Systematic Analysis of Silicates

By LEE C. PECK

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*Methods for silicate analysis
and a discussion of problems
involved in their use*

UNITED STATES DEPARTMENT OF THE INTERIOR

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ILLUSTRATIONS

[All plates are in pocket]

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By Lee C. Peck

ABSTRACT

Detailed procedures are given for the analysis for 17 constituents commonly present in silicates: SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O+, H_2O-, TiO_2, P_2O_5, MnO, CO_2, BaO, total S, and SO_3. Problems in analysis that may occur are also discussed. The use of special equipment to facilitate analysis is stressed.

INTRODUCTION

Methods are described in this bulletin for the determination of constituents that, in the Geological Survey, compose a "standard analysis" (SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O+, H_2O-, TiO_2, P_2O_5, MnO, and CO_2) and for the determination of BaO, total S, and SO_3. Once the basic techniques required for the analysis of these constituents are mastered, they may be easily applied to the determination of additional constituents.

Although this bulletin is primarily a manual for the instruction of beginners, in both the Geological Survey and other laboratories, rather than a comprehensive treatise on the subject of silicate analysis, it is directed also to experienced analysts who would like to compare procedures and to the geologists who must interpret the data furnished by analysts.

Most of the so-called conventional methods date back to the 19th century, and the ones described in this manual do not differ basically from similar ones described in available texts. The speed of these methods, however, has been increased by the use of special equipment. Detailed procedures for three relatively new methods are given: the use of the silver reductor for the determination of total iron oxide, Kitson and Mellon's method for the determination of phosphorus, and the removal of manganese before the determination of calcium and magnesium.

Special equipment is described in the immediately following section; the methods are explained, conditions are listed under which these methods fail, and some modified procedures are given for the analysis of unusual samples under "Discussion of the methods," page 2; detailed procedures are given under "Standard procedures,"

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page 53; and the preparation of apparatus and reagents is described in the section "Apparatus and reagents," page 83.

SPECIAL EQUIPMENT

Although excellent analyses have been made by using standard items of equipment, time is saved, techniques are simplified, the number of accidents is reduced, and the reproducibility of results is improved by the use of special apparatus. Thus, if adequate amounts of automatically controlled equipment are available, several operations that do not require the attention of the analyst can be carried out concurrently. Making a pyrosulfate fusion is simple when an electric radiator is used, but making this fusion without loss over a burner requires skill. Accidental boiling over or spattering of a solution containing solids can be largely eliminated by the use of electrical equipment whose temperatures can be reproduced. It is difficult to bring some precipitates to their equilibrium weights by heating them over burners, sometimes because of insufficient temperature and sometimes because of variable temperatures from burner to burner. The reproducible high temperature of the Globar furnace eliminates this difficulty, and as the furnace can be brought to temperature in a short time, it is almost as convenient to use as a burner.

Careful laboratory planning is worthwhile. Much unnecessary work is eliminated if individual equipment is supplied to each analyst and if units of equipment for successive operations are placed in proximity. The arrangement used in the Geological Survey's laboratory in Denver is pictured on figure 1. Individual pieces of equipment referred to under "Standard Procedures" (p. 53) are pictured on figures 2–14, and details of the Globar furnace, the electric radiator, the desiccator, and the water furnace are illustrated by drawings on plates 1–4.

DISCUSSION OF THE METHODS

FOREWORD TO THE GEOLOGIST

Questions are frequently asked about the size of a rock sample required. The geologist should, of course, submit a sample that is large enough to give an adequate representation of the problem at hand; the cost of preparation for even a 100-pound sample is not prohibitive. If large enough to be representative, a sample of 300–500 grams is ideal. It is small enough so that its preparation is not unduly expensive and large enough so that a reserve supply can be retained. Although a standard analysis can be made with only 10 grams of material, the analysis of so small a sample can seldom be

justified. A larger sample can generally be obtained easily, and where an expensive analysis is made, a reserve supply should be set aside for possible future uses.

The sample should be free from lichens and dirt, and weathered portions should be removed, unless the geologist desires to include these portions in the sample. Paint and adhesive tape should not be used to mark samples. Although these contaminants may cause no significant errors in macroanalysis, they may cause serious errors in the determination of minor constituents.

FIGURE 1.—Laboratory arrangement. A 12-foot bench and an 8-foot hood are assigned to each analyst. The room in the background is used to store stock solutions and equipment for common use.

A 5-gram sample is adequate for the analysis of most silicate minerals, but a larger sample is desirable so that a reserve can be retained. Because of the difficulty in making separations, however, it is seldom feasible for the geologist to supply a pure sample of optimum size. The analyst can use smaller portions. However, this practice reduces the accuracy of the analysis, and unfortunately, the greatest accuracy is desirable in the analysis of minerals. It is best to discuss the matter of sample size with the analyst before the mineral is submitted and even before separation. The minimum sample size depends upon the number of constituents that are to be

FIGURE 2.—Hood. This view of an 8-foot open-face hood shows: A, water bath; B, Globular furnace; C, four electric radiators. A two-way switch permits power input to either the furnace or the radiators to be controlled by a single variable autotransformer.

determined, and in some analyses a small sample is adequate. For example, only 1.5 grams of the sample is needed in the analysis if the nonessential determinations for total water and the alkalis are omitted.

The mineral should be as pure as possible, and special care should be used to wash it free from any heavy liquids that are used in making the separation.

The primary purpose of the following discussions is to acquaint the geologist as well as the analyst with the problems of silicate analysis. If he reads them carefully, the geologist may be able to surmise why some analyses given in the literature do not agree with the petrography of the rocks. He will be able to recognize conditions that cause the analyst difficulties, particularly in the determination of such constituents as sulfide and sulfate sulfur and ferrous oxide. He will learn that under some conditions the analyst cannot make a satisfactory determination—a determination that is often the one that he most urgently needs.

Generally the analyst is neither a geologist nor a mineralogist; he cannot, therefore, be expected to guess the presence of unusual
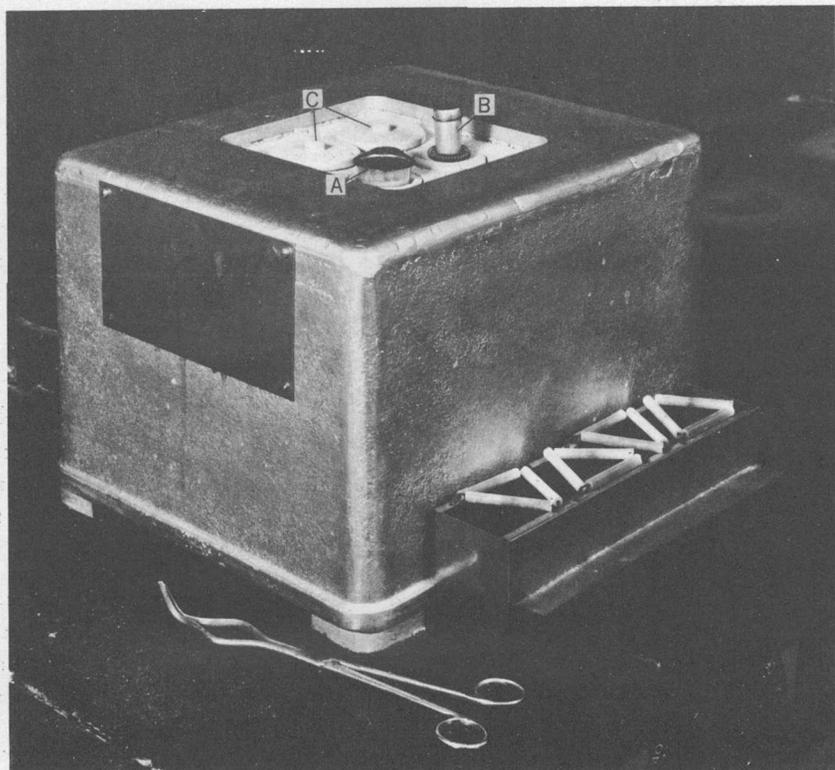
FIGURE 3.—Globar furnace. Because of its small chamber size and high power input, this furnace can be heated to 1,200°C in 40 minutes. Various uses are illustrated: A, ceramic adapter used for making a sodium carbonate fusion; B, ceramic adapter used for sintering the charge in a J. Lawrence Smith crucible; C, openings covered, as when precipitates are ignited within the furnace. For details of construction of the furnace, see plate 1.

minerals. A complete modal analysis is of little use to him, but certain minerals are troublesome, and sometimes, because he was unaware of their presence, an analysis must be repeated. The geologist, by acquainting himself with the discussions herein, should be able to supply the necessary information when he submits his sample. The use of a mineral name as a modifier is adequate for many samples, as "staurolite schist" or "garnet ijolite."

Unusual elements, if their presence in abnormal amounts is suspected, should be mentioned—for example, the rare earths, chromium, beryllium, vanadium, or any of the heavy metals. In addition, the presence of certain minerals or their polymorphs should

be mentioned, whether or not they contain unusual elements. The following minerals are in this class:

beryl	celestite	fluorite	kyanite
chromite	alunite	zircon	rutile
scapolite	pyrrhotite	siderite	pyrolusite
staurolite	graphite	garnet	psilomelane
monazite	tourmaline	andalusite	
barite	topaz	sillimanite	
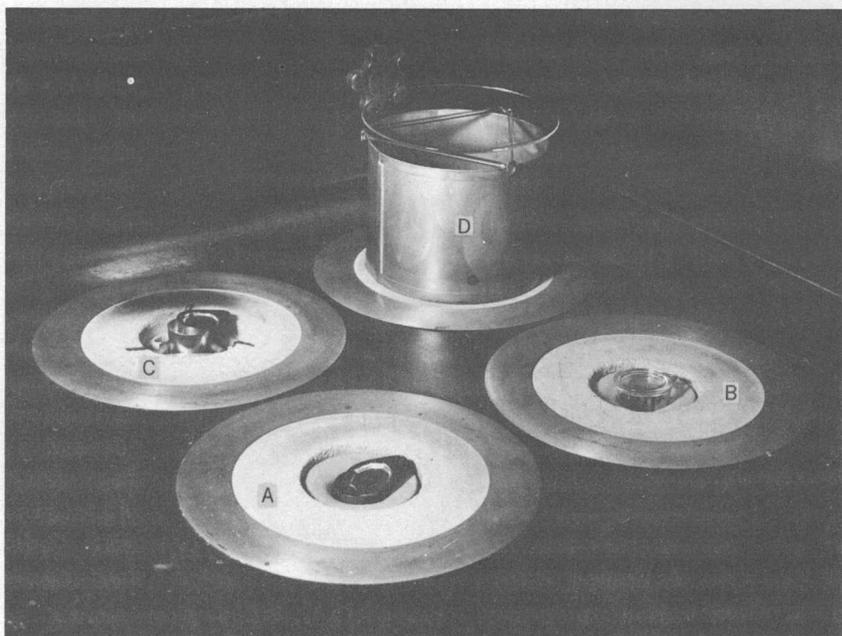
FIGURE 4.—Electric radiators. Four well-type radiators are connected in parallel and are controlled by a single variable transformer. A, ceramic ring adapter used when a filter paper is burned off (the platinum crucible is supported on an inverted porcelain crucible within the radiator); B, pyrosulfate fusion in a Vycor crucible; C, triangle supporting the crucible during the hydrofluorization of silica; D, stainless steel adapter, covered with a raised watch glass, used when ammonium chloride is sublimed in the J. Lawrence Smith method for the determination of the alkalis. For construction details of radiator, see plate 2.

No analyst is infallible. A mistake occasionally escapes detection no matter how many precautions are taken. If the geologist has reason to suspect a result he should not hesitate to report his suspicion to the analyst so that the analysis may be checked. Little harm is done if a mistake is corrected before publication.

Six portions of a sample are used in making a standard analysis, one each for total water, the "main portion" (H_2O-, SiO_2, R_2O_3, CaO, MgO, total Fe_2O_3, TiO_2, and residual SiO_2), the alkalis (Na_2O and K_2O), ferrous oxide, manganese and phosphorus oxides, and
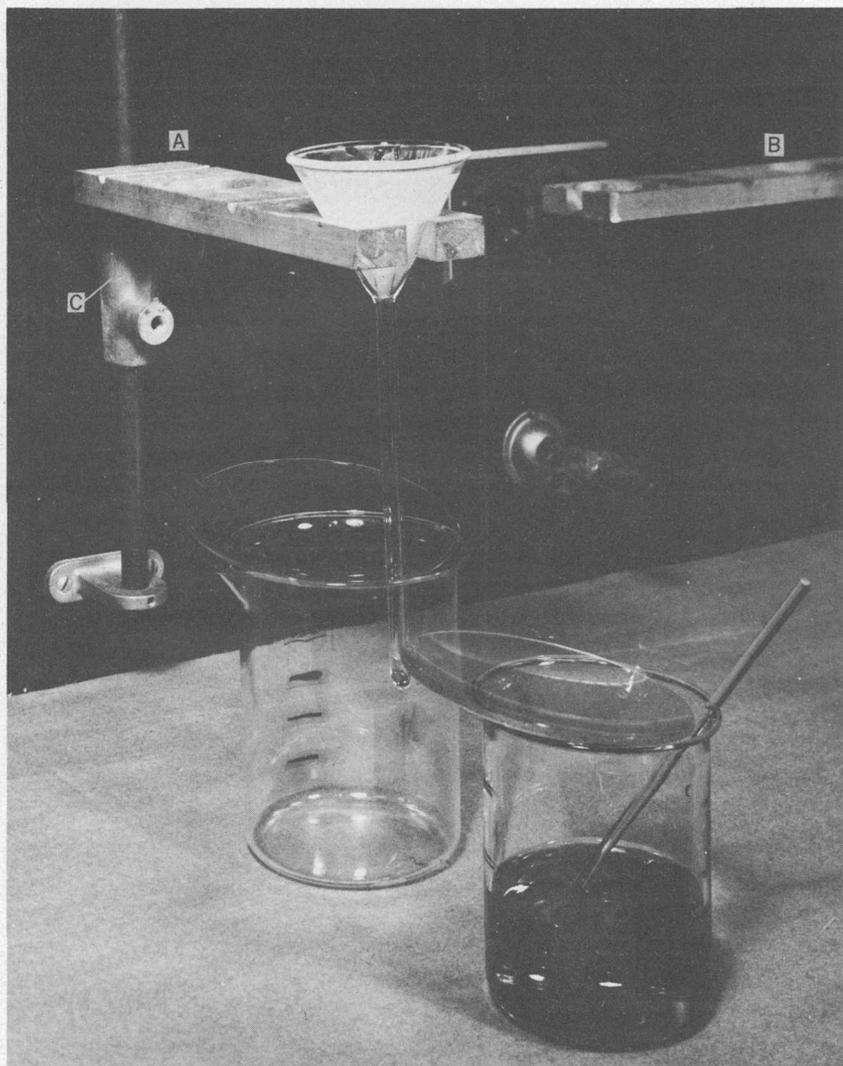
FIGURE 5.—Funnel racks (A and B). These individual, permanently mounted racks may be folded against the backboard when not in use (B). The height of the rack is maintained by a pressure device consisting of a ball and spring that is contained in the boss (C) below the wooden funnel holder.

carbon dioxide. Additional portions are needed for the determination of additional constituents. Some of the results are obtained by difference: combined water (total H_2O minus H_2O-), alumina (R_2O_3 minus total Fe_2O_3, TiO_2, P_2O_5, and residual SiO_2), ferric oxide (total iron as Fe_2O_3 minus FeO calculated to Fe_2O_3), and sodium oxide (calculated from the NaCl found by subtracting KCl from
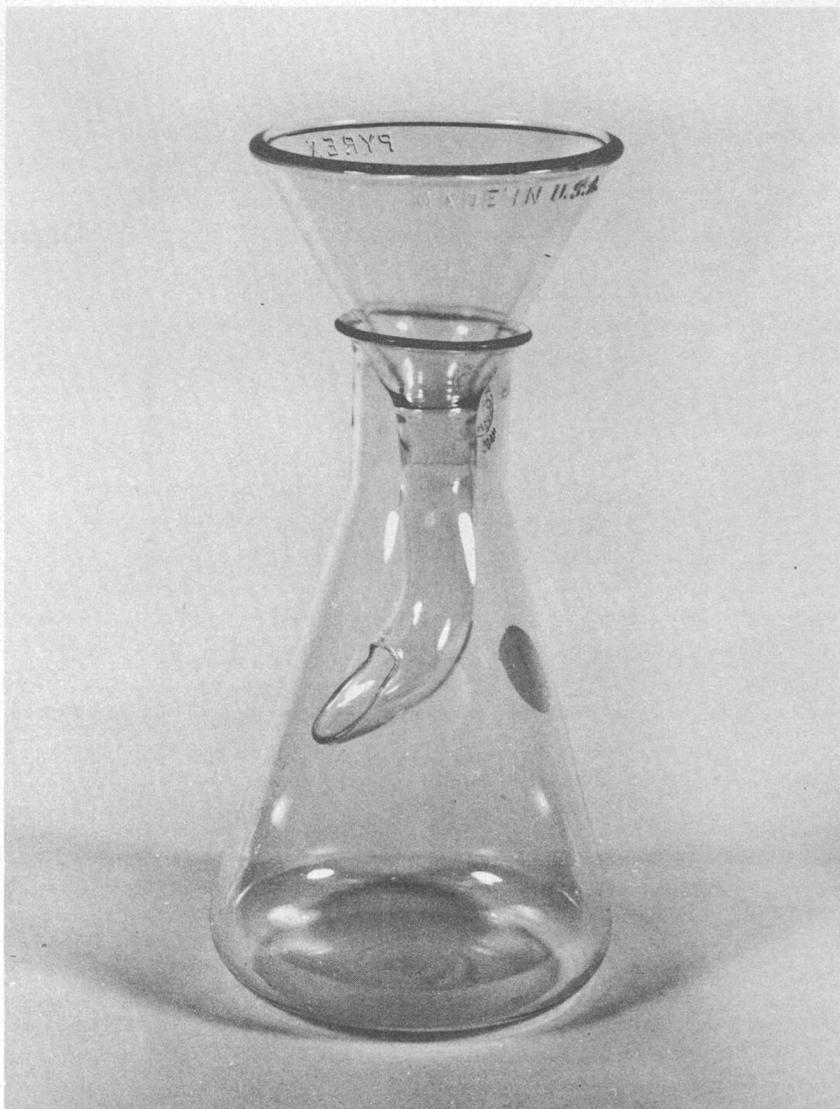
FIGURE 6.—Spray trap. This trap, made from a transfer funnel, prevents loss by spraying if a solution must be boiled.

total alkalis chlorides). Therefore, except in the analyses of ferric oxide and sodium oxide, an error in one of the foregoing results has no effect upon the summation because it is balanced by an equal and opposite error in the determination of another constituent.

Although a very high or low summation indicates that some error has been made, an acceptable summation, inasmuch as it may be the
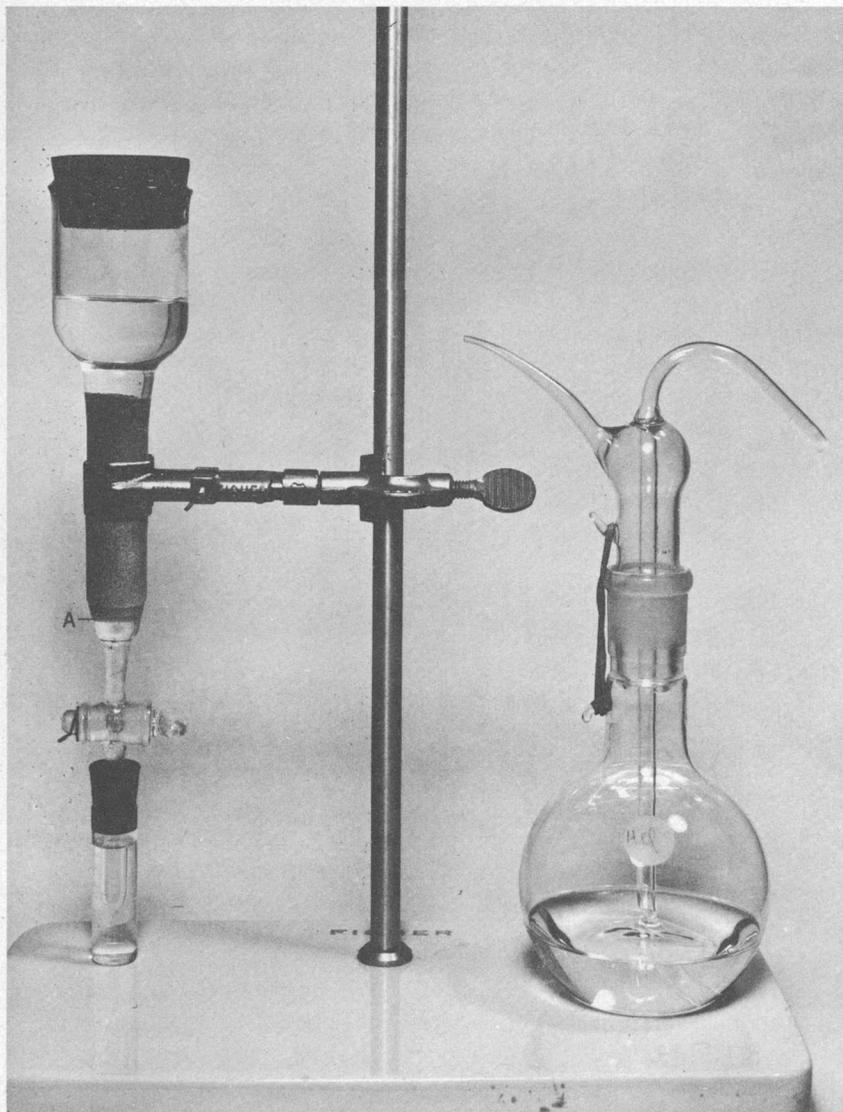
FIGURE 7.—Silver reductor. The reductor tube is fabricated from a glass Buchner funnel having a 20-mm extra-coarse porosity filtering disk (A). The column of silver is 10 cm high. The special bottle shown is used to wash down the inside of the reductor reservoir.

result of compensating errors, does not prove that an analysis is accurate. However, consistently good summations obtained by an analyst of integrity indicate that careful work has been done. A summation between 99.50 and 100.75 percent was considered acceptable by Washington (1930, p. 144); one between 99.75 and 100.50

FIGURE 8.—Four-chamber desiccator. This compact desiccator is convenient to handle. Because only one crucible is placed in each chamber, the moisture admitted when one is opened cannot be absorbed by other precipitates in a series to be weighed. For details, see plate 3.

was considered acceptable by Hillebrand (1919, p. 30). In the author's laboratory a summation between 99.50 and 100.25 is considered acceptable; values outside this range indicate the possibility of a mistake. The trend toward lower totals shows that research has reduced plus errors more than minus ones.

Because of the time required for slow operations such as evaporations, an overall time of 2 weeks is required to complete a standard silicate analysis; but if work is properly planned, only 12 working hours are needed to complete such an analysis. The average productivity over a period of a year, however, is about 24 hours per analysis, for samples and solutions must be prepared, equipment kept in order, analysis repeated because of mistakes, and disproportionate amounts of time used in the analysis of special samples.

