory, Hertfordshire, Great Britain, March 1963.

could originate from varying humidity conditions during storing and grinding. For this reason Stevens and Niles[23] have recommended that analytical data on rocks should be reported on a moisture-free basis. However, some rock analysts still prefer a reporting of the analysis on a "sample as received" basis, one of the reasons for this being that certain rocks, e.g. those containing chlorite, have a variable moisture content.

The content of combined water is obtained by subtracting the amount of hygroscopic water from the total content of water, which is determined by the Penfield[24] method or some modifications of it.

Riley[25] has discussed the sources of error in the Penfield method and has pointed out that it is almost impossible to remove all the water from minerals by heating in a glass tube and, that it is difficult to insure that all the liberated water is condensed in the Penfield tube. Both sources of error will lead to low results. Riley recommends a method based upon heating of the sample at 1100—1200 in a combustion tube swept with dry nitrogen. By this method total water and carbon dioxide can be determined simultaneously. It is shown that higher results are obtained by this method than by the conventional Penfield technique.

g. Manganese

The standard method for the determination of manganese is based upon oxidation of manganese(II) to manganese(VII) and subsequent photometric measurement of the permanganate. Due to incomplete oxidation some methods for manganese may exhibit a systematic negative error. Oxidizing agents normally applied are bismuthate, periodate or peroxidisulphate. As to the choice between the two latter reagents, statements in the literature on the subject are controversial. Some authors, e.g. Willard and Greathouse[26] have stated that oxidation is incomplete with peroxidisulphate and that the colour frequently fades after a short time, these authors advocate the use of periodate. Sandell[27] also considers periodate to be the best reagent for this purpose. However,

23. R. E. Stevens and W. W. Niles, U. S. Geol. Surv. Bull., No. 1113 (1960) 10.
24. S. L. Penfield, Z. Anorg. Allgem. Chem., 7 (1894) 22.
25. J. P. Riley, Analyst, 83 (1958) 42.
26. H. H. Willard and L. H. Greathouse, J. Am. Chem. Soc., 39 (1917) 2366.
27. E. B. Sandell, Colorimetric Determination of Traces of Metals. Third edition, Interscience Publishers, Inc., New York, 1959, p. 608.

objections have also been made about the use of periodate, Nydahl[28] experienced incomplete oxidation of small amounts of manganese. He made a comprehensive study of the use of peroxidisulphate and conclu-ded by recommending this reagent.

In the present investigation the procedure advocated by Nydahl was tested, but it proved impossible to obtain complete oxidation. Periodate was then tried (see chapter IV.Q.9.) and satisfactory results were obtai-ned. On the basis of these experiments periodate was preferred as the oxidizing agent.

h. Iron (II)

The conventional method for the determination of iron(II) is beset with a number of disadvantages and errors which make the determina-tion difficult and in certain cases, e.g. in the presence of sulphide miner-als, yields results which are less dependable.

One of the conditions that must be fulfilled in order to obtain reliable results is that the sample must be completely decomposed by the mix-ture of hydrofluoric and sulfuric acids. The efficiency of the decomposi-tion can normally be increased by grinding the sample to a very fine state of subdivision, but to avoid oxidation of iron(II) during grinding a comparatively coarse powder (e.g., a powder that passes a 100 mesh sieve) is always used in the first attack.

After titration with an oxidizing agent (e.g. permanganate or dichro-mate) the analyst is often faced with a difficult decision. According to one author[29] no unattacked residue should be visible after the titration. Another author[30] specifies that the attack should be continued until gritty matter can no longer be felt, or until experience tells that decom-position must be complete.

In practise, small amounts of undecomposed material will nearly al-ways be present after the first attack. This residue may consist of resist-ant minerals, such as staurolite, tourmaline, axinite and others, but in most cases it is likely to contain pyrite. According to Hillebrand[31] pyrite is nearly universally present in rocks and is only partly attacked (the sulphide minerals chalcopyrite and pyrrhotite are completely de-

28. F. Nydahl, Anal. Chim. Acta, 3 (1949) 144.
29. B. A. Soule, J. Am. Chem. Soc., 50 (1928) 1691.
30. J. P. Cooke, Am. J. Sci., Second series, 44 (1867) 347.
31. W. F. Hillebrand, U. S. Geol. Surv. Bull., No. 700 (1919) 194.

composed) by the boiling mixture of hydrofluoric and sulfuric acids.* By filtering off the residue and regrinding it to a very fine state it is possible to bring some minerals completely into solution by a second attack, but not pyrite. Thus, one of the errors inherent in the conventional method for iron(II) is that the main part of the pyrite present is left undecomposed.

In addition to undecomposed sample the solid phase remaining after the attack may also contain slightly soluble compounds (simple fluorides and/or complex fluorides) formed during the decomposition. It appears from Hillebrand[33] that insoluble fluorides and fluorosilicates may be present in the solid phase. In an investigation of the precipitates formed by the decomposition of olivine, oligoclase and labradorite in hydrofluoric acid, and in mixtures of this acid with perchloric acid, Langmyhr and Graff[34] were unable to detect (with the use of emission spectrography) more than traces of silicon. It was concluded that fluorosilicates are not likely to be met with in the solid phase. An investigation of the composition of the precipitates formed during the attack of some minerals by hydrofluoric acid and by mixtures of this acid with perchloric acid was carried out by Langmyhr and Sveen[32]. The precipitates that resulted from the use of the different acid solutions were practically identical in composition. It is important to note that some of the precipitates were found to contain iron(II). In a later investigation Langmyhr and Kringstad[35] examined the precipitates formed by the decomposition of 2 granites and the standard rock W 1 in 38—40 % hydrofluoric acid. In addition to confirming the absence of silicon, the following main compounds were detected in all precipitates: CaF_2, $MgAlF_5 \cdot xH_2O$, $NaAlF_4 \cdot xH_2O$ and $Fe(II)Al(Fe(III))F_5 \cdot xH_2O$. Consequently, in the determination of iron(II) by the conventional method it is imperative that the slightly soluble fluorides be brought into solution before the titration is finished.

The normal procedure after the decomposition is to transfer the contents of the decomposition vessel into a solution of boric acid containing

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* It was demonstrated recently[32] that by using a bomb technique pyrite was completely decomposed by hydrofluoric acid.

32. F. J. Langmyhr and S. Sveen, Anal. Chim. Acta, 32 (1965) 1.
33. W. F. Hillebrand, U. S. Geol. Surv. Bull., No. 700 (1919) 201.
34. F. J. Langmyhr and P. R. Graff, unpublished results.
35. F. J. Langmyhr and K. Kringstad, to be published.

sulfuric acid* and to titrate the iron(II) immediately, without, however, making certain that precipitated fluorides are dissolved. A survey of the literature showed that only one author[38] had called attention to the formation of slightly soluble compounds and had stated that it is desirable to bring them into solution before titration. This author assumed that the precipitates consisted mainly of calcium and magnesium fluorides.

The presence of sulphides, vanadium and carbonaceous matter in rocks will introduce different errors and problems affecting the analytical results for iron(II) and iron(III). These relations have been discussed in detail by Hillebrand[39]. Statements in the literature regarding the effect of the presence of sulphides on the results for iron are controversial. Hillebrand[39] believes that most of the hydrogen sulphide is expelled without affecting iron(III), while other authors[40] state that pyrite, pyrrhotite and presumably other sulphides reduce iron(III).

The lack of agreement as to the effect of sulphides on the results for iron(II) and iron(III) makes a further investigation highly desirable.

II. Novel schemes of rock analysis.

During the last two decades a number of novel schemes[41] have been proposed for the analysis of silicate minerals, rocks and related materials. These schemes are characterized by the extensive use of instrumental

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* A comparison between different reagents for complexing fluoride ions was made by Tarutani[36], who found aluminium and beryllium salts to be more effective than boric acid. Graff and Langmyhr[37] confirmed this statement and demonstrated that an excess of boric acid added to a solution of hydrofluoric acid did not prevent glass from being attacked, while no attack took place in the presence of an excess of aluminium trichloride.

36. T. Tarutani, Nippon Kagaku Zasshi, 77 (1956) 1292; C. A. 52 (1958) 974.
37. P. R. Graff and F. J. Langmyhr, Anal. Chim. Acta, 21 (1959) 429.
38. A. D. Wilson, Analyst, 85 (1960) 823.
39. W. F. Hillebrand, U. S. Geol. Surv. Bull., No. 700 (1919).
40. C. V. Clemency and A. F. Hagner, Anal. Chem., 33 (1961) 888.
41. R. Hedin, Proc. Swed. Cement and Concrete Res. Inst., No. 3 (1947);
    L. Shapiro and W. W. Brannock, U. S. Geol. Surv. Circ., No. 165 (1952);
    L. Shapiro and W. W. Brannock, U. S. Geol. Surv. Bull., No. 1036-c (1956);
    C. C. Miller and R. A. Chalmers, Analyst, 78 (1953) 636;
    R. B. Corey and M. L. Jackson, Anal. Chem., 25 (1953) 624;
    R. A. Durie and N. N. S. Schafer, Private communication to W. Schmitz, out-

methods which are rapid and have the important advantage of permitting the determination of one constituent in the presence of others. It has thus been possible to get away from the classical system of analysis and many of its tedious and timeconsuming chemical separations.

A common feature of these new schemes is that 2 or 3 solutions are prepared from the sample to be analyzed and separate determinations are made on aliquot parts of these solutions. The methods most frequently employed are based upon spectrophotometry, flame photometry and titrimetry. Another feature is that many of them are on a smaller, mostly semi-micro, scale of operation.

It has been claimed by some authors that their novel schemes are rapid and simple, and that the analyses can be executed by analysts having less skill and training. In a critical review Chirnside[42] has justifiably challenged these statements. After having had personal experience with some of the proposed methods, he concludes that they are not rapid, requiring long standing, e.g. overnight, for sample decomposition. He also points out that some of the classical separations, which the authors of these novel schemes are driven to employ, are not satisfactory because they are being based on a single instead of double precipitation. As to the statement that analysts of lesser skill can utilize these methods, Chirnside again disagrees, his experience being that some methods could at first not be made to work even by analysts of the highest skill.

A serious objection to some of the novel schemes is that they are published without sufficient data to demonstrate their accuracy and precision. Some of these schemes are also subject to serious sampling errors caused by the use of a small amount of a sample which has not

42. R. C. Chirnside, J. Soc. Glass Technol., 43 (1959) 5 T.

line of scheme published in Leitz-Mitt. Wiss. u. Tech., 1 (1960) 154;
E. L. P. Mercy, Geochim, Cosmochim. Acta, 9 (1956) 161;
W. Radmacher and W. Schmitz, Brennstoff-Chem., 38 (1957) 225, 38 (1957) 270, 38 (1957) 308;
K. Archer, D. Flint and J. Jordan, Fuel, 37 (1958) 421;
J. P. Riley, Anal. Chim. Acta, 19 (1958) 413;
J. P. Riley and H. P. Williams, Mikrochim. Acta, 4 (1959) 525, 6 (1959) 804, 6 (1959) 825;
R. L. O'Neil, J. Sediment. Petrol., 29 (1959) 267;
A. Behr, M. L. Blanchet and L. Malaprade, Chim. Anal., No. 10 (1960) 501. No. 11 (1960) 557;
M. Weibel, Schweiz. Mineral. Petrog. Mitt., 40 (1960) 5, 41 (1961) 285;
C. O. Ingamells, Talanta, 11 (1964) 665.

been ground to a sufficiently fine state of subdivision (for a discussion of the sampling of silicate rock powders for chemical analysis, see a paper by Wilson[43]).

Although various novel schemes have been introduced into rock analysis laboratories, a large number of analysts still prefer to use a modified conventional scheme. One reason for this could be that rock analysts are inclined to be conservative in outlook, but another could be because of a feeling of uncertainty as to the applicability, accuracy and precision of these new, and very often inadequately tested, schemes.

It should be mentioned also that special instrumental techniques, such as emission spectrography and X-ray fluorescence spectrometry, are being used for the analysis of rocks.

The advantages of emission spectrochemical methods are well known and include rapidity, the use of a small amount of sample and the determination of several elements in one operation. The method, however, is beset with systematic errors due to matrix and self-absorption effects, and the precision is generally inferior to that obtained by chemical methods. This makes the method less suitable for the determination of the major constituents of rocks, while it is superior to chemical methods for the determination of certain trace components. Contributions to the spectrochemical analysis of rocks and related materials have been made by Ahrens and Taylor[44], Price[45], Ward[46], Ward and Hartley[47], and Hawley and MacDonald[48].

Analysts are at present taking great interest in the potential usefulness of X-ray fluorescence spectrometry, for it is now possible[49] to determine the major constituents of rocks with a reasonable degree of accuracy

43. A. D. Wilson, Analyst, 89 (1964) 18.
44. L. H. Ahrens and S. R. Taylor, Spectrochemical Analysis, Second edition, Addison-Wesley Publ. Co., Inc., U.S.A., 1961.
45. W. J. Price, Spectrochim. Acta, 6 (1953) 25.
46. W. Ward, J. Soc. Glass Technol., 42 (1958) 240 T.
47. W. Ward and F. Hartley, J. Soc. Glass Technol., 37 (1953) 113 T, 40 (1956) 37 N.
48. J. E. Hawley and G. MacDonald, Geochim. Cosmochim. Acta, 10 (1956) 197.
49. R. J. Langobucco, Anal. Chem., 34 (1962) 1263;
H. J. Rose, I. Adler and F. J. Flanagan, Appl. Spectroscopy, 17 (1963) 81;
A. Volborth, X-Ray Spectrographic Determination of SiO_2 in Fifteen Igneous Rocks, and two Plagioclase Feldspars, and Precision and Accuracy as Compared with Gravimetric Methods. Tenth Annual Norelco Western X-Ray Diffraction and Spectrographic School in San Fransisco, September 14th, 1962.

and precision. The technique has also been employed[50] for the determination of trace constituents in rocks. The method is still in its infancy, and further refinements will undoubtedly improve the results.

It should be noted, however, that neither the emission spectrographic nor the X-ray fluorescence methods can be used for the determination of all 14 major components of silicate rocks.

III. Hydrofluoric acid as decomposing agent for silicate rocks.

In 1771 Scheele[51] reported that glass and silica were attacked by hydrofluoric acid. Berzelius seems to have been the first to employ hydrofluoric acid as decomposing agent in the chemical analysis of silicate minerals and rocks*. It was known at Berzelius' time that silicon was volatilized during evaporation in the presence of hydrofluoric acid, and consequently the silicon content could not be determined on the sample attacked by this acid.

Fresenius[54] advocated the use of hydrofluoric acid for the decomposition of the main portion, while Hillebrand[55] adviced against it. The latter author experienced difficulties in completely removing fluorine after the decomposition, and this resulted in incomplete precipitation of the constituents of the mixed oxide group. In his first enlarged and revised edition of the conventional scheme of analysis Hillebrand[56] resumed the

* In his textbook of chemistry Berzelius[52] describes the use of hydrofluoric acid for breaking up the separate sample weighed out for the determination of the alkalis. The present authors were unable to find a paper by Berzelius describing the attack of the main portion by hydrofluoric acid. Holmberg[53] does not — in his bibliography of Berzelius — list any paper with a title indicating the introduction of hydrofluoric acid as decomposing agent.

50. M. J. Kaye, Geochim. Cosmochim. Acta, 29 (1965) 139.
51. C. W. Scheele, Kgl. Svenska Vetenskapsakad. Handl., 32 (1771) 120.
52. J. J. Berzelius, Lehrbuch der Chemie, Third edition, Dresden and Leipzig, 1841, vol. 10, p. 46.
53. A. Holmberg, Bibliografi över J. J. Berzelius. Published by Kungl. Svenska Vetenskapsakademien, Stockholm and Uppsala, 1933.
54. C. R. Fresenius, Anleitung zur Quantitativen Chemischen Analyse, Fifth edition, Friedrich Vieweg and Son, Braunschweig, 1864, p. 374.
55. W. F. Hillebrand, U. S. Geol. Surv. Bull., No. 700 (1919) p. 89.
56. W. F. Hillebrand, U. S. Geol. Surv. Bull., No. 148 (1897).

use of sodium carbonate as the deomposing flux, and continued its use in later editions. In this scheme the use of hydrofluoric acid for decomposition purposes is restricted to the attack of the separate sample weighed out for the determination of iron(II). In modified conventional schemes hydrofluoric acid is also employed in connection with the flame photometric determination of sodium and potassium.

To the authors' best knowledge, hydrofluoric acid does not seem to have been used previously as the decomposing agent for the sample weighed out for the determination of silicon. Since the days of Berzelius, it seems to have been a common assumption among analysts that silicon is lost by evaporation when silicon-containing materials are in contact with hydrofluoric acid. However, it has been demonstrated recently[57] that there is no, or only a negligible, loss of silicon from solutions prepared by dissolving silicon dioxide (and presumably also other siliceous materials, e.g. rocks) in an excess of concentrated (38—40 %) hydrofluoric acid. By this reaction a ternary system consisting of hydrofluoric acid, fluorosilicic acid and water is formed. The reason why there is no loss of silicon under the conditions given above is found in the investigation made of this ternary system by Muster, Aepli and Kossatz[58]. From the vapour-liquid equilibrium diagram worked out by these authors it can be seen that in the vicinity of constant-boiling hydrofluoric acid the liquid ternary mixture is in equilibrium with a vapour phase in which the concentration of fluorosilicic acid is very much lower than in the liquid. The results of these two investigations encourage the possibility of determining silicon, e.g. spectrophotometrically, in all types of siliceous materials decomposable by hydrofluoric acid.

The corrosive nature of hydrofluoric acid, which previously restricted the use of this reagent, does not represent any problem in handling to-day, because of the availability of relatively inexpensive plastic equipment.

There are some definite advantages to be gained from employing hydrofluoric acid as the decomposing agent for silicate rocks:

a. Silicon may be determined irrespective of the presence of fluorine and boron.

57. F. J. Langmyhr and P. R. Graff, Anal. Chim. Acta, 21 (1959) 334.
58. P. A. Muster, O. T. Aepli and R. A. Kossatz, Ind. Eng. Chem., 39 (1947) 427.

b. Methods for the determination of the alkalis and iron(II)* can be incorporated in the scheme for the analysis of the main portion.

c. Decompositions and evaporations can be done in plastic vessels and thus expensive platinum equipment is no longer a prerequisite for the analysis of rocks.

d. The sample is not contaminated through attack of the vessel used in the decomposition, as in the case of a fusion.

e. There is no risk of losing iron by reduction and reaction with the vessel used for the decomposition.

f. The decomposing agent can be removed quantitatively by evaporation.

The objection that is raised against the use of hydrofluoric acid as decomposing agent is that very few, if any, constituents of rocks can be determined in the presence of an excess of hydrofluoric acid or of fluoride. To avoid the disturbing effects of fluorine, it is necessary either to make it harmless by adding a strong complexing agent, or to remove it by evaporation.

In the present scheme both methods are employed for removing the difficulties occasioned by the presence of fluorine. Because the statements in the literature concerning the complete expulsion of fluorine by evaporation are controversial, however, this latter approach will be discussed in more detail. Hillebrand[55] seems to have experienced difficulties in completely removing fluorine by evaporation and advised against the use of hydrofluoric acid as the decomposing agent for the main portion. As reported by various workers[59], the presence of fluorine results in incomplete precipitation of aluminium (and presumably also of other members of the mixed oxide group). However, as early as in 1915, Selch[60] demonstrated that complete expulsion of fluorine was obtained after two evaporations to dryness with sulfuric acid and this was confirmed by Langmyhr and Graff[61]. It should be noted that in order to expel the last traces of fluorine it is necessary to evaporate the

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* As will be apparent from later experiments (see chapter IV.E.), it was found not advisable to determine iron(II) in samples decomposed in polytetrafluoroethylene (teflon) vessels.

59. F. P. Veitch, J. Am. Chem. Soc., 22 (1900) 246.
     F. W. Hinrichsen, Ber., 40 (1907) 1497.
     H. Cavaignac, Compt. Rend., 158 (1914) 948.
60. E. Selch, Z. Anal. Chem., 54 (1915) 395.
61. F. J. Langmyhr and P. R. Graff, unpublished results.

solution twice, not only to dense fumes but to complete dryness. The latter authors recommended a final heating temperature of $280 \pm 10°$. Hinrichsen[59] recommended ignition of the dry residue, but without indicating the temperature to be used. Thus, the chief objection of Hillebrand to the use of hydrofluoric acid has long been invalidated.

A study of the development of rock analysis has led to the conclusion that the replacement of hydrofluoric acid by sodium carbonate as the decomposing agent for the main portion was, to a large extent, influenced by the objections Hillebrand had to the use of the former reagent, his authority seems to have been so great that his colleagues, more or less uncritically, stopped using hydrofluoric acid. It is unfortunate that Hillebrand did not support his wide-ranging decision with experimental data.

In connection with the development of a scheme based on decomposition by hydrofluoric acid, it is of importance to know whether the acid acts upon all types of minerals or if it has limited applicability. The scattered data to be found in the literature on this subject deal chiefly with those minerals found to be resistant to such attack. Riley[62] reported that a mixture of hydrofluoric and perchloric acids did not completely decompose corundum, rutile, spinel, tourmaline and staurolite, he was able to decompose these minerals by applying a bomb technique. Ito[63] also introduced a bomb technique and demonstrated that a number of resistant minerals were decomposed successfully in this way, however, under the conditions employed, pyrite was found to be resistant to attack. On the other hand, Ito demonstrated that zircon was decomposable by hydrofluoric acid alone, but not so by a mixture of hydrofluoric and sulfuric acids.

A more systematic study of the decomposability of minerals in a mixture of hydrofluoric and perchloric acids was made by Langmyhr and Sveen[64] on 28 main, and some minor and trace, minerals of silicate rocks. The majority of the specimens were decomposed by simple heating on the water bath, while the remaining minerals, including pyrite, but with the only exception of topaz, were decomposed successfully in a bomb.

From the above it seems obvious that the composition of the attacking solution is of considerable importance. The attacking solution normally

62. J. P. Riley, Anal. Chim. Acta, 19 (1958) 413.
63. J. Ito, Bull. Chem. Soc. Japan, 35 (1962) 225.
64. F. J. Langmyhr and S. Sveen, Anal. Chim. Acta, 32 (1965) 1.

consists of a mixture of hydrofluoric and concentrated or dilute sulfuric acids, although some authors[65] have used hydrofluoric acid alone during the first stage of attack and have later added sulfuric acid. The volumes and concentrations of acid prescribed in the various procedures differ widely, however, and systematic studies to develop the most effective composition have not been made. Instead of sulfuric acid, some authors[66] recommend concentrated perchloric acid*. Mixtures of hydrofluoric and hydrochloric acids[68], and of hydrofluoric, sulfuric and nitric acids[69] have also been applied. No reasons are found in the literature for the presence of a second mineral acid during the decomposition stage, however, and the investigations of Langmyhr and Sveen[64] and of Ito[64] indicate that hydrofluoric acid is more effective alone than in a mixture with another acid.

One complication that arises from the use of hydrofluoric acid as the decomposing agent for silicate rocks is that slightly soluble fluorides are formed during the attack. The chemical composition of the precipitates likely to be met with in silicate rock analysis is discussed in chapter I. B. For the subsequent analysis it is thus necessary that these precipitated fluorides be brought into solution. This can be done either by the addition of a strong complexing agent for fluoride (suitable agents for this purpose were discussed in chapter I. B.) or by transforming the fluorides into sulphates by evaporation in the presence of sulfuric acid.

IV. The present scheme.

A. Introduction.

From the discussions in the preceding chapters it is obvious that the present state of rock analysis is less than satisfactory. The serious systematic errors inherent in the classical methods for such important constituents as silicon and aluminium make it desirable to get away altogether from these methods, and these, as well as other errors and drawbacks

* It has been observed[67] that fluorine is less easily expelled by evaporation from perchloric acid solution than it is from sulfuric acid.

65. C. R. Fresenius, Anleitung zur Quantitativen Chemischen Analyse, Sixth edition, Friedrich Vieweg and Son, Braunschweig, 1875, Vol. 1, p. 461.
66. J. P. Riley, Anal. Chim. Acta, 19 (1958) 413.
67. A. D. Wilson, private communication.
68. C. R. Fresenius, Anleitung zur Quantitativen Chemischen Analyse, Sixth edition, Friedrich Vieweg and Son, Braunschweig, 1875, Vol. 1, p. 462.
69. R. L. O'Neil, J. Sediment. Petrol. 29 (1959) 267.

connected with the modified conventional schemes, indicate the need for further development in the field of rock analysis.

This situation encouraged the present authors to consider the possibility of reintroducing hydrofluoric acid as the main decomposing agent for silicate rocks. It was apparent in the preceding chapter that this acid has definite advantages to offer, some of which have been obvious since the days of Berzelius, while others stem from the development of new, plastic laboratory materials and recent investigations of the hydrofluoric acid solvent system.

B. An outline of the scheme.

The separate methods of separation and determination are described in detail in section Q, but the chief features of the proposed scheme will be outlined here. The proposed scheme includes methods for the determination of 11 of the 14 constituents normally sought. Methods for hygroscopic water, the total content of water and carbon dioxide are not given. It is assumed that these components will be determined on separate samples according to established methods.

The determination of the 11 constituents are based upon the decomposition of 3 separate samples which will be designated A, B and C.

Sample A is decomposed by hydrofluoric acid in a closed teflon vessel (decomposition vessel A). After decomposition the precipitated fluorides are dissolved and the excess of hydrofluoric acid is made harmless by the addition of aluminium trichloride solution. From the resulting solution (solution A) two aliquot portions are taken for the determination of silicon which is determined spectrophotometrically as the yellow α,12-molybdosilicic acid. A special feature of the scheme is that the blank solution is prepared from a portion of solution B (see below) representing the same amount of the sample, the blank solution does not contain silicon and fluorine, but contains, and automatically compensates for, all of the other, known or unknown, interfering constituents of the solution.

Sample B is attacked in an open teflon vessel (evaporation vessel B) by a mixture of hydrofluoric and sulfuric acids. After decomposition all fluorine, as well as silicon, is removed by a double evaporation to

dryness. The remaining sulphates are dissolved and the solution is transferred to a volumetric flask (solution B). From this solution the following aliquot portions are pipetted:

One aliquot portion to serve as a blank solution in the determination of silicon. One aliquot portion for the spectrophotometric determination of total iron with sodium 1,2-dihydroxybenzene-3,5-disulfonate (tiron). After the determination of total iron, a reducing agent is added and titanium is determined spectrophotometrically in the same solution. One aliquot volume for the determination of phosphorus spectrophotometrically as molybdovanadophosphoric acid. One aliquot portion for the spectrophotometric determination of manganese as permanganate. One aliquot portion for the determination of aluminium, calcium, magnesium, sodium and potassium. A double precipitation with ammonia solution separates the constituents of the mixed oxide group from magnesium and the members of the alkaline earth and alkali groups. The filtrate is transferred to a volumetric flask (solution b).

The precipitate containing the hydrous oxides is dissolved in acid and a chloroform extraction of the cupferrates is made. The aluminium remaining in the aqueous phase is determined titrimetrically by adding an excess of a standard solution of the sodium salt of ethylenediaminetetraacetic acid (EDTA) and back-titrating the excess in about 50 % ethanol with a standard zinc solution, using diphenylthiocarbazone (dithizone) as the indicator.

From solution b aliquot portions are taken for the determination of calcium and magnesium. Calcium is determined by titration with a standard solution of EDTA using 3-hydroxy-4-(2-hydroxy-4-sulfo-1-naphthylazo)-2-naphthoic acid (calcon carboxylic acid) as indicator. Magnesium is determined by difference from the sum of calcium and magnesium obtained by titrating with a standard solution of EDTA using sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonate (eriochrome black T) as indicator. Finally, sodium and potassium are both determined in solution b by flame photometry.

Because it was found inadvisable to determine iron(II) in samples decomposed in teflon vessels, it is necessary to resort to the method used in the modified conventional schemes. A separate sample (sample C) is decomposed in a crucible of recrystallized alumina or platinum by a mixture of hydrofluoric and sulfuric acids, the fluoride is complexed by boric acid and the iron(II) is titrated with a standard solution of dichromate using sodium diphenylaminesulfonate as the indicator.

The proposed analytical scheme will be found applicable to most ordinary rocks. If the sample contains unusual, acid-resistant minerals, it may be necessary to modify the decomposition technique. Procedures for decomposing such samples are given in sections O. and P.

C. Factors considered in the selection of methods for separation and determination.

The separate methods of separation and determination were selected after thorough testing. During these preliminary investigations a considerable number of methods were rejected for various reasons.

The methods of determination were selected mainly on the basis of accuracy and precision, but it was also considered as an advantage if the method was direct, simple, rapid and uninfluenced by the presence of other elements. It was not, however, always possible to find satisfactory direct methods. In general, an indirect method was preferred if it proved to be better than a direct one and, similarly, a slow method was preferred if it proved to be better than a more rapid one.

D. Scope of the scheme.

The proposed scheme is intended for the analysis of all types of silicate rocks decomposable by hydrofluoric acid and containing as essential components the 14 constituents normally sought.

The possible application of the proposed scheme to the analysis of related natural or artificial materials, such as meteorites, glass, porcelain and refractories was not investigated. It is, however, very likely that the scheme, with or without modification, will be found applicable to the analysis of some of these materials.

E. The behaviour of iron(II).

At the start of the present work it was assumed that iron(II) could be determined in solution A. The only precaution believed to be necessary in connection with this determination was that of preventing oxidation of iron(II) by air during the steps required for the preparation of solution A.

In the analysis of solutions representing a rock of known composition, and of standard rocks with a low content of iron(II), no difficulties

were encountered in the spectrophotometric method originally employed for the determination of iron(II). However, when the method was tested on a standard rock having a relatively high concentration of iron(II) a systematic negative error was observed. No explanation was found for the low results for iron(II)* and as a result the method was discarded and the conventional method was used instead.

During the decomposition of sample A according to the final procedure of the proposed scheme the solution is in contact with air, and under these conditions some of the iron(II) present in the sample is likely to be oxidized. During the later manipulations no precautions are taken to avoid oxidation and more iron(II) is probably transformed to the trivalent state. In solution A the iron(II) can thus be expected to be found both as iron(II) and iron(III).

Sample B is decomposed under strongly oxidizing conditions and in solution B all of the iron can be assumed to be present as iron(III).

Sample C is attacked according to the modified conventional procedure for the determination of iron(II). For a discussion of the errors that may effect the determination of iron(II), see chapter I.B.

F. The behaviour of manganese.

In the proposed scheme the conventional group separation of the mixed oxide group has been retained and in this connection the presence of manganese gives rise to difficulties. If no attempt is made to oxidize manganese(II) to the quadrivalent state, some of the manganese is precipitated together with the hydrous oxides and the rest passes into the filtrate. From an analytical point of view, it would be desirable to collect all manganese in the mixed oxide group, but as the oxidation of manganese to the quadrivalent state has been found to be incomplete, this method is not recommended[70]. In the proposed scheme the components of the mixed oxide group are precipitated without prior oxidation of manganese(II), and consequently the distribution of this constituent between the hydrous oxides and the filtrate after the precipitation with ammonia solution must be considered.

* There is a discrepancy between the present results and those of Ito[83]. Using a teflon-lined bomb, he decomposed the same standard rock (high in iron(II)) that was used by the present authors and obtained satisfactory results.

70. See e.g. I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, Third edition, Macmillan Co., New York, 1959, p. 368 and 701.

The group precipitation of the hydrous oxides also serves the purpose of separating constituents which would interfere in the subsequent determinations. In the hydrous oxide precipitate only one component, aluminium, is determined; the hydrous oxides are filtered off, dissolved in acid and a chloroform extraction of the cupferrates is made[*]. From the data given by Starý and Smiżanská[72] it was concluded that manganese(II) would remain together with aluminium in the aqueous phase. To this aqueous phase a standard solution of EDTA is added in excess and the excess in back-titrated at a pH of about 4.5 with a standard zinc solution. At this pH manganese(II) reacts with EDTA, as is apparent from the conditional constant of the manganese(II) EDTA complex (log $K_{pH\ 4.5} = 6.5$). However, if the conditional constant of the zinc EDTA complex is higher at the pH of the titration, the manganese(II) EDTA complex will not be stable. As the conditional constant at pH 4.5 of the zinc EDTA complex is higher (log $K_{pH\ 4.5} = 8.9$), it was concluded that manganese(II) would not interfere in the determination of aluminium.

The rest of the manganese originally present in the sample is found in the filtrate after the precipitation of the hydrous oxides and this may interfere in the determination of calcium, magnesium, sodium and potassium. As apparent from the discussions of the methods for these 4 components (section Q.6.), manganese(II) will only interfere in the titrimetric method for the determination of the sum of calcium and magnesium and this interference is removed by precipitating and filtering it off as hydrous manganese dioxide prior to titration.

To verify the assumptions made above as to the distribution of manganese in the proposed scheme, the following experiments were carried out. From the "main solution" (the preparation of this solution is described in chapter V. B.) 25 ml were pipetted into a 200 ml beaker. The amounts of the different constituents of this solution are given in Table 1. An aliquot of a standard solution of iron(III) equivalent to 10 mg of iron(III) oxide was added. A double precipitation of the hydrous oxides was made according to the procedure employed in the present scheme (section Q.2.). The filtrate (collected in a beaker) was evaporated to a small volume, 0.5 ml of concentrated sulfuric acid were added and the

[*] A survey of the literature relating to the extraction of cupferrates is given by Sandell[71]. More recent data on this extraction are published by Starý and Smiżanská[72].

71. E. B. Sandell, Colorimetric Determination of Traces of Metals, Third edition, Interscience Publishers, Inc., New York, 1959, p. 60.
72. J. Starý and J. Smiżanská, Anal. Chim. Acta, 29 (1963) 545.

solution was evaporated to copious, white fumes. After dilution to about 40 ml, 2 ml of concentrated orthophosphoric acid and 0.5 g of potassium periodate were added. The solution was heated and kept just below the boiling point for 15 ± 3 min. A blank solution, prepared from about 40 ml of water, 2 ml of concentrated orthophosphoric acid and 0.5 g of potassium periodate, was given the same treatment as the sample solution. Both solutions were transferred to 50 ml volumetric flasks, diluted to volume and the extinction of the sample solution was measured against the blank under the conditions of the present method for the determination of manganese (section Q.9.). The result is given in Table 1. The hydrous oxides, which had been collected on a glass filter crucible (porosity 20—30 μm), were now treated according to the procedure given for the determination of aluminium (section Q.2.). After the extraction of the cupferrates with chloroform, the content of manganese in the chloroform and aqueous phases was determined. The chloroform phase was transferred to a porcelain dish and the organic solvent was removed by evaporation to dryness. Organic matter was destroyed by heating in the presence of nitric acid, sulfuric acid was added and the solution was heated to dense, white fumes. Manganese was then determined as given above. Similarly, the manganese content of the aqueous phase was found by adding sulfuric acid, evaporating to fumes and determining the amount spectrophotometrically. The analytical results are given in Table 1.

Thus, under the conditions of the proposed scheme, 0.600 mg of manganous oxide (MnO) were distributed as shown in Table 1.

Table 1.

Distribution of 0.600 mg of manganous oxide in the proposed scheme.

Constituents present (amounts given in mg)	mg of manganese (as MnO) found		
	in the chloroform phase after extraction	in the aqueous phase after extraction	in the filtrate after the precipitation of the hydrous oxides
Al_2O_3 – 32.00 Fe_2O_3 – 10.00	0.000	0.451	0.153
TiO_2 – 1.40 MnO – 0.600 CaO – 10.00 MgO – 5.00 Na_2O – 10.00 K_2O – 10.00	Total found 0.604 mg of MnO, as against 0.600 mg taken.		

G. The behaviour of minor and trace elements.

1. Introduction

In addition to the 14 components normally sought, all rocks contain a number of elements in minor or trace amounts. These are not usually determined in the course of an ordinary analysis, and their interfering effect is usually considered to be negligible. However, in certain types of rocks minor and trace elements may occur in sufficient amounts as to cause some interference.

In the proposed scheme the occurrence and possible interfering effect of the minor and trace elements lithium, rubidium, strontium, barium, lead, zirconium, thorium, chromium, vanadium, nickel, cobalt, copper, zinc, sulphur, boron and fluorine were considered. Their possible interfering effect upon the separate methods of determination is discussed in section Q., which contains the detailed analytical procedures; however, it is also necessary to know the general behaviour and distribution of minor and trace elements in the course of the analysis, and these considerations are discussed in the present section.

2. Lithium and rubidium

These elements accompany and behave like the other members of the alkaline group and no problems were expected to arise from their presence during the decomposition of samples A and B, and the preparation of the solutions A and B. A double precipitation with ammonia solution is made on one of the aliquot portions withdrawn from solution B, the filtrate of which is designated solution b. All of the alkaline group will be found in solution b in which sodium and potassium are determined by flame photometry. Lithium and rubidium may be determined in the same solution with the use of a sensitive flame photometer or, preferably, by atomic absorption spectroscopy.

3. Strontium, barium and lead

Of these three elements, barium is most abundant in rocks, followed by strontium and then lead (in the divalent state)[73].

The solubility of the fluorides of barium, strontium and lead is low, and during the decomposition of sample A these compounds may precipitate. However, the subsequent addition of a large excess of aluminium

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73. See e.g. J. Green, Bull. Geol. Soc. Am., 70 (1959) 1127.

trichloride, combined with heating, will usually result in complete dissolution of any slightly soluble fluorides of barium, strontium and lead. Provided that sulphate ions are absent, the three constituents are found in solution A.

Sulphate-containing minerals are rarely found in silicate rocks, but if sulphate occurs together with barium, strontium and lead, a precipitate of sulphate(s) is to be expected in solution A. The solubility of these sulphates is also discussed below.

After the decomposition of sample B a double evaporation to dryness is made and barium, strontium and lead, if present, will be found as sulphates in the residue. This is then dissolved in dilute hydrochloric acid containing a small amount of sulfuric acid. The resulting solution is transferred to a 250 ml volumetric flask and is diluted to volume with water. In this solution (solution B) the concentration of hydrochloric acid is about 0.05 molar.

In aqueous solution the sulphates of barium, strontium and lead are slightly soluble (the solubility products at room temperature are 1.3×10^{-10}, 3.2×10^{-7} and 1.6×10^{-8}, respectively[74]). The concentration of sulphate ions in solution B was calculated to be about 4×10^{-3} molar. Concentrations of barium, strontium and lead above 3×10^{-8}, 8×10^{-5} and 4×10^{-6} molar, respectively, can thus be expected to result in the formation of a precipitate in solution B.

The situation likely to be encountered in silicate rock analysis is best illustrated by the following example.

The proposed scheme was employed in the analysis of the standard rock G 1 (a granite issued by the U. S. Geological Survey). According to a report by Ahrens and Fleischer[75], who discussed the content and determination of trace constituents in this sample, the recommended values (in ppm) for barium (as Ba), strontium (as Sr) and lead (as Pb) are 1220, 280 and 50, respectively. In the analysis of G 1 a small, white precipitate was observed in solution B. Precipitates from two solutions were recovered and ignited in porcelain crucibles to constant weight at 800—900°. The ignited residues weighed 0.6 and 0.9 mg. They were examined by emission spectrography and was found to consist essentially of a barium compound. Assuming that the precipitates consisted of barium sulphate, the amounts found corresponded to 883 and

74. Data taken from J. Bjerrum, G. Schwarzenbach and L. G. Sillén, Stability Constants, The Chemical Society, London, 1958.

75. L. H. Ahrens and M. Fleischer, U. S. Geol. Surv. Bull., No. 1113 (1960) 83.

1324 ppm of barium. These results fall close to those given above for the content of barium in G 1. Presupposing the presence of the average, small amounts of barium, strontium and lead, it was concluded that, in solution B, barium would be precipitated as sulphate, while the two other constituents would remain in solution[*]. If a precipitate appears in solution B it should be removed by filtration. However, it is not recommended that barium be determined by igniting and weighing this precipitate. It is better to base such a determination on emission spectrography or atomic absorption spectroscopy.

Thus, solution B can be expected to contain the strontium and lead present in the sample. In the aliquot portion which is submitted to a double precipitation with ammonia solution, strontium will accompany the other alkaline earth metals and will thus be found in solution b.

The small amount of lead present in solution B will, according to Hillebrand, Lundell, Bright and Hoffman[76], be caught quantitatively in the ammonia precipitate. After the extraction of the cupferrates from approximately 4 normal acid lead is left in the aqueous phase.

4. Zirconium, thorium and chromium

In silicate rocks these constituents are normally present as zirconium(IV), thorium(IV) and chromium(III). According to Goldschmidt[77] the latter component occurs mainly in the trivalent state.

During the decomposition of sample A and the preparation of solution A, the amounts of zirconium, thorium and chromium(III) normally occurring in rocks are not likely to introduce any difficulties. In the rare cases when chromium(VI) is present oxidation of iron(II) can be expected to take place during decomposition. In silicate rocks iron(II) is normally present in excess of chromium(VI), and the latter ion is therefore quantitatively reduced to chromium(III).

Sample B is decomposed in a mixture of hydrofluoric and sulfuric acids to which a small amount of nitric acid is added. Oxidation of chromium(III) to chromium(VI) is not likely to occur during this attack. During the analysis of solution B an aliquot portion is sub-

[*] From a preliminary spectrographic investigation of the sample conclusions can be drawn as to the probability of obtaining a precipitate in solution B.

76. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, Applied Inorganic Analysis, Second edition, John Wiley & Sons, New York, 1953, p. 223.
77. V. M. Goldschmidt, Geochemistry, Clarendon Press, Oxford, 1954, p. 547.

mitted to a double precipitation with ammonia solution and in this group separation zirconium, thorium and chromium(III) will precipitate as hydrous oxides. The ammonia precipitate is dissolved in acid, cupferron is added and a chloroform extraction is made from approximately 4 normal acid. According to Dyrssen[78] thorium will not be extracted under these conditions. Similar data on the extraction of zirconium and chromium(III) from strongly acid solution were not found, but from available data[79] on the precipitation and extraction of cupferrates, it was concluded that zirconium will be extracted with chloroform, while chromium(III) will be left in the aqueous phase.

5. Vanadium

Minor or trace amounts of vanadium can be assumed to be present in most rocks. Goldschmidt[80] and Hillebrand, Lundell, Bright and Hoffman[81] have discussed the distribution and the many valence states of vanadium in rocks. In igneous rocks vanadium is chiefly present in the trivalent state, but in other types of rocks, such as those which have been weathered, it may be present in other states of oxidation, e.g. as vanadium(V).

During the decomposition of sample A by hydrofluoric acid it is likely that reactions involving vanadium will occur. Wilson[82] has shown that during this decomposition iron(II) is oxidized by vanadium(V), the reaction products being iron(III) and vanadium(IV). In most rocks iron(II) is found in excess of vanadium(V) and consequently, after decomposition, the latter component will be present as vanadium(IV). Thus, in solution A vanadium may be found in both the tri- and tetravalent states. In the aliquot portion of solution A used for the determination of silicon, the addition of a few drops of concentrated nitric acid will oxidize all vanadium to the pentavalent state.

Sample B is decomposed by an oxidizing attack, and in solution B all vanadium will be found as vanadium(V). One of the aliquot portions

78. D. Dyrssen, Svensk Kem. Tidskr., 65 (1953) 43.
79. N. H. Furman, W. B. Mason and J. S. Pekola, Anal. Chem., 21 (1949) 1325; K. L. Cheng, Chemist-Analyst, 50 (1961) 126; H. Freiser, Chemist-Analyst, 51 (1962) 62; J. Starý and J. Smižanská, Anal Chim. Acta, 29 (1963) 545.
80. V. M. Goldschmidt, Geochemistry, Clarendon Press, Oxford, 1954, p. 485.
81. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, Applied Inorganic Analysis, Second edition, John Wiley & Sons, New York, 1953, p. 452.
82. A. D. Wilson, Analyst, 85 (1960) 823.

withdrawn from solution B is submitted to a precipitation with ammonia solution and, according to tests made by Knowles and reported by Hillebrand, Lundell, Bright and Hoffman[83] practically all of the comparatively small amount of vanadium in rocks will be caught in the mixed oxide group. The constituents of this group are then separated by a chloroform extraction of the cupferrates from approximately 4 normal acid and under these conditions vanadium(V) is quantitatively extracted[84].

6. Nickel, cobalt, copper and zinc

In silicate rocks these constituents (all in the divalent state) are normally present only in trace amounts. No problems are likely to be encountered by their presence during the decomposition of samples A and B, and the preparation of the solutions A and B.

According to Hillebrand, Lundell, Bright and Hoffman[85] nickel is not carried down with the mixed oxides. Other analysts[86] have, however, experienced that nickel may be caught with the mixed oxides. It was demonstrated by Lundell and Knowles[87] that appreciable amounts of cobalt are retained by the ammonia precipitate. The small amounts of nickel and cobalt normally occurring in rocks are therefore assumed to be distributed between the mixed oxide group and the filtrate and the interfering effect of these elements on the methods of the proposed scheme is considered as negligible.

Lundell and Knowles[67] also showed that some of the copper is precipitated with the mixed oxides. Data in the literature on the extraction of copper cupferrate with chloroform from approximately 4 normal acid, are, however, controversial[88]. To elucidate the behaviour of copper in the proposed scheme the following experiment was made. From a standard solution of copper(II) sulphate a volume corresponding to 50 mg of copper was transferred to a separating funnel. The solution was

83. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, Applied Inorganic Analysis, Second edition, John Wiley & Sons, New York, 1953, p. 455.
84. N. H. Furman, W. B. Mason and J. S. Pekola, Anal. Chem., 21 (1949) 1325.
85. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, Applied Inorganic Analysis, Second edition, John Wiley & Sons, New York, 1953, p. 404.
86. J. A. Maxwell, private communication.
87. G. E. F. Lundell and H. B. Knowles, J. Am. Chem. Soc. 45 (1923) 680.
88. See e.g. N. H. Furman, W. B. Mason and J. S. Pekola, Anal. Chem., 21 (1949) 1325.

made approximately 4 normal with regard to sulfuric acid. The solution was cooled, 20 ml of a 10 % aqueous solution of cupferron were added and the solution was extracted 3 times with 20 ml portions of chloroform. The aqueous phase was transferred to a beaker, the pH was adjusted to between 7.5 and 8.0 and the content of copper was determined titrimetrically with a standard solution of approximately 0.05 molar EDTA using ammonium purpureate (murexide) as indicator. The result showed that only about 20 % of the copper was extracted with chloroform.

The trace amounts of copper present will thus be distributed between the mixed oxides and solution b, with that portion retained by the mixed oxides again beeing distributed between the chloroform and aqueous phases.

A small part of the zinc present is likely to be retained by the ammonia precipitate[89], but the main part of the zinc will be found in solution b. It was demonstrated by Pinkus and Katzenstein[90] that zinc is not precipitated by cupferron from 0.4 to 0.5 normal nitric acid and it was concluded by the present authors that in the chloroform extraction of the cupferrates from approximately 4 normal sulfuric acid a negligible amount of zinc will be left in the aqueous phase.

7. Sulphur

The present discussion of the behaviour of sulphur will be limited to sulphur present as sulphate and sulphide.

If barium, strontium and lead are absent from sample A, any sulphate present will not participate in any reactions and the total content will be found in solution A; if they are present a precipitate of slightly soluble sulphate(s) is to be expected in solution A*. In sample A the decomposition of sulphides results in the generation of hydrogen sulphide. This decomposition takes place in a closed system and under these conditions the hydrogen sulphide is likely to participate in reactions with reducible species. During these reactions sulphide is oxidized to sulphur.

* A discussion of the behaviour of barium, strontium and lead in the proposed scheme is found above (see section G. 3.).

89. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, Applied Inorganic Analysis, Second edition, John Wiley & Sons, New York, 1953, p. 425.
90. A. Pinkus and M. Katzenstein, Bull. Soc. Chim. Belges, 39 (1930) 179.

Sample B is attacked under oxidizing conditions and in the presence of sulfuric acid. The possibility of formation of slightly soluble sulphates was discussed in the sections dealing with the behaviour of the cations. Sulphide present in sample B is likely to be oxidized to sulphate and thus, in solution B, sulphur will be present only as sulphate.

8. Boron and fluorine

In the proposed scheme boron behaves similarly to silicon. During the decomposition of sample A boron will go into solution as fluoroboric acid. By the addition of aluminium trichloride the fluoroboric acid is transformed into boric acid and thus in solution A the element can be assumed to be present as boric acid. To the authors' best knowledge an investigation of the loss of boron by volatilization of fluoroboric acid from hydrofluoric acid solution has not been carried out, and it was therefore not known whether the total amount of boron present in the sample would be found in solution A.

During the decomposition of sample B boron is quantitatively removed by volatilization as fluoroboric acid and is therefore not found in solution B.

After the decomposition of sample A all fluorine is complexed by the addition of an excess of aluminium trichloride and is present in solution A in a complexed state.

After the decomposition of sample B all fluorine is removed by a double evaporation to dryness in the presence of sulfuric acid and consequently no fluorine in present in solution B.

H. The importance of a preliminary qualitative analysis.

In the analysis of silicate rocks it is not common practise to carry out a preliminary qualitative analysis. However, some rock analysis laboratories have introduced the excellent habit of examining all samples spectrographically and if this examination is made prior to the chemical analysis, as it should be, both the analyst and the geologist get valuable additional information.

The analyst learns about the presence of uncommon elements which enables him to modify his methods and to correct his results, whereas the geologist gets information on the presence or absence of minor and trace components. The spectrographic qualitative examination can easily

be extended to comprise a quantitative determination of such constituents as strontium, barium, zirconium, vanadium, chromium, cobalt, nickel and copper.

I. Statement of analytical results.

In compliance with the wishes of the geologists it is common practise to tabulate the results of silicate rock analyses in a certain order which facilitates comparison and study. The arrangement which is universally followed to-day was strongly advocated by Washington[91] and the tabulation of analytical results is discussed in his manual on methods of rock analysis[92]. The arangement recommended by Washington has been followed in the present investigation.

In a discussion of the results of chemical analyses of some standard rocks Stevens and Niles[93] have pointed out that, because the moisture content of a rock sample will vary from place to place, analytical results should be reported and compared on a moisture-free sample. They have also stated that the results of rock analyses would be improved if all constituents were reported to the limit of accuracy of the determination. In the present work an attempt has been made to follow these recommendations.

J. Sampling.

All analytical work is based upon the obvious presupposition that the sample weighed out for analysis represents the average content of a certain amount of material.