SAMPLE PREPARATION

Mineral samples are submitted generally as powders that need only to be ground in an agate mortar to pass a 100-mesh screen.
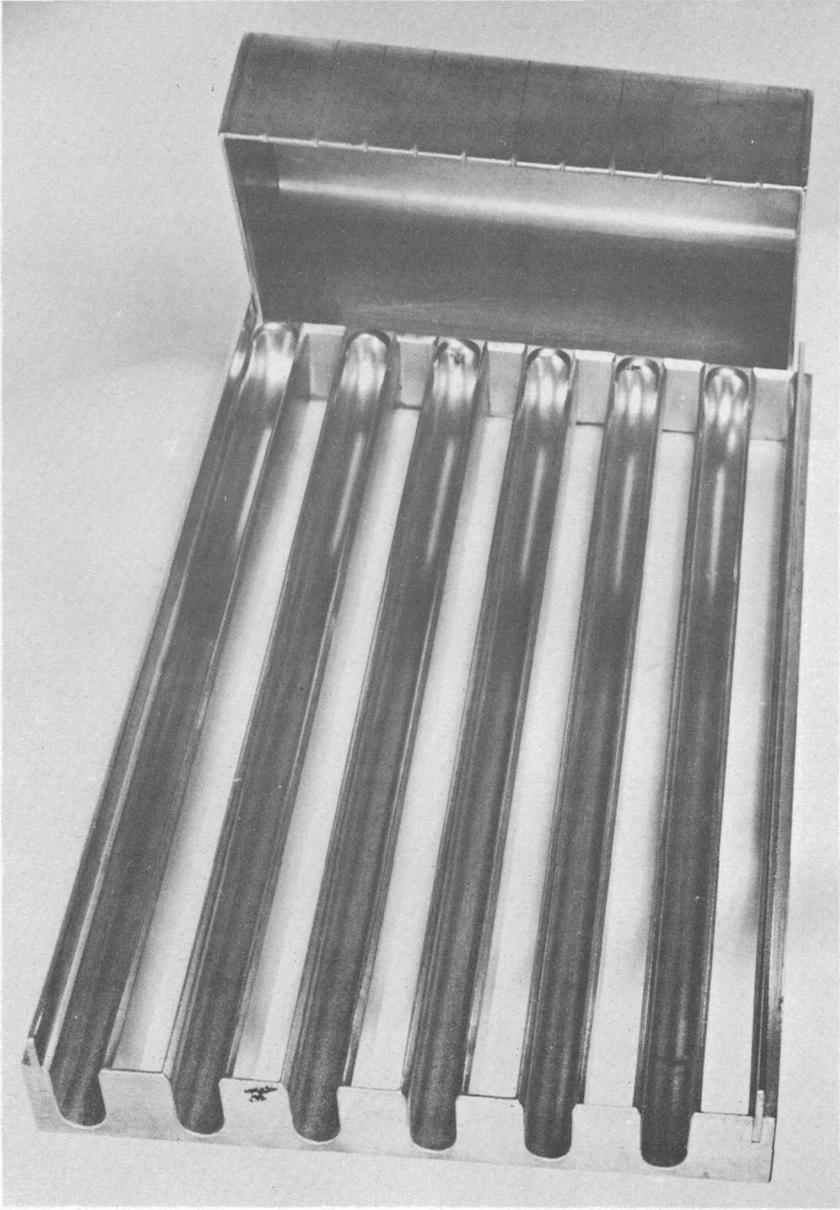
FIGURE 9.—Sample splitter. This splitter, which is milled from an aluminum block 14 inches long by 8 inches wide by 1 inch high, consists of a series of equally spaced troughs and slots. The troughs and slots are half an inch wide; the troughs are seven-eighths of an inch deep. Half of the sample is retained in the troughs; the other half falls through the slots onto the paper beneath.
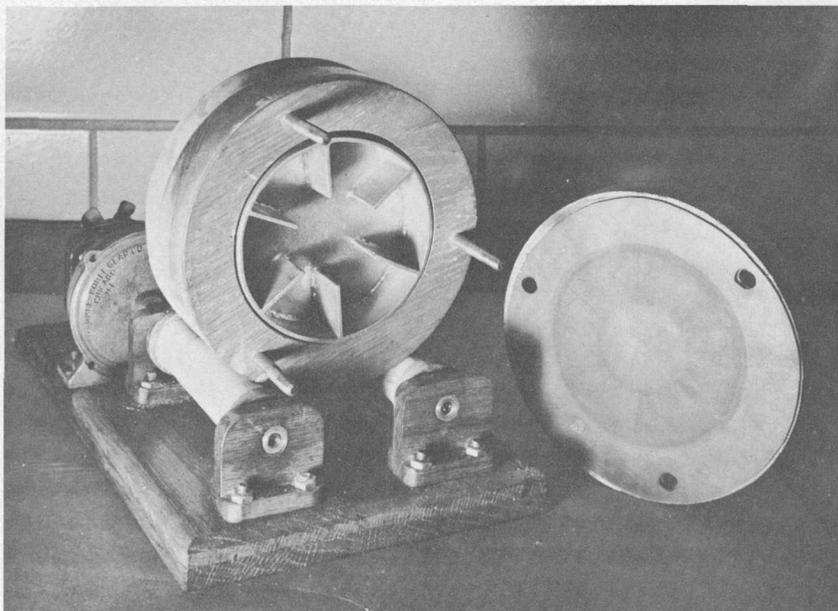
FIGURE 10.—Sample mixer. The aluminum chamber, 4 inches in diameter and 1 inch in depth, rotates at 40 rpm. The front of the chamber is closed by the rubber gasket shown on the cover.

A rock is broken down on a hardened steel plate, by blows from a hammer, to pieces having maximum dimensions of 1 inch and is crushed further by using a Plattner (diamond) mortar. The size of the sample is progressively reduced as the particle size decreases, and crushing is continued with the Plattner mortar until the portion selected for analysis passes a 60-mesh screen. This portion is ground in an agate mortar to pass a 100-mesh screen and is then mixed thoroughly and transferred to a vial.

DISCUSSION

A very common source of error in the analysis of silicate rocks is improper sampling. The powder may not be representative of the rock, the powder itself may be segregated, and contaminants may have been introduced during the crushing and grinding. Preparation by hand grinding is extremely tedious, and for this reason, machinery is generally used. Except for the substitution of ceramic plates (Barnett and others, 1955) for steel plates in attrition grinders, machinery now available is little different from that used in Hillebrand's time, and most of the objections of Hillebrand (1919, p. 57–64) to the use of machinery are still valid. Excessive amounts of tramp iron are introduced, and the composition of the sample,
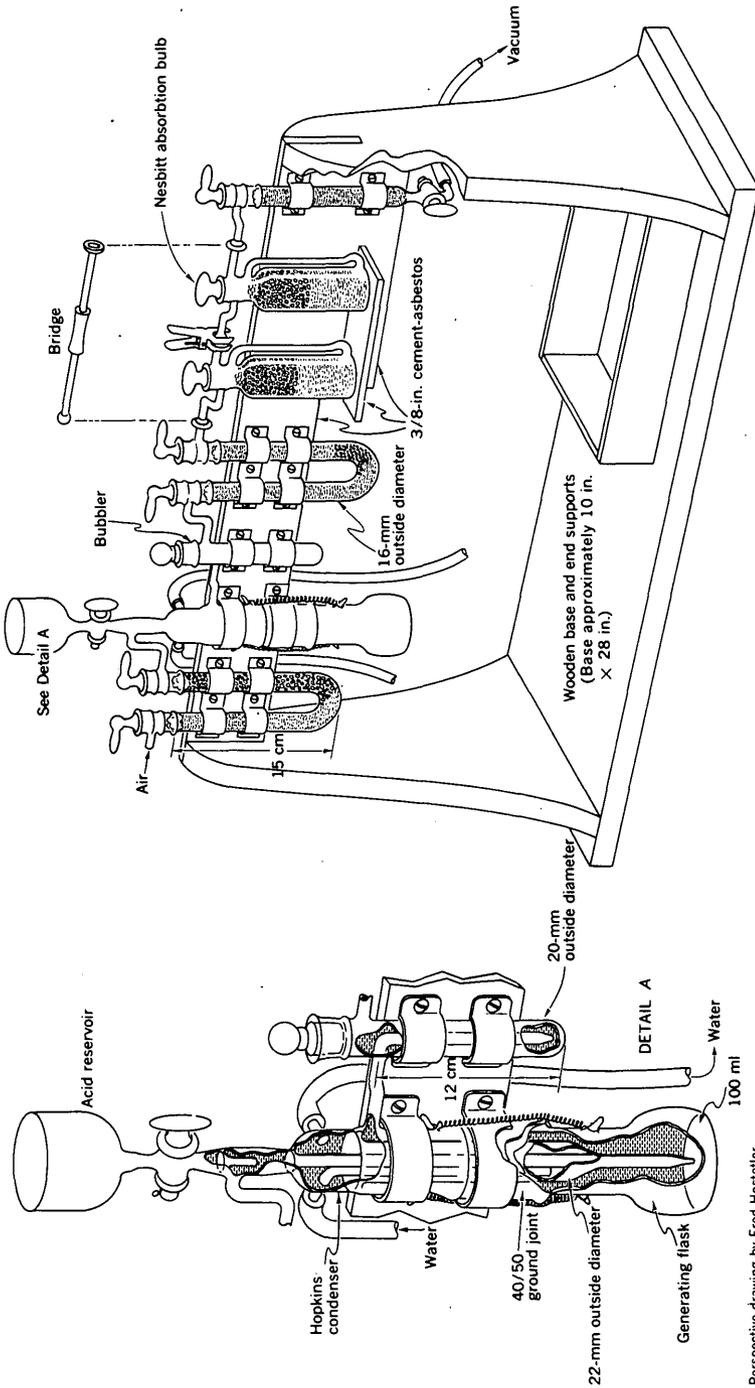
FIGURE 11.—Carbon dioxide apparatus. This compact portable apparatus has the glassware mounted on a cement-asbestos board that may be lifted from the side supports when the absorbants are replaced. Leakage is minimized by using fused glass connections wherever possible. A Hopkins condenser, modified as shown above, is built into the tube above the generating flask.
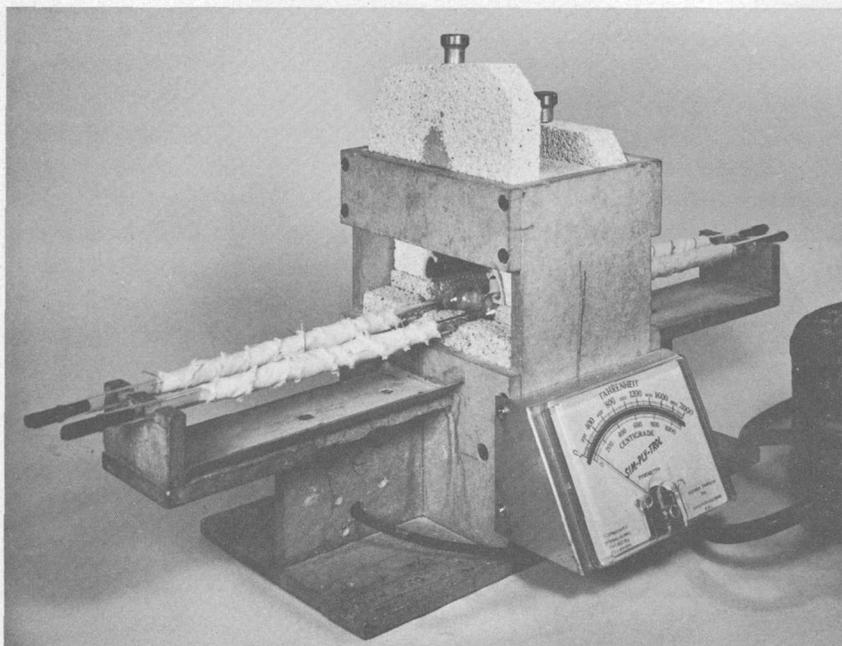
FIGURE 12.—Total water furnace. Excellent temperature control is obtained by using this furnace. The bulbs are heated from the top only, by means of a semicylindrical heating element. For construction details, see plate 4.

particularly in the ferrous iron and water content, may be changed by attrition grinding. Careful hand grinding adds no more than 0.05 percent of iron to the sample, and changes in composition are minimized by the use of impact crushing.

The use of a splitter to reduce the size of a sample lessens the possibility of obtaining a nonrepresentative portion. A special type of splitter (fig. 9) minimizes the loss of dust, which in general is different in composition from the rest of the sample. If the mixed sample is poured into a vial, segregation occurs. Such segregation can be prevented by using a spatula to transfer the powder in small portions to the vial.

Tests made in the author's laboratory indicate that a representative portion of a sample can be obtained by using proper technique. In one test, a 100-pound drill-core sample of a pegmatite was used to determine the reproducibility of splits taken for analysis. Because some pieces of the core contained layers of muscovite 1–2 inches thick, the pegmatite presented a difficult sampling problem.

The whole 100 pounds was reduced to a maximum particle size of about 1 inch with a jaw crusher. A Plattner and then an agate
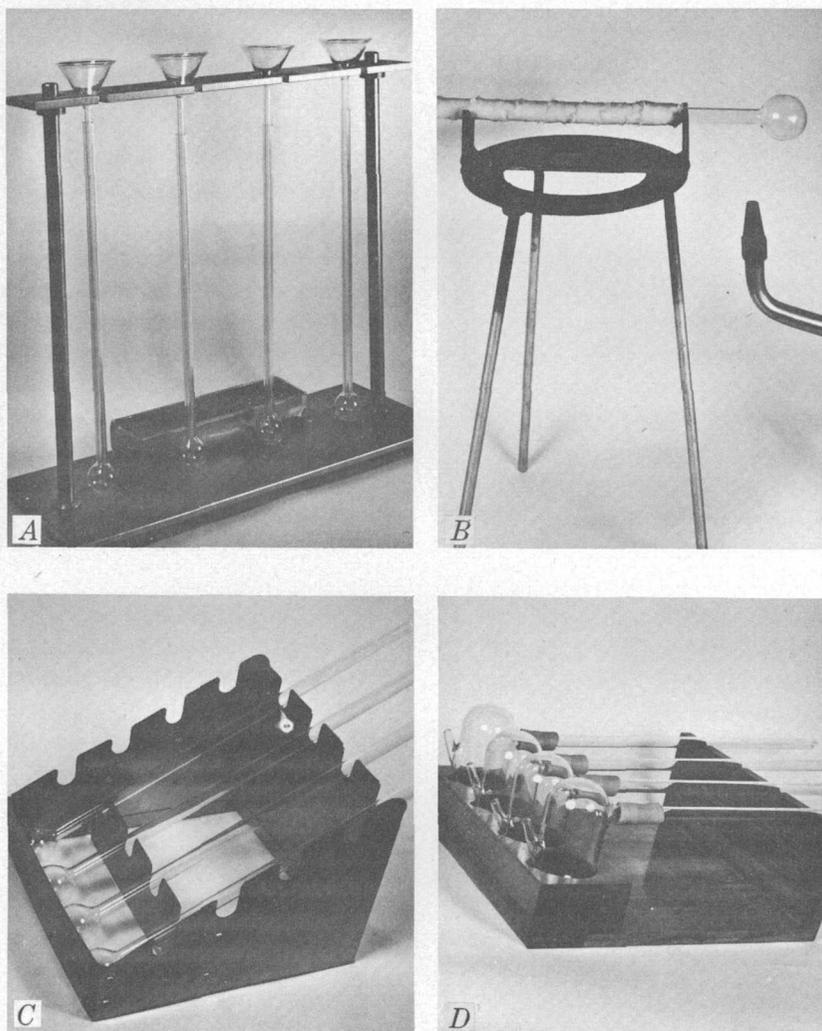
FIGURE 13.—Accessory equipment for total-water determination. A, funnels used to load Penfield tubes; B, jig used when bulb is fused from tube; C, tube rack; D, apparatus used for the diffusion of carbon dioxide. The bulbs, which are fabricated from tubing whose outside diameter is 45 mm, are 8 cm high.

mortar were used for subsequent grinding. The 100 pounds of jaw-crushed material was split into 2 portions. One split was reduced to a smaller particle size before it was split again. This procedure was repeated until about 200 grams of 10-mesh material were obtained. Without further grinding, the 200-gram portion was split repeatedly until 25 grams of material was separated. The 25-gram portion was reduced to 80 mesh powder (A). The rest of the origi-

nal material was reworked in exactly the same way to obtain a second 25-gram portion (B). The remainder of the original material was then crushed mechanically to produce a third portion (C). A disk mill having ceramic plates was used for the final grinding. The three carefully mixed portions were analyzed by Marjorie Balazs. Results, in percent, are shown in the following table:

Constituent	Sample		
	Hand ground		Machine ground
	A	B	C
SiO_2	73. 39	73. 45	73. 25
Al_2O_3	15. 14	15. 14	15. 20
Fe_2O_3	. 30	. 26	. 26
FeO	. 27	. 27	. 54
MgO	. 04	. 03	. 03
CaO	. 24	. 20	. 21
Na_2O	4. 52	4. 51	4. 51
K_2O	5. 08	5. 07	5. 07
H_2O+	. 04	. 04	. 04
H_2O-	. 40	. 41	. 36
TiO_2	. 01	. 01	. 01
CO_2	. 01	. 00	. 01
P_2O_5	. 32	. 31	. 32
MnO	. 02	. 02	. 02
F	. 07	. 07	. 07
Cl	. 00	. 00	. 00
Subtotal	99. 85	99. 79	99. 90
Less O	. 03	. 03	. 03
Total	99. 82	99. 76	99. 87

Although the very close agreement between analyses A and B may be fortuitous, the preceding data show that a reasonably representative sample can be prepared if proper precautions are taken. The amount of iron introduced from steel machinery during the preliminary crushing is shown by the increased ferrous iron content of sample C; this increase probably represents normal contamination. Samples ground in machines having steel grinding plates have been submitted for analysis that contained as much as 3 percent of tramp iron.

Because samples prepared for macroanalysis are frequently used for spectrographic analysis or for the chemical determination of trace elements, no metal that might be present in the sample in trace amounts should be used in crushing or screening equipment. Sieves having aluminum frames and iron or cloth screens are used in the Geological Survey.

The cost of hand grinding is small compared to that of a complete silicate analysis; therefore, no method of sample preparation should
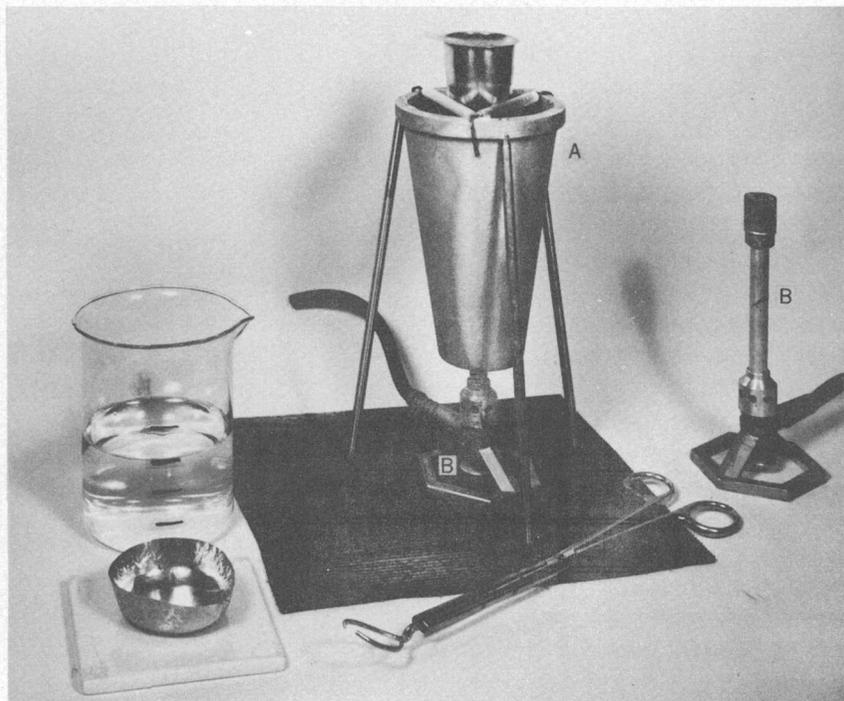
FIGURE 14.—Apparatus used for the determination of ferrous oxide. A, special tripod
with burner shield ; B, Terrill burners.

be considered that would cause serious errors in the analytical re-
sults. Because it is difficult, however, to obtain competent person-
nel to prepare samples by tedious hand methods, the development
of a reliable machine method is desirable.

TOTAL WATER

A mixture of sample and flux is transferred to a bulb at the end
of a borosilicate glass tube. The bulb containing the charge is
heated by means of a special electric furnace. The tube, which is
cooled by a strip of wet cloth wrapped around it, serves as a con-
denser for the water driven from the sample. The juncture of the
bulb and tube is heated; the bulb is pulled off, and at the same time,
the bulb end of the tube is sealed. The tube is then placed in a hori-
zontal position, and its open end is connected to a glass bulb that
is partly filled with water. After the tube stands for sufficient time
to allow any carbon dioxide it may contain to be substantially
replaced by air, it is weighed, dried, and reweighed. The loss in
weight represents the total water content of the sample.

DISCUSSION

The water content of a silicate is divided into two classes: that released at and below 105°C is reported as moisture, or H_2O-; that released above this temperature is reported as combined water, or H_2O+. This division, which is based on accepted usage, is arbitrary. Combined water is determined by difference after separate determinations for total water and moisture.

Among earlier analysts, total water was customarily determined by loss on ignition, a method that has long been discredited. Results so obtained are poor approximations because the loss in weight may be due not only to loss of water but also to the loss of carbon dioxide, the alkalis, sulfur, fluorine, and chlorine. Oxidation may decrease loss or even produce a gain.

Now only two methods are commonly used. In one method, the sample is heated with a flux in a combustion tube and the water evolved is carried by a stream of dry air into a weighed tube containing a suitable absorbant. This method is time consuming, but it has one advantage—carbon dioxide does not interfere. Because of its simplicity, the method of Penfield (1894), or some modification of it such as that outlined in the foregoing descriptive paragraph, is preferred by most analysts. This method has one disadvantage: interference from carbon dioxide is difficult to overcome.

The use of a furnace rather than a flame for heating the charge has several advantages: the operation requires little attention, the heating cycle can be controlled, and four determinations can be made concurrently.

The flux has a threefold purpose: it destroys the structure of the minerals present, some of which do not give up their water when heated to 900°C (Smethurst, 1935)—the maximum temperature that a glass bulb can withstand; it retains elements such as sulfur, fluorine, and chlorine, which would otherwise interfere; and it prevents the reduction of water to hydrogen by ferrous oxide present in the sample.

Sodium tungstate, lead oxide, and lead chromate are the three fluxes commonly used. None is completely satisfactory. Hornblende, one of the most difficult minerals to decompose, was used to test the reactivity of various fluxes. Water is completely released from this mineral when it is heated with lead oxide, but lead oxide is frequently troublesome when used with silicates containing carbon dioxide or carbon. If the mixture of flux and sample fuses before carbon dioxide is expelled, the melt intumesces until it blocks the opening to the tube; then the bulb swells and finally ruptures.

Intumescence does not occur if either lead chromate or sodium

tungstate is used in the analysis of silicates containing carbon or carbon dioxide, but neither of these fluxes completely releases water from hornblende. In addition to being insufficiently reactive, sodium tungstate is hygroscopic. Its use is not recommended.

A mixture of two parts of lead oxide and one part of lead chromate is sufficiently reactive to decompose hornblende, and intumescence is not troublesome when this mixture is used in the analysis of samples containing carbon or carbon dioxide.

A ratio of 3 grams of flux to 1 gram of sample is satisfactory for the analysis of most silicates; micas, however, are an exception. Because of its bulk, a mica makes inadequate contact with the flux, and some of it remains undecomposed. Excellent results are obtained if 3 grams of flux are used with a 0.5-gram portion of a mica.

Immediately after preparation, the flux is moisture free and reabsorbs water very slowly if kept in a tightly sealed bottle. It is advisable, however, to make a blank determination from time to time, particularly in humid climates.

Carbon dioxide, if released from a sample and then left in the tube, makes the value for total water too high. By connecting the tube to a bulb containing water and air and by allowing the tube to stand for sufficient time, the saturated carbon dioxide becomes so thoroughly diluted with saturated air that it no longer has any effect on the results. The speed of the diffusion is not increased, nor is the replacement more complete if the tube is laid at an angle, as some texts suggest, to permit the carbon dioxide to "drain." It is advantageous to keep the tube in a horizontal position because then no center bulb is needed to retain the water.

In some analyses, the foregoing method for eliminating the interference of carbon dioxide is unsatisfactory. If the carbon dioxide content of the sample is high, some water is carried from the tube with the carbon dioxide released while the charge is heated. The error is negligible if the content is below 5 percent, but it increases rapidly as the amount of carbon dioxide increases. Thus, in the analysis of a mixture of 0.4 gram of marble and 1 gram of hornblende containing 21.8 mg of water, only 20.1 mg was recovered.

Organic matter, if present, may be converted to water and carbon dioxide, or it may volatilize; hence, the Penfield method fails to give the correct value for total water if the sample contains organic matter.

Research is handicapped by the lack of suitable silicate standards containing known amounts of water. Recently, Friedman and Smith (1958, p. 218) described a method in which the sample is fused in an evacuated system by means of an induction furnace. The water

thus released is reduced to hydrogen by passing it over hot uranium metal, and the volume of hydrogen is measured. This method is theoretically sound, and it is reasonable to assume that results obtained by using this method are nearly correct; but the method is rather complex for use in routine silicate analysis. Two amphiboles analyzed by Friedman for combined water were used to check the results obtained by the modification of Penfield's method described in this bulletin. The figures in the following table are expressed as percent combined water:

Analysis	Method	
	Friedman and Smith	Penfield
Uralite		
1	1. 99	1. 98
2	1. 97	1. 99
3	1. 92	1. 98
4		1. 97
Average	1. 96	1. 98
Hornblende		
1	2. 11	2. 06
2	2. 02	2. 06
3		2. 05
4		2. 06
Average	2. 07	2. 06

MOISTURE

A 1.000-gram portion of the sample is added to a weighed platinum crucible; the crucible and its contents are weighed, heated for 1 hour in an oven having a temperature of $105 \pm 5°C$, cooled in a desiccator, and reweighed. The sample is reserved for the determination of silica.

DISCUSSION

In the analysis of most silicates, the heating temperature is not critical, and no more moisture is released at 150°C than at 105°C. Some silicates, such as clays and zeolites, release water more or less continuously from below 105°C to considerably above, and erratic results may be obtained because of small differences in the oven temperature. The analyst should not be overly concerned by these erratic results because the values obtained have little meaning to the geologist. Useful information is obtained in other ways, such as by X-ray, differential thermal, or thermogravimetric methods.

Many clays and zeolites and some other types of samples may be extremely hygroscopic, and their moisture contents may vary with changing atmospheric humidity. Because of water that is lost or absorbed when a vial is opened, the content may vary from day to day; furthermore, the content may change while the sample is being weighed. If a sample is hygroscopic, it is spread in a thin layer and allowed to stand overnight in the balance room, so that its moisture content comes to equilibrium with the atmospheric humidity. Portions for the water determinations and for the determinations of major constituents are then weighed within a few minutes of each other.

The crucible is weighed at the start of the analysis, although this weight is not used in subsequent calculations. The weight of sample taken is determined both by direct weighing and by difference. If the two weights do not agree within 0.2 mg, either the sample is hygroscopic or the transfer of the powder to the crucible was carelessly made. Because this portion is used in the determination of most of the major constituents, it is important that the weight of the portion be nearly correct.