Field specimens of rocks are normally selected by the geologists, but to the analyst falls the job of preparing a representative sample from the bulk of material received. In order to make the final sample representative it is necessary to reduce the particle size as the bulk of the sample is reduced. The sampling of silicate rock powders for chemical analysis is discussed by Wilson[94] who, on the basis of theoretical considerations, states that the amount of sample and the particle size prescribed by the

91. H. S. Washington, Am. J. Sci., Fourth series, 10 (1900) 59.
92. H. S. Washington, Manual of the Chemical Analysis of Rocks, First edition, John Wiley & Sons, New York, 1904, p. 26.
93. R. E. Stevens and W. W. Niles, U. S. Geol. Surv. Bull., No. 1113 (1960) 3.
94. A. D. Wilson, Analyst, 89 (1964) 18.

conventional and modified conventional schemes (usually 1 g of 72 mesh* powder) is adequate for the accurate determination of the main constituents in most rock types. Wilson calculated that 1 g of rock powder (density 2.63), consisting of uniformly sized spheres just passing a 72 mesh sieve would contain $0.77 \cdot 10^5$ particles. If less than 1 g is weighed out for analysis, it is desirable that the particle size is diminished accordingly so that the sample contains approximately this same number of particles.

As apparent from the subsequent section dealing with the preparation of the sample, 40, 100 and 120 mesh sieves were used to ensure that the maximum size of the particles was below a certain value. Using the simplified method given by Wilson[94], the number of particles per g of rock powder just passing 40, 100 and 120 mesh sieves were calculated and the data are listed in Table 2**.

* In most textbooks it is prescribed that crushing and grinding should be continued until the powder passes a sieve having a square opening of a certain size, as indicated by a mesh number. The sieve opening recommended by the different authors varies considerably, as apparent from the following list:

	mesh number recommended
Washington[95]	about 65
Hillebrand[96]	75
Groves[97]	90 or 100
Kolthoff and Sandell[98]	100

It should be noted that Washington and Hillebrand give the sieve opening in mesh per lineal centimeter, while the other authors only state the mesh number. For the latter group it can be assumed that the authors, according to modern practice, mean mesh per lineal inch. In the list above the mesh numbers of Washington and Hillebrand were calculated to mesh per inch. It should further be noted that the different sieve series are not always equivalent. Thus, the 100 mesh sieves of the British Standard and the U.S. Standard series have sieve openings of 0.152 and 0.149 mm, respectively.

** Data relating to the sieves were taken from Handbook of Chemistry and Physics, 41st edition, Chemical Rubber Publishing Co., U.S.A., 1959—60.

95. H. S. Washington, Manual of the Chemical Analysis of Rocks, First edition, John Wiley & Sons, New York, 1904, p. 51.
96. W. F. Hillebrand, U. S. Geol. Surv. Bull., No. 700 (1919) 58.
97. A. W. Groves, Silicate Analysis, Second edition, George Allen & Unwin Ltd., London, 1951, p. 22 and 23.
98. I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, Third edition, Macmillan Co., New York, 1959, p. 700.

Table 2.

Mesh number of sieve	Sieve opening in mm	Particles per g of sample
40	0.42	$0.98 \cdot 10^4$
100	0.149	$2.15 \cdot 10^5$
120	0.125	$5.89 \cdot 10^5$

Precautions should be taken at all stages of the sample preparation to ensure that the sample taken containes at least $0.77 \cdot 10^5$ particles.

K. Preparation of the sample.

From one or more representative field specimens, a sample of about 100 g, ground to pass a 40 mesh sieve, is prepared by crushing, splitting and grinding as described in standard textbooks of inorganic quantitative analysis[*]. These operations are conveniently done by laboratory crushing and grinding machines and by sample splitters. Rock samples containing exceptionally hard minerals should preferably be crushed and ground with the use of a hard metal mortar and pestle.

From the 100 g main sample a quantity of about 10 g is taken for analysis. This amount is first sieved gently on a 100 mesh sieve and the coarse powder is ground in a mortar or mill until all has passed through the sieve. For this operation it is recommended to employ an automatic mortar or a laboratory mill. This quantity of finely-ground material will more than suffice for the chemical determination of the 14 main constituents, as well as for the determination of minor and trace components by emission spectrography or other methods.

From the 10 g portion of 100 mesh rock powder the amount needed for sample C (for the determination of iron(II)) is taken. However, the particle size is too large for the amount (0.2000 g) weighed out for sample A and consequently about 1 g of 100 mesh powder is submitted to further grinding to pass a 120 mesh sieve. From the 120 mesh powder portions are taken for samples A and B.

[*] If the rock is exceptionally coarse-grained, it is necessary to use a larger sample. For the size of such samples, reference is made to a paper by E. S. Larsen (Am. J. Sci., Fifth series, 35 (1938) 94).

During the crushing, splitting and grinding, precautions should be taken to minimize the absorption of moisture and also to minimize the introduction of contamination from the equipment*.

L. Drying of the sample prior to analysis.

The question whether or not the sample should be dried before analysis has been discussed by various authors. Hillebrand[99] advised against the practice of drying the specimen before analysis and stressed the importance of maintaining the hygroscopic conditions constant during the analysis. He recommended the use of an air-dried powder and that a special determination of the moisture content was made. This practice was followed in the present scheme.

M. Instruments, photometric cells, laboratory equipment, reagents, glassware, plastic materials, water, nitrogen and pH-standard.

1. Instruments

The photometric measurements were made with a Zeiss spectrophotometer PMQ II equipped with a quartz prism and covering the wavelength range 200—1000 nm. In the range 200—600 nm the measurements were made with a photomultiplier tube, the sensitivity of which could be varied by changing the voltage. Above 600 nm an ordinary photocell was used.

The same instrument was employed for the flame photometric measurements, using a flame attachment based on direct spray and hydrogen and oxygen as fuel gases.

For the measurement and adjustment of pH a Beckman Zeromatic pH meter (glass (pH range 0—11) and calomel electrodes) was used.

Weighings were made to the nearest tenth of a milligram with a macro single pan substitution balance. The weights and the optical scale of the balance were calibrated against a certified set of weights.

99. W. F. Hillebrand, U. S. Geol. Surv. Bull., No. 700 (1919) 71.

* Contaminations originating from metal sieves are avoided by using nylon-meshed plastic sieves.
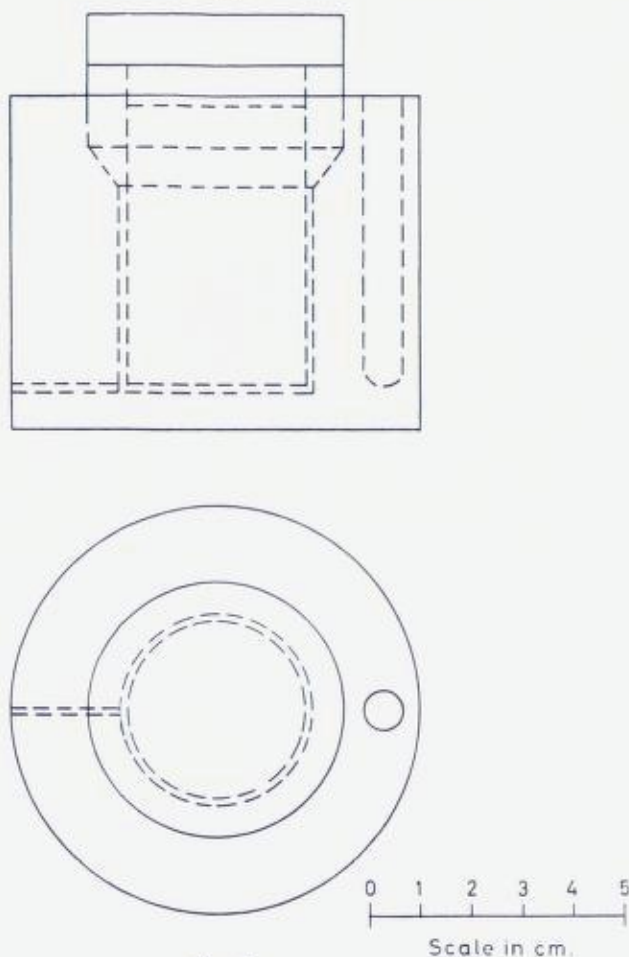
Fig. 1.
Decomposition vessel A.

2. Photometric cells

The photometric measurements were made in 1, 2 or 5 cm cells of glass or silica.

3. Laboratory equipment

For purposes of decomposition and evaporation 3 types of vessels were constructed. The vessels consisted of an inner teflon container enclosed in an aluminium block. The teflon container (a dense quality of teflon should be used) was machined from 2″-diameter rod and the
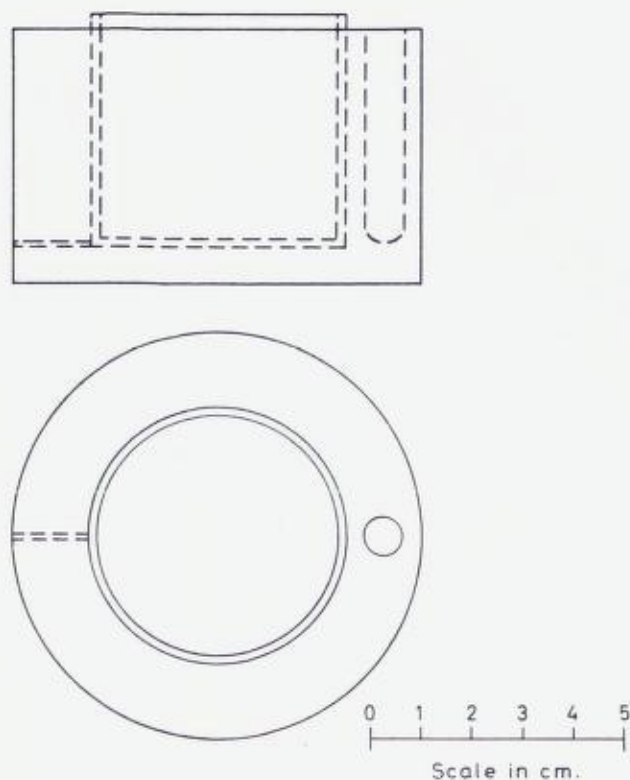
Fig. 2.
Evaporation vessel B.

blocks were made from commercially pure aluminium. The constructional details are shown in Figs. 1, 2 and 3.

For the decomposition of the separate sample for the determination of iron(II) 2 other types of crucibles were employed. The traditional type is a platinum crucible with a capacity preferably about 40 ml equipped with a tightly fitting cover of the same material. However, it is also possible to use less expensive crucibles made from recrystallized alumina. These crucibles, which are supplied in different forms, are impervious to acid aqueous solutions and their content of iron(II) can be considered to be negligible. In the present investigation a conical crucible with a capacity of 50 ml, and equipped with a plane, circular cover of the same material, was used.
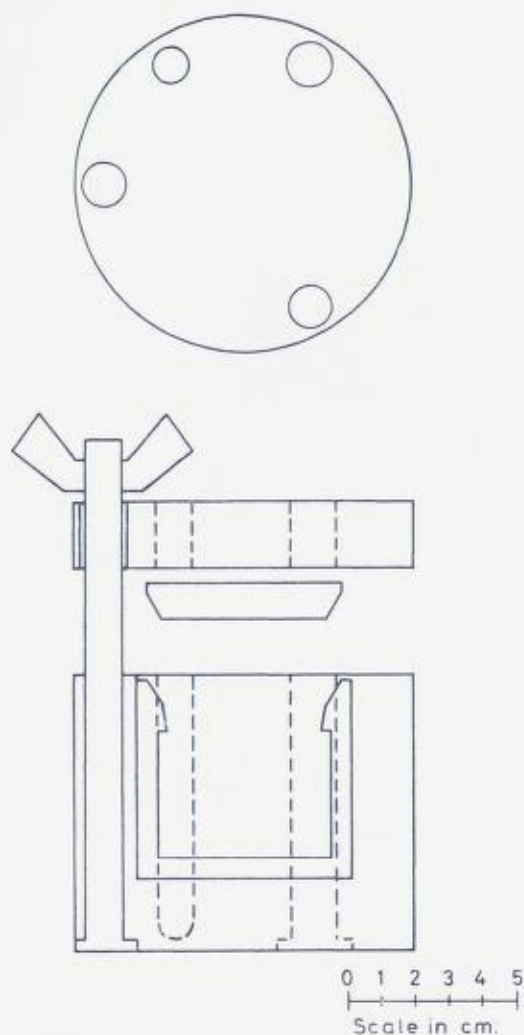
Fig. 3.
The bomb.

For the regulation of the temperature of certain solutions an ordinary thermostat was used. If the cell house permits the circulation of water, the circulation pump of the thermostat can be used to maintain a constant temperature during photometric measurement.

Special equipment for heating consisted of an electrically heated hot plate and a water bath, both equipped with devices to maintain the temperature within ± 3°.

Combined heating and stirring was obtained with the use of electrically heated magnetic stirrers, capable of maintaining the temperature within ± 2°.

4. Reagents

The reagents employed in the present investigation may be classified into three groups, as follows:

a. Reagents with a specification showing the actual content of impurities

To this group belong the analyzed substances and the high purity metals listed below. These reagents were used for the preparation of the majority of the standard solutions. The analysis was either issued by the manufacturer or resulted from a later analysis. In the present investigation it is specified when reagents of this group are employed.

Aluminium metal (bar from Vigelands Brug, Vikeland, Norway); 99.997 %.

Iron metal (sponge from Johnson, Matthey & Co., Ltd., Great Britain). The product contained only traces of metals, but appreciable amounts of non-metals (probably oxygen).

Manganese metal (flakes from Electro Manganese Corp., U.S.A.); 99.9 + %.

Titanium metal (rod from A. D. Mackey, Inc., U.S.A.); 99.99 %.

Zinc metal (rod from American Smelting & Refining Co.); 99.98 %.

Calcium carbonate, magnesium oxide, potassium chloride, potassium dihydrogen phosphate, silicon doxide and sodium chloride (all substances in the form of powder from Johnson, Matthey & Co., Ltd., Great Britain). The reagents contained only traces of metals. It should be noted, however, that the silicon dioxide was found to contain appreciable amounts of water; in one of the portions purchased for the present investigation the content of water, determined by ignition to constant weight at 1150 ± 25°, was 16 %.

b. Reagents with a specification showing the permitted maximum content of impurities

In these reagents the actual content of impurities is usually well below the limit indicated. To this group belong the majority of reagents employed.

A reagent of special importance belonging to this group is hydrofluoric acid. The concentrated hydrofluoric acid (38—40 %, E. Merck, Darm-

stadt, Germany) was controlled as to the content of silicon. Using the method of Graff and Langmyhr[100] the content of silicon (as fluorosilicic acid) was found to be practically constant (0.01 %), and well below the permitted maximum content (0.15 %).

c. Reagents without any specification showing the actual, or permitted maximum, content of impurities

To this group belong a limited number of reagents including aluminium trichloride hexahydrate.

5. Glassware

Ordinary laboratory glassware of the resistant, borosilicate type was employed.

6. Plastic materials

The decomposition vessels were made from a dense form of teflon (from Hammarby Bakelit Industri AB, Sweden). The magnets used in the decomposition vessels were covered with teflon.

Some alkaline and other solutions that would attack glass were stored in polyethylene bottles.

7. Water

Purified water was obtained from an ion exchange column (Research Model type from Illinois Water Treatment Co., U.S.A.) capable of removing all ionizable solids. This unit also removes silicon and carbon dioxide.

8. Nitrogen

Purified nitrogen was used to remove oxygen from certain solutions and to maintain a non-oxidizing atmosphere. The producer of the gas (Norsk Hydro-Elektrisk Kvælstofaktieselskab, Norway) specified that the content of oxygen did not exceed 6 ppm.

9. pH-standard

The pH meter was standardized with the use of a 0.05 molar solution of potassium hydrogen phthalate which, according to Bates and Guggenheim[101], has a pH of 4.00 at 20°.

100. P. R. Graff and F. J. Langmyhr, Anal. Chim. Acta, 21 (1959) 429.
101. R. G. Bates and E. A. Guggenheim, Pure Appl. Chem., 1 (1960) 163.

N. Calibration of instruments, photometric cells, laboratory equipment and volumetric glassware.

1. Instruments

The wavelength scale of the spectrophotometer was adjusted with a hydrogen lamp and the line at 486.1nm.

2. Photometric cells

The 4 cells of a set were cleaned, numbered and filled with water. The 3 cells were calibrated against the fourth at the wavelength(s) of the later measurement(s). 10 Readings were taken of each cell and the arithmetic mean was used for correction purposes. The cells should be calibrated regularly.

3. Laboratory equipment

The thermostat was calibrated with a precision thermometer graduated to 0.02°.

4. Volumetric glassware

A comparatively large number of volumetric flasks, pipettes and burettes were employed in the different determinations. The majority of items used had been tested by the manufacturer and were supplied with a certificate of examination. Pieces of apparatus without a certificate were tested by weighing with water, and, if necessary, corrections were made.

O. Choice of equipment and procedure for decomposition.

Sample A may be decomposed either in the decomposition vessel A or in the bomb. If the mineral composition of the rock is known, a choice of suitable equipment can be made on the basis of the known decomposability of the separate minerals*. Samples of unknown mineral composition are first attacked in the decomposition vessel A according to the general procedure given in the next chapter. If unattacked material is visible after the decomposition, as apparent from an inspection of solution A, two ways of action are open, i. e. either to repeat the

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* Data on the decomposability of minerals in hydrofluoric acid have been presented by Langmyhr and Sveen[64].

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attack using material ground to a finer state of subdivision and an increased decomposition time, or to employ the bomb technique*. The former method is recommended when the amount of undecomposed material is small, while comparatively large amounts call for the use of the bomb.

Sample B is always decomposed in the evaporation vessel B. Most rock samples are decomposed by the mixture of concentrated hydrofluoric and sulfuric acids. Samples which contain extremely resistant minerals should be ground more finely than usual and the duration of the attack may be extended by adding a third portion of hydrofluoric and sulfuric acids to the residue after the first double evaporation to dryness.

Sample C is decomposed either in a 50 ml crucible of recrystallized alumina or in a platinum crucible. If a comparatively large amount of unattacked material is visible after the decomposition, a new sample should be used and the duration of the attack increased. If undecomposed material is still present, it should be filtered off, ground further under non-oxidizing conditions to a very fine state of subdivision and reattacked.

P. Methods for the decomposition of samples A, B and C; and for the preparation of solutions A and B.

1. Decomposition of sample A and preparation of solution A

a. *Decomposition in decomposition vessel A*

A 0.2000 g sample is weighed into the decomposition vessel A which also contains a teflon-covered magnet. The powder is moistened with 6—8 drops of water, 4.5 ± 0.2 ml of hydrofluoric acid are added carefully and the vessel is closed. The vessel, supported in the aluminium block containing a thermometer, is then placed on an electrically heated magnetic stirrer. During decomposition the teflon stopper of the vessel is held in place by means of a weight or with the use of a laboratory clamp.

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* Inspection of the contents of the decomposition vessel A will, because of the likely presence of precipitated fluorides, reveal only the presence of resistant dark minerals.

It should also be noted that solution A may contain precipitated sulphates, but these can in most cases be distinguished from undecomposed rock.

The magnetic stirrer is started and the block is heated to, and maintained at, $110 \pm 2°$ for 45 min. The block is then removed from the stirrer and the vessel is cooled to room temperature without removing the teflon stopper (the rate of cooling can be increased by keeping the block in water).

Approximately 100 ml, of a total volume of 225 ml, of 25 % aluminium trichloride hexahydrate solution are added to a 300 ml plastic beaker. The contents of vessel A are transferred to the beaker and the remaining volume of aluminium trichloride solution is used to wash the vessel and the stopper. The plastic beaker, equipped with a plastic cover, is placed on a boiling water bath for 5—10 min with frequent stirring. This heating serves to dissolve precipitated fluorides and a clear solution should be obtained. If unattacked material is visible, repeat the attack as described in section O.

The contents of the beaker are cooled to room temperature, transferred to a 250 ml volumetric flask and diluted to volume with water. This solution is designated solution A. To avoid polymerization of the silicic acid, the time between the addition of the sample solution A to the aluminium trichloride solution and the later addition of molybdate solution to the aliquot portions pipetted from solution A for the determination of silicon should not exceed 0.5 h.

b. *Decomposition with the use of the bomb*

A 0.2000 g sample is weighed out into the inner teflon vessel of the bomb. The powder is moistened with 6—8 drops of water and 4.5 ± 0.2 ml of hydrofluoric acid are added carefully. The bomb is closed, a reliable thermometer is inserted and the bomb is heated to $240 \pm 10°$ and maintained at this temperature for 1 h.

After cooling, the procedure to be followed is the same as that given above for the use of the decomposition vessel A. Extremely resistant minerals, such as topaz, may not be completely decomposed in the first attack. In this case the attack should be repeated with a portion ground to an impalpable powder.

The final solution, in a 250 ml volumetric flask, is designated solution A. As emphasized in the preceding section, aliquot portions of solution A must be withdrawn and molybdate must be added as soon as possible after the preparation of solution A.

2. Decomposition of sample B and preparation of solution B

A 0.4000 g sample is weighed* into the evaporation vessel B. The powder is moistened with 10—12 drops of water and 0.5 ± 0.1 ml of concentrated sulfuric acid (95—97 %), 4—5 drops of concentrated nitric acid (65—70 %) and 10 ± 1 ml of hydrofluoric acid are added. The vessel is placed in its aluminium block (equipped with a thermometer) and the block is heated on a hot plate. Heating should always take plase in a fume cupboard. During the decomposition stage the temperature should be kept in the range 160 ± 20°. When most of the hydrofluoric acid has been removed, the temperature is increased to 280 ± 10°** and the evaporation is continued to complete dryness***. The vessel is then cooled, the residue is moistened with concentrated sulfuric acid and the evaporation to dryness is repeated. The block with the vessel is cooled and 1.0 ± 0.1 ml of concentrated hydrochloric acid (36—38 %), 2 drops of concentrated sulfuric acid (95—97 %) and enough water to cover the residue are added. The vessel is covered and is heated in its aluminium block on the boiling water bath until all salts are dissolved, stirring when necessary to speed up the dissolution. The cooled solution is transferred to a 250 ml volumetric flask and diluted to the mark with water. This solution is designated solution B.

Solution B may contain a precipitate of slightly soluble sulphates of barium, lead and strontium****. The precipitate should be removed by filtration, preferably before solution B is diluted to the mark.

The procedure given above will decompose the majority of rocks usually encountered. If unattacked material is detected in solution B, a redetermination according to the directions given in section O. should be made.

3. Decomposition of sample C

It was stated in the discussion of the rôle of iron(II) in the proposed scheme (see section E.) that the original plan of determining this constituent in an aliquot portion of solution A was not successful. It was

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* The amount of sample B should be exactly twice the amount of sample A.

** The temperature should not exceed 300°. Above this temperature teflon starts to decompose, giving off poisonous fumes.

*** The problems relating to the removal of fluoride by evaporation were discussed in chapter III

**** A preliminary emission spectrographic investigation will indicate the probability of obtaining sulphate precipitates.

necessary to resort to the conventional method by which a separate portion of the sample is decomposed by a mixture of hydrofluoric and sulfuric acids, with air being excluded by the generation of water vapour. After decomposition the fluorine is complexed by boric acid.

Contributions to the development of the hydrofluoric acid method* for iron(II) were made by Cooke[103] and Pratt[104]. In the present investigation the method of Pratt, with some modification, is used.

For this decomposition comparatively large platinum crucibles (capacity about 40 ml) are normally employed. Because such crucibles are very expensive, attempts have been made to use crucibles of other materials and one analyst[105] has successfully used crucibles made of recrystallized alumina for a number of years.

The following procedure is used for the decomposition of sample C.

0.4 g or more** of the sample are weighed into a 50 ml crucible of recrystallized alumina or a capacious platinum crucible, and the powder is moistened with 8—10 drops of water. Some pieces of recrystallized alumina or a coil of platinum wire are placed in the crucible to prevent bumping. Then 10 ml of sulfuric acid (1:1) are added, the solution is heated to boiling and boiled gently for approximately 5 min. The burner is removed, 5 ml of hydrofluoric acid are quickly added, the crucible is covered without delay and the solution is boiled uninterruptedly for 10 min. The solution is treated as described in section Q.5.

If decomposition is not complete the measures prescribed in section O. should be taken.

Q. Methods for the determination of the separate constituents.

1. Determination of silicon

a. *Principle*

Silicon, in the form of silicic acid, is determined spectrophotometrically, as the yellow α,12-molybdosilicic acid (later referred to as molyb-

* For a survey of methods for the determination of iron(II), see Hillebrand, Lundell, Bright and Hoffman[102].

** In order to prevent sampling error, amounts less than 0.4 g of 100 mesh powder should not be taken.

102. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, Applied Inorganic Analysis, Second edition, John Wiley & Sons, New York, 1953.
103. J. P. Cooke, Am. J. Sci., Second series, 44 (1867) 347.
104. J. P. Pratt, Am. J. Sci., Third series, 48 (1894) 150.
105. B. Bruun, private communication.

dosilicic acid) in an aliquot part of solution A. The method was originally introduced by Jolles and Neurath[106]. The blank solution is prepared from an aliquot portion of solution B.

b. *Reactions*

When silicon dioxide* or silicates are decomposed by hydrofluoric acid, silicon is transformed into fluorosilicic acid. If the decomposition is carried out in the presence of an excess of hydrofluoric acid, silicon is kept quantitatively in solution as fluorosilicic acid and reacts with molybdate to form a heteropolyacid which, according to Langmyhr and Stige[107], is identical with that resulting from the reaction of silicic acid with molybdate. These authors assumed that the former reaction took place in two steps, the first producing silicic acid and an oxofluoromolybdate and the second resulting in the formation of a 12-molybdosilicic acid. Similar reactions probably take place when aluminium ions are added to solutions of fluorosilicic acid, the primary reaction producing silicic acid and a fluoroaluminate.

In these reactions silicic acid is formed initially in the monomeric state, but by standing the monomer undergoes polymerization. It was demonstrated by Alexander[108] that silicic acid is most reactive in the monomeric or dimeric form. The higher polymeric forms do not react, or react much more slowly with molybdate than the monomeric or dimeric species. Molybdate should therefore be present or be added as soon as possible after the formation of silicic acid. Langmyhr and Stige[109] found that, after the addition of an aluminium salt to a solution of silicon dioxide in hydrofluoric acid, the solution should not be left for more than about 1 h before the addition of molybdate. If left for a longer period the results for silicon were found to be low.

In the heteropolyacid-forming reactions discussed above the pH plays an important rôle. In their studies of the spectrophotometric determination of silicon in materials decomposed by hydrofluoric acid Langmyhr and Graff[110] recommended that the pH of solutions of molybdosilicic

* A discussion of the reaction of silicon dioxide with hydrofluoric acid (the system water-hydrofluoric acid-fluorosilicic acid) is also found in chapter III.

106. A. Jolles and F. Neurath, Angew. Chem., 11 (1898) 315.
107. F. J. Langmyhr and L. Stige, unpublished results.
108. G. B. Alexander, J. Am. Chem. Soc., 75 (1953) 5655.
109. F. J. Langmyhr and I. Stige, unpublished results.
110. F. J. Langmyhr and P. R. Graff, Anal. Chim. Acta, 21 (1959) 334.

acid be maintained in the range 0.5—1.5. Andersson[111] prepared a series of solutions containing constant amounts of silicic acid, sodium molybdate and sodium fluoride; by varying the concentration of aluminium and the pH, and plotting the extinction of the molybdosilicic acid as a function of pH, he obtained curves demonstrating that the upper pH-limit for complete colour development was below pH 1.5.

Under the experimental conditions of the present determination Langmyhr and Stige[109] found that complete and reproducible development of molybdosilicic acid was possible up to pH 2.3. The determination of silicon in the present scheme is made at pH 1.90 ± 0.05.

e. Interfering elements

A comparatively large number of the constituents of silicate rocks interfere in the present determination. These constituents may be divided into two groups, one comprising anions which react with molybdate to form heteropolyacids, and another consisting of cations which either absorb at the wavelength of the measurement, or react with molybdate to form absorbing species.

Constituents of the first group are phosphorus, vanadium, arsenic and germanium (in the form of orthophosphate, vanadate, arsenate and germanate, respectively). In the photometric determination of silicon it is customary to concentrate on the removal of the interference from phosphorus, and to consider the interfering effects from other heteropolyacid-forming species as negligible.

The removal of the interfering effect of phosphorus has been the object of a large number of investigations. A common procedure is to add oxalic, citric or tartaric acid, or a salt of these acids, but recent studies[109,112] have shown that this addition did not completely remove the colour of molybdophosphoric acid, and that the reagents also affected the colour of molybdosilicic acid. A number of other methods have been suggested for the separation of interfering elements from silicon, such as precipitation, extraction, volatilization (of arsenic and germanium with hydrochloric acid), and the use of ion exchange and mercury cathode electrolysis. Without further testing, nothing can be said about the applicability of these methods to the present determination. Some of the

111. L. H. Andersson, Acta Chem. Scand., 14 (1960) 1571.
112. L. H. Andersson, Arkiv Kemi, 19 (1963) 223.

methods are lengthy and tedious, and have only been used in connection with the determination of small amounts of silicon.

The other group of interfering elements consists of coloured ions and ions that react with molybdate to form absorbing species. The dominant ion of this group is iron(III). The interfering effect of this ion upon the photometric determination of silicon was studied by Andersson[111] and by Langmyhr and Stige[100]. These authors concluded that iron(III), when present in amounts normally met with in silicate rocks, will not affect the results for silicon.

It is thus obvious that the presence of interfering elements, especially those belonging to the first group, seriously affects the results for silicon, and that it is extremely difficult to eliminate the effect of all these ions.

In the present scheme the problems relating to the interfering effect of other constituents on the photometric measurement of molybdosilicic acid were solved in a way which, to the authors' best knowledge, does not seem to have been previously employed. This method is based upon the use of a blank solution prepared from solution B and representing exactly the same amount of rock as the sample solution, this solution, from which silicon and fluorine have been quantitatively removed, thus automatically compensates for orthophosphate, vanadate, arsenate and germanate as well as for other known* and unknown interfering substances.

d. *Reagents*

    Acetic acid (96 %)

    Aluminium trichloride hexahydrate — this reagent had no specification showing the actual, or permitted maximum, content of impurities.

    Ammonium molybdate tetrahydrate

    Hydrochloric acid (36—38 %)

    Hydrofluoric acid (38—40 %)

    Nitric acid (65—70 %)

    Silicon dioxide, spectrographically analyzed (see section M.4.)

    Sodium acetate trihydrate

* In the present method the possible effect of iron was compensated for by oxidizing all of the iron in both sample and blank solutions to the trivalent state.

Aluminium trichloride hexahydrate solution (25 %). This solution should be filtered before use.

Ammonium molybdate tetrahydrate solution (10 %)

Buffer solution (pH 4.76). 62.6 g of acetic acid and 136.1 g of sodium acetate trihydrate are transferred to a 1000 ml volumetric flask. The reagents are dissolved in water and the solution is diluted to volume with water.

Hydrochloric acid (1:3).

e. *Calibration curve*

A 0.2000 g portion of silicon dioxide, ignited to constant weight at $1150 \pm 25°$, was weighed into the decomposition vessel A, the powder was moistened with 6—8 drops of water and 4.5 ± 0.2 ml of hydrofluoric acid were added cautiously. Without delay a teflon-covered magnet was placed in the vessel, the vessel was closed, placed in the aluminium block and the block (equipped with a thermometer) was placed on the electrically heated magnetic stirrer. The contents of the vessel were stirred continuously while the block was heated to $110 \pm 2°$ and maintained at this temperature for 45 min. Without being opened, the vessel was cooled to room temperature. The contents were then transferred to a 300 ml plastic beaker containing 100 ml of 25 % aluminium trichloride hexahydrate solution. Another portion of 125 ml of the same solution was used to wash the vessel and the stopper* and the solution was then transferred to a 500 ml volumetric flask and diluted to volume with water.

Aliquots of the silicon standard solution (Table 3) were added from a 50 ml burette to 9, of a series of 10, plastic beakers of 300 ml capacity. In order to compensate for the absorption of aluminium trichloride and the content of silicon in the hydrofluoric acid** it is necessary to maintain the same amounts of the two reagents in both sample and blank solutions. These constant amounts (22.5 ml of 25 % aluminium trichloride hexahydrate solution and 0.45 ml of hydrofluoric acid) are present in the sample and blank solutions prepared in connection with the later determinations of silicon. The amounts of aluminium trichloride hexahydrate and hydrofluoric acid present in the aliquots of the silicon

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* At this stage a white precipitate may appear. The precipitate is dissolved by heating the solution for some minutes on the water bath.

** A determination of the silicon content of the hydrofluoric acid used in the present investigation is described in section M. 4.

standard solution added from the burette, as well as the amounts to be added, are tabulated in Table 3.

Table 3.

Volumes (in ml) of silicon standard solution taken	Amounts (in mg) of SiO_2 taken	Volumes (in ml) of 25% $AlCl_3 \cdot 6H_2O$ solution and of hydrofluoric acid originating from the silicon standard solution		Additional volumes (in ml)	
		25% $AlCl_3 \cdot 6H_2O$ solution	hydro-fluoric acid	of 25% $AlCl_3 \cdot 6H_2O$ solution	of hydro-fluoric acid
10	4	4.50	0.090	18.00	0.360
15	6	6.75	0.135	15.75	0.315
20	8	9.00	0.180	13.50	0.270
25	10	11.25	0.225	11.25	0.225
30	12	13.50	0.270	9.00	0.180
35	14	15.75	0.315	6.75	0.135
40	16	18.00	0.360	4.50	0.090
45	18	20.25	0.405	2.25	0.045
50	20	22.50	0.450	0.00	0.000

The additional volumes of aluminium trichloride hexahydrate solution and hydrofluoric acid were added as a combined reagent solution which was prepared in the following way: 200 ml of 25 % aluminium trichloride hexahydrate solution were pipetted into a 300 ml plastic beaker, the beaker placed on the water bath and the solution evaporated to a volume of about 190 ml. From a 5 or 10 ml plastic graduated measuring cylinder (the same cylinder should be used for all additions of hydrofluoric acid) 4.0 ± 0.2 ml of hydrofluoric acid were added and the solution was transferred to a 200 ml volumetric flask and diluted to the mark with water. By adding from a burette the additional volumes of 25 % aluminium trichloride hexahydrate solution given in Table 3, the correct amounts of both reagents were added. A 22.5 ml aliquot of the combined aluminium trichloride hexahydrate and hydrofluoric acid solution was transferred to the beaker reserved for the blank solution. Water was added to all beakers to give a total volume of 225 ± 5 ml, followed by 2—3 drops of concentrated nitric acid and 10 ml of ammonium molybdate solution. The pH of all solutions was adjusted to 1.90 ± 0.05 by the addition of either buffer solution* (pH 4.76) or hydro-

* To avoid the precipitation of hydrous alumina buffer solution (pH 4.76) was used instead of ammonia solution to increase the pH of the solutions.

chloric acid (1:3). The beakers were covered and were kept in the water bath for 3 h[*]. After cooling the solutions to room temperature, the pH was checked and if not within 1.90 ± 0.05 it was adjusted as described above. The solutions were transferred to 250 ml volumetric flasks and water was added to a point just below the graduation mark. The flasks were placed in the thermostat[**] (20.0 ± 0.2°) for 30 ± 5 min, the solutions were diluted to volume with water of temperature 20.0 ± 0.2° and the extinction of each solution was measured 10 times against the blank at 415 nm using 1 cm silica cells[***]. A second series of calibration data were recorded in the same way as described above and with the use of a new portion of ignited silicon dioxide.

The extinction data and the resulting extinction index are shown in Table 4.

f. *Procedure*

Two 25 ml aliquot portions of solution A are pipetted into 300 ml plastic beakers[****]. The blank solution is prepared by transferring from a burette or graduated pipette 12.5 ml of solution B[*****] into a 300 ml plastic beaker. The blank should also contain the same amounts of aluminium trichloride and hydrofluoric acid as the sample solutions, and

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[*] The purpose of the heating is to transform molybdosilicic acid from the unstable β- to the stable α-modification. During heating, the beakers should be kept in the hot water of the bath.

[**] The effect of the temperature on the extinction of solutions of molybdosilicic acid is considerable. According to Andersson[113] the temperature coefficient at 20° is 0.2—0.3 % per degree.

[***] If possible, the temperature of the cell house should be maintained at 20.0 ± 0.2° by the circulation of water from the thermostat.

[****] In order to avoid any effect from polymerization of silicic acid, it is strongly recommended not to let the time interval, between the transference of the content of the decomposition vessel A to the aluminium trichloride hexahydrate solution, and the addition of molybdate to the aliquot portions pipetted from solution A, exceed 0.5 h.

[*****] In the analysis of rocks it is presupposed that 0.2000 g and 0.4000 g are weighed out for the preparation of solution A and B, respectively. In the analysis of the test solution (described in chapter V. B.) 25 ml of solution B were withdrawn for the preparation of the blank solution.

113. L. H. Andersson, Acta Chem. Scand., 12 (1958) 495.

Table 4. *Calibration data for the determination of silicon.*

Amounts (in mg) of SiO_2 per 250 ml (C)	Extinctions				Arithmetic mean (E)	Extinction index (I) (I = E/C)
	first series		second series			
4	0.186	0.186	0.186	0.187	0.1863	0.04658
	0.187	0.186	0.187	0.186		
	0.185	0.186	0.186	0.186		
	0.186	0.186	0.187	0.187		
	0.186	0.186	0.186	0.187		
6	0.280	0.279	0.280	0.279	0.2799	0.04665
	0.279	0.281	0.280	0.279		
	0.281	0.281	0.279	0.280		
	0.279	0.280	0.281	0.280		
	0.280	0.281	0.279	0.280		
8	0.370	0.371	0.370	0.371	0.3709	0.04636
	0.371	0.371	0.371	0.371		
	0.371	0.371	0.372	0.371		
	0.372	0.371	0.372	0.371		
	0.370	0.371	0.371	0.370		
10	0.461	0.460	0.462	0.461	0.4618	0.04618
	0.461	0.462	0.462	0.463		
	0.462	0.463	0.462	0.461		
	0.463	0.462	0.462	0.461		
	0.462	0.463	0.461	0.462		
12	0.559	0.558	0.558	0.559	0.5596	0.04663
	0.559	0.558	0.559	0.559		
	0.560	0.560	0.560	0.560		
	0.560	0.560	0.560	0.560		
	0.559	0.561	0.561	0.561		
14	0.649	0.650	0.649	0.650	0.6497	0.04640
	0.650	0.650	0.650	0.650		
	0.650	0.649	0.650	0.649		
	0.650	0.649	0.650	0.650		
	0.650	0.650	0.649	0.650		
16	0.739	0.739	0.740	0.739	0.7408	0.04630
	0.740	0.743	0.741	0.740		
	0.740	0.743	0.741	0.741		
	0.742	0.743	0.740	0.741		
	0.743	0.740	0.741	0.740		
18	0.832	0.830	0.830	0.832	0.8327	0.04626
	0.834	0.832	0.832	0.831		
	0.834	0.834	0.832	0.834		
	0.834	0.834	0.833	0.832		
	0.835	0.834	0.833	0.833		
20	0.933	0.934	0.934	0.933	0.9330	0.04665
	0.934	0.933	0.933	0.934		
	0.933	0.932	0.933	0.932		
	0.933	0.932	0.931	0.932		
	0.933	0.934	0.934	0.933		

Arithmetic mean for extinction index = 0.04645.

consequently 22.5 ml of aluminium trichloride hexahydrate solution and 4.5 ± 0.2 ml of hydrofluoric acid (1:9)* are added.

The 3 solutions are diluted with water to a volume of 225 ± 5 ml, 2—3 drops of nitric acid (to maintain oxidizing conditions) and 10 ml of ammonium molybdate solution are added. The pH of the solutions is then adjusted to 1.90 ± 0.05 with the addition of either hydrochloric acid (1:3) or buffer solution (pH 4.76). The beakers are covered and kept in the boiling water bath for 3 h. The pH is checked and if not within 1.90 ± 0.05 it is adjusted as described above. The solutions are transferred to 250 ml volumetric flasks, diluted with water to a point just below the graduation mark, left in the thermostat (20.0 ± 0.2°) for 30 ± 5 min, diluted to volume with water of temperature 20.0 ± 0.2° and measured at 415 nm using 1 cm silica cells. Each solution is measured 10 times, the arithmetic mean of each series of extinction readings is calculated and the content (in per cent) of silicon (as silica) is found from the formula:

$$SiO_2 \text{ (in per cent)} = \frac{0.1 \cdot E \cdot V}{I \cdot v \cdot G}$$

where

E = arithmetic mean of extinction readings
V = volume (in ml) of solution A — usually 250 ml
I = extinction index determined from the calibration data
v = volume (in ml) pipetted from solution A — usually 25 ml
G = weight (in g) of sample — usually 0.2000 g

From the 2 separate results the arithmetic mean is calculated.

2. Determination of aluminium

a. *Principle*

Aluminium is determined titrimetrically in an aliquot portion of solution B. To the aluminium solution, from which interfering elements have been removed by a chloroform extraction of the cupferrates, an excess of a standard solution of EDTA is added. The excess of EDTA is back-titrated with a standard solution of zinc, dithizone being used as an indicator,

* Dilute 5.0 ± 0.2 ml of hydrofluoric acid with 45 ml of water in a plastic beaker, and store in a plastic bottle.

as originally proposed by Wänninen and Ringbom[114]. Nydahl[115] studied the Wänninen-Ringbom method and demonstrated that the aluminium-EDTA complex behaves as an indifferent substance, this resulting in a considerable reduction of the titration error.

b. *Separations*

Before the determination of aluminium it is necessary to carry out 2 separations. In the first separation, which is the classical double precipitation by ammonia solution of the constituents of the mixed oxide group, aluminium and the other components of the group are separated from magnesium and the alkali and alkaline earth metals. A further separation of the constituents of the mixed oxide group is indispensable, as EDTA reacts with practically all members of this group. The second separation is based upon a chloroform extraction from approximately 4 normal acid of the cupferrates of the interfering elements.

c. *Interfering elements*

The present discussion is restricted to those constituents which, after the chloroform extraction of the cupferrates, accompany aluminium into the aqueous phase.

From the discussion of the rôle of manganese in the present scheme (section IV.F.), it follows that this component does not interfere with the determination of aluminium.

Orthophosphate is found in the aqueous phase, but this constituent does not react with EDTA.

Of the trace elements, the total content of chromium(III) and thorium(IV) accompany aluminium. Some other trace metals, e.g. lead(II), nickel(II), cobalt(II) and zinc, may be partly or completely caught with the hydrous oxides and are found in the aqueous phase. However, in silicate rocks each of these metals are normally present in amounts well below 0.1 per cent, and their interference will usually be negligible.

d. *Reagents*

Acetic acid (96 %)
Ammonia solution (about 25 %)
Ammonium chloride

114. E. Wänninen and and A. Ringbom, Anal. Chim. Acta, 12 (1955) 308.
115. F. Nydahl, Talanta, 4 (1960) 141.

Ammonium N-nitrosophenylhydroxylamine (cupferron)

Chloroform (the reagent contained about 1 % of absolute ethanol)

4-Dimethylaminoazobenzene-2'- carboxylic acid, sodium salt (methyl red)

Diphenylthiocarbazone (dithizone)

Disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA)

Ethanol (96 %)

Hydrochloric acid (36—38 %)

Sodium acetate trihydrate

Sulfuric acid (95—97 %)

Zinc, analyzed (see section M. 4.).

Zinc standard solution (0.025 molar)

3.2690 g of zinc were transferred to a 200 ml beaker and 100 ml of water and 5 ml of sulfuric acid were added. The beaker was covered with a watch glass and was kept on the water bath until the dissolution of the metal was complete. The cooled solution was transferred to a 2000 ml volumetric flask, 1000 ml of buffer solution (pH 4.76) were added and the contents of the flask were made up to volume with water. The solution, which was stored on a plastic bottle, had a pH of 4.70.

EDTA solution (about 0.05 molar)

93.06 g of EDTA were transferred to a 5000 ml volumetric flask, dissolved in water and then diluted to volume with water. The solution was stored in a plastic bottle.

Standardization of the EDTA solution

A 20 ml aliquot of the EDTA solution was pipetted into a 400 ml beaker, and 20 ml of buffer solution (pH 4.76), about 60 ml of water and 100 ml of ethanol were added. If the solution became turbid by precipitation of salts, water was added in small increments until a clear solution was obtained. After the addition of 2 ml of dithizone solution the solution was titrated with zinc standard solution (0.025 molar) until the colour changed from greenish-violet to red. At least two aliquots should be titrated and the arithmetic mean molarity calculated.

Ammonia solution (1:1)

Ammonium chloride solution (2 %)

Buffer solution (pH 4.76). The preparation of the buffer solution is described in section Q. 1. d.

Cupferron solution (10 %). 1.0 ± 0.1 g of cupferron was dissolved in 10 ml of cold water. A freshly-prepared solution should be used.

Dithizone solution (0.025 %). 0.025 g of dithizone were transferred to a 100 volumetric flask, dissolved in ethanol and diluted to volume with the same solvent. Only a freshly-prepared solution should be used.

Hydrochloric acid (1:1)
Hydrochloric acid (1:1000)
Methyl red solution (0.1 %).

e. Procedure

From solution B 125 ml are pipetted into a 300 ml beaker and 0.5 ± 0.1 g of ammonium chloride are added and dissolved. The solution is heated to boiling and ammonia solution (1:1) is added until the hydrous oxides are precipitated and there is a distinct odour of ammonia from the solution. The pH of the solution, as measured by pH indicator paper or a pH meter, should be adjusted to 6.5—7.5. The precipitate is allowed to settle for some minutes and is then collected in a glass filter crucible (porosity 20—30 μm) the filtrate (and wash water) being collected in a 300 ml beaker. The precipitate is washed 2 or 3 times with hot ammonium chloride solution (2 %) made alkaline to methyl red with ammonia solution (1:1). (The total amount of wash water should be 10 ± 1 ml.) By means of a jet of water, the hydrous oxides are transferred from the crucible (it is not necessary to remove the precipitate completely) into the beaker used for the precipitation, dissolved in 10.0 ± 0.5 ml of hot hydrochloric acid (1:1) and reprecipitated as described above, this time omitting the addition of ammonium chloride. The hydrous oxides are collected in the original filter crucible and are washed 4 or 5 times with hot ammonium chloride solution (2 %) made alkaline to methyl red with ammonia solution (1:1). (The total amount of wash water should be 10 ± 1 ml.) The hydrous oxides are again washed from the crucible into the original beaker (more than 25 ml of water should not be used for this operation), and the crucible is placed in an upright position in the beaker. Sufficient hydrochloric acid (36—38 %) is poured into the crucible to give a final acid concentration in the beaker of about 1:1. The beaker is covered and is left overnight, preferably on the water bath. It is then heated to boiling and is kept just below the boiling point for at least 1 h. The crucible is removed after being washed with hydrochloric acid (1:1000) and the contents

of the beaker are transferred to a 350 ml separating funnel. The beaker
is washed with hydrochloric acid (1:1000). The solution is cooled in ice
water and 10 ml of cupferron solution are added to precipitate the
cupferrates, which are then extracted by three 20 ml portions of chloro-
form. The organic phase is discarded after the extraction and the aque-
ous phase is transferred to a 500 ml beaker, the funnel being washed with
hydrochloric acid (1:1000). From a pipette 20 ml of EDTA standard
solution are added and, with continuous stirring, ammonia solution
(1:1) is added slowly until the pH is 4.7 ± 0.2, pH indicator
paper being used for this adjustment. The solution is heated to boiling
and is kept just below the boiling point for 15 ± 3 min. After cooling
to room temperature, 20 ml of buffer solution (pH 4.76) and 2 ml of
dithizone solution are added. If the solution is yellow, hydrochloric acid
(1:1) is added slowly until the colour changes to greenish. The volume
of the solution is then doubled by the addition of ethanol*, and the
excess of EDTA is back-titrated with zinc standard solution until the
colour changes from greenish-violet to red. The content (in per cent) of
aluminium (as aluminium oxide) is calculated from the equation:

$$Al_2O_3 \text{ (in per cent)} = \frac{(VM - V'M') \cdot E \cdot V''}{20 \cdot v \cdot G}$$

where

V = volume (in ml) of EDTA standard solution added

M = molarity of EDTA standard solution

V' = volume (in ml) of zinc standard solution added

M' = molarity of zinc standard solution

E = molecular weight of Al_2O_3 ; 101.96

V'' = volume (in ml) of solution B — usually 250 ml

v = volume (in ml) pipetted from solution B — usually 125 ml

G = weight (in g) of sample — usually 0.4000 g.

* If the solution becomes turbid at this point, water is added in small increments
until a clear solution is obtained.

f. *Notes*

Hydrous alumina is extremely resistant to dissolution by acids*, and it is only by prolonged standing and heating that the last traces are brought into a form which reacts with EDTA. It is therefore recommended that the hydrous oxides are left overnight in contact with strong acid, and it is imperative that the strongly acid solution is maintained near the boiling point for some time.

At an early stage of the development of the scheme, the hydrous oxides were collected in filter paper. The paper with its content was transferred to a beaker containing strong acid and was disintegrated by stirring and heating. Even by prolonged heating and stirring it was impossible to transform all aluminium into a state which reacted with EDTA, the reason for this probably being that aluminium was strongly adsorbed on the cellulose fibers.

3. Determination of the total content of iron

a. *Principle*

In an aliquot portion of solution B (in which all iron is present as iron(III)) the total content of iron is determined spectrophotometrically with sodium 1,2-dihydroxybenzene-3,5-disulfonate (tiron). Titanium is determined in the same aliquot portion.

b. *Interfering elements*

Yoe and Jones[117] (who introduced the reagent) studied the colour formation of 78 ions with tiron, and stated that the following ions produced a colour, Fe^{3+}, Ti^{4+}, Cu^{2+}, MoO_4^{2-}, OsO_5^{2-}, UO_2^{2+} and VO^+. With the exception of Fe^{3+} and VO^+, all ions formed yellow or greenish yellow complexes. The VO^+ ion produced a purple colour which faded to colourless within 15 min.

In a later paper Yoe and Armstrong[118] described the simultaneous determination of iron and titanium with tiron. These authors stated that at pH 4.7 the blue iron(III) tiron complex was not affected by the

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* The reactivity of hydrous alumina toward acids was studied by Graham and Thomas[116].