SILICA

The powder that was reserved after the determination of moisture is ignited briefly at a dull-red heat and then fused with sodium carbonate. The cooled cake is transferred to a platinum dish. Sodium carbonate and sodium silicate are leached from the cake with water containing a little alcohol, and the resulting solution is acidified with hydrochloric acid. The crucible is cleaned with acid, the washings are transferred to the dish, and the crucible is ignited and weighed. The solution in the dish is evaporated to dryness. After the soluble salts are dissolved by heating the residue with dilute hydrochloric acid, silica is filtered from the solution. The filtrate is evaporated to dryness, the residue is heated with dilute hydrochloric acid, and additional silica is filtered from the solution on a separate paper.

Both papers are burned off in a single platinum crucible, and the silica is ignited and weighed. The precipitate is dissolved in hydrofluoric acid containing a few drops of sulfuric acid, the solution is evaporated to dryness, and the crucible containing a small residue is ignited and weighed.

The crucible, which contains a residue that is part of the ammonium hydroxide group, is set aside and is used later to burn off the paper containing the bulk of this group.

Not all the silica is recovered. The few milligrams that pass into

the second filtrate are gathered by and recovered from the ammonium hydroxide group.

In order to prevent excessive attack on the crucible during the fusion, any carbon, organic matter, or sulfides present are removed by igniting the sample briefly over a Tirrill burner. The ignition described in the standard procedures is satisfactory for most silicates, but the ignition of a sample containing large amounts of organic matter, such as a shale, serves only to char the organic matter and to leave a cokelike residue. An electric radiator is used to make the ignition of such samples. The partially open crucible is brought slowly to a dull-red heat and is heated at this temperature for about 3 hours.

Sodium carbonate is a satisfactory flux for almost any silicate; therefore, no other flux—for example, a mixture of sodium carbonate and potassium carbonate—need be considered. The ratio of 5 parts of sodium carbonate to 1 part of sample can be used for the fusion of any silicate, regardless of its composition.

If the crucible is cooled after the fusion and then heated over a Meker burner for 30 seconds, the cake generally loosens and can be removed and transferred to a platinum dish. With a little practice, this technique can be mastered. If the cake fails to loosen, the crucible is laid on its side in the platinum dish and is covered with water; the solution is then heated. The solution is cooled, acidified, and then heated to expel carbon dioxide before the crucible is removed from the dish.

The loss in weight of the crucible during the sodium carbonate fusion seldom exceeds 1 mg. For a sample rich in iron or calcium, attack is more severe, and the loss may be as much as 5 mg. If the crucible gains weight, the gain may be due to alloying of iron with the crucible or to careless washing after removal of the cake. This alloying practically never occurs in analyses in which the Globar furnace is used for the fusion, but it is quite common in analyses in which a burner is used for the fusion of iron-rich samples. Sometimes a residue that cannot be removed by washing or by policing with acid remains in the angle of the crucible. In this event, the crucible is dried, and the residue is fused with a little sodium carbonate. The cooled melt is dissolved in acid, and the solution obtained is transferred to the dish containing the bulk of the sample.

Leaching the cake with water dissolves most of the sodium silicate and sodium carbonate and leaves a porous residue that can be crushed with a stirring rod. Alcohol is added in order to reduce tetravalent manganese, which would subsequently react with hydro-

chloric acid to form chlorine. Chlorine causes severe attack on platinum ware.

When hydrochloric acid is added to the solution, most of the residue dissolves, but little of the silica precipitates. During the evaporation, silica precipitates to form a fine powder, which is easy to filter and wash. If hydrochloric acid is added directly to the cake, lumps of siliceous material form. These lumps are difficult to break up and tenaciously retain impurities.

In the first evaporation, the residue need be brought only to apparent dryness by heating it on a water bath. The practice of first drenching the dried salts with concentrated hydrochloric acid and then diluting the acid is unnecessary. The salts will dissolve just as well if diluted hydrochloric acid is used. When the second dehydration is made, the residue should be heated on the water bath for at least an hour after it appears dry; but it should never be heated in an oven at temperatures above 100°C. Only slightly better dehydration is obtained, and the high temperature makes some of the salts insoluble thereby increasing the amount of impurities retained by the silica. The second filtration must be made through a separate paper. If the original paper is used, some silica from the bulky first precipitate is redissolved.

The papers containing the precipitates are burned off slowly by means of an electric radiator. If the ignition is too rapid, carbonized paper may be trapped beneath the silica. This paper does not burn until after the silica is hydrofluorized, and the loss in weight causes high results for silica.

The precipitate is extremely hygroscopic after the paper is burned off, and will absorb water if it is exposed to the atmosphere. If this hydrated precipitate is brought to a high temperature quickly, it decrepitates violently, and loss of silica may occur even if the crucible is covered. When the ignition cannot be carried out immediately, the precipitate is stored in a desiccator. As a further precaution, the covered crucible is heated over a Meker burner before it is transferred, uncovered, to the Globar furnace.

To insure its complete dehydration, the silica precipitate is heated at 1,200°C for 1 hour. Constant weight is sometimes attained by heating for 1 hour at 1,100°C, but it probably cannot be attained at the temperature of a Meker burner regardless of the length of time that the precipitate is heated.

Heating at 1,200°C slowly volatilizes any phosphorus pentoxide from precipitates, and the loss in weight causes low results for alumina. Precipitates of this type seldom occur, but if a substantial loss in weight is noted after a second heating at 1,200°C, the

presence of phosphate should be suspected. A correction can be made by assuming that the amount of phosphorus pentoxide lost is equivalent to twice the loss in weight that occurs during a second 1-hour heating period, but the correction is approximate; the platinum crucible also loses weight.

Because the precipitate contains impurities, the difference in weight of the crucible and its contents before and after volatilizing the silica as silicon fluoride is used to determine the true value for silica. Sulfuric acid must be present during this hydrofluorization so that residual fluorides are converted to sulfates; otherwise, titanium fluoride is volatilized in the subsequent ignition of the crucible. Titanium phosphate is sparingly soluble in hydrochloric acid, and in the analysis of a sample rich in phosphorus and titanium, as much as 20 mg of titanium phosphate can be present in the silica precipitate. Except in the foregoing analysis or in the analysis of a sample containing chromite or zircon, the weight of the residue should not exceed 1 mg; a larger residue indicates that the sample was not completely decomposed during the sodium carbonate fusion.

Some texts warn against a differential error caused by weighing the sodium left in the residue, as sodium sulfate, after the silica has been hydrofluorized (Hillebrand and others, 1953, p. 681). In tests carefully made with a flame photometer, no more than 0.1 mg of sodium oxide was found in any of the unignited precipitates obtained from a series of samples of varying composition.

A few refractory silicates, for example beryl and kyanite, may be incompletely decomposed by a sodium carbonate fusion. The presence of a gritty light-colored residue in the platinum dish after the dried salts have been dissolved in hydrochloric acid indicates incomplete decomposition. If decomposition is incomplete, the first filtrate is evaporated to dryness and set aside. The paper containing the precipitate is burned off in a platinum crucible, and the silica and residue are fused with 3 grams of sodium carbonate. The cooled melt is treated exactly as was the melt from the original fusion; when the silica is filtered off, the filtrate is caught in the dish containing the residue of the filtrate previously set aside. The second silica recovery is made in the usual way.

Zircon, another refractory silicate that is difficult to decompose completely by means of a sodium carbonate fusion, is generally present in such small amounts that it is filtered unnoticed with the silica precipitate. If zircon were decomposed in the subsequent hydrofluorization of silica, its presence would cause no error; but it is generally not decomposed, and the silica it contains is reported as alumina. Toleration of this small error is generally best; the

expenditure of the time required to correct the error can seldom be justified.

Chromite is not completely decomposed during the sodium carbonate fusion. It may be detected as a black gritty residue in the platinum dish after decomposition of the fusion cake with acid. The presence of this mineral causes no error in the silica determination, but it may cause an error in the subsequent determination of alumina.

In the analysis of boron-rich minerals, or of rocks containing them, boron must be removed by volatilization as methyl borate before the determination of silica (Hillebrand and others, 1953, p. 752–753). If boron is not removed, it coprecipitates with silica, and because boron fluoride is volatile, high results are obtained for silica.

Many analysts believe that as much as 2 percent of fluorine may be present in the sample without having significant effect upon the determination of other constituents. In order to obtain more specific data, Elaine Munson made a series of experiments in which 1-gram portions of sample W-1 (Fairbairn and others, 1951) were fused with sodium carbonate. The cakes were leached with water, and amounts of sodium fluoride to simulate fluoride contents of 0, 2, 5, and 10 percent were added to the various leachates. The analyses were continued as described under "Standard procedures" (p. 62). Results of the analyses, in percent, are given in the following table:

Analysis	Simulated percentages of fluorine			
	0	2	5	10
Silica				
1_____	52. 47	52. 49	52. 41	51. 34
2_____	52. 46	52. 53	52. 41	52. 26
3_____	52. 49	52. 49	52. 26	51. 29
4_____	52. 53	52. 52	52. 33	51. 42
Average_____	52. 49	52. 50	52. 35	51. 33
Ammonium hydroxide group (less silica)				
1_____	27. 42	27. 39	27. 27	27. 03
2_____	27. 35	27. 35	27. 25	26. 93
3_____	27. 39	27. 35	27. 28	27. 13
4_____	27. 32	27. 33	27. 35	26. 97
Average_____	27. 37	27. 36	27. 31	27. 02

Analysis	Simulated percentages of fluorine			
	0	2	5	10
Calcium oxide				
1	10. 92	10. 87	10. 85	10. 61
2	10. 93	10. 88	10. 88	10. 60
3	10. 91	10. 89	10. 85	10. 53
4	10. 90	10. 90	10. 88	10. 60
Average	10. 92	10. 89	10. 87	10. 59
Magnesium oxide				
1	6. 57	6. 57	6. 58	6. 56
2	6. 59	6. 58	6. 57	6. 52
3	6. 57	6. 56	6. 58	6. 52
4	6. 59	6. 58	6. 58	6. 54
Average	6. 58	6. 57	6. 58	6. 54
Titanium oxide				
1	1. 07	1. 07	1. 07	1. 07
2	1. 06	1. 06	1. 07	1. 07
3	1. 07	1. 07	1. 07	1. 07
4	1. 07	1. 07	1. 07	1. 07
Average	1. 07	1. 07	1. 07	1. 07
Total Iron oxide (as ferric oxide)				
1	10. 98	10. 99	11. 01	11. 00
2	11. 00	11. 00	11. 00	10. 96
3	10. 99	11. 00	11. 02	10. 98
4	11. 00	11. 00	11. 02	11. 00
Average	10. 99	11. 00	11. 01	10. 99

Previous observations about the effect of 2 percent or less of fluorine were confirmed. Larger amounts interfere in the determinations of silica, the ammonium hydroxide group, and calcium oxide. They interfere little in the determination of magnesium oxide and not at all in the determinations of titanium oxide or total iron oxide.

AMMONIUM HYDROXIDE GROUP

The solution reserved from the silica determination is neutralized with ammonium hydroxide, made slightly acid, and boiled; the solution is then neutralized with ammonium hydroxide. After an addition of paper pulp, the precipitate is separated by filtration. It is redissolved in hydrochloric acid, and the ammonium hydroxide group

is reprecipitated from the resulting solution by neutralization with ammonium hydroxide. A second filtration is made through the paper used in the first filtration. The combined filtrates are reserved for the determinations of calcium and magnesium, after the removal of manganese.

The paper containing the precipitate is burned off in the platinum crucible containing the residue that was reserved after the hydrofluorization of silica; the precipitate is ignited at a suitable temperature, and the crucible and its contents are weighed. Because the crucible loses weight during the ignition of. the silica and the ammonium hydroxide group, the weight of the empty crucible is determined after removal of the precipitate. (See "Recovery of silica," p. 69.)

DISCUSSION

Although the ammonium hydroxide (R_2O_3) group consists generally of aluminum, iron, titanium, phosphorus (as phosphate), and the residual silicon (as silicate), other elements may be present. Aluminum is determined by difference after separate determinations for all other elements in the group have been made, and if uncommon elements that are not detected and determined are present in the precipitate, values that are too high are obtained. A preliminary spectrographic analysis of the sample is invaluable to determine whether such uncommon elements are present in macroamounts. Chromium, vanadium, zirconium, the rare earths, and beryllium are some of the uncommon elements that may be present. Silicates containing members of the hydrogen sulfide group are seldom submitted for analysis, but if this group is present, it must be removed before the determination of the ammonium hydroxide group.

Pure ammonium hydroxide, prepared by pasing ammonia gas into distilled water contained in a polyethylene bottle, is used for the precipitation. Reagent-grade ammonium hydroxide contains silica.

Because of the gelatinous nature of the precipitate, paper pulp is added to the solution prior to the first filtration, not only to increase the rate of filtration but also to obtain better washing.

The group precipitate is ignited in a furnace at a temperature of 1,100°C; at higher temperatures, ferric oxide may be converted to magnetite. Contrary to common belief, the dehydration of alumina in amounts commonly present in silicates is substantially complete at 1,100°C. However, in the analysis of a sample such as kyanite in which the amount of aluminum is very high and the amount of iron is low, it is best to ignite the precipitate at 1,200°C for 30 minutes.

Enough ammonium chloride, formed by the neutralization of hydrochloric acid, is present to prevent the coprecipitation of magnesium. The separation of the ammonium hydroxide group from magnesium is so nearly complete that a third precipitation is never required. In a set of experiments, solutions were prepared containing various amounts of magnesium and aluminum and the amounts of ammonium salts that would be present in an analysis. In each experiment, the aluminum was separated by a double precipitation, as described in the standard procedures for the ammonium hydroxide group. In order to determine the amount of magnesium retained by the aluminum hydroxide precipitate after the separation, the precipitate was redissolved, and a third precipitation was made. The amount of magnesium found in the third filtrate was considered to be the amount retained by the aluminum hydroxide after two precipitations. The following table presents the results of four analyses:

Analysis	Constituents taken (mg)		MgO in third filtrate (mg)
	Al_2O_3	MgO	
1	400	100	0. 13
2	300	200	. 11
3	200	300	. 02
4	100	400	. 01

The separation of a few milligrams of manganese oxide from the ammonium hydroxide group presents no problem; but where larger amounts (5 mg or more) are present, complete separation is difficult. Because alumina is determined by difference, manganese oxide present in the precipitate will be reported as alumina. The amount of manganese coprecipitated depends upon the composition of the precipitate and the pH of the solution. Coprecipitation with aluminum hydroxide is negligible regardless of the technique used, but the coprecipitation with iron hydroxide is serious and with titanium hydroxide even worse. If the iron and titanium hydroxides are precipitated from faintly acid solution, coprecipitation is minimized.

In the commonly used technique of Lundell and Knowles (1923), the boiling solution is neutralized with dilute ammonium hydroxide to the distinct yellow color of methyl red. The success of this method depends upon a very close adjustment of the final pH, which should be between 6.8 and 7.0. Recognition of the methyl red end point in the presence of ferric hydroxide is difficult, and a pH of 7 is likely to be exceeded more often than not. If two precipitations are made, separation from manganese, at least in amounts up to

20 mg, is substantially complete. However, the author was unable to verify claims by Lundell and Knowles that nearly complete separation from large amounts of manganese can be obtained in a single precipitation.

Equally good results are obtained if, in the first precipitation, the cold solution is neutralized with ammonium hydroxide to the brom cresol purple end point, made just acid, boiled, and again made just ammoniacal to assure complete precipitation of aluminum before the solution is filtered. Methyl red and brom cresol purple change color at approximately the same pH (6.4 and 6.8), but the color change of brom cresol purple is easier to see in solutions containing ferric hydroxide. Care must be taken not to pass the end point appreciably in the initial neutralization. The amount of manganese coprecipitated increases greatly with an increasing excess of ammonium hydroxide. This manganese does not redissolve if the solution is brought back to the neutral point with acid; the precipitate must be completely redissolved and the neutralization procedure repeated.

In the rare analyses in which a silicate contains more than 2 percent of manganese oxide, the ammonium hydroxide group cannot be assumed to be free from manganese, particularly if the iron or titanium content is also high, as in many iron garnets. It is safest to determine manganese after solution of the precipitate and to make a suitable correction for the manganese present (calculate manganese as Mn_3O_4). Total iron oxide and titanium oxide must then be determined from a separate portion of the sample.

Sometimes because of improper adjustment of pH, the combined filtrates contain aluminum. The faintly ammoniacal filtrates are heated to determine whether precipitation was complete before they are used in the next determination.

Fluorine does not interfere in the precipitation of either iron or titanium, but if the fluorine content of the sample exceeds 2 percent, the precipitation of aluminum may be incomplete. (See "Silica," p. 25.)

Chromite that is not decomposed during the fusion with sodium carbonate is eventually weighed with the ammonium hydroxide group. No error would result if the mineral were pure ferrous chromite, but the magnesium it generally contains will be reported as alumina unless a special procedure is used. Magnesium must be separated if the amount of chromite is large. The residue remaining after the hydrofluorization of silica is fused with potassium pyrosulfate, and the cake is dissolved in dilute hydrochloric acid. Magnesium is separated from iron and chromium by filtration after

an ammonium hydroxide precipitation. The precipitate is combined with the main ammonium hydroxide group precipitate, and the filtrate is added to the group filtrate.

A solution used for the determination of the ammonium hydroxide group contains more than 5 grams of sodium chloride. If the amount of aluminum is large, its voluminous precipitate retains sodium chloride in spite of a double precipitation. A high summation in the analysis of an aluminum-rich sample, which is generally attributed to incomplete dehydration of alumina, is often caused by the retention of sodium chloride. If the sample contains more than 30 percent of alumina, a triple precipitation should be made, or a smaller portion of the sample should be used for the determination.

Platinum, most of which is dissolved from the dish during the dehydration of silica, is always present in the second filtrate from the silica determination. The amount increases with increasing iron content of the sample. Unless prior techniques were so faulty that an excessive amount is present, this platinum passes completely into the filtrate when the ammonium hydroxide group is separated by a double precipitation.

REMOVAL OF MANGANESE

The combined acidified filtrates, reserved after the ammonium hydroxide group determination, are evaporated to a small volume. Zirconyl chloride is added; the solution is first made ammoniacal and then just acid. After the addition of ammonium persulfate and paper pulp, the solution is heated on the water bath, made ammoniacal, and then heated for a short additional period.

The precipitate of hydrated manganese dioxide and zirconium hydroxide is removed by filtration and discarded; the filtrate is reserved for the determinations of calcium and magnesium.

DISCUSSION

Although a prior separation of manganese simplifies the subsequent determinations of calcium and magnesium, this separation has generally been avoided. Most analysts prefer to omit the troublesome precipitation with ammonium sulfide and to make suitable corrections for the coprecipitated manganese. In a few analyses, however, in which manganese predominates over magnesium, a prior separation is mandatory because manganese partially precipitates as hydrated manganese dioxide. If no separation is made, the error caused by the contamination of calcium oxide with manganese is generally negligible; most of the manganese precipitates with magnesium as manganous ammonium phosphate.

Since the development of the simple, rapid method outlined above (Peck and Smith, 1961, p. D401), the objection to the prior removal of manganese is no longer valid, and this separation should be made routinely.

A solution containing colloidal hydrated manganese dioxide filters slowly, and the precipitate tends to pass the finest paper. If zirconium hydroxide is used to gather the precipitate, filtration is rapid, and the removal of manganese is complete. Paper pulp added to the solution before it is filtered prevents channeling when the precipitate is washed.

Sulfate ions from the persulfate do not interfere in subsequent determinations. If calcium is separated by two precipitations with ammonium oxalate, no calcium sulfate is present in the final precipitate. Barium and strontium behave much as they do if no separation is made.

Calcium does not coprecipitate appreciably with hydrated manganese dioxide, but magnesium does. Coprecipitation of magnesium is minimized if manganese is precipitated from acid solution, but the precipitation is incomplete. Best separation is achieved if the solution is acidified, heated, then made ammoniacal, and heated for a short additional period. In the analyses of an average sample, the amount of magnesium coprecipitated is so small that the error may be ignored, but where the manganese oxide content of the sample exceeds 2 percent, a double precipitation should be made. If two precipitations are necessary, each precipitation is made as described in the standard procedures, except that a larger initial volume of solution is used. The first precipitate is dissolved in a dilute hydrochloric acid solution containing sodium sulfite.

The following table shows the average amounts, in milligrams, of magnesium coprecipitated for various amounts of magnesium and manganese oxides for analysis in which single precipitations were made:

MnO present	MgO coprecipitated at indicated concentrations of MgO			
	400	100	50	10
20	0. 30	0. 20	0. 15	0. 10
5	. 10	. 06	. 05	. 05

CALCIUM OXIDE

The filtrate from the recovery of manganese is heated to incipient boiling, and oxalic acid is added. The solution is made ammoniacal and is allowed to stand overnight at room temperature. The pre-

cipitate, after it is filtered from the solution, is dissolved in hydro-
chloric acid. The solution obtained is diluted and heated to incipient
boiling. It is then neutralized with ammonia and, after the addi-
tion of oxalic acid, is again made ammoniacal and allowed to stand
until the precipitation of calcium oxalate is complete. The precipi-
tate is filtered from the solution, and the combined filtrates are re-
served for the determination of magnesium.

The paper containing the precipitate is burned off in a weighed
platinum crucible, and the crucible containing the precipitate is
ignited and weighed.

DISCUSSION

In the analysis of most silicates in which a second precipitation
is made separation of calcium from magnesium and the alkalis is
almost complete. Although the separation is as good when the solu-
tion is cold, the precipitation is made from hot solution in order to
obtain a precipitate coarse grained enough to be filterable.

Magnesium oxalate is relatively insoluble, but it forms supersatu-
rated solutions and, therefore, does not precipitate readily. If the
proper technique is used, no magnesium oxalate will precipitate
from 200 ml of solution containing 400 mg of magnesium oxide. In
the first precipitation of calcium after the solution has been made
ammoniacal, heating should be stopped, and the solution should not
be stirred or the bottom of the beaker scratched; the solution should
be allowed to stand overnight but no longer. Magnesium oxalate,
unlike calcium oxalate, precipitates as a film on the inside surface
of the beaker. If such a film is evident, a third precipitation must
be made in order to insure complete separation of calcium from
magnesium.

Ammonium and magnesium salts inhibit and, if the amount of
calcium is low, may even prevent the precipitation of calcium oxa-
late. The following table shows the recoveries obtained in milli-
grams, in analyses in which double precipitations were made and
the initial solutions contained various amounts of calcium and mag-
nesium and amounts of ammonium salts equivalent to those present
in a normal analysis:

MgO taken (mg)	CaO found for indicated amounts of CaO taken (mg)						
	1.0	3.0	5.0	10.0	50.0	100.0	250.0
0	0. 4	2. 7	4. 8	9. 9	50. 0	100. 0	249. 8
10	. 4	2. 7	4. 8	9. 9	50. 0	100. 1	249. 6
50	. 0	2. 2	4. 3	9. 6	49. 8	100. 1	249. 9
100	. 0	2. 2	4. 6	9. 7	50. 0	100. 2	249. 6
300	. 0	2. 5	4. 6	9. 4	49. 8	100. 1	249. 6

The exact recoveries obtained in some cases are the results of compensating errors. A few tenths of a milligram of calcium oxide are always present in the filtrate. The behavior of the calcium that escapes precipitation is discussed under "Magnesium oxide" (p. 34).

Calcium is weighed as the oxide. At the temperature of a Meker burner, calcium carbonate formed by the decomposition of calcium oxalate is readily converted to the oxide. If the standard procedure is followed, there should be no high results due to the reabsorption of either carbon dioxide or water.

If the barium oxide content of the sample is less than one percent, the calcium precipitate will not be contaminated with barium; but in the analysis of an uncommon sample that contains greater amounts, the precipitate should be examined for the presence of barium. Much of the strontium present in the sample coprecipitates with calcium, and if more than trace amounts are present, a correction should be made. The determination of strontium is one of the more complex procedures and should not be attempted by beginners (Groves, 1951, p. 165). Fortunately, strontium-rich samples are rarely submitted for analysis.

Low results are obtained for calcium oxide in the analysis of silicates containing large amounts of fluorine. (See "Silica," p. 26.)

MAGNESIUM OXIDE

Ammonium phosphate is added to the combined filtrates from the calcium determination; the solution is made strongly ammoniacal and is allowed to stand until the precipitation of magnesium is complete. The precipitate is filtered from the solution and dissolved in hydrochloric acid. A small amount of phosphoric acid is added, and magnesium is reprecipitated by making this acid solution ammoniacal. The precipitate is then filtered from the solution.

The paper containing the precipitate is burned off slowly in a weighed platinum crucible containing ammonium nitrate, and the crucible and its contents are ignited and weighed.

DISCUSSION

Magnesium is precipitated as magnesium ammonium phosphate, which when ignited is converted to magnesium pyrophosphate. Unless the conditions of precipitation are carefully controlled, other magnesium phosphates are also obtained, and the mixture forms an ignited precipitate of indefinite composition. Two precipitations are always made: the first under conditions that ensure complete precipitation of magnesium without regard to the composition of the precipitate, and the second under controlled conditions in order to obtain a precipitate having the desired composition.

Because the combined filtrates from the previous determination of calcium contain an accumulation of ammonium salts that retard the precipitation, a large excess of ammonium phosphate is used in the first precipitation of magnesium, and the solution is allowed to stand until the precipitation is complete. No better recovery of magnesium is obtained if ammonium salts are destroyed before the precipitation is made (Hillebrand and others, 1953, p. 133), and this tedious procedure should be avoided. Where large amounts of magnesium are present, precipitation is complete if the solution stands overnight; but for an average amount, it is best to allow the solution to stand for two nights and to stir the solution frequently during the intervening day. If the magnesium oxide content of the sample is a few tenths of a percent or less, the solution should be allowed to stand for a third night, the bottom of the beaker should be scratched, and the solution should be stirred frequently during the intervening days. Under these conditions, as little as one-tenth milligram of magnesium oxide precipitates.