116. R. P. Graham and A. W. Thomas, J. Am. Chem. Soc., 69 (1947) 816.
117. J. H. Yoe and A. L. Jones, Anal. Chem., 16 (1944) 111.
118. J. H. Yoe and A. R. Armstrong, Anal. Chem., 19 (1947) 100.

presence of titanium(IV) ions. As apparent from the discussion in section G. 5., vanadium is only present in the pentavalent state in solution B and consequently will not interfere in the present determination*. Because the remaining colour-forming ions are present only in trace amounts in rocks, and as their tiron complexes absorb mainly at other parts of the spectrum, it was concluded that none of the constituents normally met with in silicate rocks would interfere in the determination of the total content of iron.

c. *Reagents*

Acetic acid (96 %)
Hydrochloric acid (36—38 %)
Hydrogen peroxide solution (30 %)
Iron, spectrographically analyzed (see section M. 4.)
Sodium acetate trihydrate
Sodium 1,2-dihydroxybenzene-3,5-disulfonate (tiron).

Iron(III) standard solution (0.02 mg of iron(III) oxide per ml)

From a standard solution of iron(III) containing 1 mg of iron(III) oxide per ml (the preparation of this solution is described in chapter V. B. 1.) 50 ml were pipetted into a 250 ml volumetric flask and diluted to volume with water. From this solution 25 ml were transferred to another 250 ml volumetric flask and again diluted to volume with water. The latter solution contains 0.02 mg of iron(III) oxide per ml.

Buffer solution (pH 4.76). The preparation of this solution is described in section Q. 1. d.

Tiron solution (4 %). 4.0 g of tiron were transferred to a 100 ml volumetric flask, dissolved in water and the solution was made up to volume with water. Freshly-prepared solutions of tiron are colourless, but by prolonged standing they turn yellow. Only colourless solutions should be used.

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* It should be noted that Yoe and Jones[117] reported that VO^+ ions gave a purple colour with tiron, while Yoe and Armstrong[118] stated that VO^{++} produced a purple complex.

d. *Calibration curve*

From a 100 ml burette 20, 30, 40, 50, 60 and 70 ml of iron(III) standard solution (0.02 mg of iron(III) oxide per ml) were run into 6 of a series of seven 100 ml volumetric flasks. To all flasks water was added to a volume of about 70 ml, followed by 5 ml of tiron solution, 20 ml of buffer solution and 2—3 drops of hydrogen peroxide solution. After dilution to volume with water and 15 min standing, the extinctions were measured against the blank at 560 nm using 1 cm cells. Each sample solution was measured 4 times against the blank. The recorded data are reproduced in Table 5. The extinctions were remeasured after 20 h and, as apparent from Table 5, the colour was stable for this period of standing.

Table 5.

Calibration data for the determination of the total content of iron.

| Amounts (in mg) of Fe_2O_3 per 100 ml (C) | Arithmetic mean of 4 extinction readings | | | Extinction index (I) $(I = E/C)$ |
| | with addition of H_2O_2 | | without addition of H_2O_2 | |
	15 min standing (E)	20 h standing	15 min standing	
0.4	0.214	0.213	0.211	0.535
0.6	0.316	0.315	0.314	0.527
0.8	0.424	0.424	0.420	0.530
1.0	0.529	0.524	0.524	0.529
1.2	0.631	0.633	0.628	0.526
1.4	0.732	0.738	0.713	0.523

Arithmetic mean for extinction index = 0.528.

In an effort to determine whether or not the addition of hydrogen peroxide was necessary a second series of solutions was prepared, but this time without the addition of the oxidizing agent. As seen from Table 5, the extinctions (measured after 15 min) are distinctly lower, and it was concluded that the presence of hydrogen peroxide is necessary. The probable explanation of the lower extinctions of solutions not containing hydrogen peroxide is that the tiron solution either contained reducing agents or acted as a reducing agent. A reducing effect of tiron solutions has been observed by Yoe and Jones[117].

e. Procedure

From solution B 25 ml are pipetted into a 100 ml volumetric flask and water is added to a volume of about 70 ml, followed by 5 ml of tiron solution, 20 ml of buffer solution and 2—3 drops of hydrogen peroxide solution. A blank solution is prepared in another 100 ml volumetric flask by adding to about 70 ml of water the volumes of reagent solutions given above. The sample and blank solutions are diluted to the mark with water and, after 15 min standing, the extinction is measured 4 times against the blank at a wavelength of 560 nm. using 1 cm cells. The total content (in per cent) of iron (as iron(III) oxide) is calculated as follows:

$$Fe_2O_3 \text{ (in per cent)} = \frac{0.1 \cdot E \cdot V}{I \cdot v \cdot G}$$

where

E = arithmetic mean of extinction readings
V = volume (in ml) of solution B — usually 250 ml
I = extinction index determined from the calibration data
v = volume (in ml) pipetted from solution B — usually 25 ml
G = weight (in g) of sample — usually 0.4000 g.

f. Notes

In order to obtain complete and rapid development of the colour of the titanium(IV) tiron complex, it is necessary that the different reagent solutions be added strictly in the order given in the above procedure. The reason for this is apparent from the experiments described below (section Q. 7.).

4. Determination of iron(III)

The content of iron(III) (as iron(III) oxide) is found by subtracting the result for iron(II) (see below), recalculated to iron(III) oxide, from the result for the total content of iron.

The recalculation of iron(II) oxide to iron(III) oxide is done by multiplying the figure for the former constituent by the factor 1.1113.

5. Determination of iron(II)

a. Principle

A separate portion of the sample is decomposed by a mixture of hydrofluoric and sulfuric acids and the iron(II) content is determined titrimetrically with a standard solution of potassium dichromate, using sodium diphenylaminesulfonate as indicator.

b. *Interfering elements*

For a discussion of the difficulties adhering to the conventional method for iron(II), and for the elements that may interfere, reference is made to chapter I. B.

c. *Reagents*

Boric acid

Orthophosphoric acid (85 %)

Potassium dichromate

Sodium diphenylaminesulfonate.

Potassium dichromate standard solution (0.03 normal)

1.4711 g of potassium dichromate, previously dried to constant weight at $175 \pm 25°$, were transferred to a 1000 ml volumetric flask, dissolved in water and the solution diluted to volume with water.

Boric acid solution (saturated)

Sodium diphenylaminesulfonate solution (0.2 %).

d. *Procedure*

While the sample is being decomposed according to the procedure given in section P. 3., 25 ml of boric acid solution, 200 ml of freshly boiled water and 5 ml of orthophosphoric acid are added to a 600 ml beaker.

After decomposition the covered crucible is quickly transferred to the beaker, the contents of the crucible are mixed with the solution in the beaker, 5—6 drops of sodium diphenylaminesulfonate solution are added, and potassium dichromate standard solution is added from a burette until the colour changes from green to violet.

The content (in per cent) of iron(II) (as iron(II) oxide) is found from the equation:

$$\text{FeO (in per cent)} = \frac{M \cdot N \cdot E}{10 \cdot G}$$

where

M = volume (in ml) added of potassium dichromate standard solution

N = normality of potassium dichromate standard solution

E = molecular weight of FeO ; 71.85

G = weight (in g) of sample.

e. *Notes*

After the titration the beaker should be inspected for the presence of undecomposed material. If more than a trace amount is found, the precautions given in section P. 3. should be taken.

One of the main sources of error in the determination of iron(II) is partial oxidation because of incomplete exclusion of air before the titration is made. This source of error is completely eliminated by decomposing the sample in the presence of an excess of either potassium dichromate standard solution, as suggested by L. E. Reichen and J.J. Fahey, U. S. Geol. Surv. Bull., No. 1144-B (1962); or ammonium vanadate standard solution, as described by A. D. Wilson, Analyst, 85 (1960) 823.

6. Determination of calcium, magnesium, sodium and potassium

a. *Introduction*

Calcium, magnesium, sodium and potassium are all determined in the filtrate after the double precipitation with ammonia solution of the members of the mixed oxide group. The collected filtrates and wash water are transferred to a 250 ml volumetric flask and diluted to volume with water; this solution is designated solution b.

Solution b may contain some or all of the following constituents:

1. Main constituents: The total content of calcium, magnesium, sodium, potassium and a part of the manganese.
2. Minor and trace constituents: lithium, rubidium, strontium, nickel, cobalt, copper and zinc.

Of the elements listed above the main constituents can always be assumed to be present in appreciable amounts, while the minor and trace elements are often absent or present in such low concentrations that their interfering effect can be considered as negligible.

In addition to the constituents originating from the sample, the effect of added reagents upon the determination of calcium, magnesium, sodium and potassium also has to be taken into account. Ions belonging to the latter category are chloride and sulphate and in order to compensate for the effect of these ions it is desirable that their concentrations in solution b be maintained approximately constant.

b. *Determination of calcium*

α. Principle

Calcium is determined titrimetrically in an aliquot portion of solution b. For this titration (carried out at pH 12—14) a standard solution of EDTA and the indicator 3-hydroxy-4-(2-hydroxy-4-sulfo-1-naphthylazo)-2-naphthoic acid (calcon carboxylic acid) are employed.

β. Interfering elements

The ions that may be present in solution b were listed above (see section a).

Because of the low stability of the alkali metal EDTA complexes, these do not affect the present determination.

At the high pH values used in the determination of calcium and in the presence of a reducing agent (e.g. ascorbic acid or hydroxylamine hydrochloride) magnesium and manganese are quantitatively precipitated as hydroxides* and do not react with EDTA.

Patton and Reeder[119] discussed the interfering effect of a number of ions on the present determination, and stated that barium, strontium, lead, zinc, copper, cobalt and nickel interfered. These authors also suggested measures to be taken to avoid the interferences, such as the addition of cyanide to complex zinc, cobalt, nickel and copper, the addition of sodium diethyldithiocarbamate to complex lead and the precipitation of barium as sulphate.

To avoid the interference from nickel, cobalt, copper and zinc** (barium and lead*** are not present in solution b) potassium cyanide is added before the titration of the calcium. The anions (chloride and sulphate) present in solution b are without effect in the present titration.

The only interfering ion is strontium. However, in silicate rocks the strontium content rarely exceeds a few hundredths of one per cent, and consequently its effect can usually be considered to be negligible****.

* In the presence of large amounts of magnesium some calcium is likely to be coprecipitated with the magnesium hydroxide and will not react with EDTA.

** As pointed out in section G. 6., a portion of these metals is likely to be coprecipitated with the mixed hydroxides.

*** The behaviour of barium and lead was discussed in section G. 3.

**** If a preliminary spectrographic investigation was carried out, it is possible to correct for the presence of strontium.

119. J. Patton and W. Reeder, Anal. Chem., 28 (1956) 1026.

γ. *Reagents*

Ascorbic acid
3-Hydroxy-4-(2-hydroxy-4-sulfo-1-naphthylazo)-2-naphthoic acid
  (calcon carboxylic acid)
Potassium cyanide
Sodium chloride
Sodium hydroxide.

EDTA standard solution (about 0.005 molar). This solution is pre-
  pared by diluting the standard solution described in section Q. 2.
Calcon carboxylic acid — sodium chloride solid mixture (1:100). 0.020 g
  of calcon carboxylic acid and 2.0 g of sodium chloride are triturated
  together in an agate mortar.
Sodium hydroxide solution (about 50 %).

δ. *Procedure*

The filtrate and wash water from the double precipitation with
ammonia solution are transferred to a 250 ml volumetric flask and dilu-
ted to volume with water (solution b). A 125 ml portion is pipetted into
a 250 ml beaker, water is added to a volume of about 200 ml and 20 ±
5 mg of ascorbic acid and 20 ± 5 mg of potassium cyanide are added.
The pH is increased to 12.5—13.5 by the addition of sodium hydroxide
solution, the beaker is covered and the solution is left for 2—3 min
to let the hydroxides of magnesium and manganese coagulate. Indicator
mixture is then added to give a suitably coloured solution and EDTA
standard solution is added from a 25 ml burette until the colour chan-
ges from red to pure blue. The titration should be made under good
lighting conditions and on a white sheet of paper or glass plate.

The content (in per cent) of calcium (as calcium oxide) is calculated
from the expression:

$$\text{CaO (in per cent)} = \frac{0.1 \cdot V \cdot M \cdot E \cdot V' \cdot V''}{v \cdot v' \cdot G}$$

where

V = volume (in ml) of EDTA standard solution added
M = molarity of EDTA standard solution
E = molecular weight of CaO ; 56.08
V' = volume (in ml) of solution B — usually 250 ml
V'' = volume (in ml) of solution b — usually 250 ml

v = volume (in ml) pipetted from solution B — usually 125 ml
v = volume (in ml) pipetted from solution b — usually 125 ml
G = weight (in g) of sample — usually 0.4000 g.

ε. Notes

Among the methods considered for the determination of calcium was flame photometry. This technique was tried, but because of the disturbance caused by the presence of other constituents it was abandoned. Satisfactory results could only be obtained if the standard solutions of calcium contained the same amounts of magnesium, sodium, potassium, chloride and sulphate as the sample solution.

c. Determination of magnesium

α. Principle

The content of magnesium is also determined in an aliquot portion of solution b. In this aliquot portion the sum of calcium (and strontium) and magnesium is determined by titration at pH 10—11 with a standard solution of EDTA using sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonate (eriochrome black T) as indicator.

β. Interfering elements

The ions to be considered in the present discussion were listed in section a.

Due to the low stability of the complexes formed between EDTA and the members of the alkali metals, these ions do not interfere in the titration of magnesium.

The interfering effect of zinc, cobalt, nickel and copper is avoided by adding potassium cyanide to the solution before titration. The portion of the manganese that is present in solution b will react with EDTA under the present conditions and is therefore removed by precipitation as hydrous manganese dioxide and filtration. The other interfering elements are calcium and strontium which are both titrated under the conditions of the determination of calcium, and consequently a correction can be made for their presence.

The anions chloride and sulphate do not affect the present determination.

γ. *Reagents*

    Ammonia solution (about 25 %)
    Ammonium chloride
    Ascorbic acid
    Sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonate
      (eriochrome black T)
    Potassium cyanide
    Sodium chloride
    Sodium chlorite.

EDTA standard solution (about 0.005 molar). See under the determination of calcium (section b.).

Eriochrome black T — sodium chloride solid mixture (1:100). 0.020 g of eriochrome black T and 2.0 g of sodium chloride are triturated together in an agate mortar.

δ. *Procedure*

    A 100 ml aliquot of solution b is pipetted into a 250 ml beaker, 75 ± 25 mg of sodium chlorite are added and the solution is heated to boiling*. After 5 min of boiling to precipitate hydrous manganese dioxide and expel the oxides of chlorine, the hot solution is filtered through a glass filter crucible (porosity 20—30 μm) and the precipitate is washed with water. To avoid adsorption of calcium and magnesium the solution should be filtered without delay. The filtrate and wash water are collected in a 250 ml beaker, 20 ± 5 mg of ascorbic acid and 20 ± 5 mg of potassium cyanide are added, the pH is adjusted to 10.6 ± 0.2 by the addition of ammonia solution, indicator mixture is added to give a suitably coloured solution and the EDTA standard solution is added from a 25 ml burette until the colour changes from red to pure blue (no tinge of violet should be visible at the end point).

    The content (in per cent) of magnesium (as magnesium oxide) is calculated from the formula:

$$\text{MgO (in per cent)} = \frac{0.1 \, (V \cdot M - \dfrac{V'}{V''} V''' \cdot M) \, E \cdot V'''' \cdot V'''''}{V' \cdot v \cdot G}$$

* This method is described by Riley and Williams[120].

120. J. P. Riley and H. P. Williams, Mikrochim. Acta, No. 6 (1959) 804.

where

V = volume (in ml) of EDTA standard solution added in the present titration of the sum of calcium and magnesium

M = molarity of EDTA standard solution

V' = volume (in ml) pipetted from solution b for the present determination — usually 100 ml

V'' = volume (in ml) pipetted from solution b for the titration of calcium (according to the procedure given in section 6. b. δ.) — usually 125 ml

V''' = volume (in ml) of EDTA standard solution added in the titration of calcium (according to the procedure given in section 6. b. δ.)

E = molecular weight of MgO ; 40.32

V'''' = volume (in ml) of solution b — usually 250 ml

V''''' = volume (in ml) of solution B — usually 250 ml

v = volume (in ml) originally pipetted from solution B — usually 125 ml

G = weight (in g) of sample — usually 0.4000 g.

d. *Introduction to the determination of sodium and potassium*

α. Principle

Sodium and potassium are determined in solution b by flame photometry, the wavelengths employed for these determinations being 589 nm and approximately 767 nm, respectively.*

β. *Introductory remarks on interferences*

Data on the interfering effect of other elements on the flame photometric determination of sodium and potassium have been collected by different investigators using widely different types of instruments and flames. Differences in the nature of the flame, atomizer, monochromator etc. may result in considerable variations in the interfering effect of a certain foreign element, and consequently published data on interferences should be critically evaluated. To guard against the possibility of

* As many ordinary colour filters are likely to transmit light from other elements, e.g. the potassium filter transmitting light of sodium, and the sodium filter transmitting light of calcium, it is recommended that an instrument equipped with a prism or grating monochromator is employed.

experiencing unexpected interfering effects, it is recommended that adequate experiments on the interfering effect of other elements are carried out with each instrument.

In an excellent treatise on flame photometry Dean[121] critically surveyed the large number of data on the influence of foreign elements on the flame photometric determination of sodium and potassium. The present discussion of this influence is partly based on the data compiled by Dean.

As discussed above (see section 6. a.) a number of foreign cations and anions may be present in solution b. The influence of some of the cations, viz. those which can always be expected to be present, was studied experimentally. With regard to the anions occuring in solution b, it was only necessary to consider the effect of chloride and sulphate. To compensate for the effect from these ions, hydrochloric and sulfuric acids were added to the standard solutions of sodium and potassium.

A more detailed discussion of the interferences will be found under the separate methods.

c. Determination of sodium

α. Interfering elements

The sodium emission line at 589 nm* is very little affected by spectral interference from other elements. The high sensitivity of the sodium emission permits the use of relatively narrow slit widths (about 0.02 mm with the instrument employed in the present work) which in turn reduces the background emission. According to Dean[121] spectral interference may be encountered in the presence of large amounts of calcium, cerium, lanthanum, strontium and a number of rare earth elements. However, in silicate rocks none of these elements (with the possible exception of calcium) are found in amounts such as to cause interference. From the data tabulated by Dean[121] on the interfering effect of cations on the emission intensity of sodium it was concluded that none of the cations that may be present in solution b would interfere.

To confirm the conclusions on the spectral interference and the effect of some major cations on the determination of sodium the experiments outlined in Table 6 were made.

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* This line is actually a closely spaced doublet at 589.0 and 589.6 nm.

121. J. A. Dean, Flame Photometry, McGraw-Hill Book Company, Inc., New York, 1960.

Table 6. *Effect of diverse elements upon the flame emission of sodium. Wavelength 589 nm. Slit width 0.02 mm. All constituents present as chlorides.*

Effect of potassium		
Concentrations (in mg) per 100 ml		Scale reading [*]
of sodium	of potassium	
2	0	36.5
2	20	36.4
2	40	36.5
2	200	36.7

Effect of calcium		
Concentrations (in mg) per 100 ml		Scale reading [*]
of sodium	of calcium oxide	
2	0	36.5
2	20	36.6
2	40	36.7

Effect of magnesium		
Concentrations (in mg) per 100 ml		Scale reading [*]
of sodium	of magnesium oxide	
2	0	34.0
2	20	34.0
2	40	34.0

Effect of manganese		
Concentrations (in mg) per 100 ml		Scale reading [*]
of sodium	of manganous oxide	
2	0	37.4
2	2	37.4
2	4	37.4
2	12	37.5

[*] Each figure is the arithmetic mean value of 4 separate measurements.

From the data of Table 6 it was concluded that none of the major cations of solution b would interfere in the determination of sodium.

As to the possible influence of anions, it should be remembered that chloride and sulphate are added to solution B and are thus always found in solution b, while other anions originating from the sample, such as orthophosphate, have been removed by the precipitation with ammonia solution. The concentration of chloride in solution b is considerable (about 0.36 molar), while the concentration of sulphate is appreciably lower (about 0.01 molar). Traces of some other anions, e. g. vanadate, may be present, but in the analysis of silicate rocks the concentration of anions other than chloride and sulphate can be regarded as negligible. From the data compiled by Dean[121] it is obvious that the interfering effect of chloride and sulphate upon the flame emission of sodium is considerable and must be taken into account. In the present scheme it was decided to compensate for the interference from chloride and sulphate by maintaining the same concentrations of these ions in the standard solutions of sodium.

β. Instrument

For the flame photometric determinations the Zeiss spectrophotometer PMQ II with flame attachment was employed.

Flame: hydrogen — oxygen
Working pressures: hydrogen — 0.29 lb/sq in
oxygen — 4.3 lb/sq in
Slit width: 0.02 mm
Photodetector: photomultiplier
Volume aspirated per min — 1.8 ml.

γ. Reagents

Hydrochloric acid (36—38 %)
Sodium chloride — spectrographically analyzed (see section M. 4.)
Sulfuric acid (95—97 %).
Sodium chloride standard solution (1 mg of sodium oxide per ml).

Sodium chloride was ignited to constant weight in a porcelain crucible at 500 ± 25° and 1.8858 g were transferred to a 1000 ml volumetric flask, dissolved in water and the solution was made up to volume with water. From this primary standard solution a series of secondary standard solutions were prepared in the following way.

From the primary standard solution 20, 24, 28, 32, 36, 40 and 44 ml aliquots were transferred to a series of 1000 ml volumetric flasks. To compensate for the practically constant amounts of chloride and sulphate present in solution b, hydrochloric and sulfuric acids were added at this stage, in the amounts given below. The relatively small amount of chloride originating from the sodium chloride primary standard solution was not taken into account. To each flask 30.1 ml of hydrochloric and 0.60 ml of sulfuric acids were added and the solutions were made up to volume with water. The series of secondary standard solutions contained 5, 6, 7, 8, 9, 10 and 11 mg of sodium oxide per 250 ml (which is the usual volume of solution b), and the concentrations of chloride and sulphate were 0.36 molar and 0.01 molar, respectively.

8. Procedure

The flame photometer is set up according to the instruction manual. The flame is lighted and the pressures are adjusted to the values recommended. With maximum sensitivity and a slit width of 0.02 mm the wavelength is set to about 589 nm. Water is now aspirated and the galvanometer scale is adjusted to zero.

A suitable secondary standard solution, e.g. one containing 5 mg of sodium oxide per 250 ml, is aspirated and the wavelength is adjusted to maximum response. This setting must not be disturbed until all measurements are completed. Water is aspirated again and the zero is adjusted. Solution b is then aspirated and from the reading 2 adjacent secondary standards are selected, of which one will give a higher and the other a lower reading than solution b. Water and the 3 solutions are now aspirated twice in the following order: distilled water, lower standard, solution b, higher standard. The arithmetic mean of the readings are determined and the content (in per cent) of sodium (as sodium oxide) is calculated from the following equation:

$$\text{Na}_2\text{O (in per cent)} = \frac{0.1 \left(a + \dfrac{E_x - E_1}{E_2 - E_1} \right) \cdot V}{v \cdot G}$$

where

a = the content (in mg per 250 ml) of sodium oxide in the standard solution of lower concentration

E_1 = arithmetic mean of readings for the standard solution of lower concentration

E_2 = arithmetic mean of readings for the standard solution of higher
    concentration

E_x = arithmetic mean of readings for solution b

V = volume (in ml) of solution B — usually 250 ml

v = volume (in ml) originally pipetted from solution B — usually
    125 ml

G = weight (in g) of sample — usually 0.4000 g.

r. Notes

a. Calculation of the approximately constant content of chloride present in solution b

The chloride found in solution b originates from the following sources:

1. From the 1.0 ml of concentrated hydrochloric acid added to dissolve the residue after the evaporation to dryness with sulfuric acid. This amount of acid is present in solution B (volume 250 ml) from which 125 ml are pipetted for the preparation of solution b. Consequently, the latter solution contains 0.50 ml of concentrated hydrochloric acid.

2. From the amount of ammonium chloride (0.50 g) added to the aliquot portion of 125 ml pipetted from solution B before the precipitation with ammonia solution of the components of the mixed oxide group. This amount of salt corresponds to 0.78 ml of concentrated hydrochloric acid.

3. From the total volume of ammonium chloride solution (40 ml of 2 % solution) employed to wash the precipitated mixed hydroxides. The total volume of wash solution (corresponding to about 0.80 g of ammonium chloride) is found in solution b and is equivalent to 1.25 ml of concentrated hydrochloric acid.

4. From the 10 ml of hydrochloric acid (1:1) used for the dissolution of the hydrous oxides after the first precipitation with ammonia solution. This amount of acid enters solution b.

The total amount of chloride present in solution b corresponds to a molarity of 0.36 and to a volume of 7.53 ml of concentrated hydrochloric acid.

b. Calculation of the approximately constant content of sulphate present in solution b.

The sulphate found in solution b originates from:

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1. The residue of sulphates left after the evaporation to dryness with sulfuric acid.

The amount of sulphate in this residue will vary with the chemical composition of the sample. However, an approximate value can be calculated by assuming a chemical composition corresponding to that of an intermediate rock, e. g. the composition chosen in the testing of the present scheme (see chapter V. B. 1.).

Presupposing this intermediate composition and the presence of the compounds tabulated in Table 7, the amount of sulphate in the residue was calculated to 0.3333 g.