In the second precipitation, which also serves to separate remaining traces of sodium, proper composition of the precipitate is attained by the slow addition of ammonia to a solution containing only a slight excess of phosphate.

If the filter paper is burned too rapidly, the precipitate may be nearly black or may contain a core of unburned carbon. Additional heating does not remove this carbon. By using an electric radiator to burn the paper at a controlled low temperature in the presence of ammonium nitrate, a faintly gray precipitate is obtained that contains negligible amounts of carbon.

As discussed under "Calcium oxide" (p. 32), the oxalate precipitation of calcium is never quite complete, but the amount that escapes precipitation is generally so small that the error in the calcium results may be ignored.

No simple method is known for the recovery of the calcium that escapes precipitation. In the absence of ammonium salts, it coprecipitates with magnesium as calcium phosphate; but if ammonium salts are present, particularly the oxalate, coprecipitation is incomplete. If the amount of magnesium is low, calcium may not precipitate at all. Hillebrand's method (Hillebrand and others, 1953, p. 613), in which calcium is precipitated as calcium sulfate from an alcohol-sulfuric acid solution of the combined phosphate precipitates, is sometimes used to recover calcium. Even if the complete coprecipitation of calcium is ensured by the prior destruction of ammonium salts, this method has little application. If the magnesium content of the sample is low, the amount of calcium that

escapes the oxalate precipitation is so small that no correction is needed. If a magnesium-rich sample contains little calcium, as does dunite, all the calcium escapes the oxalate precipitation, and the problem is to separate about one milligram of calcium oxide from the several hundred milligrams of magnesium oxide contained in the phosphate precipitate. If Hillebrand's method is used, so much 80-percent alcohol is required to keep the magnesium in solution that most of the calcium sulfate also remains in solution. A better alternative, if calcium must be determined, is to make a spectrographic analysis on a portion of the sample.

Strontium, if present, partially coprecipitates with magnesium; nickel, a common constituent of magnesium-rich silicates, does not. Contrary to a statement by Hillebrand and others (1953, p. 640), barium, in the amounts commonly present in silicates, does not coprecipitate with magnesium. For example, 200 mg of magnesium oxide were separated by a double precipitation from a solution containing 10 mg of barium oxide and the amounts of ammonium salts that are normally present in an analysis at this stage. The final precipitate was dissolved in dilute sulfuric acid. No barium sulfate formed.

RECOVERY OF SILICA

The bulk of the ammonium hydroxide group precipitate is transferred to a Vycor crucible and fused with potassium pyrosulfate; the residue in the platinum crucible is fused with a small amount of potassium pyrosulfate. The cooled melts from both crucibles are transferred to a single beaker, where they are dissolved in dilute sulfuric acid. The solution is evaporated to fumes, diluted with water, heated to dissolve the soluble salts, and filtered to remove the silica. The filtrate is caught in a volumetric flask and reserved for the determination of titanium.

The empty platinum crucible is ignited and weighed, and the weight is used in calculating the weight of the ammonium hydroxide group precipitate.

The paper containing the silica is burned off in a platinum crucible and its contents are ignited and weighed both before and after hydrofluorizing silica. The small residue is fused with potassium pyrosulfate, and the cooled melt, which generally contains iron, is reserved for addition to the solution used in the determination of total iron oxide. (See "Total iron oxide," p. 37.)

DISCUSSION

In the initial determination of silica, the temperature of the steam bath is insufficient to completely dehydrate silica, and, even after a

double dehydration, some silica passes into the filtrate used for the determination of the ammonium hydroxide group. The amount not dehydrated increases as the silica content of the sample decreases, but it should not exceed 5 mg; a larger amount indicates that the initial separation of silica was faulty. All but a few tenths of a milligram of silica in the solution coprecipitates with the ammonium hydroxide group, except in rare samples in which the amount of this group is very small.

When the ammonium hydroxide group is fused with potassium pyrosulfate and the cooled melt is dissolved in dilute sulfuric acid, some of the silica dissolves. If the solution is evaporated to fumes, dehydration of the silica is complete. Silica can be filtered from the solution after the sulfuric acid has been diluted and heated to dissolve the salts.

Because dissolved platinum interferes in the subsequent determination of total iron, the bulk of the ammonium hydroxide group precipitate is fused in a Vycor crucible. The short fusion needed to clean the platinum crucible does not dissolve appreciable amounts of platinum.

TITANIUM OXIDE

The filtrate from the recovery of silica, which was caught in a volumetric flask, is diluted to the mark and mixed. A standard titanium peroxide solution is used to adjust the spectrophotometer to the proper wavelength. Then the transmittance of a specific volume of the sample solution is measured, hydrogen peroxide is added, and the transmittance is measured again. Two wavelengths are used: one to measure average amounts of titanium oxide, and the other to measure larger amounts. Suitable tables, which are prepared for each wavelength by measuring the transmittances of standard titanium solutions, are used to determine the titanium oxide content of the sample. The sample solution is reserved for the determination of total iron oxide.

DISCUSSION

Interferences caused by the presence of a faint turbidity or of a colored ion such is iron or chromium are eliminated if the transmittance of the solution is measured before and after the addition of hydrogen peroxide. The amount of titanium oxide equivalent to the transmittance of the unperoxidized solution is subtracted from that equivalent to the transmittance of the peroxidized solution in order to obtain the correct value for titanium oxide.

The foregoing method also eliminates temperature effects. The color intensity due to titanium peroxide in solution changes little

with temperature, but that due to ferric sulfate changes sharply. Because the transmittances of the peroxidized and unperoxidized solutions are always measured at the same room temperature, no error is caused by the presence of iron.

For the color to reach full intensity, the solution must contain at least 5 percent of sulfuric acid, but larger amounts do no harm. Potassium sulfate from the pyrosulfate bleaches the titanium peroxide color slightly, and an equivalent amount of potassium sulfate is therefore added to each solution used in the preparation of transmittance tables.

If the transmittance is measured at about 410 $m\mu$, 1 percent or less of titanium oxide can be measured. If the amount exceeds this figure, it is unnecessary to dilute the solution. Instead, a longer wavelength can be used to increase the range with no change in the relative accuracy.

The 3-percent hydrogen peroxide commonly available deteriorates rapidly and should not be used. Where high concentrations of titanium oxide are measured, the strength of the hydrogen peroxide must be at least 3 percent. Thirty-percent peroxide is very stable, and solutions diluted from it can be depended upon to have the calculated strength. If kept in a tightly sealed bottle, a 6-percent solution can be used for a month, but at the end of this time it should be discarded.

TOTAL IRON OXIDE

The cake from the pyrosulfate fusion made after the recovery of silica is dissolved in the solution that was used for the determination of titanium. This solution is partially neutralized with ammonium hydroxide and is evaporated to reduce its volume and to expel hydrogen peroxide. Potassium dichromate is used to test for the complete removal of hydrogen peroxide. Ammonium chloride is added, and the solution is passed through the silver reductor. The effluent is titrated with potassium dichromate solution; sodium diphenylamine sulfonate is used as the indicator.

DISCUSSION

By convention, the term "total iron oxide" is considered to mean the total amount of iron present in the sample calculated as ferric oxide.

Iron oxide is often a major constituent of the ammonium hydroxide group. Because alumina is determined by difference, accurate values for total iron oxide are essential if accurate results are to be obtained for alumina. The silver reductor method is ideally suited

for the determination of total iron oxide—it is accurate and is substantially free from interference by other elements.

If the reductor is properly prepared, solutions flow through it by gravity. The fine-grained silver prepared by the method of Walden, Hammett, and Edmonds (1934, p. 350) packs so tightly in the reductor tube that the flow rate is extremely slow. Coarse-grained silver prepared by the author's method can be compacted to give a specific, rapid flow rate. For most samples, complete reduction of the iron contained in 100 ml of solution is obtained by means of a 10-cm high column of silver and a flow rate of 60 ml per minute. For uncommon samples containing more than 25 percent of iron oxide, the column does not give complete reduction, and the iron solution is diluted with water before it is passed through the reductor. If the volume of the iron solution is increased, the volume of the effluent collected is increased by a like amount.

Before the solution is passed through the reductor, the acid concentration is reduced by the addition of ammonium hydroxide. Acid stronger than $1N$ attacks the silver, and the hydrogen evolved causes a gas lock. If a gas lock forms, the solution will no longer flow by gravity and the reductor must be emptied and reloaded.

Hydrogen peroxide, if not previously removed, passes through the reductor and reoxidizes ferrous iron in the effluent. Peroxide is readily removed by heating when enough iron is present to catalyze the decomposition of titanium peroxide, but the complete removal of peroxide from titanium-rich solutions containing little iron is difficult. The solution, after its evaporation to a volume of 75 ml, is cooled and tested with potassium dichromate. If the yellow dichromate color fades, peroxide is present, and the solution is further heated and tested at intervals until the color persists.

Chloride ions, which are added as ammonium chloride, must be present in order to precipitate silver ions as they form; otherwise, the reduction of ferric iron is incomplete (Walden and others, 1934, p. 350).

Most of the reduction takes place in the upper part of the silver, and the precipitated silver chloride darkens on exposure to light forming a dark layer. As the reductor is used on successive samples, this layer extends farther down the column; when the upper three-fourths of the silver is dark, the reductor is reloaded.

Few elements interfere. Manganese present is divalent and is not oxidized by potassium dichromate. Titanium is not reduced. Chromium is reduced to the trivalent state and vanadium, to the tetravalent state; neither of these is reoxidized by the dichromate.

Platinum interferes if it is present, but during the separation of

the ammonium hydroxide group by two precipitations with ammonium hydroxide, platinum passes completely into the filtrate. If the pyrosulfate fusion is made in a Vycor crucible, as described under "Recovery of silica," page 36, the solution used for the determination of iron is platinum free.

Copper interferes by catalyzing the oxidation of iron by air present in the effluent. The following table shows the amount of ferric oxide found in the effluent when various amounts of copper were added to copper-free iron solutions containing 225 mg of Fe_2O_3 before the solutions were passed through the reductor.

Cu added (mg)	Fe_2O_3 in effluent (mg)
0.0	0.01
.1	.14
.3	.34
1.0	.58

Two precipitations with ammonium hydroxide do not separate less than milligram amounts of copper from the ammonium hydroxide group, and these amounts, if originally present in the sample, are in the solution used for the determination. No method has been devised to prevent this catalytic action of copper; however, few rocks contain more than 0.02 percent copper (some ultrabasic rocks contain 0.05 percent), and the error due to this amount can be tolerated. A few rocks, such as those taken near an ore body, may contain large amounts. For such rock, copper must be removed by precipitation with hydrogen sulfide before the separation of the ammonium hydroxide group.

FERROUS OXIDE

A 0.5000-gram portion of the sample is transferred to a platinum crucible; a mixture of sulfuric acid and hydrofluoric acid is added; the acids are boiled to dissolve the sample; and the crucible is immersed in a solution containing boric, sulfuric, and phosphoric acids. The final solution is titrated with potassium dichromate; sodium diphenylamine sulfonate is used as the indicator.

DISCUSSION

Because the oxidation of ferrous sulfate in air is strongly catalyzed by hydrofluoric acid (Hillebrand and others, 1953, p. 914), air must be excluded during solution of the sample. If a hot solution formed by adding concentrated sulfuric acid to dilute hydrofluoric acid is transferred to the crucible and brought to a boil quickly, air is displaced by steam and the oxidation of ferrous iron is negli-

gible. It is unnecessary to use methods in which the air is removed before solution of the sample is started, such as the one in which air is displaced with carbon dioxide or the one in which dilute sulfuric acid in the crucible is boiled before the addition of hydrofluoric acid.

The final solution contains phosphoric acid, which reduces the oxidation potential by complexing ferric iron and thus prevents the oxidation of the indicator before the end point of the titration is reached (Kolthoff and Sandell, 1952, p. 579–580). Boric acid prevents the catalytic oxidation effect of hydrofluoric acid by converting it to fluoboric acid (Hillebrand and others, 1953, p. 914). This conversion serves also to minimize the attack by hydrofluoric acid on the glassware used.

Some texts state that the final solution must be air free. Replicate analyses were made by Faye Neuerburg on four samples in which both air-free and air-saturated solutions were used. The following table, giving results in percent of ferrous oxide found, indicates that the use of air-free solutions is unnecessary:

| Analysis | Type of sample | | | |
	Banded magnetite-chlorite	Olivine basalt	Hornblendite	Granite
Air-free solution				
1	20. 52	10. 20	7. 00	1. 80
2	20. 59	10. 19	6. 97	1. 80
3	20. 61	10. 17	6. 95	1. 82
4	20. 65	10. 18	6. 92	1. 80
Average	20. 59	10. 18	6. 96	1. 80
Aerated solution				
1	20. 66	10. 19	7. 02	1. 79
2	20. 68	10. 22	6. 97	1. 84
3	20. 66	10. 16	6. 91	1. 80
4	20. 63	10. 20	6. 94	1. 81
Average	20. 66	10. 19	6. 96	1. 81

Good results are obtained in the analysis of most silicates; but for a few silicates, the method must be modified, and for a few others it is unsatisfactory. In the absence of complications, replicate determinations should agree within 0.1 percent (absolute). Failure to achieve such agreement is caused either by mineral segregation or by incomplete solution of the sample.

Some micas dissolve quickly, and clear solutions of these minerals tend to bump. The first sign of bumping indicates that solution of the mineral is complete, and heating should be discontinued, lest there be a loss.

Finely divided carbon obscures the end point of the titration. If the amount is small, the end point can be seen if a strong light is placed behind the solution; if it is large, the titration can be made electrometrically.

Tramp iron introduced during grinding causes high results, not only because of the additional ferrous iron introduced but also because ferric iron may be reduced by the metal. Where careful hand grinding is used, the error can be tolerated, but enough iron is introduced from steel plates used in mechanical grinders to cause a serious error. If machine grinding is carelessly done, the error is so large that the ferrous oxide determination is worthless.

The decomposition of garnet is seldom complete after a single treatment with the mixed acids. Usually the solution must be decanted from the residue and the residue redigested with a new portion of mixed acid (sometimes several times) to obtain complete solution. The solutions obtained are titrated separately. Fine grinding, which facilitates solution, is not advisable because such treatment oxidizes ferrous iron (Hillebrand and others, 1953, p. 907).

Chromite is not dissolved, and other oxide minerals such as ilmenite and magnetite may be incompletely dissolved if present in large amounts. Complete solution of ilmenite and magnetite may be effected by repeated treatments, as with garnet. Because of the uncertain composition of chromite, a correction for its ferrous iron content based on the amount of chromium present is only approximate.

Siderite dissolves slowly in the mixed acids, and a residue generally remains after the normal digestion period. This mineral occurs in many sedimentary or metamorphic rocks containing finely divided carbon, which obscures the presence of a siderite residue. If a sample is known to contain siderite, the residue should be tested.

Certain silicate minerals that contain ferrous oxide, such as staurolite and tourmaline, are insoluble in the mixed acids. Other methods must be used to determine their ferrous iron content. The Mitscherlich method (Hillebrand and others, 1953, p. 911–912), in which the sample is decomposed by heating it with sulfuric acid in a sealed tube, is not entirely satisfactory. A recent discussion of this method and its modifications is given by Dinnin (1959, p. 56–59). In another method, the sample is decomposed by fusion with sodium

metafluoborate in an inert atmosphere (Groves, 1951, p. 183–186).
Sulfides interfere in both methods.

Because pyrite is not appreciably attacked by the mixed acids, the ferrous iron present in pyrite is not included in the reported value for ferrous oxide but is included in the value for ferric oxide. If pyrite is the only mineral containing sulfur, a correction can be calculated from the sulfur content of the sample.

The method fails if any constituents in the sample are either oxidizing or reducing agents. Some of these are mentioned in the following paragraph. If corrections cannot be made, the analyst should note in his report that the ratio of ferrous oxide to ferric oxide is unreliable.

Pyrrhotite and a few other sulfide minerals are decomposed by the action of the mixed acids, and hydrogen sulfide released may reduce ferric iron. Manganese dioxide will oxidize ferrous iron when the sample is dissolved. Vanadium in the trivalent state reduces ferric iron and in the pentavalent state, oxidizes ferrous iron. Tetravalent vanadium does not react with iron in either of its valences nor is it oxidized by potassium dichromate. Many kinds of organic matter reduce potassium dichromate and consequently result in high results for ferrous iron. Potassium permanganate is a less satisfactory oxidant than is potassium dichromate; because of its high oxidation potential, it reacts with an even greater variety of organic compounds. The determination of ferrous iron in the presence of organic matter is discussed by Nicholls (1960).

THE ALKALIS

A 0.5000-gram portion of the sample is ground to an impalpable powder in an agate mortar and thoroughly mixed with ammonium chloride and calcium carbonate. The mixture is transferred to a special finger-shaped crucible in which it is heated by means of an electric furnace.

The resulting sinter cake is transferred to a beaker. Barium hydroxide is added, the cake is leached with boiling water, and the solution is filtered from the residue. The residue is again leached with boiling water, and a second filtration is made. Alkali earths in the combined filtrates are separated from alkali chlorides by repeated precipitations with ammonium carbonate. Between precipitations and filtrations, the filtrates are evaporated to dryness and ammonium chloride is sublimed before the residue is redissolved in water for the next precipitation. The final filtrate, now free from alkaline earths, is evaporated to dryness in a weighed platinum dish, and the remaining ammonium chloride is sublimed. The alkali

chlorides are heated to incipient fusion; then the dish and its contents are cooled in a desiccator, and weighed.

The chlorides are dissolved in water, transferred to a porcelain dish, and converted to their respective chloroplatinates by adding chloroplatinic acid and evaporating the solution to dryness. Sodium chloroplatinate contained in the mixed salts is dissolved with 80-percent alcohol, and the insoluble potassium chloroplatinate is collected in a weighed, glass filtering crucible. The crucible and its contents are heated in an oven, cooled, and weighed.

The amount of potassium chloride present in the combined chlorides is calculated from the weight of potassium chloroplatinate. The amount of sodium oxide is calculated from the weight of sodium chloride obtained by difference.

DISCUSSION

The method of J. Lawrence Smith (1871, p. 269), as previously outlined, is intended only for the determinations of sodium and potassium oxides. Lithium oxide, if it is present and not determined, is included in the reported sodium oxide; caesium and rubidium oxides, if they are present and not determined, are included in the reported potassium oxide. Gravimetric methods that are given in the literature for the determinations of lithium, caesium, and rubidium are not very satisfactory, and these elements, particularly when they are present in small amounts, are best determined by flame photometric methods.

The success of the Smith method is dependent to a large extent upon the preparation of the mixture before the fusion is made. The sample must be ground to an impalpable powder and then thoroughly mixed with the ammonium chloride and calcium carbonate. If the grinding and mixing are inadequate, the conversion of the alkalis to alkali chlorides is incomplete.

Only the lower part of the crucible containing the charge is heated; the upper part serves as a condenser for alkali chlorides that may volatilize. A low temperature is used at first so that the ammonium chloride can react with the calcium carbonate to form calcium chloride and ammonia; if the temperature is too high, ammonium chloride is volatilized without reacting. When this reaction is complete, the mixture is brought to a high temperature. Calcium carbonate is converted to calcium oxide, and the mixture of calcium oxide and calcium chloride reacts with the silicate to form a sinter cake containing insoluble high-calcium silicates and soluble alkali and alkaline earth chlorides.

When the sinter cake is leached with water, the added barium

hydroxide precipitates any sulfate that is present. Calcium hydroxide, formed by the reaction of calcium oxide and water, precipitates magnesium hydroxide. After filtration, the solution contains only the chlorides of calcium, barium, and the alkalis and a small amount of alkaline earth hydroxides.

The alkaline earth carbonates are somewhat soluble, especially in the presence of ammonium chloride; therefore, repeated precipitations from decreasing volumes of solution are necessary to separate the alkaline earths completely from the alkalis. After each filtration, the filtrates are evaporated to dryness, and the ammonium chloride formed during the neutralization is sublimed before the salts are redissolved in water for the next precipitation. In each precipitation an excess of ammonium hydroxide must be present to prevent the formation of soluble alkaline earth bicarbonates.

In the determination of potassium, enough chloroplatinic acid is added to convert both sodium and potassium chloride to their respective chloroplatinates. Sodium chloride is insoluble in 80-percent alcohol and, if present, would be filtered from the solution with the potassium chloroplatinate. A porcelain dish must be used for the evaporation; platinum would reduce chloroplatinic acid to chloroplatinous acid, which is insoluble in 80-percent alcohol.

It has been stated that the theoretical composition of potassium chloroplatinate is not obtained, and therefore, empirical factors should be used to convert the weight of potassium chloroplatinate to the weights of potassium chloride and potassium oxide. Careful experiments showed that the best average values are obtained by using theoretical factors, although results tend to be slightly low for small amounts of potassium and slightly high for large amounts.

A special problem is entailed in the analysis of a mica. Because of its platy cleavage, a mica cannot be finely ground in an agate mortar, and therefore, a double fusion is made to insure complete decomposition. Without attempting to grind it to an impalpable powder, the mica is carried through the sintering, leaching, and filtering operations. The initial precipitation with ammonium carbonate is made, the solution is filtered, the filtrate is evaporated to dryness, and ammonium chloride is sublimed. The residue from the sinter cake is dried, ground to break up lumps, and mixed with a new portion of ammonium chloride. The mixture is sintered and extracted with water; the solution is filtered. Calcium and barium are also precipitated from this filtrate with ammonium carbonate. The solution is filtered and caught in the dish containing the salts from the first extraction. The balance of the determination is carried out as described in the standard procedure.

MANGANESE AND PHOSPHORUS OXIDES

After its ignition in a platinum dish, a 1.0000-gram portion of the rock powder is treated twice with a mixture of nitric and hydrofluoric acids; after each treatment, the mixed acids are evaporated to dryness. The residue is then taken up with nitric acid, and the acid is evaporated to dryness. The dried salts are dissolved in a mixture of nitric and boric acids; the solution obtained is filtered into a volumetric flask, diluted to the mark with water, and mixed.

Separate portions of the sample solution are used for the determination of manganese and for the determination of phosphorus. Manganese, after its oxidation to permanganate with periodic acid, is determined colorimetrically (Willard and Greathouse, 1917, p. 2366). Phosphorus is precipitated as ammonium phosphomolybdate. The precipitate is dissolved in ammonium hydroxide, and the solution is diluted and acidified with nitric acid. Phosphorus is determined colorimetrically as the yellow vanadium molybdiphosphate complex formed when a vanadate-molybdate reagent is added to this solution (Kitson and Mellon, 1944, p. 379).

DISCUSSION

Soluble organic matter interferes with the determination of manganese by reducing permanganate and with the determination of phosphorus by inhibiting the precipitation of ammonium phosphomolybdate. If the powder is ignited, the organic matter is charred or burned off; any remaining carbon is removed during the filtration of the sample solution. The ignition may be omitted if organic matter is known to be absent.

Both silica and fluorine, if present in too large amounts in the sample solution, interfere with the determination of phosphorus. If the recommended procedure is followed, no more than 600 mg of fluorine nor 40 mg of silica will be present regardless of the composition of the sample, and these amounts can be tolerated. To dissolve the sample, most procedures require a single evaporation with a mixture of hydrofluoric and nitric acids followed by several evaporations with nitric acid alone. R. B. Ellestad of the Lithium Corp. of America (oral communication, 1944) obtained better removal of silica by making two evaporations with the mixed acids. Only one evaporation with nitric acid need be made. Repeated evaporations do not remove enough aditional fluorine or silica to justify the time required.

A 2-hour heating period on the water bath is necessary to dissolve the dried salts in the mixture of nitric and boric acids. If solution is incomplete, the subsequent filtration is slow. The high nitric acid

concentration assures complete solution of titanium phosphate and gives the correct acidity for the determination of both manganese and phosphorus in portions of the filtrate. Boric acid protects glassware from attack by residual hydrofluoric acid.

A residue of minerals insoluble in the hydrofluoric acid-nitric acid mixture will frequently be present in the solution before it is filtered. Chromite, hematite, kyanite, rutile, and graphite are some of these insoluble minerals. Monazite, beryl, tourmaline, staurolite, zircon, garnet, and quartz may be incompletely dissolved.

Although silica is soluble in hydrofluoric acid, quartz dissolves slowly, and in the analysis of rocks containing quartz, a residue usually remains. Phosphorus is most always present as apatite, which is readily soluble, although a few samples contain monazite. If the standard procedure is followed, solution of monazite may be incomplete, and some phosphorus is lost. Dark-colored minerals are very likely to contain manganese, but unless the manganese content of the sample is high and the amount of the insoluble minerals large, the amount of manganese lost is too small to be worth recovering. In the analysis of an iron garnet, which generally contains 2–3 percent of manganese oxide, such a large residue is obtained that the recovery of manganese is mandatory. The light-colored fine-grained residue remaining after decomposition of a titanium-rich metamorphic rock is generally rutile or anatase, which may be discarded without causing an error.

Manganese is oxidized to permanganate generally by boiling it in a 20-percent nitric acid solution containing solid potassium periodate. Because the periodate dissolves slowly, the concentration of periodate ions at the start of the oxidation is low, and hydrated manganese dioxide may precipitate unless a high concentration of nitric acid is present (Willard and Greathouse, 1917, p. 2366). If the periodate is added initially as a solution, such precipitation will not occur, even if the acid concentration is as low as 5 percent. It is convenient to oxidize manganese in a 10-percent acid solution because this concentration is required for the precipitation of ammonium phosphomolybdate from a similar portion of the sample solution. If solid periodate is used, the solution must be boiled to dissolve the periodate, but if a solution of periodate is used, the oxidation may be made by immersing in boiling water a volumetric flask containing the solution. Oxidation is complete, or very nearly so, if the manganese content of the sample is 0.01 percent or higher.

Because it is readily soluble in water, periodic acid is used as the oxidant. Periodate in solution is relatively stable; results obtained

with a year-old solution were identical with those obtained by using a freshly prepared one.

Iron is decolorized by the addition of phosphoric acid and does not interfere with the colorimetric determination of manganese. Chromium does interfere, but, fortunately, it is almost always present in the sample as chromite, one of the minerals that is not dissolved by the hydrofluoric-nitric acid mixture.

Before its determination, phosphorus is separated from diverse ions by precipitating it as ammonium phosphomolybdate. The determination of phosphorus by the direct addition of a vanadate-molybdate reagent to the sample solution is subject to a variety of interferences: colored ions may be present, fluorine decreases the intensity of the color by complexing molybdenum, and silica forms a colored complex with the reagent. Colored ions such as chromium and iron cause a serious error only if the amount of phosphorus is low. For example, the color produced by 40 percent of ferric oxide is equivalent to that of 0.03 percent phosphorus pentoxide.

The precipitation of ammonium phosphomolybdate is inhibited by the presence of fluoride and many other ions. This inhibiting action can be overcome by the addition of a large excess of ammonium molybdate, provided that no more than 200 mg of fluoride are present. Silica coprecipitates from a hot solution as ammonium silico-molybdate, and the mixed precipitate may dissolve incompletely in ammonium hydroxide. On the other hand, ammonium phospho-molybdate precipitated from a cold solution is free from silica, but precipitation may be incomplete. By heating the solution for an optimum length of time, after the addition of the ammonium molyb-date-ammonium nitrate reagent, complete precipitation of phosphorus can be obtained; yet, the amount of silica present in the precipitate is so small that it neither prevents solution of the precipitate nor interferes in the subsequent colorimetry. When only a few hundredths of a percent of phosphorus oxide are present, the bottom of the beaker must be scratched in order to start precipitation. However, as soon as a turbidity is evident, this practice must be stopped, or molybdic oxide will precipitate.

Erratic results are obtained if a combined nitric acid-molybdate-vanadate reagent is added to the ammoniacal solution of ammonium phosphomolybdate or if the ammonium molybdate and ammonium vanadate are added before the solution is acidified. Nitric acid must be added first, but the ammonium molybdate and ammonium vanadate may be added as a combined solution.

If more than 5 mg of phosphorus pentoxide are present in the ammoniacal solution, a precipitate may form when the solution is

acidified; this precipitate does not redissolve upon the addition of the combined reagent. In such an analysis, a smaller portion of the sample solution is used.

Although the color of the vanadium molybdiphosphate complex does not vary appreciably with temperature, the color of the vanadate-molybdate reagent does; therefore, when a few hundredths of a percent of phosphorus pentoxide are determined, variations in room temperature cause significant errors unless a reference solution containing the reagents is used in place of water. Although the color intensities of the reference and standard solutions are stable for at least 1 day, they change slowly, and new solutions should be prepared for each set of determinations.

Special precautions must be taken if a few hundredths of a percent of phosphorus oxide are to be determined accurately. The paper used for filtering the yellow precipitate may contain enough extractable coloring matter to cause an error of 0.005 percent (absolute), and therefore, the paper should be prewashed. Because 5-percent ammonium hydroxide stored in glass bottles absorbs silica, silica-free ammonium hydroxide from polyethylene containers should be used to dissolve the yellow precipitate.

In the analysis of the uncommon sample that is both phosphorus rich and titanium rich, a white precipitate of titanium phosphate forms when the yellow precipitate is dissolved with ammonia, and the filtrate from such a solution may be turbid. The turbidity disappears when the solution is acidified and therefore does no harm, but any of this precipitate retained on the filter contains phosphorus that must be recovered.

At least if the vanadium pentoxide content of the sample is less than 2 percent, vanadium does not interfere with the precipitation nor does it coprecipitate as ammonium vanadomolybdate, but large amounts of vanadium form a soluble vanadium molybdiphosphate complex. Fortunately, silicates containing more than 2 percent of vanadium pentoxide are rarely analyzed.

CARBON DIOXIDE

A 5.000-gram portion of the sample is transferred to the generating flask of the carbon dioxide apparatus (fig. 11). Water is added to form a slurry with the powder, and the water is heated to incipient boiling. A stream of air carries the carbon dioxide liberated by the addition of acid through a series of absorbents that remove interfering substances and finally into weighed absorbers that remove the carbon dioxide.

The apparatus differs somewhat from those commonly used in that acid may be added to the slurry while air is being drawn through the system. This arrangement allows the analyst to control the rate of acid addition so that excessive pressure does not build up in the reaction flask. Fused glass joints between the various parts, except for the necessary ground-glass joints at the generating flask and absorbers, minimize the possibility of leakage. The design also permits the system to be tested for leaks before the analysis is run.

The procedure also differs from that normally used in that the slurry of the sample and water is heated before the addition of acid. Some carbonates, for example siderite, release little if any carbon dioxide when they are treated with acid at room temperature. If all of the acid is added to the cold solution, the violent evolution of carbon dioxide when the solution is heated may cause the solution to back up into the U-tube containing solid reagents.

When air is drawn through the system, it passes first through a column of magnesium perchlorate to dry it and then through a column of sodium hydroxide asbestos to remove the carbon dioxide it contains. When it passes through the generating flask, the air gathers the carbon dioxide that is liberated from the sample, and the combined gases pass through a condenser where much of the water and most of the hydrochloric acid are removed. The air then passes through a sulfuric acid bubbler to remove additional water and through a column of magnesium perchlorate to remove most of the remaining moisture. A layer of copper sulfate absorbs hydrogen sulfide and traces of hydrochloric acid, and another column of magnesium perchlorate absorbs the last trace of moisture. The carbon dioxide is removed as the gas passes through two weighed absorbers, each of which contains layers of sodium hydroxide asbestos and of magnesium perchlorate. Sodium hydroxide asbestos absorbs carbon dioxide; magnesium perchlorate absorbs the water that is released in the reaction between carbon dioxide and sodium hydroxide. All of the carbon dioxide is generally absorbed in the first of the two absorbers; the second serves to indicate when the absorbents in the first are spent. The air, after it leaves the absorbers, passes through a guard tube containing magnesium perchlorate, which prevents entrance of water from the vacuum pump.

A few carbonate minerals release carbon dioxide very slowly when they are boiled with dilute hydrochloric acid. If fine bubbles can be seen rising from the residue after the solution has been boiled for the 2-minute period specified in the procedure, incomplete decomposition of the carbonate is indicated, and the solution should be

boiled until decomposition is complete. Some silicates containing carbonate do not release their carbon dioxide when treated with hot acid, and such silicates must be analyzed by other methods (Borgström, 1914).

Judgment is occasionally needed in selecting the size portion to be used in the analysis. For most silicates, the 5-gram portion specified in the procedure is satisfactory, but if the apparatus is used for the analysis of a carbonate, a 1-gram portion is used. In the analysis of mixed silicate and carbonate rocks in which the carbon dioxide content may be 10 percent or higher, an intermediate-sized portion should be used, otherwise carbon dioxide may be incompletely absorbed.

BARIUM OXIDE

A 1.0000-gram portion of the sample is fused with sodium carbonate and a small amount of potassium nitrate. The cake formed is leached with water containing a little alcohol, and the resulting solution is filtered. If total sulfur is to be determined, the filtrate is reserved.

The residue is washed back into the extraction beaker; water and sulfuric acid are added, and the solution is heated until most of the residue dissolves and barium sulfate is precipitated. The barium sulfate plus any other residue that does not dissolve is filtered from the solution, and the filtrate is discarded. After the paper is burned off in a platinum crucible, the residue is fused with sodium carbonate; the cake is leached with water, and the resulting solution is filtered. The filtrate is discarded. The residue on the paper is dissolved in dilute hydrochloric acid, and barium is precipitated from the solution obtained by the addition of sulfuric acid. The precipitate is filtered from the solution; the paper is burned off in a weighed platinum crucible, and the crucible and its contents are ignited and weighed.

DISCUSSION

After the sample is fused with sodium carbonate, the cake is leached with water, and the solution is filtered. All the alkaline earths remain in the residue as carbonates, and all the sulfate is in the filtrate. Addition of dilute sulfuric acid dissolves most of the residue and precipitates barium sulfate, which is contaminated not only by coprecipitated calcium sulfate but also by the insoluble portions of the residue. To purify the barium sulfate, the residue is separated by filtration and, after the paper is burned off, is fused with sodium carbonate in order to convert sulfates to carbonates. The cake is leached with water, and the resulting solution is filtered in order to separate sodium sulfate from the insoluble carbonates.

The carbonates are dissolved in dilute hydrochloric acid, and barium sulfate is precipitated from the solution by the addition of sulfuric acid.

Strontium oxide is generally present in silicates in far less amounts than barium oxide and does not interfere with the determination of barium. A few samples may contain very large amounts of strontium oxide and little barium oxide. The analysis of such samples gives a final precipitate that consists largely of strontium sulfate, if the foregoing procedure is followed. Barium can be separated from strontium by precipitating it the second time as barium chromate instead of a barium sulfate (Groves, 1951, p. 166).

TOTAL SULFUR

If barium oxide was determined, the reserved filtrate is used for the determination of total sulfur; otherwise, the procedure for barium oxide is followed until such a filtrate is obtained.

This filtrate is diluted and slightly acidified with hydrochloric acid; sulfate is precipitated with barium chloride. The solution is filtered, and the paper containing the precipitate is burned off in a weighed platinum crucible. A drop of sulfuric acid and a few milliliters of hydrofluoric acid are added, and the solution is evaporated to complete dryness. The crucible and its contents are then ignited and weighed.

DISCUSSION

If this procedure is used, sulfur is assumed to be present as sulfides, sulfates, or a mixture of the two. Native sulfur or organic sulfur compounds can be present, but occurrence of either in a silicate is extremely rare.

In the method outlined, sulfur is determined as sulfate regardless of whether it was originally present as a sulfide or sulfate. The fusion with sodium carbonate and potassium nitrate oxidizes sulfides to sulfates. Alkaline-earth sulfates react with sodium carbonate to form alkaline-earth carbonates and sodium sulfate, and all the sulfur originally present is in the filtrate as sulfate.

Some barium sulfate precipitates contain a little silica that precipitates when the filtrate is acidified, and the precipitate is therefore hydrofluorized before it is weighed.

The amount of potassium nitrate specified in the procedure is sufficient to oxidize the sulfides present in most samples. Some samples contain a large amount of pyrite and also organic matter. In such samples, the oxidation of sulfides may not be complete, and sodium sulfide is present in the filtrate. Satisfactory results are generally obtained if the amount of potassium nitrate is increased,

but if the pyrite content of the sample exceeds 2 percent, another method is best used for the analysis (Hillebrand and others, 1953, p. 712–713).

Sulfide sulfur is determined by difference after separate determinations for total sulfur and for sulfur trioxide. In the final summation of the complete analysis, an oxygen correction must be subtracted if sulfides are present in the sample, but such a correction is unsatisfactory unless the type of sulfide is known. Where the amount of sulfide is small, it is best to make a correction equal to one-half the percentage of sulfide sulfur present and to tolerate the small error that results. This correction is nearly right if sulfide is present as pyrrhotite; however, if a large amount of pyrite is present, such a correction will lead to an unsatisfactory summation. To correct for pyritic sulfur, only one-fourth of the percentage of sulfide sulfur should be subtracted as the oxygen correction, and a correction must also be made in the ferrous iron value calculated from the amount of sulfur present as pyrite. (See "Ferrous oxide," p. 42.)

SULFUR TRIOXIDE

Water is added to a 1.0000-gram portion of the sample. The water is boiled, and after hydrochloric acid is added, boiling is continued for an additional 15 minutes. The solution is filtered, and the filtrate is neutralized with ammonium hydroxide and then reacidified with hydrochloric acid. Sulfate ions are precipitated by the addition of barium chloride. The solution is filtered, and the paper containing the precipitate is burned off in a weighed platinum crucible. The crucible and its contents are ignited and weighed.

DISCUSSION

Pyrite and some related minerals do not dissolve in hydrochloric acid. Other sulfide minerals dissolve and liberate hydrogen sulfide, in some reactions, precipitate sulfur. The added water is first boiled to expel air. The hydrochloric acid is added, and hydrogen sulfide, if liberated, is expelled by boiling, without danger of being oxidized to the sulfate. Pyrite and any precipitated sulfur are filtered from the solution.

Without considerable knowledge of the mineralogy of the sample, a reliable analysis for sulfur trioxide cannot be made. Sulfur trioxide is generally present as one or more of the calcium sulfate minerals, which dissolve readily in hydrochloric acid, and if they are the only sulfate minerals present, the analysis is accurate.

Barite and scapolite do not dissolve in hydrochloric acid, and if routine procedures for the determination of sulfur are followed, their

sulfur will be reported as sulfide sulfur. The sulfate in celestite is probably incompletely dissolved.

The sulfate contained in alunite and some related sulfate minerals is only partly extracted by boiling the sample with hydrochloric acid. Alunitic sulfate is almost completely extracted by boiling the sample with 5-percent sodium hydroxide, but this treatment does not dissolve calcium sulfate. If a mixture of alunite and calcium sulfate minerals are present, the sample must be boiled first with sodium hydroxide and then with hydrochloric acid in order to recover all of the sulfate. If the analysis is made by boiling with sodium hydroxide, the solution is filtered, and the filtrate is acidified with hydrochloric acid; the sulfate is precipitated as barium sulfate. Only a few analyses have been made by using this procedure, and how sulfide minerals are affected by treatment with sodium hydroxide is not known.

Although procedures can be planned by which the various sulfates and sulfides can be determined separately, it is rarely advisable to attempt such separations. The total amount of sulfur is generally so small that the errors in the individual determinations would be larger than the sulfur content of a particular mineral. If small amounts of sulfur are present, it is best to determine and report total sulfur and to allow the petrographer to estimate its mineralogical distribution.

STANDARD PROCEDURES

FOREWORD TO THE ANALYST

The beginner should start by analyzing common igneous rocks such as granites and basalts. If he does so, he need be little concerned about the difficulties described in the preceding section. Most igneous rocks can be adequately analyzed by meticulously following the standard procedures. He should make analyses in duplicate until he is satisfied with his precision, although to do so routinely thereafter is too expensive.

If he has not done so, the analyst should take or audit courses in general geology, elementary mineralogy, and petrography. As it will be necessary for him to work closely with geologists, he should learn their terminology.

Best use of time is attained if analyses are made in sets of four—a number that keeps the analyst busy during slow operations such as filtrations. If a larger number of analyses are determined concurrently, the design of special equipment is complex, excessive amounts of platinum are required, and each operation becomes unduly tedious.

In making parallel determinations, special care must be taken to avoid transposition of samples, a common error that causes much loss of time. The analyst should school himself to work systematically. Equipment should be numbered from 1 to 4, and the lowest number in the series kept at the left. Before a transfer is made, the numbers of both the containing and receiving vessels should be checked.

When the main portion is started first, all other determinations in a standard analysis can be completed during waiting periods before this portion is finished; it is therefore often necessary to work on two sets of main portions at the same time. Although an exact routine cannot be prescribed, an order of running the various determinations should be selected to make the best possible use of time and equipment. The total water determination should be made on the day that the main portion is started, because this portion contains most of the major constituents whose values are affected by a change in the water content of the sample.

Precision of a method is measured by the difference between results obtained in replicate determinations by the method; accuracy of a method is measured by the difference between the result obtained and the correct result. Although precise results are not necessarily accurate, lack of precision is a good indication of inaccuracy.

For many problems, geologists are more immediately interested in determining differences among samples in a suite and are therefore more concerned with precision than accuracy. Nevertheless, every analyst should strive for the greatest accuracy practical so that his results will be comparable with other accurate results.

It is difficult to specify values for the precision of a method that apply in all analyses. Further, the analyst should recognize that to stay within rigid limits is not always possible, since he may otherwise spend unjustifiable amounts of time trying to do so. Sometimes differences are caused by factors that he cannot completely control, such as the presence of a troublesome mineral or the marked tendency of a rock powder to segregate. If he does his best at all times, his least precise results will probably be acceptable.

Where there are no complications, determinations made in parallel should be expected to agree within the following percentages (absolute): silica, 0.1; alumina, 0.15; calcium and magnesium oxides, 0.05; sodium oxide, 0.1; potassium oxide, 0.05; total iron oxide, 0.1; ferrous oxide, 0.1; and carbon dioxide, 0.02.

The summation is of far more value to the analyst than to the geologist; consistently good totals assure him that his work is of

generally high quality, and an unsatisfactory summation helps him detect a mistake. If errors were proportional to the amounts of the constituents and were either all plus or all minus, an analysis having a summation of 99 or 101 percent would be satisfactory to the geologist for many purposes. A bad total, however, is almost never the result of such bias; it generally indicates that a gross error has been made in the determination of a single constituent.

Although the summation should be between 99.50 and 100.25 percent if the analyst has determined everything except trace elements, no such variation should occur in replicate analyses of the same sample. Generally, summations for analyses made in parallel agree within 0.2 percent (absolute). Therefore, a summation that is substantially higher or lower than that generally obtained for a specific type of sample is another indication that a mistake has been made in the determination of one constituent.

There are reasons why totals for the same type of sample generally fall within the same range and why those for one type of sample tend to be high and for another type tend to be low. Replicate results for determinations made by a specific method are apt to be predominantly high or predominantly low; they tend to be slightly biased and rarely bracket the true value. Furthermore, in some analyses the absolute error may be proportional to the amount of the constituent present, whereas in others it may be nearly constant. In the analysis of a given constituent, results obtained by two equally accurate methods may show trends in opposite directions; therefore, the statements in the following paragraph apply only to analyses made by the methods described in this bulletin.

In general, highly acidic silicates tend to have low totals, and highly basic ones tend to have high totals. Samples having a large number of major constituents are more apt to have totals close to 100 percent than ones having only a few because errors tend to cancel each other. Therefore, summations for basalts are generally between 99.9 and 100.1 percent. A summation of 100.25 percent obtained on a granite or even a basalt should be viewed with suspicion, whereas a similar total is normal for a magnesium-rich olivine.

Unsatisfactorily high totals are generally the result of slovenly work, such as the incomplete washing of precipitates, the failure to ignite precipitates to their equilibrium weights, and the introduction of extraneous material through failure to keep vessels covered. If the Globar furnace is used as directed, high totals are not obtained because of failure to achieve the equilibrium weights of the silica and ammonium hydroxide group precipitates, but if Meker burners are used for the ignitions, these weights are apt to be high. Samples

may also have high totals for the following reasons: the retention of manganese oxide by the ammonium hydroxide group precipitate in the analysis of manganiferous samples; the incomplete recovery of ferrous iron from slowly soluble or insoluble minerals such as iron garnet and staurolite; and the retention of sodium chloride by the ammonium hydroxide group precipitate in the analysis of aluminum-rich samples.

In general, results obtained by the methods of this bulletin tend to be slightly low; totals predominantly below 100 percent should therefore be expected. If the analyst is careless, as by making an incomplete transfer of a precipitate, this tendency is aggravated, and he will be plagued by unacceptably low totals. A low total obtained after careful work has been done may be due to: the presence of an uncommon mineral containing a constituent that has not been determined; or the loss of silica, as silicon fluoride, from samples containing amounts of fluorine; or the presence of sulfate which has been reported as sulfide. Where spectrographic services are available, the presence of many uncommon elements can be quickly detected. Some elements that cannot be so detected are chlorine, fluorine, and sulfur.

A mistake in the determination of a single constituent that causes an unsatisfactory summation is difficult to correct. If the analyst attempts to guess the source of error, he usually guesses wrong and wastes time by making piecemeal determinations. It is best to start a completely new analysis and to continue with it, at least until the mistake is discovered.

The limits given for an acceptable summation are intended to be used as a guide. In spite of the length of time that conventional methods have been used and the amount of research that has been done to test them, summations on some kinds of samples are routinely outside these limits. A specific example is the analysis of a siliceous volcanic ash having a high water content. This material commonly has a total as low as 99.30 percent and has nearly the same total if the analysis is repeated. Although the cause of such a total could doubtless be determined by research, attempts to find the cause by superficial tests are usually futile. When the tendency for a specific type of sample to have totals somewhat higher or lower than the accepted limits has been established, it is best to tolerate the total obtained and to postpone research until time is available to conduct a thorough investigation.

If the analyst is unable to determine certain constituents, or to make the necessary oxygen corrections, it is best to omit the total, which can only confuse the geologist. Thus, for a sample containing

both pyrite and pyrrhotite, neither a satisfactory determination for ferrous iron nor an oxygen correction for the sulfur present can be made. Accordingly, all iron should be reported as ferric oxide, the total should be omitted, and the reasons for so doing should be made part of the report.

Sometimes the analyst may justifiably be unable to make a satisfactory determination for a certain constituent, but there is no excuse for his failure to advise the geologist of the fact. Furthermore, if he knows in advance that a determination cannot be made—such as the determination of ferrous iron in the presence of pyrolusite or psilomelane—he should say so firmly. He can do the geologist no greater disservice than to supply him with inaccurate data—no information is better than bad information.

GENERAL INSTRUCTIONS

WEIGHING

An analytical balance having a notched beam and chain is adequate for general use. It should have a capacity of 200 grams and a sensitivity of 0.05 mg; the vernier should read to 0.1 mg. Not enough weighing is done to justify the additional cost of a single pan balance; furthermore, this type is not very satisfactory for some purposes, for example, the determination of specific gravity. (An excellent discussion of balances and weighing is given by Kolthoff and Sandell, 1952, p. 203–207.)

Use of the single deflection method of weighing is advantageous (Brinton, 1919). It is rapid and as accurate in practice as other common methods. Because of its speed, its use is especially advantageous when hygroscopic materials are weighed.

In the single deflection method, the right arm of the balance is made slightly lighter than the left by turning an adjusting nut on the beam. The pan rest button is pressed and released two or three times to center the pans, otherwise a motion may be imparted to them when they are released. The beam is lowered, the pans are quickly released, and the maximum deflection of the pointer is noted. The pointer should start from a dead stop and swing smoothly to the right; if it does not do so, the pan rests are adjusted so that they release evently. If necessary, the weight of the right arm is readjusted so that the deflection of the pointer is from 3 to 7 divisions, and the new deflection point is noted. Now the weight on the right arm is increased by 0.2 mg, and the deflection point is again observed. It should be one division less than before; if not, the bobbin on the pointer is adjusted so that a deflection of one division is equivalent to 0.2 mg. To make a weighing, the pan rest button is

pressed and released two or three times, the beam is lowered, the pans are released quickly, and the deflection point is noted. The object to be weighed is placed on the left-hand pan and the procedure is repeated until the weights have been adjusted to give the original deflection.

When a check weighing is made after reheating, particularly of a hygroscopic material, the weight found in the first weighing is put on the balance. The material to be weighed is then transferred to the left-hand pan, and the weight is determined by a single swing. The change in weight, if small, is estimated from the difference in the pointer deflection.

The balance should be checked occasionally against an accurate set of weights. Although minor adjustments such as resetting the pan rests or the chain can be made by the analyst, major repairs should be undertaken only by an expert.

COLORIMETRY

Although the colorimetric methods described in the following procedures are based on the use of a Beckman Model B spectrophotometer, any similar instrument can be used. It must have a stable electronic circuit, a dark current adjustment, and a tube carrier. An electronic voltage regulator is used to obtain adequate stability.

Because tubes presently available for the Model B instrument do not have enough volume for the determination of titanium, Leitz 1-cm X 1-cm tubes are used after they have been cut to a length of 8 cm and calibrated with 5-ml marks. When the Beckman instrument is used, a reinforcing vane is removed from the tube compartment cover so that these longer tubes will fit into the compartment.

To save time and to avoid calculations that might introduce errors, a system of colorimetry is employed in which percentages are read directly from transmittance tables. Use of this system requires reproducible readings for a given concentration, and a standard solution is therefore used to set the instrument before a measurement is made. A transmittance of 20.0 percent is arbitrarily selected as the lower limit of measurement, and the instrument is adjusted so that a standard solution reads 20.0 percent when the reference solution reads 100.0 percent. If the transmittance curve is a straight line, or nearly so, readings for intermediate concentrations will then be reproducible.

Most spectrophotometers have a multiplying arrangement in the mechanism for setting the wavelengths. Because of play in this mechanism, different wavelengths can be obtained for the same dial setting; therefore, a standard solution may give different readings

for the same apparent wavelength. The standard can be set to a reading of 20.0 percent by changing the wavelength, but to do so exactly is difficult. A final adjustment—and this adjustment must be small or an error will result—is made by varying the dark current.

Since transmittances of titanium peroxide solutions deviate slightly from Beer's law, tables are constructed from closely spaced calibration points. (See "Preparation of apparatus and reagents," p. 84.) Even where transmittances of other solutions obey Beer's law, it is advisable to construct tables from calibration points to correct for possible nonlinearity of the instrument.

Wavelengths for each element were selected to permit measurement of an optimum range of concentrations which is a range that gives adequate sensitivity where small amounts are determined and which is so wide that most samples can be analyzed by one procedure. If larger amounts must be measured, a longer wavelength is used in conjunction with a more concentrated standard.