Of the total amount of sulphate (333.3 mg) found in the residue, one half (166.7 mg) enters into solution b. This corresponds to a concentration of sulphate in solution b of 0.007 molar.

2. The sulfuric acid added to solution B.

Two drops of concentrated sulfuric acid are added, of which one half, assumed to correspond to 0.05 ml, is found is solution b. This volume of acid (0.05 ml) corresponds to a sulphate concentration of about 0.0036 molar.

Thus the total concentration of sulphate in solution b is approximately 0.01 molar.

Table 7.

Constituent	Chemical composition (in per cent) of sample	Compounds assumed to be present in residue after the double evaporation to dryness with sulfuric acid	Amounts (in mg) of sulphate held by the different constituents after the decomposition of 0.4000 g of sample and the double evaporation to dryness with sulfuric acid
SiO_2	60.00	not present	—
Al_2O_3	16.00	$Al_2(SO_4)_3$*	181.0
Fe_2O_3	2.50	⎫ $Fe_2(SO_4)_3$**	37.9
FeO	2.50	⎭	
MgO	2.50	$MgSO_4$	23.8
CaO	5.00	$CaSO_4$	34.2
Na_2O	5.00	Na_2SO_4	31.0
K_2O	5.00	K_2SO_4	20.4
TiO_2	0.70	$TiOSO_4$	3.4
P_2O_5	0.50	$AlPO_4$	—
MnO	0.30	$MnSO_4$	1.6
			Total 333.3 mg of sulphate

* Not corrected for the amount of aluminium held as phosphate.

** Iron(II) is oxidized to iron(III) during evaporation.

f. *Determination of potassium*

α. Interfering elements

The emission line employed for the present determination is the un-resolved doublet appearing at approximately 767 nm. The slit width used — 0.1 mm — gives a relatively broad spectral band. However, as pointed out by Dean[121], the background emission is negligible in this part of the spectrum.

The foreign elements to be considered in the present discussion, i. e., those that may occur in solution b, are listed in section 6. a. With regard to spectral interferences at the wavelength employed, Dean[121] reported that some interference from rubidium and lanthanum is expe-rienced when medium and broad spectral bandwidths are employed. However, in silicate rocks these constituents are present only in trace amounts and their interfering effect can be considered to be negligible.

From the data tabulated by Dean[121] on the change of emission inten-sity of potassium in the presence of other cations, it was concluded that, with the possible exception of sodium, none of the cations that may be encountered in solution b would interfere.

In the presence of an excess of sodium the emission of potassium may be enhanced[121], at least when flames other than hydrogen-oxygen are used. It was therefore considered necessary to study the influence of sodium with the present instrument, and, at the same time, to include the cations which always can be expected to be found in solution b. The experimental results are given in Table 8.

The results confirmed that when sodium is present in excess, the results for potassium will be high. None of the other elements studied (calcium, magnesium and manganese) had any effect on the determina-tion of potassium.

The emission intensity of potassium may also be influenced by anions. In solution b the only anions that have to be considered are chloride and sulphate. From the data compiled by Dean[121] it can be concluded that the effect of these anions differ widely with the type of flame employ-ed. In the development of the proposed scheme it was found most satis-factory to compensate for the effect of chloride and sulphate by main-taining the same concentration of these ions in both sample and stan-dard solutions.

Table 8. *Effect of diverse elements upon the flame emission of potassium. Wavelength approximately 767 nm. Slit width 0.1 mm. All constituents present as chlorides.*

Effect of sodium		
Concentrations (in mg) per 100 ml		Scale reading*
of potassium	of sodium	
2	0	17.7
2	2	17.7
2	20	18.5
2	40	19.1
2	200	19.9

Effect of calcium		
Concentrations (in mg) per 100 ml		Scale reading*
of potassium	of calcium oxide	
2	0	18.0
2	20	18.0
2	40	18.1

Effect of magnesium		
Concentrations (in mg) per 100 ml		Scale reading*
of potassium	of magnesium oxide	
2	0	17.7
2	20	17.6
2	40	17.2

Effect of manganese		
Concentrations (in mg) per 100 ml		Scale reading*
of potassium	of manganous oxide	
2	0	19.6
2	2	19.8
2	4	19.6
2	12	19.7

* Each figure is the arithmetic mean value of 4 separate measurements.

The approximately constant concentrations of chloride and sulphate that are present in solution b were calculated above (see section 6. e. ɛ.).

β. Instrument

Zeiss spectrophotometer PMQ II with flame attachment.
Flame: hydrogen — oxygen
Working pressures: hydrogen — 0.29 lb/sq in
oxygen — 4.3 lb/sq in
Slit width: 0.1 mm
Photodetector: photocell
Volume aspirated per min — 1.8 ml.

γ. Reagents

Hydrochloric acid (36—38 %)
Potassium chloride — spectrographically analyzed (see section M. 4.)
Sulfuric acid (95—97 %).

Potassium chloride standard solution (1 mg of potassium oxide per ml).

Potassium chloride was ignited to constant weight in a porcelain crucible at $500 \pm 25°$, and 1.5830 g were transferred to a 1000 ml volumetric flask, dissolved in water and the solution diluted to volume with water. A series of secondary standard solutions were prepared exactly as prescribed in the preceding section for the preparation of the corresponding series of sodium chloride solutions. The same volumes of primary standard solution were taken and the same volumes of hydrochloric and sulfuric acids were added. The secondary series contained 5, 6, 7, 8, 9, 10 and 11 mg of potassium oxide per 250 ml.

δ. Procedure

The procedure followed in the determination of potassium and the calculation of the percentage of potassium oxide in the sample are exactly the same as described in the preceding section on sodium.

7. Determination of titanium

a. Principle

Titanium is determined spectrophotometrically in an aliquot part of solution B with sodium 1,2-dihydroxybenzene-3,5-disulfonate (tiron). The total content of iron is determined in the same aliquot portion.

b. *Interfering elements*

The use of tiron for the photometric determination of titanium was first suggested by Yoe and Jones[122]. Yoe and Armstrong[123] later applied the reagent for the simultaneous determination of titanium and iron. The latter authors found that the interference of iron(III) ions upon the determination of titanium could be removed by the addition of sodium dithionite. Yoe and Armstrong[123] reported that the ions VO^{2+}, MoO_4^{2-} and UO_2^{2+} formed coloured complexes with tiron and specified that, in the presence of 0.03 mg of titanium, the limiting concentrations of these ions were 0.01 mg, 0.01 mg and 0.1 mg, respectively.

Rigg and Wagenbauer[124] studied the use of tiron for the photometric determination of titanium in silicate rocks and investigated the interfering effect of constituents normally found in rocks. In the presence of thioglycolic acid (added as reducing agent) these authors reported that none of the major constituents of silicate rocks interfered, while interferences were received from: Cr_2O_3, V_2O_3, CuO, WO_3, MoO_3 and U_3O_8. The limiting concentrations (in per cent) for these substances in the analysis of a rock containing 0.50 % TiO_2 (and assuming a permissible error of $\pm$ 0.01 % TiO_2) were: Cr_2O_3 — 0.84 (0.029); V_2O_3 — 0.13 (0.022); CuO — 0.06 (0.013); WO_3 — 0.19 (0.010); MoO_3 — 0.01 (0.002) and U_3O_8 — 0.60 (0.0005). (The data given in parenthesis are, according to the same authors, the average content (in per cent) of these elements in the earth's crust.) Rigg and Wagenbauer concluded by stating that a very unusual enrichment of the interfering substances would have to occur before a serious error would be met with in a titanium determination.

On the basis of the investigations referred to above, and presupposing the use of sodium dithionite, it was assumed that none of the ordinary constituents of rocks would interfere in the present method for titanium.

c. *Reagents*

Acetic acid (96 %)
Bromine
Sodium acetate trihydrate
Sodium 1,2-dihydroxybenzene-3,5-disulfonate (tiron)
Sodium dithionite

122. J. H. Yoe and A. L. Jones, Anal. Chem., 16 (1944) 111.
123. J. H. Yoe and A. R. Armstrong, Anal. Chem., 19 (1947) 100.
124. T. Rigg and H. A. Wagenbauer, Anal. Chem., 33 (1961) 1347.

Sulfuric acid (95—97 %)

Titanium, analyzed (see section M. 4.).

Titanium standard solution (0.0417 mg of titanium dioxide per ml). 0.5000 g of titanium drillings were weighed out and transferred to a 150 ml beaker. 10 ml of sulfuric acid (1:3) were added, the beaker was covered and left on the water bath until complete dissolution of the metal. The coloured solution was heated to about 90° and bromine water was added in excess. To ensure complete oxidation of titanium to the quadrivalent state and to remove the excess of bromine, the cover was removed and the solution was heated to boiling and kept just below the boiling point for about 0.5 h. The solution was cooled to room temperature, 20 ml of sulfuric acid were added, the solution was transferred to a 1000 ml volumetric flask and diluted to volume with water. From this standard solution 25 ml were pipetted into a 500 ml volumetric flask and diluted to volume with water to give a standard solution containing 0.0417 mg of titanium dioxide per ml.

Bromine water (saturated)

Buffer solution (pH 4.76). For the preparation see section Q. 1. d.

Sulfuric acid (1:3)

Tiron solution (4 %). For the preparation see section Q. 3. c.

d. *Calibration curve*

From the standard solution of titanium containing 0.0417 mg of titanium dioxide per ml, 2, 4, 6, 8 and 10 ml portions were added from a 10 ml burette to 5 of a series of six 100 ml volumetric flasks. To all 6 flasks 5 ml of tiron solution, 20 ml of buffer solution and 20 ± 5 mg of solid sodium dithionite were added. The sodium dithionite was dissolved, and the solutions were made up to the mark with water. The extinctions of the sample solutions were measured 4 times against the blank at 410 nm using 1 cm cells*. The calibration data are given in Table 9.

° As pointed out by Yoe and Armstrong[123] the absorption maximum of the titanium(IV) tiron complex is found at 380 nm, but as sodium dithionite solutions start to absorb at wavelengths below 410 nm, the latter wavelength is recommended for the determination of titanium.

Table 9. *Calibration data for the determination of titanium.*

Amounts (in mg) of TiO₂ per 100 ml	Arithmetic mean of 4 extinction readings	Extinction index (I)
(C)	(E)	$(I = E/C)$
0.0834	0.139	1.67
0.1668	0.275	1.65
0.2502	0.416	1.66
0.3336	0.550	1.65
0.4170	0.685	1.64

Arithmetic mean for extinction index = 1.65.

e. *Procedure*

To the sample and blank solutions prepared or used for the determination of the total content of iron (section Q. 3.) 20 ± 5 mg of solid sodium dithionite are added and the solutions are mixed. As soon as the colour of the iron(III) tiron complex has disappeared the extinction of the sample solution is measured 4 times against the blank at 410 nm and with the use of 1 cm cells. The content (in per cent) of titanium (as titanium dioxide) is calculated from the formula:

$$\text{TiO}_2 \text{ (in per cent)} = \frac{0.1 \cdot E \cdot V}{I \cdot v \cdot G}$$

where

E = arithmetic mean of extinction readings
V = volume (in ml) of solution B — usually 250 ml
I = extinction index determined from the calibration data
v = volume (in ml) — pipetted from solution B for the determination of titanium (and the total content of iron) — usually 25 ml
G = weight (in g) of sample — usually 0.4000 g.

f. *Notes*

During the testing of the present method it was found that the order of addition of the reagents played an important rôle, as demonstrated by the following experiments.

Experiment 1

The following amounts of titanium standard solution and reagent solutions were pipetted into a 100 ml volumetric flask in the following order: 10 ml of titanium standard solution (containing 0.0417 mg of titanium dioxide per ml); 20 ml of buffer solution and 5 ml of 4 % tiron solution. A blank solution was also prepared from the reagents, these being added in the amounts and order given above. After dilution to volume with water the extinction was measured after the intervals given below (wavelength 410 nm and 1 cm cells):

Table 10

Time of standing (in min)	Extinctions
20	0.335
25	0.352
30	0.364
35	0.376
40	0.380
70	0.426
100	0.453
130	0.480
1200	0.687

From Table 10 it is seen that the colour development was extremely slow. A standing time of 1200 min was necessary to obtain the final value (compare with data in Table 9).

The order of addition given in Experiment 1 was that used by Rigg and Wagenbauer[124]. These authors reported that the extinction continued to increase after 1 h standing, and recommended that the solutions be allowed to stand overnight before measurement.

Experiment 2

The amounts of titanium and reagents, as well as the order of addition, were as described for experiment 1. However, in this experiment the mixtures were prepared in beakers which were then heated to boiling, cooled to room temperature and the contents transferred to 100 ml volumetric flasks, diluted to volume with water and measured against the blank under the conditions given in experiment 1. The extinction of the solution was now 0.688. Thus the rate of reaction was increased by heating, the extinction value obtained by this treatment now being the same as the final value in experiment 1.

Experiment 3

The amounts of titanium and reagents were as given for experiments 1 and 2, but the order of addition was now: titanium solution, tiron solution and buffer solution. The mixtures were not heated. The extinction of the solution was measured as before after the time intervals specified in Table 11.

Table 11

Time of standing (in min)	Extinctions
10	0.688
15	0.689
20	0.689
25	0.689
35	0.689
60	0.689

The order of addition used in experiment 3 should therefore be applied in the determination of titanium.

8. Determination of phosphorus

a. *Principle*

In an aliquot part of solution B phosphorus, in the form of orthophosphate, is determined spectrophotometrically as molybdovanadophosphoric acid. This method was originally proposed by Misssion[125] for the determination of phosphorus in steel.

b. *Interfering elements*

Kitson and Mellon[126] studied the interfering effect of 60 ions upon the photometric determination of phosphorus as molybdovanadophosphoric acid. None of the ions studied by these authors seemed to form a heteropoly compound, but some ions (Bi(III), Th(IV), AsO_4^{3-}, Cl^- and F^-) slowed down the rate of colour formation and the authors recommended that the colour was allowed to develop for 30 min before measurement. Other ions (Fe(II), S^{2-}, $S_2O_3^{2-}$ and CNS^-) were found

125. G. Mission, Chem. Ztg., 32 (1908) 633.
126. R. E. Kitson and M. G. Mellon, Anal. Chem., 16 (1944) 379.

to reduce the molybdovanadophosphoric acid or the excess of molybdate to molybdenum blue.

In the proposed scheme phosphorus is determined in an aliquot part of solution B. This solution does not contain reducing substances, and ions which may slow down the reaction have either been removed (as is the case with fluoride) or they are present only in trace amounts. If the recommendation of Kitson and Mellon is followed, viz. to measure after 30 min standing, no interferences should be expected from other constituents.

c. *Reagents*

Ammonium metavanadate

Ammonium molybdate tetrahydrate

Nitric acid (65 %)

Potassium dihydrogen phosphate, spectrographically analyzed (see section M. 4.).

Phosphorus standard solution (0.02 mg of phosphorus pentoxide per ml).

From the standard solution of phosphorus containing 0.2 mg of phosphorus pentoxide per ml (the preparation of this solution is described in chapter V. B.) 25 ml were pipetted into a 250 ml volumetric flask and diluted to volume with water.

Combined molybdate-vanadate solution.

1.25 g of ammonium metavanadate were transferred to a 600 ml beaker, 400 ml of nitric acid (1:1) were added and the salt was dissolved. An amount of 50.0 g of ammonium molybdate tetrahydrate were transferred to a second 600 ml beaker and dissolved in 400 ml of water. The 2 solutions were combined in a 1000 ml volumetric flask and diluted to volume with water.

Nitric acid (1:1).

d. *Calibration curve*

From the standard solution containing 0.02 mg of phosphorus pentoxide per ml 5, 10, 15, 20, 25 and 30 ml portions were added from a 50 ml burette into 6 of a series of seven 50 ml volumetric flasks. To all 7 flasks water was added to a total volume of about 40 ml, 5 ml of the combined molybdate-vanadate solution were added by pipette and the solutions were diluted to the mark with water. After 30 min standing the extinctions of the sample solutions were measured 4 times at 430 nm using 2 cm cells. The calibration data are shown in Table 12.

Table 12. *Calibration data for the determination of phosphorus.*

Amounts (in mg) of P_2O_5 per 50 ml (C)	Arithmetic mean of 4 extinction readings (E)	Extinction index (I) $(I = E/C)$
0.1	0.070	0.700
0.2	0.142	0.710
0.3	0.215	0.717
0.4	0.292	0.730
0.5	0.358	0.716
0.6	0.430	0.717

Arithmetic mean for extinction index = 0.715.

c. *Procedure*

From solution B a 25 ml portion is pipetted into one of two 50 ml volumetric flasks. To both flasks water is added to a volume of about 40 ml and then, by a pipette, 5 ml of the combined molybdate-vanadate solution are added. After dilution to the mark with water and 30 min standing the extinction of the sample solution is measured 4 times against the blank at 430 nm using 2 cm cells. The content (in per cent) of phosphorus (as phosphorus pentoxide) is calculated from the expression:

$$P_2O_5 \text{ (in per cent)} = \frac{0.1 \cdot E \cdot V}{I \cdot v \cdot G}$$

where

E = arithmetic mean of extinction readings
V = volume (in ml) of solution B — usually 250 ml
I = extinction index determined from the calibration data
v = volume (in ml) pipetted from solution B — usually 25 ml
G = weight (in g) of sample — usually 0.4000 g.

9. Determination of manganese

a. *Principle*

In an aliquot part of solution B manganese is determined spectro-photometrically as permanganate, periodate being employed as the oxidizing agent.

b. *Interfering elements*

Under the conditions of the present determination no interference was expected from other constituents.

Constituents which form coloured ions, e. g. Cu(II), Ni(II), Co(II), Cr(III) and Cr(VI) are present only in trace amounts, and their interfering effect can be considered as negligible. Iron(III) ions are transformed into a colourless complex by the addition of orthophosphoric acid*. It has been stated[127] that small amounts of chloride may be oxidized by periodate and that chloride therefore should be removed before the addition of the oxidizing agent. Other authors[128] have found that the permanganate colour was stable in the presence of small amounts of chloride. No difficulties were encountered in the present scheme when the determination was made in the presence of chloride ions.

c. *Reagents*

Manganese, analyzed (see section M. 4.)
Orthophosphoric acid (85 %)
Potassium periodate
Sulfuric acid (95—97 %).

Two manganese standard solutions (corresponding to 0.2 and 0.01 mg of manganous oxide per ml) were prepared. For the preparation of the first solution 0.1549 g of manganese were transferred to a 150 ml beaker, the beaker was covered and the metal was dissolved in 20 ml of sulfuric acid (1:3). The solution was transferred to a 1000 ml volumetric flask and diluted to volume with water. The second standard solution was prepared by pipetting 25 ml of the first solution into a 500 ml volumetric flask and diluting to volume with water.

Sulfuric acid (1:3).

Experiments relating to the choice of oxidizing agents for manganese are described below. The extinction data from one of the series of experiments (see Table 13) were used for the calculation of the extinction index.

* The addition of orthophosphoric acid also serves the purpose of preventing the precipitation of the slightly soluble iron(III) periodate.

127. See e.g. E. B. Sandell, Colorimetric Determination of Traces of Metals, Third edition, Interscience Publishers, Inc., New York, 1959, p. 609.
128. D. Williams and R. V. Andes, Anal. Chem., 17 (1945) 28.

e. *Procedure*

From solution B a 25 ml aliquot is pipetted into a 150 ml beaker and water is added to a volume of about 40 ml. 2 ml of orthophosphoric acid and a part of 0.5 ± 0.1 g of potassium periodate are added, the solution is heated to boiling and kept just below the boiling point for 15 ± 3 min. During this period the remaining amount of periodate is added in 2 or 3 increments. After being cooled to room temperature, the solution is transferred to a 50 ml volumetric flask and is made up to volume with water. In another 50 ml volumetric flask the blank solution is prepared by adding to a volume of about 40 ml of water 2 ml of orthophosphoric acid and a part of 0.5 ± 0.1 g of potassium periodate. The subsequent treatment is the same as for the sample solution. After 15 min standing the extinction of the sample solution is measured 4 times against the blank at 525 nm using 5 cm cells and the arithmetic mean is calculated. The content (in per cent) of manganese (as manganous oxide) is calculated from the expression:

$$MnO \text{ (in per cent)} = \frac{0.1 \cdot E \cdot V}{I \cdot v \cdot G}$$

where

E = arithmetic mean of extinction readings
V = volume (in ml) of solution B — usually 250 ml
I = extinction index determined from the calibration data
v = volume (in ml) pipetted from solution B — usually 25 ml
G = weight (in g) of sample — usually 0.4000 g.

e. *Choice of oxidizing agent and preparation of the calibration curve*

As mentioned previously (chapter I. B.) it proved impossible to obtain complete oxidation to permanganate by using peroxidisulphate according to the procedure described by Nydahl[28], while oxidation with periodate gave satisfactory results, as demonstrated by the following experiments.

From a standard solution of manganese (the preparation of this solution is described above) containing 0.01 mg of manganous oxide per ml, 2, 4, 6, 8 and 10 ml portions were added from a 10 ml burette to 5 of a series of six 150 ml beakers. Then 5 ml of the combined reagent solution described by Nydahl (containing mercuric sulphate, silver nitrate, nitric and orthophosphoric acids) were pipetted into all beakers. After dilution with water to about 40 ml, the solutions were heated to boiling and

Table 13. *Extinctions of permanganate solutions oxidized by either ammonium peroxidisulphate or potassium periodate. Wavelength 525 nm. 5 cm cells.*

Amounts (in mg) of MnO per 50 ml (C)	Extinctions of solutions oxidized by peroxidisulphate. Standing time before measurement				Extinctions* of solutions oxidized by periodate. Standing time before measurement – 15 min (E)	Extinction index I (I = E/C) for solutions oxidized by periodate
	15 min	30 min	60 min	24 h		
0.02	0.040	0.040	0.029	0.066	0.068	3.40
0.04	0.106	0.102	0.086	0.133	0.138	3.45
0.06	0.160	0.160	0.174	0.210	0.211	3.52
0.08	0.225	0.222	0.210	0.272	0.277	3.46
0.10	0.325	0.324	0.306	0.350	0.353	3.53

* Arithmetic mean of 4 readings.

Arithmetic mean for extinction index = 3.47.

2.0 ± 0.1 g of ammonium peroxidisulphate were added. The beakers were removed from the source of heating and were left for 1 min, cooled in tap water to room temperature and the contents transferred to 50 ml volumetric flasks and diluted to volume with water. The blank solution was prepared and treated as described for the sample solutions. The extinctions of the sample solutions were measured 4 times against the blank after the time intervals specified in Table 13. The wavelength was 525 nm and 5 cm cells were used.

In the next series of experiments the same amounts of manganese were taken and water was added to a volume of about 40 ml. After addition of 2 ml of orthophosphoric acid and 0.5 ± 0.1 g of potassium periodate, the solutions were heated to boiling and kept just below the boiling point for 15 ± 3 min. The blank solution was prepared by adding the same amounts of the reagents and in the same order to a volume of about 40 ml of water. The further treatment was as for the sample solutions. The beakers were cooled to room temperature, the solutions were transferred to 50 ml volumetric flasks and diluted to the mark with water. After 15 min the solutions were measured 4 times under the conditions given for the first series. The data recorded are reproduced in Table 13.

As seen from Table 13 the extinctions of solutions oxidized by peroxidisulphate are nearly constant for the first 30 min. In the interval from 30 to 60 min the extinction of 4 of the 5 solutions decrease. After 24 h standing the extinctions seem to have reached their final values which are practically identical with those oxidized by periodate after 15 min of standing.

On the basis of these results periodate was preferred as the oxidizing agent.

V. Testing and applications of the scheme.

A. Introduction.

In analytical chemistry some sort of measure is required by which methods can be evaluated and compared. Although many different factors may be considered to be of importance in the evaluation of analytical methods, it is probably generally accepted that the two major factors serving this purpose are accuracy and precision. Data on the accuracy and precision of a single method or a number of methods incorporated in

a scheme are obtained by testing, i.e. by analyzing repeatedly some natural or synthetic sample of suitable composition.

The data which are most easily acquired are those indicating the precision, by carrying out a number of analyses of a suitable rock sample, for which the exact chemical composition need not be known, data on precision can be calculated. On the other hand, it is more difficult to get data on accuracy. Such data can only be obtained if the "true" value for each constituent is known.

In the field of rock analysis it is customary to test the accuracy of a method or an analytical scheme by analyzing a rock whose composition has been determined previously by the conventional or a modified conventional scheme. In view of the serious systematic errors adhering to some of the methods of the conventional and modified conventional schemes, it is obvious that this way of establishing the accuracy is misleading and highly unsatisfactory. An excellent agreement with the value given on the certificate of analysis may only demonstrate that both methods are encumbered with the same systematic error.

Few attempts have been made to get away from this unsatisfactory practice. A survey of the literature showed that Fairbairn and Schairer[129] prepared a glass of known chemical composition and used it to test the accuracy of some of the methods of modified conventional schemes.

In the present investigation another way of establishing the accuracy and precision of the proposed scheme of rock analysis was employed, by analyzing a solution containing known amounts of the constituents covered by the scheme. In this solution the content of the different constituents is known within such narrow limits that the "true" values can be assumed to be known. To the authors' best knowledge, such a solution of known composition has not been employed before in the testing of schemes of rock analysis.