ELECTRIC RADIATOR

The temperature of the electric radiator is controlled by varying the voltage across the elements by means of an autotransformer. Line voltage is sufficiently constant to give adequate reproducibility. The voltage settings given in the procedures are based on an average line voltage of 115 volts. If the radiator is operated at a different voltage, suitable changes must be made in these settings.

GLOBAR FURNACE

The power input to the Globar furnace is regulated by a variable transformer that is in series with a tap transformer (pl. 1). Because the resistances of the heating elements increase with use, the voltage across them must be increased periodically by means of the tap transformer. Since the power input may vary for the same setting of the autotransformer, the input is determined by the amperage at line voltage.

At 1,100° to 1,200°C, the furnace has a temperature gradient of about 100°C between the tip of the thermocouple and a precipitate within a platinum crucible. The pyrometer is therefore adjusted by means of a variable resistance so it reads 1,150°C when the temperature within the crucible is 1,150°C. If this adjustment is made, the critical temperatures for the ignition of the silica and ammonium hydroxide group precipitates, 1,200°C and 1,100°C, respectively, are correctly given by the reading of the pyrometer. The other temperatures specified in the procedures are the readings of a pyrometer that has been so adjusted. The temperature given for a sodium

carbonate fusion is not the temperature of the charge within the crucible.

Elements must have matched resistances; otherwise, the furnace will heat unevenly. If an element has a hot spot or burns out, all of the elements must be replaced by a matched set. Used Globar elements can be matched and reused.

SAMPLE PREPARATION

1. Using an agate mortar, grind minerals, with the exception of micas and a few others that cannot be ground by attrition, to pass a 100-mesh sieve.

2. If a rock sample is large, reduce it to particles having a maximum size of about one-half inch by passing it through a jaw crusher; then by means of a sample splitter (fig. 9), halve the sample and reject one of the portions. Continue to halve the sample and reject portions, if necessary, until about 2,000 grams of material remains. If a sample is a hand specimen weighing only a few pounds, break it on a hardened steel plate into pieces having maximum dimensions of 1 inch by blows from a hammer.

3. Transfer the sample to a sieve having a quarter-inch mesh screen, and crush the oversize with a Plattner (diamond) mortar until all the sample passes the sieve. In using the mortar, strike straight down on the pestle so that iron will not be gouged from the mortar sleeve. Do not rotate the pestle between blows.

4. Reduce the amount of sample by halving and rejecting portions until about 200 grams of material remains, and transfer the sample to a 10-mesh sieve. Using a Plattner mortar, crush the oversize until all the sample passes the sieve.

5. Reduce the amount of sample until between 25 and 35 grams remains. Store the rejected part of this portion in a 4-ounce bottle for possible future use.

6. Transfer the sample to a 60-mesh sieve, and crush the oversize with the Plattner mortar until all the material passes this sieve.

7. Screen the sample on a 100-mesh silk sieve, and grind the oversize in an agate mortar. To avoid excessive grinding by attrition and the formation of too much fine material, alternately grind and sieve the oversize until it all passes the sieve.

8. Transfer the sample to the powder mixer (fig. 10), and let the sample mix for 10 minutes. Open the mixer, brush loose material from the cover into the mixing chamber, and remove the chamber from the wooden support. Lay a sheet of paper and a board over the mixing chamber; then invert the chamber and board together so that the powder falls on the paper. Brush the small amount of powder left in the mixer onto the paper.

9. Roll the powder into a pile by folding in the corners of the paper; then, using a spatula, transfer small portions of the powder from four sides of the pile to a glass vial. Again roll the powder into a pile, and transfer four more portions. Continue in this manner until most of the material is transferred or until the vial is almost full. Discard the remaining material; do not pour it into the vial. Keep the vial upright and place it in the balance room.

TOTAL WATER

1. Lay a Penfield tube (see "Preparation of apparatus and reagents," p. 83) with its open end up on a steel rack (fig. 13C), and heat the tube and rack for at least 2 hours in an oven having a temperature of at least 110°C.
2. Place 3 grams of lead oxide-lead chromate flux and a 1.0000-gram portion of the sample in a porcelain crucible, and mix with a glass rod. Using a long-stemmed funnel (fig. 13A), transfer this mixture to the bulb of a Penfield tube, and brush any remaining powder into the funnel. Brush down the inside of the funnel, lift the funnel slightly, tap it with a policeman, and withdraw it from the tube. Close the tube with a capillary stopper.
3. Carefully lower the tube to a horizontal position. Tap the bulb as the tube is tipped so that the powder will settle to the bottom of the bulb and will not fall into the tube. Thereafter, keep the tube horizontal except where otherwise noted. Starting about 4 cm from the bulb, wrap a strip of damp cloth spirally around the tube and away from the bulb until a 16-cm section of the tube is covered. Insert the bulb of the tube into the special electric furnace illustrated in figure 12.
4. Set the variable transformer so that the furnace temperature rises to 900°C in 20 minutes (about 85 volts). When this temperature is reached, rotate the tube one-half turn, and maintain this temperature for 30 minutes. Keep the cloth wet throughout the heating period.
5. Lay the tube on a suitable jig (fig. 13B), and while rotating the tube, heat the juncture of the tube and bulb with a gas-oxygen torch until the bulb sags. Stop rotating the tube, pull off the bulb with a pair of iron tongs, and heat the sealed end of the tube for a few seconds to round off the sharp tip.
6. Let the tube cool, unwrap the cloth, and blot the water from the outside of the tube with a towel. If the sample is carbon dioxide free, omit step 7. Let the stoppered tube stand in the balance room for 30 minutes, remove the stopper, weigh the tube, and proceed to step 8. If the sample contains carbon dioxide, proceed to step 7.
7. Remove the capillary stopper, and connect the open end of the tube to a glass bulb containing water (fig. 13D). After 2 hours, disconnect the tube from the bulb and weigh.
8. Place the tube on the steel rack with its open end up, and heat the tube and rack for 2 hours in an oven having a temperature of at least 110°C. Let the tube cool for 30 minutes and weigh it.
9. Calculations:

Loss in weight of tube during drying × 100 = percent total water.

Percent total water—percent moisture = percent combined water.

MOISTURE (H_2O-)

1. Sand a 25-ml platinum crucible inside and outside until it is highly polished and its surface shows no evidence of crystallized platinum. Shape the crucible so that the top edge is round and the bottom is flat. Ignite it over a Meker burner. Let it cool below red heat; place it in a desiccator for 30 minutes, and weigh it.
2. Transfer a 1.0000-gram portion of the sample to the crucible. Reweigh the crucible, and heat the uncovered crucible and its contents for 1 hour in

an oven having a temperature of 105 $\pm$ 5°C. Place the covered crucible in a desiccator for 30 minutes; then weigh it. Reserve the powder for the determination of silica.

3. Calculation:

$$\text{Loss in weight} \times 100 = \text{percent moisture.}$$

SILICA

1. Heat the crucible containing the powder used for the determination of moisture over a Tirrill burner. Start with a small flame and gradually increase the flame until the bottom of the crucible is just red. Partially open the crucible, and continue heating it for 5 minutes.

2. Let the crucible cool. Add one-fourth of a 5-gram portion of sodium carbonate, and mix this carbonate and the rock powder using a glass rod. Add two more like portions of sodium carbonate, and mix after each addition. Tap the rod on the inside of the crucible, and then rub it in the remainder of the sodium carbonate. Add the rest of the sodium carbonate, and tap the crucible gently to spread this sodium carbonate over the mixture.

3. Place a ceramic adapter (fig. 3) in one of the holes of the Globar furnace, and set the covered crucible in the adapter. Adjust the current input to 19 amperes, and let the furnace heat for 15 minutes. Increase the input 2 amperes, let the furnace temperature rise to 1,075°C, and maintain this temperature for 20 minutes. Sometime during this 20-minute period (without removing the cover from the crucible) heat the crucible cover with a Tirrill burner for about 1 minute. Lay the cover upside down on a silica triangle. Then with a pair of platinum-shod tongs, grasp the crucible at its edge, remove it from the furnace, and, if the melt is fluid enough to do so, roll the crucible to spread the melt around the inside of it. Set the crucible on a silica triangle, replace the cover, and let the crucible cool. Heat the crucible over a Meker burner for 30 seconds; then let it cool again.

4. Cover the cake with water from a wash bottle. With the aid of a stirring rod, loosen the cake, and transfer it to a 300-ml semiround-bottom platinum dish. Wash the inside of the crucible, and catch the washings in the dish, but do not attempt to dislodge firmly adhering material. Wipe the outside of the crucible, and set it aside. Add 75 ml of water and a few milliliters of alcohol to the dish; then wash off the glass rod, and remove it. Let the solution stand overnight.

5. Pulverize the cake with a glass rod, and stir the solution. Insert the tip of a curved-stem funnel between the lip of the dish and the watch glass. Pour 25 ml of hydrochloric acid into a graduate, and add about 5 ml of this acid to the crucible. Pour the remainder of the acid through the funnel in portions small enough to avoid violent effervescence. Hold the crucible cover over the funnel and wash it with water; rub it with a policeman that has been dipped into the acid contained in the crucible, and again wash it with water. Dry the cover, and set it aside. Scrub the inside of the crucible with a policeman. Transfer the acid to the funnel; wash the policeman and the inside of the crucible with water, and catch the washings in the funnel. Finally, wash the inside of the funnel and the outside of the funnel tip, and remove the funnel from the dish.

6. Let the dish stand until most of the effervescence stops. Wash the underside of the cover glass; transfer the dish to the water bath, and cover it quickly. When no more carbon dioxide is evolved, wash the underside of the cover glass, and replace it on the dish with a triangle under it. Let the solution evaporate to dryness. Stir the residue as the solution goes dry.

7. While the solution is evaporating, ignite the crucible. Cool it in a desiccator for 30 minutes, and weigh it.

8. Add 50 ml of 1-to-4 hydrochloric acid to the dish; cover the dish, and heat the solution for 30 minutes. Sometime during this 30-minute period, sluice the salts on the inside of the dish into the solution using 1-to-19 hydrochloric acid, and stir the solution until the gritty crystals of sodium chloride dissolve.

9. Decant the solution through a 9-cm coarse-porosity paper into a 250-ml beaker. Wash the residue once with hot 1-to-19 hydrochloric acid. Stir the solution, and pour it quickly into the filter so that most of the silica is carried into the filter. Wash the rod with 1-to-19 hydrochloric acid, scrub it with a policeman, wash it again, and place it in the beaker. Police the inside of the dish, and pour the wash solution into the paper. Wash the dish twice more with 1-to-19 hydrochloric acid, and scrub the inside of the dish with a policeman each time before transferring the wash to the filter; then wash off the policeman into the filter, and lay it aside. Wash the precipitate 15 times with hot 1-to-19 hydrochloric acid. Cover the precipitate each time, and allow the solution to drain before the next wash is added. Lift the paper to drain the funnel stem.

10. Transfer the filtrate quantitatively to the platinum dish. Place the dish on the water bath, cover the dish with a raised watch glass, and evaporate the solution to dryness. Stir the residue as the solution goes dry; then continue heating the dry residue for 1 hour.

11. Add 50 ml of 1-to-4 hydrochloric acid, and heat the solution for 30 minutes on the water bath. During this 30-minute period, wash the salts on the inside of the dish into the solution with 1-to-19 hydrochloric acid, and stir the solution until crystals of sodium chloride dissolve.

12. Filter the solution through a 7-cm coarse-porosity paper into a 400-ml beaker. Wash the stirring rod with 1-to-19 hydrochloric acid, scrub it with a policeman, wash it again, and lay it aside. Police the inside of the dish, and transfer the wash solution to the filter. Wash the inside of the dish twice more. Police the dish, and transfer the solution to the filter after each wash. Wash off the policeman into the filter, and lay it aside. Let the filter drain; then hold the dish over the filter, completely wash the inside surface of the dish, and sluice any remaining silica into the filter. Wash the precipitate on the paper 10 times with hot 1-to-19 hydrochloric acid.

13. Fold the two papers containing the silica and lay them side by side in the crucible. Transfer the crucible to the radiator (ceramic ring adapter, fig. 4). Set the transformer at 90 volts, open the crucible cover, and heat the crucible until only a little carbon is left on top of the silica precipitate. Advance the potential to 125 volts, and continue heating until the silica is white. If step 14 cannot be performed at once, place the crucible in a desiccator.

14. Turn on the Globar furnace (19 amperes), and let it heat to 1,200°C. Heat the covered crucible containing the silica over a Meker burner for 30

minutes; then transfer the uncovered crucible to the Globar furnace, and heat it for 1 hour at 1,200°C. Set the crucible on a silica triangle, cover the crucible, transfer it to a desiccator, and weigh it after 30 minutes. Reheat the crucible in the furnace for 30 minutes, cool the crucible in a desiccator, and reweigh it. If the weighings do not agree within 0.2 mg, heat for 30 minutes, cool, and reweigh the crucible, repeatedly if necessary, until consecutive weights agree within 0.2 mg.

15. Moisten the silica with 1 ml of water; then add six drops of 1-to-1 sulfuric acid and 10 ml of hydrofluoric acid. Heat the covered crucible on the electric radiator (fig. 4) at 65 volts until everything is in solution. Partially open the crucible. Advance the potential to 85 volts, and evaporate the solution until fumes of sulfuric acid appear. Increase the potential to 110 volts, and continue heating until no more fumes can be seen. Heat the crucible over a Meker burner for 5 minutes with the cover open. Cool the crucible in a desiccator for one-half hour, and weigh it.

16. Reserve the crucible and its contents for the ignition of the ammonium hydroxide group.

17. Calculations:

Loss in weight during hydrofluorization $\times$ 100 $+$ percent SiO_2 recovered from R_2O_3 group $=$ percent SiO_2.

AMMONIUM HYDROXIDE GROUP

1. Dilute the filtrate from the determination of silica to 200 ml. Stir in 5 ml of ammonium hydroxide, and continue stirring until any precipitate that forms dissolves.

2. If the color of the solution is between light amber and colorless, add five drops of brom cresol purple indicator; then, while stirring the solution, add ammonium hydroxide to it—rapidly at first until a precipitate forms and then dropwise until the solution turns purple. If the solution has a dark amber color do not add the indicator. Add ammonium hydroxide rapidly until a brown precipitate forms and then by drops until the solution is neutral. Test for completeness of neutralization during the dropwise addition of ammonium hydroxide by stirring the solution and adding a drop of indicator to the solution as it swirls. If the spot of indicator turns brown or disappears completely, the solution is acid; if the spot remains purple, the end point has been reached.

3. Add two drops of 1-to-1 hydrochloric acid and 0.5 gram of dry dispersed paper pulp, and stir the solution. Cover the beaker. Bring the solution to a full boil over a Tirrill burner, turn off the burner, and let the beaker stand until boiling stops.

4. Wash the underside of the cover glass and lay the glass aside. Add one drop of ammonium hydroxide to the solution; stir the solution, and let the precipitate settle somewhat. If the supernatant liquid is purple, neutralization is complete. If it is not, repeat the procedure as often as necessary until the solution is purple.

5. Filter the solution through a 12.5-cm medium-porosity paper into a 600-ml beaker. Fill the paper only to the level that the precipitate and paper pulp are expected to occupy. Wash the inside of the beaker twice with a hot 2-percent solution of ammonium nitrate, and transfer the washings to the filter.

6. Direct a stream of the hot wash solution against the inside of the funnel above the paper, and wash slowly around the funnel 10 times. Let the solution drain; then wash the precipitate four times. Cover the precipitate with wash solution each time, and allow the solution to drain before the addition of the next wash.

7. Hold the funnel over the beaker in which the precipitation was made. Loosen the precipitate from the paper with a stirring rod; then transfer the precipitate to the beaker with a stream of ammonium nitrate solution. Wash off the edge of the funnel to remove any precipitate clinging to it; then invert the funnel, and wash the under edge. Return the funnel to the rack.

8. Adjust the volume of the solution in the precipitation beaker to 150 ml. Add 5 ml of hydrochloric acid; stir the solution, and heat it over a Tirrill burner until the precipitate dissolves. Neutralize the solution with ammonium hydroxide as before. When the neutral point is reached, add one more drop of ammonium hydroxide; stir the solution, and bring it to a full boil over a Tirrill burner. Turn off the burner, and let the solution stand until boiling stops.

9. Wash the underside of the cover glass, and let the precipitate settle somewhat. If the supernatant liquid is purple, proceed to step 10; if it is not, add ammonium hydroxide by drops, and inspect the liquid after each addition until the solution is purple.

10. Filter the solution through the original paper into the beaker containing the first filtrate. Wash the inside of the beaker once with a hot 2-percent ammonium nitrate solution. Swirl the beaker, and transfer the wash quickly to the filter so that most of the remaining precipitate will be transferred with it. Wash the stirring rod with ammonium nitrate solution, scrub it with a policeman, wash it again, and lay it aside. Scrub the inside of the beaker with a policeman, and pour the wash into the filter. Lay the policeman aside, and sluice any remaining precipitate into the filter.

11. Wash the inside of the beaker with 1-to-19 hydrochloric acid. Heat the solution on the water bath for 5 minutes; then police the inside of the beaker with the hot acid. Wash off the policeman, and lay it aside; wash down the inside of the beaker with water. Add one drop of brom cresol purple indicator and, as the beaker is swirled, add ammonium hydroxide dropwise until the solution turns purple. Heat the solution for 5 minutes on the water bath; then pour the solution into the filter, and sluice the remaining precipitate into the filter with a stream of hot ammonium nitrate wash solution. Wipe the lip of the beaker with a piece of damp filter paper, and place this paper into the filter.

12. Direct a stream of hot wash solution against the inside of the funnel above the paper, and wash slowly around the funnel 10 times. Let the paper drain; then wash the precipitate nine more times. Cover the precipitate with wash solution each time, and allow the solution to drain before addition of the next wash. Drain the funnel stem.

13. Cover the funnel with a filter paper. Lay a glass triangle on the paper to hold it in place, and let the precipitate stand overnight to partially dry it.

14. Add 1 ml of 1-to-1 hydrochloric acid to the combined filtrates, and evaporate them to a volume of 200 ml. Just neutralize the solution with ammonium hydroxide, and heat it below the boiling temperature for

15 minutes. If no precipitate is evident, reserve the solution for the next operation, the removal of manganese. If a precipitate is present, proceed to step 15.

15. Filter the solution through a 9-cm medium-porosity paper. Wash the beaker three times with hot 2-percent ammonium nitrate solution, and transfer the washings to the filter. Wash the paper 10 times with the same solution. Fold the paper, and place it in the funnel containing the main part of the ammonium hydroxide group precipitate. Reserve the filtrate for the next operation, the removal of manganese.

16. Without folding it, place the paper in the crucible containing the residue that was left after hydrofluorizing silica. Wipe the inside of the funnel with a piece of damp filter paper, and place it in the paper containing the precipitate. Fold in the sides of the paper, starting with the thin nest part, until it is pleated enough to fall into the crucible; then fold over the triple thickness, and push the paper down into the crucible.

17. Heat the partially opened crucible on the electric radiator set at 80 volts until the paper smokes. Increase the potential to 90 volts, and continue heating until all of the carbon except a little at the top of the precipitate is burned off; then set the transformer at 125 volts, and continue heating until all of the carbon disappears.

18. Preheat the Globar furnace to 1,100°C; then heat the uncovered crucible containing the precipitate in the furnace for 30 minutes. Remove the crucible, set it on a silica triangle, cover it, and transfer it to a desiccator. Weigh the crucible after 30 minutes. Repeat the heating, cooling, and weighing until consecutive results agree within 0.2 mg. Reserve the precipitate for operation 19, the recovery of silica.

19. Calculations:

$$\text{Weight } R_2O_3 \times 100 = \text{percent } R_2O_3.$$

$$\text{Percent } R_2O_3 - (\text{percent recovered } SiO_2 + \text{percent total } Fe_2O_3 +$$

$$\text{percent } TiO_2 + \text{percent } P_2O_5) = \text{percent } Al_2O_3.$$

REMOVAL OF MANGANESE

1. Acidify the solution reserved after the separation of the ammonium hydroxide group with 1-to-1 hydrochloric acid, and evaporate it to a volume of 100 ml.

2. Add 1 ml of a 5-percent zirconyl chloride solution and 0.1 gram of dry dispersed paper pulp. Make the solution ammoniacal and then just acid with 1-to-1 hydrochloric acid. Add 1 gram of ammonium persulfate. Stir the solution, and heat it for 20 minutes on the water bath. Add 1 ml of ammonium hydroxide, and continue heating the solution for an additional 5 minutes.

3. Stir the solution, and filter it at once through a 7-cm coarse-porosity paper into a 400-ml beaker. Wash the inside of the precipitation beaker three times with a hot 2-percent ammonium nitrate solution, and transfer the washings to the filter. Wash the precipitate on the paper 10 times with the same solution.

4. Discard the precipitate, and reserve the filtrate for the determination of calcium.

5. Clean the glassware used for this determination with a dilute acid solution containing hydrogen peroxide.

CALCIUM OXIDE

1. Heat the solution that was reserved after the removal of manganese to incipient boiling. Add 30 ml of 10-percent oxalic acid solution—rapidly at first, then slowly if a precipitate forms. Add 2 ml of ammonium hydroxide by drops to the solution while stirring; then add 5 drops of brom cresol purple indicator. Continue adding ammonium hydroxide by drops while stirring the solution until the indicator turns purple. Add 1 ml of ammonium hydroxide. Stir the solution, remove it from the burner, and let it stand at room temperature overnight.

2. Filter the solution through a 9-cm fine-porosity paper into a 600-ml beaker. Retain as much of the precipitate as possible in the beaker. Wash down the inside of the precipitation beaker with 0.1-percent ammonium oxalate solution, and transfer the wash to the filter. Wash the paper three times with the same solution; then fold back the paper to drain the funnel stem. Replace the beaker containing the filtrate with a 150-ml beaker. Reserve the filtrate.

3. Wash the inside of the precipitation beaker with hot 1-to-19 hydrochloric acid. Heat the solution in the beaker over a small flame, and if necessary, add 1-to-1 hydrochloric acid to bring the precipitate into solution. Pour the solution through the filter. Wash the inside of the beaker three times with hot 1-to-19 hydrochloric acid, and transfer the washings to the filter. If calcium oxalate can be seen on the paper, dissolve this precipitate with small portions of hot hydrochloric acid from the wash bottle. When no more precipitate is visible, wash the paper five times with the hot acid and five times with water. Discard the paper.

4. Dilute the solution in the 150-ml beaker to 90 ml. Add 2 drops of brom cresol purple indicator, and heat the solution to incipient boiling. Add ammonium hydroxide by drops while stirring the solution until the indicator turns purple. Add 10 ml of 10-percent oxalic acid solution and again neutralize the solution by the dropwise addition of ammonium hydroxide. Add 1 ml of ammonium hydroxide in excess. Remove the solution from the burner, and let it stand for at least 4 hours. (If the calcium oxide content of the sample exceeds 20 percent, make the second precipitation from a volume of 200 ml, and use a 9-cm paper for the subsequent filtration.)

5. Filter the solution through a 7-cm fine-porosity paper into the beaker containing the first filtrate. Wash the beaker with 0.1-percent solution of ammonium oxalate, and transfer the wash to the filter. Scrub the stirring rod with a policeman; wash the rod, and lay it aside. Scrub the inside of the beaker with a policeman, and pour the wash solution in the filter. Lay the policeman aside, and sluice the inside of the beaker with a stream of liquid from the wash bottle in order to transfer loose precipitate to the filter. Again wash the beaker, and police it; transfer the wash to the filter, and sluice the beaker. Wash off the policeman into the filter. Then wash the precipitate on the paper five times with the oxalate wash solution. Lift the paper to drain the funnel stem. Reserve the combined filtrates for the determination of magnesium.

6. Fold the paper, and place it in the platinum crucible that was weighed after the ammonium hydroxide precipitate was removed from it. (See "Recovery of silica," p. 69. Wipe the inside of the funnel with a piece of damp filter paper, and place the paper in the crucible. Heat the par-

tially opened crucible over a small flame until volatile matter is expelled and the paper is completely charred. Increase the flame until the bottom of the crucible is red, and continue heating in this manner until the precipitate is white. Heat the covered crucible over a Meker burner for 20 minutes; then cool it for 30 minutes in a desiccator, and weigh it. Repeat the heating and weighing until successive weights determined agree within 0.2 mg.

7. Discard the precipitate. Wash out the crucible, dry it, and reserve it for use in the silica recovery determination.

8. Calculations:

$$\text{Weight CaO} \times 100 = \text{percent CaO.}$$

MAGNESIUM OXIDE

1. To the combined filtrates from the calcium determination, add 25 ml of a 20-percent solution of dibasic ammonium phosphate. Add 40 ml of ammonium hydroxide, stir, and let the solution stand overnight. Stir occasionally the next day, and let the solution stand an additional night. If no precipitate forms after the first night, let the solution stand two additional nights; during the intervening days, occasionally scratch the bottom of the beaker, and stir the solution.

2. Filter the solution through a 9-cm fine-porosity paper. Wash the inside of the beaker with 1-to-19 ammonium hydroxide, and pour the wash into the filter. Wash the paper three times with the same solution; then fold back the paper to drain the funnel stem. Discard the filtrate, and place a clean 150-ml beaker under the funnel.

3. Wash the inside of the precipitation beaker with 1-to-19 hydrochloric acid, and stir to bring the precipitate into solution. Add more acid if the precipitate does not dissolve completely. Pour the solution through the filter; then wash the inside of the beaker three more times with 1-to-19 hydrochloric acid, and transfer the washes to the filter. Dissolve any precipitate remaining on the paper with small amounts of acid from the wash bottle. Finally wash the paper five times with 1-to-19 hydrochloric acid and five times with water. Discard the paper.

4. Dilute the solution in the 150-ml beaker to 90 ml. Add 1 ml of 1-to-19 phosphoric acid and two drops of brom cresol purple indicator. Add ammonium hydroxide by drops until a permanent precipitate forms or until the solution turns purple, whichever occurs first. Let the solution stand for a few minutes; add one drop of ammonium hydroxide, and stir. Continue in this manner until 10 drops of ammonium hydroxide have been added. Add 10 ml of ammonium hydroxide. Stir the solution, and let it stand overnight. (If the magnesium oxide content of the sample exceeds 20 percent, make the second precipitation from a volume of 200 ml, and use a 9-cm paper for the subsequent filtration.)

5. Filter the solution through a 7-cm fine-porosity paper. Wash the inside of the beaker once with 1-to-19 ammonium hydroxide, and transfer the wash to the filter. Wash the stirring rod with ammonium hydroxide solution, scrub it with a policeman, wash it again, and lay it aside. Police the inside of the beaker. Transfer the wash solution to the filter, lay the policeman aside, and wash loose precipitate into the paper. Wash the beaker, police and sluice as many times as necessary to effect complete transfer of the precipitate. Wash the precipitate on the paper three times

with 1-to-19 ammonium hydroxide. Drain the funnel stem, and discard the filtrate.

6. Add 0.5 gram of ammonium nitrate to the crucible that was cleaned, ignited, and weighed after the recovery of silica. Fold the filter paper, and place it in the crucible. Then wipe the funnel with a piece of damp filter paper, and place the paper in the crucible.

7. Heat the crucible on the electric radiator set at 80 volts until the paper is charred. Then set the transformer at 90 volts, and when the precipitate is nearly white, increase the potential to 125 volts; continue heating for 30 minutes. Heat the crucible over a Meker burner for 30 minutes, transfer it to a desiccator, and weigh it after 30 minutes. Repeat the heating, cooling, and weighing until the consecutive weights determined agree within 0.2 mg.

8. Calculations:

Weight magnesium pyrophosphate $\times$ 36.23 = percent magnesium oxide.

RECOVERY OF SILICA

1. Place a 30-ml Vycor crucible upside down over the platinum crucible containing the ammonium hydroxide group precipitate. Invert the two crucibles together so that the precipitate falls into the Vycor crucible. Tap the bottom of the platinum crucible, and hold it in place for a few seconds to allow dust to settle. Brush the loose precipitate from the platinum crucible into the Vycor crucible, but do not attempt to dislodge firmly adhered material.

2. Add 7 grams of potassium pyrosulfate to the Vycor crucible, and place it on a cold radiator (fig. 4). Set the transformer at 75 volts, and heat the crucible until the pyrosulfate melts; then increase the potential 2 volts every 5 minutes until the setting is 85 volts.

3. While step 2 is being carried out, add 1 gram of potassium pyrosulfate to the platinum crucible, and rotate the crucible over a small flame until the pyrosulfate melts and fumes of sulfuric acid appear. Continue heating just long enough to dissolve the small amount of precipitate left in the crucible.

4. Cool the crucible, add a little water to its contents, and heat it on top of the water bath for 5 minutes. Police the inside of the crucible to loosen the cake; then transfer the contents to a 250-ml beaker. Add 20 ml of 1-to-1 sulfuric acid to the beaker, and set it aside.

5. Ignite the crucible over a Meker burner, cool it for 30 minutes in a desiccator, and weigh it. (This weight is used in calculating the weight of ammonium hydroxide group.)

6. Pick up the Vycor crucible with a pair of platinum-shod tongs, and rotate it over a Meker burner to mix the precipitate and flux. Return the crucible to the radiator, and continue heating. After about an hour, increase the potential to 90 volts. Rotate the crucible over a burner from time to time to mix the contents. When the fusion appears to be complete, examine the melt by looking through it over a light. If pieces of precipitate can be seen, heat for a while longer on the radiator, and examine the melt again. When fusion is complete, set the crucible on a silica triangle to cool.

7. Insert the tip of a wash bottle under the lid of the crucible, and blow enough water into the crucible to cover the melt. Wash off the cover,

and lay it aside. Police the inside of the crucible to loosen the melt; then transfer the contents of the crucible to the beaker containing the cake from the platinum crucible.

8. Place the beaker on the water bath, and heat the solution until the solids dissolve. Transfer the beaker to the radiator (wire gauze). Uncover the beaker, and evaporate the solution at 65 volts until fumes of sulfuric acid appear. Continue heating for 15 minutes.

9. Cool the solution, dilute it with water to 60 ml, stir it, and heat it on the water bath until everything dissolves except a fleecy residue of silica.

10. Filter the solution, which must have a volume of 60 ml, through a 7-cm fine-porosity paper into a 100-ml volumetric flask. (Do not use a flask that has been previously used for solutions containing fluorides.) Wash the stirring rod with 1-to-99 sulfuric acid, scrub it with a policeman, wash it again, and lay it aside. Police the inside of the beaker, and pour the wash solution into the filter. Lay the policeman aside, and sluice any precipitate remaining in the beaker into the filter with a stream of 1-to-99 sulfuric acid. Wash the inside of the beaker, and scrub it again; transfer the wash to the filter, and sluice again. Wash off the policeman into the filter. Wash the precipitate on the paper 10 times with 1-to-99 sulfuric acid; then drain the funnel stem. Reserve the filtrate for the determination of titanium and total iron oxide.

11. Transfer the paper to the crucible that was cleaned after the determination of calcium. Heat the crucible over a Tirrill burner with a small flame until volatile matter is expelled and the paper is completely charred. Increase the flame until the bottom of the crucible is red, and continue heating until the precipitate is white.

12. Heat the crucible over a Meker burner for 10 minutes; cool it for 30 minutes in a desiccator, and weigh it. Add one drop of 1-to-1 sulfuric acid and a few milliliters of hydrofluoric acid to the crucible. Transfer the crucible to the radiator (silica triangle), and partially open the crucible; set the transformer at 85 volts, and heat the crucible until fumes of sulfuric acid appear. Advance the potential to 110 volts, and continue heating until all of the sulfuric acid is expelled. Heat the covered crucible over a Meker burner for a few seconds; open the cover, and continue heating the crucible for 5 minutes. Transfer the crucible to a desiccator; let it cool for 30 minutes, and weigh it.

13. Add 1 gram of potassium pyrosulfate to the crucible, and fuse this pyrosulfate over a flame to dissolve the small remaining residue. Cool the crucible; add a little water, and heat it on top of the steam bath for 5 minutes. Transfer the contents of the crucible to the beaker containing the solution that is reserved after the determination of titanium (p. 72).

14. Ignite the crucible, cool it in a desiccator, weigh it, and reserve it for use in the magnesium determination.

TITANIUM OXIDE

1. Turn on the spectrophotometer, and allow it to warm up for 15 minutes.

2. Add cleaning solution to each of three matched 1-cm × 1-cm tubes. Pour out the cleaning solution, and rinse the tubes thoroughly—first with tap water, then with distilled water. Dry the outsides of the tubes with a towel.

3. Half fill the first tube with distilled water. Polish the outside surface of the tube with a piece of lens paper, and put it in the No. 1 position in the tube rack.

4. Dilute the filtrate from the recovery of silica to the mark, and mix it. Fill the No. 2 tube nearly full with this solution. Empty the tube into a 250-ml beaker. Wash the underlip of the tube with water. Hold the tube in a horizontal position, and wipe off the outside surface with a piece of filter paper. Fill it to the 5-ml mark with the sample solution. Polish the outside surface of the tube, and place it in the No. 2 position in the tube rack.

5. Rinse and fill the No. 3 tube with low-standard titanium solution in the manner described above, except discard the rinse, and place this tube in the No. 3 position in the tube rack. Add 0.2 ml of 6-percent hydrogen peroxide to this tube, and mix the solution thoroughly with a flat-end stirring rod.

6. Place the tube rack in the photometer. Set the dark current at 0.0, and adjust the wavelength so that the standard reads 20.0 ± 0.2 when water reads 100.0. (about 435 mμ). Adjust the dark current so that the standard reads exactly 20.0 when water reads 100.0; then measure and record the percent transmittance of the sample solution.

7. Add 0.2 ml of 6-percent hydrogen peroxide to the No. 2 tube. Mix this solution with a flat-end rod, and wash off the rod into the beaker. Again measure and record the percent transmittance of the solution; the measurement is made after the dark current has been adjusted so that the standard reads 20.0 when water reads 100.0. If the reading is below 20.0, proceed as in step 9.

8. From the tables for this wavelength (see "Preparation of apparatus and reagents," p. 84), determine the percent titanium equivalent to the reading for the peroxidized solution. Subtract from this value the percent titanium equivalent to the reading for the unperoxidized solution.

9. If the reading in step 7 is below 20.0, empty and wash out the No. 2 tube into the beaker, and refill the tube with the sample solution as described in step 4. Empty the No. 3 tube, wash it, and fill it to the 5-ml mark with high-standard titanium solution. Add the peroxide, and mix as before. Set the dark current to 0.0, and adjust the wavelength so that the high standard reads 20.0 ± 0.2 when water reads 100.0 (about 510 mμ). Then adjust the dark current so that the dark standard reads exactly 20.0 when water reads 100.0, and measure the percent transmittance of the sample solution.

10. Add peroxide to the No. 2 tube; mix as before, and wash off the stirring rod into the beaker. Again measure the percent transmittance of the sample solution after adjusting the dark current so that the standard reads 20.0 when water reads 100.0.

11. From the tables for this wavelength, determine the percent titanium equivalent to the reading for the peroxidized solution, and subtract from the value the percent titanium equivalent to the reading for the unperoxidized solution.

12. Empty the solution in the No. 2 tube into the 250-ml beaker. Wash the inside of the tube three times with water, and transfer the washings to the beaker; then wash off the outside edge of the tube.

13. Transfer the remainder of the solution in the flask to the beaker. Wash the inside of the flask three times, and transfer the washings to the

beaker. Finally wash off the outside lip of the flask. Reserve the solution for the determination of total iron oxide.

TOTAL IRON OXIDE

1. Stir 15 ml of ammonium hydroxide into the solution that was saved after the determination of titanium, and continue stirring until the precipitate that forms goes into solution. Cover the beaker with a watch glass supported by a triangle, and evaporate the solution without boiling to a volume of 75 ml. Cool the solution; add two drops of 5-percent potassium dichromate solution, and stir. If the solution does not become distinctly more yellow, evaporate it further, and retest from time to time by the addition of potassium dichromate. When the dichromate color persists, add 25 ml of 15-percent ammonium chloride solution, and adjust the volume to 100 ml.
2. Drain the reductor until the level of the liquid is about one-eighth inch above the silver. Add 20 ml of 1-to-1 phosphoric acid to a clean 600-ml beaker, and lower the reductor into the beaker until the delivery tube dips into the acid. Transfer about one-half of the iron solution to the reservoir. Fully open the stopcock on the reductor, and as the solution drains, transfer the remainder of the iron solution to the reservoir. Let the solution drain until its level is about one-eighth inch above the silver. Lift the reductor as the volume of the effluent increases, but keep the tip of the delivery tube below the level of the liquid.
3. Wash the inside of the reservoir with a small amount of 1-to-19 hydrochloric acid, and allow the solution to drain until its level is a little above the silver. Repeat this operation five times. Add more 1-to-19 hydrochloric acid, and continue draining until the volume of the solution in the beaker is almost 300 ml. Close the stopcock, and lift the delivery tube clear of the liquid. Wash the tip of the delivery tube with water; then continue draining the reductor until the volume of the effluent is 300 ml.
4. Add 2 drops only of a 0.2-percent solution of sodium diphenylamine sulfonate; then, using a 50-ml burette, titrate the solution with 0.06262N potassium dichromate solution while stirring until the purple color caused by the addition of 1 drop of titrant disappears slowly. Wash down the inside of the beaker with water. Then continue adding the titrant in fractional drops while stirring the solution until a distinct purple color forms that persists for at least 30 seconds.
5. Calculations:

$$\frac{\text{Milliliters } K_2 Cr_2O_7}{2} = \text{percent total } Fe_2O_3.$$

Percent total Fe_2O_3 — milliliters $K_2 Cr_2O_7$ used in FeO titration =

percent Fe_2O_3.

FERROUS OXIDE

1. Transfer a 0.5000-gram portion of the sample to a 50-ml platinum crucible that has a small hole in the center of its cover. Set up, in the hood, the special tripod illustrated in figure 14 and the Tirrill burner used only for ferrous iron determinations. Light the burner; adjust the flame so it is about one-half inch high, and place the burner under the tripod. Have another lighted Tirrill burner in a handy position.

2. Add 5ml of water and 5 ml of hydrofluoric acid to a 50-ml platinum dish, and add 5 ml of sulfuric acid to a graduate.

3. Add 1 ml of water to the crucible, and swirl it until the powder forms a slurry. Add the sulfuric acid to the dish; then set the crucible on the tripod, and quickly add the mixed acids. Cover the crucible, and brush a flame across the side of it until a continuous flow of steam issues from the hole in the cover. Heat the crucible intermittently with the extra burner until the heat from the burner under the crucible is sufficient to keep the steam flowing continuously. Continue heating with the small flame for 10 minutes.

4. During this 10-minute period, add 100 ml of "dissolving solution" (see "Preparation of apparatus and reagents," p. 86) to a 600-ml beaker, and dilute this solution to 300 ml. Add two drops of 0.2-percent sodium diphenylamine sulfonate indicator, and place the beaker in the hood.

5. Lift the crucible from the tripod with a pair of Blair tongs; tip the beaker forward, and lower the crucible into it until the bottom of the crucible is immersed in the liquid. Then release the crucible, and let it sink into the solution. With the aid of a stirring rod, lift the crucible from the beaker; wash it with water—inside and outside—and set it aside.

6. Titrate the solution while stirring with $0.06262N$ potassium dichromate solution until the purple color caused by the addition of one drop of the titrant fades slowly. Wash down the inside of the beaker, and continue adding the titrant in fractional drops until a purple color forms that persists for 30 seconds.

7. Calculations:

$$\text{Milliliters } K_2 Cr_2 O_7 \times 0.9 = \text{percent FeO.}$$

THE ALKALIS

1. Grind a 0.5000-gram portion of the sample in an agate mortar to an impalpable powder, being careful to avoid loss. Add 0.5 gram of ammonium chloride, and mix it with the powder by gentle rubbing with the pestle. Weigh 4.0 grams of low-alkali calcium carbonate, and cover the bottom of a Smith crucible with about 0.5 gram of it. Then transfer all but 0.5 gram of the remainder to the mortar in three equal portions, and mix the contents of the mortar after each addition by rubbing with the pestle. Continue mixing the contents until they are homogeneous. Brush off the pestle, and lay it aside. Using a spatula with a flexible blade, transfer the mixture to the Smith crucible. When all but a trace of it has been transferred, add the remainder of the calcium carbonate to the mortar, and rub it over the surface of the mortar with the pestle. Finally brush off the pestle, and transfer this calcium carbonate to the crucible. Tap the crucible gently on a pad of paper to compact the powder.

2. Place a ceramic adapter for the Smith crucible in an opening of the Globar furnace (fig. 3). Push the Smith crucible through a collar fashioned from a length of helically-wound nichrome wire (fig. 3), and set it in the adapter. Adjust the height of the crucible so that it projects $1\frac{1}{4}$ inches above the ceramic top of the furnace. Set the current input at 8 amperes, and heat the crucible for 30 minutes. Increase the input to 10 amperes, and heat for an additional 10 minutes; then increase the input to 19 amperes, and let the furnace temperature rise to 1,100°C.

Maintain this temperature for 30 minutes. Remove the crucible, and let it cool to room temperature. Add water to the crucible until it is about three-fourths full, and let the crucible stand overnight.

3. Add 0.5 gram of barium hydroxide octahydrate to a clean 150-ml beaker. Stir the contents of the crucible to a paste using a glass rod, and transfer the contents to the beaker by means of a stream of water from a wash bottle. Adjust the volume of the solution to 50 ml; heat the solution to a boil over a flame, and remove it from the flame at once. Rinse off the cover glass, and lay it aside. Filter the solution through a 9-cm coarse-porosity paper into a 400-ml beaker. Stir the solution during the course of the transfer so that most of the solids are transferred to the paper. Using hot water, wash the beaker twice, and transfer the washes to the paper. Finally sluice the remainder of the residue into the paper. Wash the residue on the paper 10 times with hot water.

4. Hold the funnel over the extraction beaker; loosen the residue with a stirring rod, and wash it back into the beaker. Dilute the solution to 50 ml, and boil it for 3 minutes. Wash off the cover glass, and lay it aside. Filter the solution as before through the original paper into the beaker containing the first filtrate. Wash the beaker twice, and transfer the washings to the paper; then sluice the remainder of the residue into the paper. Wash the residue 10 times with hot water, and discard it.

5. Add 10 ml of ammonium hydroxide to the filtrate; then while stirring the solution, add 3 ml of a saturated ammonium carbonate solution. Heat the solution on the water bath for at least 20 minutes, and stir it frequently during this period.

6. Filter the solution through a 9-cm fine-porosity paper into a 500-ml platinum dish. Stir the solution as the last 100 ml are added so that most of the precipitate is transferred to the paper. Wash the inside of the beaker twice with water, and transfer the washings to the paper; then wash the precipitate on the paper five times with water.

7. Hold the funnel over the precipitation beaker and wash the precipitate back into it. Dilute the solution to 100 ml; add 3 ml of 1-to-1 hydrochloric acid, and stir until the precipitate dissolves. Add 10 ml of ammonium hydroxide and 3 ml of a saturated ammonium carbonate solution, and heat the solution on the water bath for at least 10 minutes. Stir the solution frequently.

8. Filter the solution through the original paper into the dish containing the first filtrate. Wash the beaker twice with water, and transfer the washings to the paper. Finally wash the precipitate five times, and discard it.

9. Cover the dish with a raised watch glass, and evaporate the solution to complete dryness on the water bath. Continue heating until the salts are opaque.

10. Place the dish on the electric radiator using the special stainless steel adapter provided for this purpose (fig. 4). Cover the adapter with a raised watch glass; set the transformer at 135 volts, and heat the dish for 2 hours. Remove the cover glass and triangle; lift the dish out of the adapter with a pair of platinum-shod tongs as the dish is being covered with a clean watch glass, and set the dish on a porcelain plate to cool.

11. Add 10 ml of water, and swirl the dish to dissolve the salts. Add five drops of ammonium hydroxide, and swirl the dish. Add five drops of

a saturated ammonium carbonate solution, and swirl the dish again. Heat the covered dish on the water bath for 5 minutes.

12. Filter the solution through a 5.5-cm medium-porosity paper into a 60-ml platinum dish. Make the transfer with the aid of a short stirring rod that is kept in the filter. Wash around the bottom of the dish, and pour the wash through the filter; then completely wash the inside of the dish three times, and transfer the washings to the filter. Wash the stirring rod, and lay it aside; then wash the underlip of the dish. Wash the paper five times with water, and discard it.

13. Place the 60-ml dish on the water bath; cover it with a raised borosilicate watch glass, and evaporate the solution to complete dryness on the water bath. Continue heating until the salts become opaque.

14. Place a 2-inch porcelain filter plate on a nichrome gauze above a Tirrill burner. Dry the bottom of the platinum dish; place it on the plate, and cover it with the borosilicate watch glass. Start a small flame under the dish, and increase the flame slowly until the gauze around the plate is red hot. Continue heating in this manner until most of the brown color disappears from the salts. Lay the cover glass aside; pick up the dish with a pair of platinum-shod tongs, and rotate it over the flame of a Tirrill burner until the salts melt at the edges. Set the dish on a porcelain plate, and cover it at once.

15. Add 1 ml of water, and swirl the dish to dissolve the salts. Add 1 drop of ammonium hydroxide, and swirl the dish; add 1 drop of a saturated solution of ammonium carbonate, and observe closely as it is added. If a large precipitate of calcium carbonate forms at once, the prior removal of alkaline earths was faulty, and an additional precipitation must be carried out. If no significant amounts of precipitate forms, swirl the dish to mix the solution; cover it with a borosilicate watch glass, and heat the solution on the water bath for 5 minutes.

16. Filter the solution through a 5.5-cm fine-porosity paper into a weighed 35-ml platinum dish. Wash the 60-ml dish three times with water, and transfer the washings to the filter. Finally wash the paper five times, and discard it.

17. Cover the 35-ml dish with a raised borosilicate watch glass, and evaporate the solution to dryness on the water bath. Continue heating until the salts are opaque.

18. Dry the bottom of the dish; cover it, and heat as before over a Tirrill burner. Start with a small flame, and gradually increase it until the wire gauze becomes red hot. Continue heating in this manner until most of the brown color disappears.

19. Lay the cover glass aside, and rotate the dish over a flame until the salts melt around the edges. Place the dish in a desiccator, and quickly cover it with a porcelain cover. Weigh the uncovered dish after 30 minutes. Preheat the covered dish for a few seconds on the porcelain plate; then remove the cover. Heat the dish over a free flame until the salts melt around the edges; transfer the dish to a desiccator, cover it with a porcelain cover, and weigh it after 30 minutes. If the weighings do not agree within 0.2 mg, repeat the heating, cooling, and weighing.

20. Add about 1 ml of water to the platinum dish, and swirl the dish to bring the salts into solution. Transfer the solution to a 35-ml porcelain

dish. Wash the inside of the platinum dish three times with water, and transfer the washings to the porcelain dish.

21. From the following formula, determine the amount of chloroplatinic acid required (0.05 gram platinum per milliliter):

$$\text{Weight mixed chlorides} \times 34 + 0.2 = \text{milliliters } H_2PtCl_6$$

Add this amount to the porcelain dish, and stir the solution to mix it. Cover the dish with a raised watch glass, and evaporate the solution to dryness on the water bath.

22. Add 5 ml of 80-percent alcohol, and work the salts into the solution with a stirring rod. Break up the salts by stirring gently for 1 minute, and allow the residue to settle. Decant the solution through a weighed 15-ml glass filtering crucible having a fine-porosity disk. Wash the inside of the porcelain dish with 80-percent alcohol. Stir and break up large particles with the end of the stirring rod, and decant the solution into the filtering crucible. Repeat the last operation two more times. Wash the stirring rod, and lay it aside after pouring the last wash into the crucible. Hold the dish over the crucible, and sluice the loose precipitate into the crucible. Wash the dish with alcohol, and scrub the inside of it with a policeman; again sluice the loose precipitate into the filter. Repeat the last procedure as often as necessary to completely transfer the precipitate to the filter. Wash the salts in the crucible five times with 80-percent alcohol.

23. Wash the bottom of the crucible with water; dry the crucible, and set it on a filter paper on top of the water bath. Cover it with another filter paper, and let it dry for 1 hour. Heat the crucible in an oven at a temperature of $130 \pm 5°C$ for 1 hour; transfer it to a desiccator, and weigh it after 30 minutes.

24. Make a blank determination on each lot of calcium carbonate used. Heat a mixture of 4 grams of calcium carbonate and 0.5 gram of ammonium chloride in a Smith crucible; then proceed through all steps of this procedure.

25. Calculations:

Subtract the weights for total chlorides and potassium chloroplatinate obtained on the blank from those obtained on the sample; then calculate the values for the alkalis as shown below, using the corrected figures:

$$\text{Weight } K_2PtCl_6 \times 38.76 = \text{percent } K_2O$$

$$\text{Weight } K_2PtCl_6 \times 0.3067 = \text{weight KCl}$$

$$\text{Weight mixed chlorides} - \text{weight KCl} = \text{weight NaCl}$$

$$\text{Weight NaCl} \times 106.1 = \text{percent } Na_2O.$$

MANGANESE AND PHOSPHORUS OXIDES

PRELIMINARY PROCEDURE

1. Transfer a 1.000-gram portion of the sample to a 100-ml platinum dish; then tap the dish to spread the powder in a thin layer over the bottom. Cover the dish with a borosilicate watch glass; bring the dish to a dull-red heat over a Tirrill burner, and continue heating at this temperature for 30 minutes.

2. Wet the powder with 1 ml of water. *Add 10 ml of 1-to-1 nitric acid and*

10 ml of hydrofluoric acid, and stir the solution with a platinum rod. Place the uncovered dish on the electric radiator (ceramic ring adapter, fig. 4); set the transformer at 65 volts, and stir the solution frequently over a period of 20 minutes. Then, let the solution evaporate to dryness without further attention.

3. Remove the dish from the radiator. Add 10 ml of 1-to-1 nitric acid and 10 ml of hydrofluoric acid, and stir the solution. Again evaporate the solution to dryness on the radiator.

4. Add 20 ml of 1-to-1 nitric acid; stir the solution, and evaporate it to dryness on the radiator. Heat for an additional 15 minutes after the salts appear to be dry.

5. Add 40 ml of 1-to-1 nitric acid and 20 ml of 5-percent boric acid solution to the cooled dish; cover the dish with an etched watch glass, and heat the solution for 2 hours on the water bath. (Remove the center cover only from the water bath.) Stir the solution occasionally. If the solution contains a brown precipitate of manganese dioxide, add a few crystals of sodium sulfite, and stir the solution to dissolve the precipitate.

6. Spread a thin film of stopcock grease on the underlip of the dish; then filter the solution through a 7-cm fine-porosity paper into a 100-ml volumetric flask. (Reserve special flasks for use with hydrofluoric acid solutions.) Wash the inside of the dish three times with water, and transfer the washes to the filter. Finally wash the paper five times with water and discard it.