While the glass prepared by Fairbairn and Schairer[129] contained 6 components, the solution used in the present work comprised 11 constituents. The advantages of using a solution instead of a glass are that the former can more easily be prepared in a homogeneous condition and that such operations as crushing, pulverizing and fusion are avoided. As demonstrated by Fairbairn and Schairer[129], appreciable amounts of iron and platinum were added to the sample by these operations. The advantage of using a glass is that the analyst starts with a solid silicate material

129. H. W. Fairbairn and J. F. Schairer, Am. Mineralogist, 37 (1952) 744.

which can be subjected to the sample preparation and decomposition stages.

The present chapter describes the testing of the accuracy and precision of the proposed scheme by the use of a solution representing a rock of known composition, this solution will be designated the "compound solution". In addition the chapter also deals with application of the scheme to the analysis of the standard rock samples G 1 (issued by U. S. Geological Survey) and R 117 (issued by Dr. P. G. Jeffery, Department of Scientific and Industrial Research, Warren Spring Laboratory, Hertfordshire, Great Britain).

B. Testing of the scheme by analysis of a compound solution representing a rock of known composition.

1. The chemical composition of the compound solution

The chemical composition chosen for the compound solution corresponded to that of an intermediate rock. The percentages of the 11 main constituents that compose the compound solution are given in Table 14.

2. The preparation of the silicon dioxide and the separate solutions that compose the compound solution

For each test analysis 3 compound solutions (corresponding to solutions A, B and C in the proposed analytical scheme) had to be prepared. The compound solution was prepared by first dissolving a weighed amount of silicon dioxide in hydrofluoric acid and then adding to it certain volumes of various standard solutions.

Attempts were initially made to prepare a standard solution containing all constituents except silicon and iron(II). These attempts were unsuccessful because of the chemical reactions, such as precipitation of phosphates, that took place. After some experimental work, it was found that the compound solution could best be prepared in the following way:

a. By dissolving in hydrofluoric acid a weighed amount of silicon dioxide.

b. By adding to this hydrofluoric acid solution a known volume of a combined standard solution containing aluminium, calcium, mag-

Table 14. *Data relating to the composition and preparation of the compound solution.*

Con-sti-tuent	Chemical composition (in per cent) of sample "true" amounts	Amounts (in mg) of oxides in the compound solution	Standard solution prepared from	Volume (in ml) of standard solutions	Amounts (in mg) weighed out for the preparation of standard solutions	Amounts taken for the compound solution
SiO_2	60.00	120.0	Added as solid SiO_2	Added as solid SiO_2	120.0 mg weighed out for each analysis	120.0 mg weighed out for each analysis
Al_2O_3	16.00	32.0	Al	2000[a]	1354.8	25 ml
Fe_2O_3	2.50	5.0	Fe	1000[b]	732.1[c]	5 "
FeO	2.50	5.0	Fe	1000[b]	813.7[c]	5 "
MgO	2.50	5.0	MgO	2000[a]	400.0	25 "
CaO	5.00	10.0	$CaCO_3$	2000[a]	1427.8	25 "
Na_2O	5.00	10.0	NaCl	2000[a]	1508.8	25 "
K_2O	5.00	10.0	KCl	2000[a]	1182.3[d]	25 "
TiO_2	0.700	1.4	Ti	2000[a]	64.75[e]	25 "
P_2O_5	0.500	1.0	KH_2PO_4	1000[b]	383.5	5 "
MnO	0.300	0.6	Mn	2000[a]	37.18[e]	25 "
Total	100.00	200.0				

a These components were contained in a single standard solution having a volume of 2000 ml.

b Separate standard solutions were prepared.

c The theoretical contents, 699.4 and 777.3, respectively, multiplied by the factor 1.0469 to compensate for the content of non-metallic impurities.

d The theoretical content 1266.3 less 84.0 to correct for the amount of potassium originating from potassium dihydrogen phosphate.

e These amounts were weighed out on a semi-micro balance.

nesium, sodium, potassium, titanium and manganese. This combined standard solution is designated "the main solution".

c. By the addition of a known volume of iron(III) standard solution.
d. By the addition of a known volume of phosphorus standard solution.
e. By the final addition of a known volume of iron(II) standard solution.

The main solution and the other standard solutions were prepared from analyzed compounds or high-purity metals (the purity of these substances is discussed in chapter IV. M. 4.). A statement of the materials employed and the amounts weighed out for the preparation of the different solutions are given in Table 14.

The silicon dioxide to be used in the compound solution was ignited* to constant weight in a covered platinum crucible at 1150 ± 25°. The covered crucible was stored in a desiccator with phosphorus pentoxide as drying agent.

The different solutions were prepared as follows:

a. *The main solution*

The separate solutions that composed the main solution were prepared in the following way:

The aluminium solution

Metal drillings were washed with acetone and dried in a vacuum. The calculated amount was transferred to a 250 ml beaker, 10 ml of concentrated hydrochloric acid and 30 ml of water were added, and the covered beaker was placed on the boiling water bath. To facilitate dissolution a piece of platinum foil was placed in contact with the drillings. When the gas evolution diminished, 10 ml of concentrated hydrochloric acid and 20 ml of water were added and the heating was continued until solution was complete.

The calcium solution

Calcium carbonate was dried to constant weight at 105—110°. The weighed amount was transferred to a 250 ml beaker, the powder was moistened with water and dissolved by the dropwise addition of 10 ml of hydrochloric acid (1:3).

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* This ignition also serves the purpose of making the silicon dioxide more coarse-grained and thus less exposed to absorption of moisture. During the subsequent manipulations, however, precautions should be taken to minimize the uptake of moisture.

The magnesium solution

Magnesium oxide was ignited to constant weight at 700 ± 25°. The weighed amount was transferred to a 250 ml beaker, 10 ml of sulfuric acid (1:3) were added and the oxide was brought into solution by heating.

The sodium solution

Sodium chloride was ignited to constant weight at 500 ± 25°. The correct amount of the salt was transferred to a beaker and dissolved in water.

The potassium solution

Potassium chloride was ignited to constant weight at 500 ± 25°. The calculated amount of the salt, which corresponded to the total amount less the amount originating from the phosphate standard solution (prepared from potassium dihydrogen phosphate) was transferred to a beaker and dissolved in water.

The titanium solution

Titanium drillings were washed with acetone and dried in a vacuum. The weighed amount was transferred to a 150 ml beaker and 20 ml of sulfuric acid (1:3) were added. The covered beaker was kept on the boiling water bath until the metal had dissolved. Titanium(III) was oxidized by the dropwise addition of bromine water until the solution was clear, two drops being added in excess. The solution was finally boiled until the smell of bromine no longer could be detected.

The manganese solution

A portion of the flaky material was crushed in an agate mortar to a coarse powder. The weighed amount was transferred to a beaker, 3 ml of sulfuric acid (1:3) were added and the beaker was covered. The metal went into solution without heating.

The main solution was prepared by combining the separate solutions in a 2000 ml volumetric flask with vigorous swirling and diluting to volume with water.

b. *The iron(III) standard solution*

Preliminary gravimetric analyses of solutions prepared by weighing out known amounts of analyzed iron sponge showed the presence of 4.476 % of non-metallic impurities. The amount of impure metal to be weighed out was therefore the theoretical amount multiplied by the factor 1.0469. The correct amount was transferred to a 250 ml beaker, 30 ml of hydrochloric acid (1:3) were added and the contents were heated to 60—70° and maintained at this temperature until the metal had dissolved. The solution was diluted with 50 ml of water and bromine water was added dropwise until a small excess was present. The excess of oxidizing agent was then removed by boiling until the odour of bromine could no longer be detected. The completeness of the oxidation to iron(III) was checked by means of a freshly prepared solution of potassium ferricyanide. The solution was cooled to room temperature, transferred to a 1000 ml volumetric flask and diluted to volume.

c. *The phosphorus standard solution*

A portion of potassium dihydrogen phosphate was dried to constant weight at 105—110°. The weighed amount was transferred to a 1000 ml volumetric flask, dissolved in water and the solution was made up to the mark with water.

d. *The iron(II) standard solution*

The correct amount of iron (the theoretical amount multiplied by the factor 1.0469) was weighed out and transferred to a 250 ml beaker to which 30 ml of hydrochloric acid (1:3) were added. The contents of the beaker were heated to 60—70° and maintained at this temperature until the metal had dissolved. The solution was cooled to room temperature, transferred to a 1000 ml volumetric flask and diluted to volume with water. The solution was passed through a silver reductor and the first portion of the eluent was discarded; the main portion was collected in a two necked flask flushed with carbon dioxide. The solution was stored in the flask, one of the openings being closed with a stopcock, the other being connected to a Kipp generator (filled with marble and hydrochloric acid) which maintained an atmosphere of carbon dioxide over the solution. A wash bottle con-

taining concentrated sulfuric acid was inserted between the Kipp gene-
rator and the two necked flask.

Before each test analysis oxygen was removed from the main solution
and the standard solutions of iron(III) and phosphorus by the passing
of purified nitrogen.

3. Test analysis

For each complete test analysis 3 compound solutions were pre-
pared, 1 in decomposition vessel A (corresponding to sample A), 1
in evaporation vessel B (corresponding to sample B) and 1 in the
recrystallized alumina crucible (corresponding to sample C). The 3 solu-
tions were prepared as follows:

a. Preparation of the compound solution in decomposition vessel A

A 0.1200 g portion of ignited silicon dioxide was weighed into the
inner teflon container of vessel A and decomposed according to the
procedure given for the decomposition of sample A and preparation of
solution A (see chapter IV. P. 1.). After the decomposition the alumi-
nium block with vessel A was removed from the combined magnetic
stirrer and hotplate, and the contents were cooled to room temperature
without removing the cover. The cover was removed and 25 ml of the
main solution, 5 ml of iron(III) standard solution and 5 ml of phos-
phorus standard solution were added. The volume above the liquid was
now flushed with a stream of purified nitrogen for 1—2 min and,
without discontinuing the stream of nitrogen, 5 ml of iron(II) standard
solution were added, the pipette employed for this transference being
flushed with nitrogen before use*. The vessel was stoppered without
delay, the aluminium block was placed on the magnetic stirrer and the
contents were mixed for 1—2 min by stirring.

The further treatment was the same as that described in chapter
IV. P. 1. for the steps following the decomposition of the rock sample.
The resulting solution (solution A) was then analyzed according to the
procedures given in chapter IV. Q.

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* As mentioned in chapter IV.E., it was originally planned to determine iron(II) in
sample A, and consequently the present measures were taken to avoid oxidation of
iron(II). However, as it was found necessary to determine iron(II) in a separate
sample, the flushing with nitrogen can be omitted.

b. *Preparation of the compound solution in evaporation vessel B*

A 0.1200 g portion of ignited silicon dioxide was weighed into the evaporation vessel B and decomposed* as prescribed for sample B (see chapter IV. P. 2.). After decomposition the contents were cooled somewhat and, without taking any precautions to guard against oxidation of iron(II), 25 ml of the main solution and 5 ml of the standard solutions of iron(III), phosphorus and iron(II) were added by pipette. The vessel (in its aluminium block equipped with a thermometer) was placed on the hot plate, the further treatment continuing the procedure given for the decomposition of sample B and the preparation of solution B (see chapter IV. P. 2.). Solution B was then analyzed according to the procedures given in chapter IV. Q.

c. *Preparation of the compound solution in a crucible of
recrystallized alumina*

In the determination of iron(II) according to the modified conventional schemes, hydrofluoric acid is not added at the start of the analysis. In the preparation of this particular series of compound solutions the initial dissolution of silicon dioxide in hydrofluoric acid was omitted.

25 Ml of the main solution, 5 ml of iron(III) standard solution and 5 ml of phosphorus standard solution were pipetted into the alumina crucible, the crucible was covered and the solution was heated to boiling and kept boiling for 10 ± 2 min. The burner was removed and 5 ml of iron(II) standard solution and 5 ml of hydrofluoric acid were added quickly. The crucible was covered, heated rapidly to boiling and boiled gently for 15 ± 3 min.

The further treatment was the same as that given in the procedure for the determination of iron(II) (see chapter IV. Q. 5.). The potassium dichromate standard solution employed was 0.006 normal and was added from a 50 ml burette.

In Table 15 the results from 10 test analyses are given. The test analyses are numbered chronologically, the first series of 3 compound solutions (prepared in the decomposition vessel A, the evaporation vessel B and the recrystallized alumina crucible and corresponding to samples A, B and C, respectively) being designated no. 1, the next series no. 2, and so on.

* The decomposition of the silicon dioxide is usually complete before any appreciable amounts of hydrofluoric acid have been removed by evaporation.

Table 15. *Analytical results from 10 test analyses of a compound solution representing a rock of known composition. All data are given in per cent.*

| Constituent | Chemical composition of sample — "true" amounts | Analysis no. | | | | | | | | | | Arithmetic mean value ($\bar{x}$) | $\bar{x} - 2s$ | $\bar{x} + 2s$ |
		1	2	3	4	5	6	7	8	9	10			
SiO_2	60.00	60.12	60.18	60.05	59.96	59.89	60.07	60.28	60.19	59.87	60.11	60.07	59.81	60.33
Al_2O_3	16.00	15.80	15.80	16.19	16.09	15.01	15.14	15.63	15.68	15.60	16.02	15.70	14.94	16.46
Tot. content of iron (as Fe_2O_3)	5.28	5.42	5.44	5.26	5.28	5.02	4.98	5.25	5.10	5.22	5.22	5.22	4.92	5.52
Fe_2O_3	2.50	2.66	2.71	2.75	2.53	2.31	2.19	2.50	2.32	2.49	2.47	2.49	2.13	2.85
FeO	2.50	2.48	2.46	(2.26)	2.47	2.44	2.49	2.48	2.50	2.46	2.47	2.47	2.33	2.61
MgO	2.50	2.71	2.42	2.62	2.63	2.36	2.34	2.44	2.36	2.51	2.59	2.50	2.24	2.76
CaO	5.00	4.75	4.85	4.95	4.90	4.97	4.98	4.85	4.97	4.99	4.92	4.91	4.75	5.07
Na_2O	5.00	5.00	5.00	4.76	4.72	5.19	4.81	4.92	5.04	4.86	5.26	4.96	4.60	5.32
K_2O	5.00	5.14	5.17	5.14	5.19	5.16	5.12	5.07	5.11	5.05	5.13	5.13	5.05	5.21
TiO_2	0.700	(0.618)	0.700	0.685	0.691	0.686	0.682	0.667	0.661	0.661	0.655	0.676	0.628	0.724
P_2O_5	0.500	0.479	0.479	0.539	0.545	0.532	0.545	0.525	0.532	0.545	0.538	0.526	0.474	0.578
MnO	0.300	(0.321)	0.303	0.297	0.300	0.288	0.295	0.294	0.295	0.281	0.282	0.293	0.271	0.315
Total	100.00	99.70	100.07	100.24	100.03	98.84	98.66	99.66	99.66	99.32	100.45	99.73		

4. Statistical data from the test analyses

The analytical data given in Table 15 were examined by standard statistical methods. The following notation was used for the parameters of the observed distribution of the results:

Number of determinations, n

Arithmetic mean value, $\bar{x}$

Deviation of each determination from $\bar{x}$, d

Variance, $s^2 = \Sigma d^2/n\text{-}1$

Standard deviation, $s = \sqrt{s^2}$

Relative deviation, $C = 100\ s/\bar{x}$

Standard error, $S\bar{x} = s/\sqrt{n}$

Relative error, $E = 100\ S\bar{x}/\bar{x}$

In Table 16 the statistical data relating to the 10 test analyses are tabulated.

Table 16. *Statistical data from 10 test analyses.*

Constituent	$\bar{x}$	s^2	s	C	$S\bar{x}$	E
SiO_2	60.07	0.0177	0.13	0.22	0.042	0.07
Al_2O_3	15.70	0.1466	0.38	2.42	0.121	0.77
Total content of iron (as Fe_2O_3)	5.22	0.02294	0.15	2.90	0.048	0.92
Fe_2O_3	2.49	0.03314	0.18	7.23	0.058	2.31
FeO	2.47	0.00519	0.07	2.83	0.023	0.92
MgO	2.50	0.01760	0.13	5.31	0.042	1.68
CaO	4.91	0.00590	0.08	1.56	0.024	0.49
Na_2O	4.96	0.03158	0.18	3.58	0.056	1.13
K_2O	5.13	0.00187	0.04	0.84	0.014	0.27
TiO_2	0.676	0.000563	0.024	3.51	0.0075	1.11
P_2O_5	0.526	0.000654	0.026	4.86	0.0081	1.54
MnO	0.293	0.000138	0.011	3.91	0.0037	1.27

C. Applications of the scheme.

1. Analysis of the standard rock G 1

a. *Introduction*

The standard rock G 1 (a granite issued by the U. S. Geological Survey) has been subjected to a considerable amount of study and a large number of chemical and spectrographical analyses have been made of the major, minor and trace constituents. The chemical analyses have been made by means of conventional, different modified conventional,

Table 17. Analytical results from 10 analyses of the standard rock G 1.
All data are given in per cent.

Constituent	Analysis no.										Arithmetic mean value (x̄)	x̄ − 2s	x̄ + 2s
	1	2	3	4	5	6	7	8	9	10			
SiO$_2$	72.67	72.60	72.58	72.50	72.84	72.86	72.76	72.95	72.80	72.78	72.73	72.45	73.01
Al$_2$O$_3$	12.99	13.15	13.85	14.13	13.88	13.82	13.99	13.91	13.97	14.39	13.81	12.97	14.65
Tot. content of iron (as Fe$_2$O$_3$)	1.95	1.94	1.67	1.64	1.65	1.64	1.76	1.77	1.60	1.67	1.73	1.47	1.99
Fe$_2$O$_3$	0.79	0.79	0.57	0.56	0.64	0.63	0.74	0.70	0.54	0.61	0.66	0.48	0.84
FeO	1.04	1.03	0.99	0.97	0.91	0.91	0.92	0.97	0.95	0.95	0.96	0.86	1.06
MgO	0.38	0.39	0.41	0.38	0.40	0.38	(0.44)	0.38	0.38	0.39	0.39	0.35	0.43
CaO	1.26	1.26	1.27	1.29	1.25	1.29	1.25	1.26	1.27	1.28	1.27	1.25	1.29
Na$_2$O	3.30	3.30	3.27	3.29	3.30	3.30	3.22	3.19	3.25	3.26	3.27	3.19	3.35
K$_2$O	5.11	5.12	5.07	5.12	5.06	5.06	4.95	4.96	5.02	5.00	5.05	4.93	5.17
TiO$_2$	0.237	0.232	0.244	0.235	0.231	0.238	0.241	0.239	0.238	0.238	0.237	0.229	0.245
P$_2$O$_5$	0.087	0.073	0.070	0.073	0.077	0.070	0.066	0.070	0.056	0.063	0.071	0.055	0.087
MnO	0.034	0.030	0.036	0.032	0.037	0.035	0.030	0.030	0.035	0.040	0.034	0.028	0.040
Total	97.90	97.98	98.36	98.58	98.63	98.59	98.61	98.66	98.51	99.00	98.48		

and novel schemes, and the results and statistical treatment of these analyses have been published in 2 U. S. Geological Survey Bulletins (Nos. 980 and 1113).

The large number of analytical data on G 1 makes this rock a most valuable standard sample. The determination of some of the main constituents of this sample, e. g. silicon, has been the subject of special investigations[130], and for these constituents the "true" values can be said to be approximately known. For this reason G 1 was selected for the application of the proposed scheme.

b. *Analyses*

The results from 10 analyses of G 1 are reported in Table 17. To facilitate comparison with previous data, the results were not calculated to a moisture-free sample. The content of hydroscopic water (H_2O^-) was determined and found to be 0.001 %.

c. *Statistical data*

The data from the present analyses of G 1 were examined statistically by the same methods and with the use of the same notation as in the preceding test analyses. These data are listed in Table 18. The results of other analyses of G 1 are tabulated in the U. S. Geological Survey Bulletins 980 and 1113. Stevens and Niles[131] have examined the data statistically. For the sake of comparison, the data of Stevens and Niles are also given in Table 18.

2. Analysis of the standard rock R 117

A rock sample of granite composition (designated R 117) was distributed to a number of different laboratories by Dr. P. G. Jeffery (Department of Scientific and Industrial Research, Warren Spring Laboratory, Hertfordshire, Great Britain). The purpose of this interlaboratory investigation was to study the effect of newer modifications to the conventional schemes on the precision and accuracy of rock analysis.

In Table 19 the results from 1 analysis by the proposed scheme are given.

130. See e.g. R. E. Stevens and A. A. Chodos, U. S. Geol. Surv. Bull., No. 1113 (1960) 45.
131. R. E. Stevens and W. W. Niles, U. S. Geol. Surv. Bull., No. 1113 (1960) 3.

Table 18. *Statistical data from the analysis of the standard rock G 1. For an explanation of the notation employed — see section B. 4.*

Constituent	Data from the use of the proposed scheme							Data from U. S. Geological Survey Bulletin No. 1113*			
	n	$\bar{x}$	s^2	s	C	$\bar{s}_x$	E	n	$\bar{x}$	s	C
SiO₂	10	72.73	0.0202	0.14	0.20	0.045	0.06	60	72.35	0.48	0.66
Al₂O₃	10	13.81	0.1802	0.42	3.07	0.134	0.97	60	14.32	0.37	2.60
Total content of iron (as Fe₂O₃)	10	1.73	0.01574	0.13	7.25	0.040	2.29	60	2.04	0.28	13.90
Fe₂O₃	10	0.66	0.00868	0.09	14.12	0.029	4.46	57	0.95	0.30	31.49
FeO	10	0.96	0.00213	0.05	4.81	0.015	1.52	57	0.99	0.11	11.26
MgO	10	0.39	0.00039	0.02	5.06	0.006	1.60	59	0.40	0.13	32.15
CaO	10	1.27	0.00022	0.01	1.17	0.005	0.37	59	1.40	0.12	8.95
Na₂O	10	3.27	0.00149	0.04	1.18	0.012	0.37	59	3.31	0.23	7.06
K₂O	10	5.05	0.00394	0.06	1.24	0.020	0.39	59	5.42	0.39	7.26
TiO₂	10	0.237	0.0000152	0.004	1.65	0.001	0.52	60	0.26	0.04	16.59
P₂O₅	10	0.071	0.0000686	0.008	11.66	0.003	3.69	54	0.10	0.06	55.10
MnO	10	0.034	0.0000114	0.003	0.93	0.001	3.14	56	0.03	0.01	33.62

* The data on precision in Bulletin 1113 result from interlaboratory investigations. The authors were unable to find analytical data on G 1 showing the precision obtained by one analyst working in a given laboratory.

The content of hydroscopic water (H_2O^-) in R 117 was determined and was found to be 0.12 %. To facilitate comparison with the data collected and discussed by Jeffery[132], the results were not calculated to a moisture-free sample. The statistical data given by Jeffery for the 15 analyses made in different laboratories are also incorporated in Table 19.

Table 19. *Analytical results and statistical data from the analysis of the standard rock R 117.*

Constituent	Results (in per cent) from one analysis with the proposed scheme	Statistical data reported by Jeffery[132]. For an explanation of the notation employed — see section B.4.						
		n	$\bar{x}$	s^2	s	C	$S\bar{x}$	E
SiO_2	77.18	15	77.06	0.0637	0.25	0.33	0.065	0.08
Al_2O_3	12.11	14	12.13	0.0215	0.15	1.2	0.039	0.3
Total content of iron (as Fe_2O_3)	1.15	14	1.27*					
Fe_2O_3	0.91	14	0.91	0.0035	0.059	6.6	0.016	1.8
FeO	0.22	14	0.32	0.0015	0.039	12.2	0.010	3.1
MgO	0.11	13	0.08	0.0027	0.05	66	0.14	18
CaO	0.26	14	0.29	0.0055	0.07	25	0.02	6.8
Na_2O	3.89	15	3.94	0.1279	0.36	9.1	0.09	2.3
K_2O	4.41	15	4.57	0.1557	0.395	8.6	0.10	2.2
TiO_2	0.067	14	0.065	0.00016	0.013	20	0.003	5.2
P_2O_5	0.070**	13	0.015	0.00023	0.015	100	0.004	28
MnO	0.019	14	0.018	0.000030	0.006	30.6	0.0015	8.3

D. Rejection of analytical results.

In the statistical examination of analytical data it is common practice to reject results which fall outside some adopted limits of variation which are chosen on the basis of a calculation of the standard deviation. Stevens and Niles[133], in a discussion of the analytical results of an inter-

* Calculated from the data reported by Jeffery for Fe_2O_3 and FeO.

** The result for phosphorus, as compared with the data given by Jeffery, appears to be too high. A redetermination gave the result 0.013 % P_2O_5.

132. P. G. Jeffery, Private communication and Research Report Project No. PCS 43, Department of Scientific and Industrial Research, Warren Spring Laboratory, Hertfordshire, Great Britain, March 1963.

133. R. E. Stevens and W. W. Niles, U. S. Geol. Surv. Bull., No. 1113 (1960) 3.

laboratory investigation of the standard rock G 1, selected ± 1 standard deviation from the arithmetic mean as limits of acceptability. In discussing the results of a similar, but less extensive interlaboratory investigation, Jeffery[134] chose ± 2 standard deviation from the arithmetic mean as limits.

In Tables 15 and 17 columns (x ± 2s) are given for ± 2 standard deviation from the arithmetic mean value (x). Results falling outside these limits were rejected, as designated by a parenthesis in the tables. After rejection, a new arithmetic mean value was calculated from the remaining results. As seen from Tables 15 and 17, a total of 4 results fall outside the limits ± 2 standard deviation from the arithmetic mean. In Table 15 analysis no. 3 for FeO, nr. 1 for TiO_2 and no. 1 for MnO have to be rejected. Similarly, in Table 17 analysis no. 7 for MgO falls outside the upper limit.

If the limits of acceptability are calculated according to Graf and Henning[135], other results with regard to rejection are obtained. By this method a new calculation of the limits of acceptability was made for the 4 series in Tables 15 and 17 exhibiting results falling outside ± 2 standard deviation from the arithmetic mean value. Excluding the suspected value (x), a new arithmetic mean value $(\overline{x})$ and standard deviation (s) were calculated. The limits of acceptability were then calculated from the expression:

$$\overline{x} \pm g\,(P,N) \cdot s$$

Assuming a 95 % probability and 9 measurements, a figure (4.4) for g (P,N) was found from the figure given by Graf and Henning[135].

The new limits of acceptability were then found to be:

In the series of test analyses (Table 15):

FeO : $\overline{x}$ = 2.47 ; s = 0.03
$\overline{x} \pm g\,(P,N) \cdot s$ = 2.47 ± 0.13
TiO_2 : $\overline{x}$ = 0.676 ; s = 0.017
$\overline{x} \pm g\,(P,N) \cdot$ = 0.676 ± 0.075
MnO : $\overline{x}$ = 0.293 ; s = 0.008
$\overline{x} \pm g\,(P,N) \cdot s$ = 0.293 ± 0.035

134. P. G. Jeffery, Research Report Project No. PCS 43, Department of Scientific and Industrial Research, Warren Spring Laboratory, Hertfordshire, Great Britain.
135. U. Graf and H. J. Henning, Mitteilungsbl. math. Stat., 4 (1952) 1.

In the series of analyses of G 1 (Table 17):

$MgO : \bar{x} = 0.39 ; s = 0.01$

$\bar{x} \pm g\,(P,N) \cdot s = 0.39 \pm 0.04$

With the new limits of acceptability a study of Table 15 shows that for TiO_2 and MnO analyses no. 1 should not be rejected. On the other hand, the rejection of the two other results (Table 15, FeO, analysis no. 3 and Table 17, MgO, analysis no. 7) were confirmed.

From the above discussion it is obvious that in rejecting results of rock analysis no universally adopted rules are followed and that the limits of acceptability chosen by the different authors are arbitrary.

E. Discussion of the results of testing and applications.

1. The test analyses

a. *Accuracy*

As mentioned above (section A.) a limited number of attempts have been made to ascertain the accuracy of schemes of rock analysis.

An early investigation of this kind was made by Dittrich[136] who prepared mixtures of weighed amounts of pure salts, metals and minerals, the chemical composition of the mixtures corresponding to that of a silicate rock. The mixtures were then analyzed with the use of a contemporary scheme and the absolute errors were calculated.

Another, more recent investigation was carried out by Fairbairn and Schairer[137]. These authors prepared a 6-component silicate glass of known composition and submitted it to 11 chemical laboratories for analysis. From the difference between the arithmetic mean values and the "true" amounts Fairbairn and Schairer drew conclusions as to the accuracy of the results.

The paper of Fairbairn and Schairer does not contain any information on the methods employed in the analysis of the glass. It can, however, be assumed that most analysts used a modified conventional scheme. Thus, there should be no uncertainty with regard to the methods used for the determination of the constituents silicon and aluminium. For the determination of the other constituents, such as sodium and potassium, widely different methods are being used, and it is therefore of considerable interest and importance to know whether the satisfactory accuracy reported by Fairbairn and Schairer for sodium and potassium was ob-

136. M. Dittrich, Neues Jahrb. Mineral., 2 (1903) 69.
137. H. W. Fairbairn and J. F. Schairer, Am. Mineralogist, 37 (1952) 744.

tained by some conventional gravimetric method (which may be indirect), by flame photometry or by a mixture of different methods. As long as the methods are not known for all constituents, the results of Fairbairn and Schairer are of limited value. One important result of their investigation is the demonstration of the serious systematic errors adhering to the modified conventional methods for silicon and aluminium.

Mercy[138] made a study of the accuracy and precision of a novel scheme of rock analysis.* His conclusions with regard to the accuracy of the scheme are based on the most probable values for the components of the standard rocks G 1 and W 1. The "true" values for G 1 and W 1 are, however, not exactly known, and, as the probable values for the constituents of these standard rocks are constantly being revised, the method employed by Mercy for establishing accuracy is less satisfactory.

It may be concluded that too little emphasis has been laid on the procurement of data demonstrating the accuracy of the methods of rock analysis, and that no satisfactory practice for ascertaining such data has yet been introduced. In order to contribute to the establishment of a more satisfactory practice, it is suggested that investigations with the purpose of determining the accuracy of analytical methods are based on the following presuppositions.

The accuracy of an analytical method is established by carrying out a series of analyses of a synthetic sample or standard of known and suitable composition, and by calculating and comparing the difference between the arithmetic mean value for the series and the "true" value of the standard. The accuracy which is of primary interest is that obtained by one analyst making a consecutive series of analyses under routine conditions in a given laboratory and using the same specified method.

From the difference between the arithmetic mean value of a series of determinations and the "true" amount, it is possible to detect the presence of a systematic error and to classify the method, e.g. as suggested by Mercy[138], in the groups accurate, moderately accurate and inaccurate. For this classification it is necessary to introduce certain limits of permissable difference. In discussing the accuracy of the results of analyses of the glass, Fairbairn and Schairer[137] considered the agree-

* The scheme studied was that of Shapiro and Brannock[139].

138. E. L. P. Mercy, Geochim. Cosmochim. Acta, 9 (1956) 161.
139. L. Shapiro and W. W. Brannock, U. S. Geol. Surv. Circ., No 165 (1952).

ment to be satisfactory when the difference between the arithmetic mean value and the "true" amount was less than ± 0.1 per cent (absolute).

In order to evaluate and classify the methods of the proposed scheme, it was decided to adopt the arbitrary limit, ± 0.1 per cent (absolute), introduced by Fairbairn and Schairer. This limit was used in the classification of methods for constituents present in amounts above 1.00 per cent. For components present in the concentration range 1.00—0.10 per cent, the arbitrary limit of ± 0.05 per cent (absolute) was adopted.

In Table 20 data relating to the accuracy of the test analyses are given.

From the data in Table 20, the methods of the proposed scheme are classified as follows:

a. Accurate methods: those for silicon, the total content of iron, iron(III), iron(II), magnesium, calcium, sodium, titanium, phosphorus and manganese.
b. Methods of moderate accuracy: that for potassium.
c. Inaccurate methods: that for aluminium.

b. *Precision*

Before starting a discussion of the precision of the proposed scheme, it is necessary to stress that all calculations of precision according to the standard statistical methods are based on the two following assumptions:

a. That the errors are random in sequence.
b. That the errors are "normally" distributed.

Schlecht[140] pointed out that analytical errors are not likely to be "normally" distributed. Clancey[141] examined the results of a large number of chemical analyses of industrial products and found that only 10 to 15 per cent of the distributions could be regarded as normal. He concluded by stating that "— great caution must be exercised in applying the ordinary simple statistical methods to the data of chemical analysis —".

The following discussion of precision is based on the above presuppositions and reservations.

140. W. G. Schlecht, U. S. Geol. Surv. Bull., No. 992 (1953) 57.
141. V. J. Clancey, Nature, 159 (1947) 339.

Table 20. *Data relating to the accuracy of the test analyses*.

Constituent	Chemical composition of sample ("true" amounts)	Arithmetic mean value of 10 test analyses	Diff. betw. arithm. mean value and "true" amount		Maximum diffs. in single determinations			
			absolute diff.	relative diff. × 100	positive absolute diff.	negative absolute diff.	positive relative diff. × 100	negative relative diff. × 100
SiO_2	60.00	60.07	+0.07	+0.1	0.28	0.13	0.5	0.2
Al_2O_3	16.00	15.70	−0.30	−1.9	0.19	0.99	1.2	6.2
Tot. content of iron (as Fe_2O_3)	5.28	5.22	−0.06	−1.1	0.16	0.30	3.0	5.7
Fe_2O_3	2.50	2.49	−0.01	−0.4	0.25	0.31	10.0	12.4
FeO	2.50	2.47	−0.03	−1.2	0.00	0.06	0.0	2.4
MgO	2.50	2.50	+0.00	±0.0	0.21	0.16	8.4	6.4
CaO	5.00	4.91	−0.09	−1.8	none	0.25	none	5.0
Na_2O	5.00	4.96	−0.04	−0.8	0.26	0.28	5.2	5.6
K_2O	5.00	5.13	+0.13	+2.6	0.19	none	3.8	none
TiO_2	0.700	0.676	−0.024	−3.4	0.000	0.045	0.0	6.4
P_2O_5	0.500	0.526	+0.026	+5.2	0.045	0.021	9.0	4.2
MnO	0.300	0.293	−0.007	−2.3	0.003	0.019	1.0	6.3
Total	100.00	99.73	−0.27	−0.3				

* Results in Table 15 falling outside $x ± 2s$ were excluded from the calculations in the present table.

In Table 16 the standard statistical data from the 10 test analyses are listed.

A number of papers contain data on the precision obtained in silicate rock analysis. Data well-known to rock analysts are those reported in the U. S. Geological Survey Bulletin Nos. 980 and 1113. The statistical data given in these reports result from interlaboratory investigations of the composition of the 2 standard rocks G 1 and W 1. In these investigations some of the constituents were determined by widely different methods, the precision of which may vary considerably. It is again pointed out — see the preceding discussion on accuracy — that the data of primary interest are those demonstrating the precision obtained by one analyst using the same specified method in a consecutive series of analyses made in a given laboratory under routine conditions. Data on precision resulting from the use of different and unspecified methods are of limited value.

From the data in Table 16 on the precision of the test analyses and by introducing certain arbitrary limits of precision, the methods of the proposed scheme may be classified, e.g. according to Mercy[138], as precise, moderately precise and not precise. Mercy based his classification on the data for the relative deviation (C). He did not specify the limits, but seemed to have used the following approximate arbitrary limits:

Relative deviation (C) (in per cent)	Method classified as
$C < 3.00$	precise
$3.00 < C < 10.00$	moderately precise
$10.00 < C$	not precise

On the basis of these limits and the statistical data in Table 16, the methods of the proposed scheme fall into the following groups:

a. Precise methods: those for silicon, aluminium, the total content of iron, iron(II), calcium and potassium.

b. Methods of moderate precision: those for iron(III), magnesium, sodium, titanium, phosphorus and manganese.

It was also considered of interest to compare the precision of the methods of the proposed scheme with the precision obtained in other intralaboratory investigations of modified conventional and/or novel schemes.

A survey of the literature showed that a surprisingly small number of intralaboratory investigations had been made. The majority of those found were unsatisfactory for one reason or another, mostly because the number of analyses was too small and because the investigation did not comprise all the main constituents. With regard to the precision of a modified conventional scheme, it was not possible to find satisfactory data demonstrating the precision obtained by one analyst working in a given laboratory. An intralaboratory investigation of interest is, however, reported by Dennen, Ahrens and Fairbairn[142]. This investigation contains the results obtained by 7 analysts working in the same laboratory. As these were the only satisfactory data found for a modified conventional scheme, they are included in Table 21. It should be noted, however, that in this study some of the constituents, such as sodium and potassium, were determined by different methods.

As to data relating to the precision of novel schemes, the situation is more satisfactory. Some of the data reported by Mercy[138] are reproduced in Table 21.

A comparison between the precision of the modified conventional scheme and the proposed scheme showed:

a. That the proposed scheme exhibited better precision for the constituents silicon, sodium and potassium.

b. That the precision of the 2 schemes was approximately the same for the total content of iron, iron(III), iron(II), magnesium, calcium, titanium, phosphorus and manganese.

c. That the precision of the proposed scheme was inferior for aluminium.

142. W. H. Dennen, L. H. Ahrens and H. W. Fairbairn, U. S. Geol. Surv. Bull., No. 980 (1951) 25.

Table 21. Comparison of intralaboratory precision of some schemes of silicate rock analysis. For an explanation of the notation employed, see chapter V. B. 4.

Constituent	Modified conventional scheme[1] 7 analysts Replicate analyses of G 1			Novel scheme[2] 1 analyst 6 analyses			Present scheme[3] 1 analyst 10 test analyses				Present scheme[4] 1 analyst 10 analyses of G 1			
	$\bar{x}$	C	s	$\bar{x}$	C	E	$\bar{x}$	s	C	E	$\bar{x}$	s	C	E
SiO_2	72.64	0.31	0.23	55.9	0.38	0.16	60.07	0.13	0.22	0.07	72.73	0.14	0.20	0.06
Al_2O_3	14.13	1.22	0.17	18.4	2.5	1.0	15.70	0.38	2.42	0.77	13.81	0.42	3.07	0.97
Tot. content of iron (as Fe_2O_3)	1.43	9.30	0.13	6.3	1.4	0.58	5.22	0.15	2.90	0.92	1.73	0.13	7.25	2.29
Fe_2O_3	0.86	19.3	0.17	1.6	6.8	2.8	2.49	0.18	7.23	2.31	0.66	0.09	14.12	4.46
FeO	1.06	5.72	0.06	4.3	1.5	0.60	2.47	0.07	2.83	0.92	0.96	0.05	4.81	1.52
MgO	0.44	9.90	0.04	3.4	2.9	1.2	2.50	0.13	5.31	1.68	0.39	0.02	5.06	1.60
CaO	1.34	6.53	0.09	5.5	0.81	0.33	4.91	0.08	1.56	0.49	1.27	0.01	1.17	0.37
Na_2O	3.43	6.23	0.21	4.6	1.7	0.69	4.96	0.18	3.58	1.13	3.27	0.04	1.18	0.37
K_2O	5.43	3.83	0.21	2.7	3.3	1.4	5.13	0.04	0.84	0.27	5.05	0.06	1.24	0.39
TiO_2	0.25	11.2	0.03	1.0	7.8	3.2	0.676	0.024	3.51	1.11	0.237	0.004	1.65	0.52
P_2O_5	0.10	23.4	0.02	0.39	1.6	0.66	0.526	0.026	4.86	1.54	0.071	0.008	11.66	3.69
MnO	0.03	30.5	0.01	0.08	3.5	1.4	0.293	0.011	3.91	1.27	0.034	0.003	9.93	3.14

[1] Ref.: W. H. Dennen, L. H. Ahrens and H. W. Fairbairn, U. S. Geol. Surv. Bull., No. 980 (1951) 25.

[2] Ref.: E. L. P. Mercy, Geochim. Cosmochim. Acta, 9 (1956) 161. Data taken from the analysis of the diorite T 13.

[3] Data taken from Table 16.

[4] Data taken from Table 18.

A similar comparison between the precision of a novel scheme, as evaluated from the data in Table 21, and the proposed scheme is less easily made, but the following indications may be drawn, viz.:

a. That the precision of the proposed scheme seemed to be better for silicon, potassium and titanium.

b. That the precision of the two schemes was approximately the same for aluminium and sodium.

c. That the precision of the proposed scheme was inferior for the total content of iron, iron(III), iron(II), magnesium, calcium, phosphorus and manganese.

2. The analyses of the standard rock G 1

a. *Accuracy*

The "true" amounts of the constituents that compose this natural rock are, of course, not known.

However, the closer understanding of the systematic errors inherent in the methods used in the analysis of this sample, as well as the special investigations of the content of certain constituents, have resulted in analytical data which can be considered to be close to the actual amounts. The components that have been the subject of such special and independent investigations are silicon and aluminum, and the present discussion of accuracy will be limited to these 2 constituents.

α. *Silicon*

It has long been recognized that the conventional gravimetric method for silicon is beset with a serious negative systematic error, and a number of attempts have therefore been made to establish more accurately the content of silicon in G 1. In Table 22 a survey (with references) is given of the results of some special investigations. This table also includes some results of photometric and combined gravimetric and photometric methods, which do not posess the negative systematic error of the conventional gravimetric method.

Table 22. *Some results of special investigations of the content of silicon (as silicon dioxide) in the standard rock G 1.*

References	Content (in per cent)
Stevens and Chodos[143]	72.70
Jeffery and Wilson[144]	72.60 : 72.66
Ingamells and Shur[145]	72.52
Riley[146]	72.6
Fairbairn (calculated value)*[147]	72.86
Jeffery (calculated value)[148]	72.66
Proposed scheme	72.73

It was stated above (see footnote to Table 22) that the value calculated by Fairbairn[147] resulted from analyses of a glass of known composition. Jeffery[148] reexamined the original data for G 1 and the glass prepared by Fairbairn and Schairer[137], and concluded by recommending for the content of silicon the lower value given in Table 22 (Jeffery (calculated value)).

The value of Stevens and Chodos[143] resulted from a special combined and thoroughly planned and executed chemical and spectrographical investigation in which all losses and gains of silicon were taken into account. Their value must be considered as reliable. Similar investiga-

* On the basis of analysis of a glass of known composition Fairbairn[147] concluded that in G 1 the value for silicon was 0.5 per cent (absolute) too low. Consequently, Fairbairn added 0.5 per cent to the value 72.36 per cent, thus obtaining his calculated value of 72.86 per cent. Fairbairn, however, does not give the source of his value of 72.36 per cent. At the time when Fairbairn discussed the content of silicon in G 1, the results available were those given in the U. S. Geological Survey Bulletin, No. 980, the arithmetic mean value for silicon in this paper being given to 72.24 per cent. By adding 0.5 per cent to the latter result, a preferred estimate of 72.74 per cent is obtained. This value compares more favourably with the other results of Table 22. The preferred estimate of Fairbairn (72.86 per cent) has been considered by some authors, e. g. Stevens and Chodos[148], and Jeffery[148], to be too high. This view is supported by the other data in Table 22.

143. R. E. Stevens and A. A. Chodos, U. S. Geol. Surv. Bull., No. 1113 (1960) 45.
144. P. G. Jeffery and A. D. Wilson, Analyst, 85 (1960) 478.
145. C. O. Ingamells and N. H. Shur, Geochim. Cosmochim. Acta, 27 (1963) 897.
146. J. P. Riley, Anal. Chim. Acta, 19 (1958) 413.
147. H. W. Fairbairn, Geochim. Cosmochim. Acta, 4 (1953) 143.
148. P. G. Jeffery, Geochim. Cosmochim. Acta, 19 (1960) 127.

tions were made by Jeffery and Wilson[144] and by Ingamells and Shur[145], the principle followed by these authors being the determination of the amount of silicon that escapes dehydration.

It is the opinion of Fairbairn[147] that photometric methods are applicable to major constituents of silicate rocks. He stated that the problems relating to the determination of silicon should disappear where these methods are used. In Table 22 the value of Riley[146] was obtained photometrically by the molybdenum blue method.

The result obtained with the proposed scheme falls close to the other values given in Table 22, this confirming the accuracy of the proposed method for silicon.

β. Aluminium

In discussing the precision and accuracy of chemical analysis of silicate rocks Fairbairn[147] estimated that the value for the content of aluminium in G 1 were 0.5 per cent (absolute) too high. His preferred calculated value is given in Table 23 together with the results of other special investigations of the content of aluminium in G 1.

Table 23. *Some results of special investigations of the content of aluminium (as aluminium oxide) in the standard rock G 1.*

References	Content (in per cent)
Fairbairn (calculated value)[147]	13.94
Jeffery (calculated value)[148]	14.00
Ingamells and Shur[145]	14.08
Jeffery[148]	14.05
Milner and Woodhead[149]	14.35
Riley[146]	14.08
Proposed scheme	13.81

In Table 23 the value calculated by Jeffery[148] again resulted from a reexamination of the data for G 1. Ingamells and Shur[145] made careful determinations of all constituents of the mixed oxide group and thus found aluminium by difference.

Direct determinations of aluminium were made by Jeffery[148] and by Riley[146], the former author employing a gravimetric method based on precipitation of the 8-hydroxyquinolate and the latter author using a

149. G. W. C. Milner and J. L. Woodhead, Anal. Chim. Acta, 12 (1955) 127.

photometric method based on the measurement of the aluminium 8-hydroxyquinolate in chloroform solution. The first method requires preliminary separation of iron and titanium. In the second method titanium interferes.

The volumetric method of Milner and Woodhead[149] is interesting because it is similar to that used in the present scheme. After extraction of the cupferrates of iron and titanium with chloroform, aluminium is precipitated as benzoate, complexed with EDTA, the excess of EDTA being titrated with a standard solution of iron(III) using salicylic acid as indicator. The arithmetic mean value obtained by Milner and Woodhead is, however, appreciably higher than the other data in Table 23, this indicating the presence of a systematic positive error.

The value for aluminium resulting from the use of the proposed scheme is distinctly lower than the other values reported. Thus, it is confirmed (as already shown in chapter V. B.) that the present method for aluminium is inaccurate, suffering from a systematic negative error.

b. *Precision*

Statistical data for the standard rock G 1 are given in Table 18 which also contains statistical data for the same sample, as reported by Stevens and Niles in the U. S. Geological Survey Bulletin No. 1113. A comparison of the intralaboratory precision of the proposed scheme with the interlaboratory precision given by Stevens and Niles confirms (with the exception of aluminium) the recognized observation that the former is in general better than the latter. From the statistical data in Table 18 and by introducing certain arbitrary limits of precision, it is possible to classify the methods of the proposed scheme. Using the same limits as in section E. 1. b., the methods are classified as follows:

a. Precise methods: those for silicon, calcium, sodium, potassium and titanium.
b. Methods of moderate precision: those for aluminium, the total content of iron, iron(II), magnesium and manganese.
c. Methods that are not precise: those for iron(III) and phosphorus.

In section E. 1. b. the methods of the proposed scheme were classified on the basis of the statistical data from the test analyses. A comparison with this previous classification indicates that the methods are less precise in the analysis of G 1 than in the test analyses. Thus, in the test

analyses none of the methods are classified as not precise, while in the analysis of G 1 the methods for iron(III) and phosphorus fall into this group. In the analysis of G 1 a lower precision is also obtained for aluminium, the total content of iron, iron(II), potassium and manganese. Methods exhibiting approximately the same precision in both series are those for silicon, magnesium and calcium. In the analysis of G 1 improved precision is obtained for sodium and titanium.

In Table 21 a comparison was made between the intralaboratory precision obtained with a modified conventional, a novel and the proposed schemes. A comparison of the statistical data from the former and the latter schemes is particularly interesting because the data result from analyses of the standard rock G 1.

A study of the relative deviation (C) of the modified conventional and the proposed schemes shows, with the exception of the method for aluminium, that the methods of the latter scheme are more precise. It should be noted, however, that the precision of the modified conventional scheme would probably be better, if the analyses had been made by the same analyst.

3. Analysis of the standard rock R 117

In Table 19 the analytical results from an analysis of this standard rock is given together with data resulting from an interlaboratory investigation initiated by Jeffery[150]. The data obtained by the proposed scheme compare favourably with the arithmetic mean values given by Jeffery. As expected, the proposed scheme gives a higher value for silicon, while the corresponding tendency to obtain lower results for aluminium is absent.

An interesting comparison of interlaboratory precision can be made by studying the data given by Jeffery in Table 19 and the data in Table 18 extracted from the U. S. Geological Survey Bulletin No. 1113, both resulting from the analysis of G 1. It is seen, that for practically all constituents the precision of the more recent investigation organized by Jeffery is better. This improvement probably results from a closer understanding of the errors inherent in the modified conventional schemes, and an understanding on the part of the analysts that rock analysis must be done with constant care and attention to details.

150. P. G. Jeffery, Research Report Project No. PCS 43, Department of Scientific and Industrial Research, Warren Spring Laboratory, Hertfordshire, Great Britain, March 1963.

VI. Concluding remarks.

In the present investigation an attempt was made to contribute to the development of silicate rock analysis.

The authors are fully aware of the fact that the scheme proposed is neither final nor ideal, and that better schemes will be introduced. The authors have, however, long felt that the modified conventional schemes of rock analysis are less satisfactory, and have tried to improve upon this state by introducing, testing and applying a selection of contemporary methods.

The authors may be criticized for having gone into too many details and lengthy discussions. Admittedly, the present paper is very much larger than other, recent contributions in the field of rock analysis. The authors are, however, of the opinion that papers on schemes of rock analysis are published without due attention to the large number of details which are of importance to the rock analysts; in particular, the authors have missed sufficient data demonstrating the accuracy and precision. The authors consider as ideal, and have taken for a model, the treatises on rock analysis published by Hillebrand.

In the field of rock analysis the trend today is to replace the chemical methods by more rapid, instrumental methods, such as radiometric methods and X-ray fluorescence spectrometry. In the future these methods can be expected to predominate in the routine analysis of rocks. However, many instrumental methods require solid standard samples of known composition, and for this purpose chemical methods are indispensable. For the present instrumental methods are not either capable of taking over the determination of all the main constituents of silicate rocks.

In many laboratories the purchase of large, complicated instruments will not, for economical or technical reasons, be possible, and in these cases schemes of the type proposed may be found applicable.

It may finally be mentioned that the proposed scheme has been introduced in the laboratories of the Norwegian Geological Survey, and that parts of the scheme have been in use for about two years in the routine analysis of widely different types of silicate rocks. A number of samples has been analyzed with the use of both the proposed and a modified conventional scheme. The experiences from the applications are satisfactory.

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