7. Dilute the filtrate to the mark with water, and mix. Rinse a clean 25-ml pipet with a little of the solution; then pipet a 25-ml portion of the solution into a 50-ml volumetric flask and another 25-ml portion into a 100-ml beaker. Reserve the remainder of the solution until the determinations are completed.

MANGANESE OXIDE

8. To the portion in the 50-ml flask, add 5 ml of a 5-percent periodic acid solution. Wash down the inside of the flask with water, and swirl the flask to mix the contents.

9. Remove two rings from the water bath, and place the larger ring over the neck of the flask. Fasten a test-tube clamp to the upper neck of the flask; then lower the flask into the water bath. The water in the bath must be boiling. Heat the flask in this manner for at least 1 hour.

10. Cool the solution and add 3 ml of 1-to-1 phosphoric acid. Dilute the solution to the mark, and mix it.

11. Turn on the spectrophotometer, and let it warm for 15 minutes. Half fill the first of three matched 1-cm × 1-cm tubes with water; polish it with lens paper, and place it in the tube rack. Fill the second of the tubes with the sample solution to be measured. Pour out the solution; wash the underlip of the tube with water, and blot the water from the outside of the tube with filter paper. Half fill this tube with sample solution, and polish it with lens paper; place it in the rack. In a similar manner, add standard manganese solution to the third tube. (See "Preparation of apparatus and reagents," p. 86.)

12. Set the dark current at 0.0; adjust the wavelength so that the standard reads 20.0 ± 0.2 (about 550 mμ) when water reads 100.0. Then set the dark current so that the standard reads exactly 20.0 when water reads 100.0, and measure the percent transmittance of the sample solution.

13. If the reading is below 20.0, make a suitable dilution, and measure the percent transmittance of the diluted solution.

14. Determine percent manganese oxide from a set of tables prepared by calibrating the photometer with a series of standard solutions. If a dilution was made, be sure to multiply the figure obtained from the tables by a suitable factor.

PHOSPHORUS OXIDE

15. Heat the solution contained in the 100-ml beaker for 15 minutes on the water bath. Add 25 ml of a solution of 2.5-percent ammonium molybdate and 20-percent ammonium nitrate. Stir the solution frequently while heating it for an additional 15 minutes. If no turbidity appears within 5 minutes after the addition of the reagent, scratch the bottom of the beaker occasionally to start precipitation, but do not scratch the beaker once a precipitate forms. Let the solution stand at room temperature overnight.

16. Prewash a 7-cm fine-porosity paper three times with 5-percent ammonium hydroxide solution and once with a wash solution of 2-percent ammonium nitrate and 1-to-99 nitric acid. If the bottom of the beaker was scratched, add 0.1 gram of paper pulp to the sample solution. Decant the solution through the filter. Wash down the inside of the beaker twice with the wash solution of ammonium nitrate and nitric acid, and transfer the washings to the filter; then wash the paper five times with the same solution. Drain the funnel stem, and discard the filtrate.

17. Place a 100-ml volumetric flask under the funnel. Wash down the inside of the beaker with 1-to-19 ammonium hydroxide (contained in a polyethylene wash bottle), and stir the wash solution until the precipitate dissolves. Transfer this solution to the filter; then wash the inside of the beaker three more times with 1-to-19 ammonium hydroxide, and transfer the washes to the filter. Finally, wash the underlip of the beaker. Dissolve any yellow precipitate left on the paper with small portions of ammonium hydroxide; then completely wash the paper five times, and discard it. Use a fine wash-bottle tip so that the final volume of the ammonium hydroxide solution does not exceed 25 ml.

18. Add 60 ml of water to a 100-ml flask (reference solution). Pipet 10 ml of stock phosphorus solution (see "Preparation of apparatus and reagents," p. 87) into a second flask (low-standard solution), and dilute it to 60 ml. Add 8.0 ml of 1-to-1 nitric acid to both of these flasks. If the amount of yellow precipitate was large, make up a third solution (high standard solution) containing 20 ml of stock phosphorus solution and 8.0 ml of 1-to-1 nitric acid. Dilute the ammoniacal solution from step 17 to 60 ml, and add 10.0 ml of 1-to-1 nitric acid.

19. Pipet 10 ml of vanadate-molybdate solution into each of the sample, reference, and standard solutions; dilute each solution to volume and mix it.

20. After 30 minutes, measure the percent transmittance of the sample solution with a spectrophotometer. Add the reference solution to the first of three matched 1-cm × 1-cm tubes, the sample solution to the second, and low standard solution to the third. Set the dark current at 0.0, and adjust the wavelength so that the standard solution reads 20.0 ± 0.2 when the reference solution reads 100.0 (about 410 $m\mu$); then set the dark current so that the standard solution reads exactly 20.0 when the reference solution reads 100.0. Measure the percent transmittance of the sample solution.

21. If the reading for the sample solution is less than 20.0, replace the low standard solution with high standard solution. Set the dark current at 0.0, and adjust the wavelength so that the dark standard reads 20.0 ± 0.2 when the reference solution reads 100.0 (about 440 mμ) ; then adjust the dark current so that the standard solution reads exactly 20.0 when the reference solution reads 100.0. Measure the percent transmittance of the sample solution.

22. If the reading at 440 mμ is below 20.0, pipet a 10-ml portion of the solution from step 7 into a 100-ml beaker. Add 6 ml of 1-to-1 nitric acid and 9 ml of water. Repeat the procedure starting with the precipitation using the solution of ammonium molybdate and ammonium nitrate, and measure the percent transmittance at 440 mμ.

23. Determine percent phosphorus pentoxide from tables prepared by calibrating the photometer with a series of standard solutions at the wavelength used for the sample solution. If a 10-ml portion of the sample solution was used, multiply the figure obtained from the table by a suitable factor.

CARBON DIOXIDE

1. Start water running through the condenser of the carbon dioxide apparatus (fig. 11), and connect the tube below valve I (fig. 15) to a vacuum source. Open all valves except C and I, and make sure that the bridge is in place.
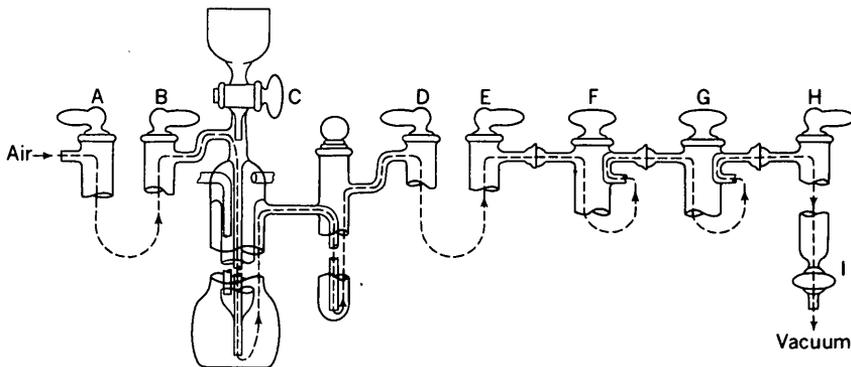

FIGURE 15.—Flow diagram of carbon dioxide apparatus.

2. With the aid of a transfer funnel, add 5.000 grams of the sample (or 1.0000 gram for carbonates) to the generating flask. Wash powder adhering to the funnel into the flask, and adjust the volume of water in the flask to 25 ml.

3. Open valve I slowly to start a stream of air through the system. Observe the rate of flow at the sulfuric acid bubbler. Swirl the flask to make a slurry of the powder; then put the flask into place at the ground joint, and watch the end of the delivery tube until bubbles appear. Turn the flask gently to seat the joint, and connect the springs that hold the flask in place. Continue drawing air through the system for 10 minutes at the rate of about three bubbles per second.

4. During the 10-minute period mentioned above, weigh each of the two absorption tubes against the tare tube. Open the stopcock of each tube momentarily before placing it on the balance pan.

5. Close valves I, H, and E, in order. Remove the bridge, and replace it with the two absorbers. Hold the absorbers so that the joints are under compression when the clamps are put in place. Open valves E, F, G, and H.

6. Adjust valve I so that a rapid stream of air flows through the system. Close valve A, wait a few seconds, and close valve I. Observe the tip of the tube in the bubbler. If sulfuric acid rises in this tube, a leak at the absorption tubes is indicated; if bubbles continue to flow, the leak is at the joint of the generating flask. Open valve A slowly to release the vacuum, and if no leak was found proceed to step 7. If a leak was found at the generating flask, remove the springs, rotate the flask to reseat the joint, and replace the springs. If a leak was found at the absorbers, remove the clamps, and move the absorbers forth and back until a position is found where the joints are under compression; then replace the clamps. Again test for leaks by putting the system under vacuum. When the system is free from leaks, proceed to step 7.

7. Add 25 ml of 1-to-1 hydrochloric acid to the reservoir. Start a moderate flow of air through the system by opening valve I; then heat the water in the generating flask almost to boiling with a Tirrill burner. Slow the rate of air flow; add a few drops of acid to the generating flask through valve C, and watch the end of the delivery tube until bubbles of air appear. Continue adding acid in small portions, but wait after each addition until bubbles of air appear at the delivery tube. Leave a little acid in the reservoir so that air will not be admitted through it.

8. Increase the air flow, and bring the solution in the flask to a gentle boil. At first, brush a flame against the flask at the surface of the liquid; when boiling starts, heat the bottom of the flask to stir up the powder. Continue boiling gently for 2 minutes. Slow down the flow of air to about three bubbles per second, and continue drawing air through the system at this rate for 20 minutes.

9. Close valves I, H, and E, in order, and immediately open valve C; close valves F and G. Remove the absorption tubes from the system, and put them in the balance room. After 1 hour weigh the absorption tubes against the tare tube. Open the valve of each tube momentarily before placing it on the balance pan. Use two sets of absorbers alternately if a series of determinations are made.

10. Remove the flask from the apparatus, and put a beaker under the delivery tube. Wash the flask thoroughly, and set it aside. Close valve B, and wash down the acid reservoir three times with a stream of water from the wash bottle; then blow a stream of water up around the Hopkins condenser to wash out the acid. Wrap a piece of filter paper around the condenser, and push the paper into the condenser chamber to remove droplets of water; then proceed with the next in a series of determinations.

BARIUM OXIDE

1. Transfer a 1.000-gram portion of the sample to a 25-ml platinum crucible. Add 0.20 gram of potassium nitrate and three-fourths of a 5-gram portion of sodium carbonate to the crucible, and mix the powder and flux. Add the rest of the sodium carbonate, and tap the crucible to spread the sodium carbonate over the mixture.

2. Place a crucible adapter in one of the top holes of a cold Globar furnace, and set the crucible in the adapter. Adjust the current input to 19

amperes, and let the furnace heat for 15 minutes. Increase the input 2 amperes, and wait until the furnace temperature reaches 1,075°C. Maintain this temperature for 20 minutes. Using a Tirrill burner, heat the crucible cover for about 1 minute without removing it from the crucible. Lay the crucible cover upside down on a silica triangle; then with a pair of platinum-shod tongs, grasp the crucible at its edge, remove it from the furnace. If the melt is fluid enough to do so, roll the crucible to spread the melt around the inside of it. Set the crucible on a silica triangle; replace the cover, and let the crucible cool. Heat the crucible over a Meker burner for 30 seconds; then let it cool again.

3. Transfer the cake to a 150-ml beaker. Scrub the crucible with a policeman, and transfer any loose material to the beaker with a stream of water from the wash bottle. Add a few milliliters of hydrochloric acid to the crucible, and heat it on top of the water bath for 30 minutes. Discard the acid, and wash out the crucible.

4. Add a few milliliters of alcohol to the beaker, and adjust the volume of the solution to 60 ml. Heat the solution on the water bath until the sodium carbonate is extracted from the cake, and break up lumps with a flat-ended stirring rod.

5. Filter the solution through a 9-cm fine-porosity paper into a 400-ml beaker. Wash the inside of the beaker three times with a 1-percent sodium carbonate solution, and transfer the washes to the filter; then sluice the balance of the residue into the filter. Wash the residue on the paper five times. Reserve the filtrate if total sulfur is to be determined.

6. Unfold the filter paper, and spread it flat along the inside of the extraction beaker. Wash the residue into the beaker with water, and discard the paper.

7. Adjust the volume of the solution to 75 ml, and slowly add 4 ml of 1-to-1 sulfuric acid. Stir vigorously during the addition. Add about 0.1 gram of sodium sulfite; stir the solution, and heat it on the water bath for 1 hour. Let the solution stand overnight at room temperature.

8. Add 0.25 gram of paper pulp, and filter the solution through a 9-cm fine-porosity paper. Transfer the precipitate to the paper with a stream of water from a wash bottle, and wash the precipitate three times with water. Discard the filtrate.

9. Burn off the paper in a platinum crucible (radiator set at 90 volts); cool the crucible, and add 1 gram of sodium carbonate to it. Heat the crucible and its contents over a Meker burner for 10 minutes.

10. Lay the crucible on its side in a clean 150-ml beaker, and add 25 ml of water. When the cake loosens, remove the crucible from the beaker, and wash the cake from the crucible into the beaker. Stir the solution occasionally until the sodium carbonate dissolves and only a fine residue remains.

11. Filter the solution through a 7-cm fine-porosity paper, and transfer the precipitate to the filter with a stream of 1-percent sodium carbonate solution. Wash the paper 10 times with the same solution. Drain the funnel stem, and discard the filtrate.

12. Place a clean 150-ml beaker under the funnel. Wash the paper three times with 1-to-19 hydrochloric acid, then 10 times with water. Discard the paper.

13. Dilute the solution to 100 ml. Add 3 ml of 1-to-1 sulfuric acid, stir, and let the solution stand overnight.

14. Filter the solution through a 7-cm fine-porosity paper, and transfer all the precipitate to the filter with water; then wash the paper five times. Discard the filtrate.

15. Burn off the paper in a weighed platinum crucible at a temperature below red heat (radiator set at 90 volts). If carbon is deposited on the underside of the crucible cover, heat the cover over a flame until the carbon disappears. Ignite the precipitate over a Tirrill burner at a dull-red heat for 15 minutes with the cover of the crucible partially open. Cool the crucible in a desiccator for 30 minutes, and weigh it.

16. Calculations:

$$\text{Weight } BaSO_4 \times 65.7 = \text{percent BaO.}$$

TOTAL SULFUR

1. If barium was determined, use the filtrate that was reserved for making the sulfur determination; otherwise follow the barium oxide procedure until such a filtrate is obtained. Dilute this filtrate to 200 ml, and cautiously add 7 ml of hydrochloric acid. Add five drops of brom phenol blue indicator, and then using dropper add and stir in 1-to-1 hydrochloric acid until the solution becomes yellow; then add 2 ml more.

2. Add 5 ml of 10-percent barium chloride solution; stir the solution, and heat it on the water bath for 2 hours. Stir occasionally during this period. Let the solution stand at room temperature overnight.

3. Filter the solution through a 7-cm fine-porosity paper into a clean 150-ml beaker. Discard the filtrate from time to time if it is clear, but refilter any portion that is turbid. Transfer the precipitate to the paper with a stream of water from a wash bottle; then wash the paper five times. Discard the filtrate.

4. Burn off the paper in the weighed platinum crucible at a temperature below red heat (radiator set at 90 volts). If a residue of carbon remains on the underside of the cover, burn off this carbon over a separate flame. When the precipitate becomes white, cool the crucible. Add 1 drop of 1-to-1 sulfuric acid and a few milliliters of hydrofluoric acid. Heat the crucible with the cover partially open at 85 volts on the radiator (triangle) until white fumes appear; then set the transformer at 110 volts, and continue heating until the sulfuric acid is expelled. Ignite the crucible with the cover partially open over a Tirrill burner at a dull-red heat for 15 minutes. Cool the crucible in a desiccator for 30 minutes, and weigh it.

5. Calculations:

$$\text{Weight } BaSO_4 \times 13.7 = \text{percent S.}$$

SULFUR TRIOXIDE

1. Transfer a 1.000-gram portion of the sample into a 250-ml Erlenmeyer flask. Place a spray trap (fig. 6) in the neck of the flask. Add 80 ml of water, and bring it to a gentle boil over a Tirrill burner. Boil the water for 1 minute; then add 20 ml of 1-to-1 hydrochloric acid through the funnel, slowly enough so that the solution does not stop boiling. Continue boiling gently for 15 minutes.

2. Wash off the inside and outside of the funnel trap, and remove it from the flask. Add 0.25 gram of paper pulp, and filter the solution through a 9-cm fine-porosity paper into a 400-ml beaker. Use a short stirring rod,

which should be kept in the funnel, to make the transfer. Wash down the inside of the flask three times with 1-to-19 hydrochloric acid, and transfer the washes to the filter. Finally, wash the paper five times with the same solution, and discard it.

3. Add five drops of brom cresol purple indicator to the filtrate. Neutralize the solution with ammonium hydroxide. Add 1-to-1 hydrochloric acid by drops until the indicator turns yellow; then add 2 ml more. Dilute the solution to 200 ml.

4. Add 5 ml of a 10-percent barium chloride solution. Heat the solution for 2 hours on the water bath, and stir it occasionally during this period; then let it stand overnight at room temperature.

5. Filter the solution through a 7-cm fine-porosity paper into a clean 150-ml beaker. Discard each 50-ml portion of the filtrate as it collects, provided it is clear; but if a portion of the filtrate is turbid, refilter it. Transfer the precipitate to the paper using water, and wash the paper five times with water.

6. Burn off the paper in a weighed 25-ml platinum crucible on the electric radiator (set at 90 volts). If carbon is deposited on the underside of the cover after the precipitate in the crucible is white, burn off the deposit over a flame. Heat the crucible with the cover partially open over a Tirrill burner at a dull-red heat for 15 minutes. Cool the crucible in a desiccator for 30 minutes, and weigh it.

7. Calculations:

$$\text{Weight } BaSO_4 \times 34.3 = \text{percent } SO_3.$$

PREPARATION OF APPARATUS AND REAGENTS

TOTAL WATER

Penfield tube. Blow a bulb on one end of a piece of 9-mm O.D. borosilicate tubing 30 cm long. Work 4 cm of the tube into a bulb having an outside diameter of 2.5 cm. Fire polish the open end of the tube without constricting it.

Capillary stopper. Draw a piece of capillary tubing to a taper; cut off the tapered section, and cover it with a piece of thin rubber tubing.

Flux. Transfer 50 grams of lead oxide to one platinum crucible and 25 grams of lead chromate to another. Heat the crucibles and their contents for 1 hour in an electric furnace having a temperature of 800°C. Combine the two components, and grind them to pass a 20-mesh sieve. Store the mixed flux in a bottle having a tight sealing cap. Do not heat the two components together. Neither attacks platinum at the specified temperature, but a mixture of the two attacks it severely.

AMMONIUM HYDROXIDE GROUP

Pure ammonium hydroxide. Add 1,300 ml of distilled water to a 2-liter polyethylene bottle; and place the bottle in a cooling bath; then bubble ammonia into the water until the volume of the solution is 2,000 ml.

Brom cresol purple indicator–0.1 percent. Wet 0.1 gram of brom cresol purple with 1 drop of ammonium hydroxide. Add 100 ml of water, and stir the solution until the dye dissolves.

REMOVAL OF MANGANESE

Zirconyl chloride solution–5 percent. Dissolve 25 grams of zirconyl chloride octahydrate in about 200 ml of water containing 5 ml of hydrochloric acid.

Let the solution stand overnight. Filter it through a fine-porosity paper, and dilute the filtrate to 500 ml.

CALCIUM OXIDE

Oxalic acid–10 percent. Dissolve 200 grams of oxalic acid in 1,800 ml of hot water. Let the solution stand overnight. Filter it through a fine-porosity paper, and dilute the filtrate to 2,000 ml.

Brom cresol purple indicator. See "Ammonium hydroxide group," page 83.

MAGNESIUM OXIDE

Ammonium phosphate–20 percent. Dissolve 400 grams of dibasic ammonium phosphate in about 1,500 ml of water. Let the solution stand overnight. Filter it through a fine-porosity paper, and dilute the filtrate to 2,000 ml.

Brom cresol purple indicator. See "Ammonium hydroxide group," page 83.

TITANIUM OXIDE

Hydrogen peroxide–6 percent. Dilute 10 ml of 30-percent hydrogen peroxide to 50 ml, and transfer the solution to a polyethylene bottle having a tight sealing cap. Make a fresh solution each month.

Potassium pyrosulfate solution–20 percent. Dissolve 400 grams of potassium pyrosulfate in about 800 ml of water. Let the solution stand overnight. Filter it through a fine-porosity paper, and dilute the filtrate to 2,000 ml.

Stock titanium solution (1 ml = 1 mg TiO_2). Transfer 1.013 grams of National Bureau of Standards titanium oxide No. 154 and 50 ml of sulfuric acid to a 250-ml Erlenmeyer flask. Swirl the flask vigorously over the flame of a Meker burner to bring the acid to incipient boiling, and continue heating until the acid becomes translucent. When the solution is cool, transfer it to a 1-liter beaker containing 500 ml of water. Let the solution stand overnight; then filter it through a small fine-porosity paper into a 1-liter volumetric flask. Wash the beaker and paper with 1-to-19 sulfuric acid. Dilute the filtrate to the mark, and mix it.

Low-standard titanium solution (1 ml = 0.1 mg TiO_2). Transfer 50.00 ml of stock titanium solution to a 500-ml volumetric flask. Add 200 ml of 20-percent potassium pyrosulfate solution and 50 ml of 1-to-1 sulfuric acid. Let the solution cool to room temperature; then dilute it to the mark, and mix it.

High-standard titanium solution (1 ml = 0.5 mg TiO_2). Pipet 50 ml of stock titanium solution into a 100-ml volumetric flask; add 40 ml of 20-percent potassium pyrosulfate solution and 5 ml of 1-to-1 sulfuric acid. Dilute the solution to the mark, and mix it.

Standardization of the photometer. Prepare, in 100-ml volumetric flasks, 10 solutions containing from 1.00 to 10.00 ml of stock titanium solution in increments of 1.00 ml. To each flask add 40 ml of 20-percent potassium pyrosulfate solution and 10 ml of 1-to-1 sulfuric acid; then dilute each solution to volume, and mix it. Following the technique described in the standard procedure for titanium oxide, measure the transmittance of each of these solutions several times, and average the values obtained for each solution. The solution containing 10 mg of titanium oxide is the same as the low standard solution described in the procedure and should be used to set the wavelength of the photometer. Prepare tables in which titanium oxide is expressed in percent based on a 1-gram sample and 100 ml of solution. Assume that the relationship between log transmittance and concentration for adjacent values is linear, and calculate percent titanium oxide for each *increment of 0.2 percent*

transmittance. In a similar manner, prepare another table for measurements at 510 mμ, using solutions containing from 10 to 50 mg of titanium oxide. The solution containing 50 mg of titanium oxide is the same as the high standard described above and should be used to set the wavelength of the photometer.

TOTAL IRON OXIDE

Preparation of silver. In a 1-liter beaker, prepare a solution consisting of 30 grams of silver nitrate in 900 ml of water. Add 10 drops of nitric acid and 25 ml of glacial acetic acid, and stir the solution. By means of a glass cradle, suspend a stick of zinc about 3 inches long and three-eighths inch in diameter in a horizontal position about 1 inch below the top level of the liquid. Let the solution stand overnight without disturbing it. Dislodge the silver formed on the zinc stick, and remove the zinc from the solution. Collect the silver on a Buchner funnel, and wash it thoroughly with water; then transfer it to a porcelain dish, and dry it in an oven at 105°C. Gently rub the silver through 20-mesh sieve to break up lumps, and discard any that fails to pass the sieve.

Loading the reductor. Turn the reductor tube (fig. 7) upside down, and immerse the reservoir in water contained in a beaker. Apply suction to the delivery tube until the reductor is filled with water; close the stopcock, and quickly invert the reductor and beaker. (If the tube is filled from the top, an air space forms below the fritted disk.) Lower the water level to the bottom of the reservoir, and add 2 ml of 1-to-1 sulfuric acid. Add silver, a spoonful at a time. After each addition, stir the silver with a glass rod just enough to break up voids until the reductor is filled with silver to the bottom of the reservoir. Using a flat-ended glass rod, compact the silver slightly; then fill the reservoir with 1-to-99 sulfuric acid. Place a graduate under the delivery tube, and allow the reductor to drain with the stopcock fully open for 15 seconds. If the flow rate exceeds 60 ml per minute, compact the silver still more, fill the reservoir, and again check the rate of flow. Add silver if necessary to maintain the level of the silver at about 1 cm below the bottom of the reservoir. Continue in this manner until the rate of flow is 60 ml per minute with the reservoir full and the stopcock fully open. Pass an additional 500 ml of 1-to-99 sulfuric acid through the column of silver; then displace the sulfuric acid with 1-to-19 hydrochloric acid.

Potassium dichromate–0.06262N at 25°C. Add about 1 liter of water that is at room temperature to a 2-liter volumetric flask. Take the temperature of the water, and from the following table determine the amount of potassium dichromate required:

Temperature of water (°C)	$K_2Cr_2O_7$ required (grams)	Temperature of water (°C)	$K_2Cr_2O_7$ required (grams)
21	6. 147	26	6. 140
22	6. 146	27	6. 138
23	6. 144	28	6. 137
24	6. 143	29	6. 135
25	6. 141	30	6. 134

Weigh this amount of potassium dichromate; transfer it to the flask, and swirl the flask until all the potassium dichromate dissolves. Dilute the solution to the mark with water, and mix it. To guard against a possible error in weighing dichromate, check the titer of the solution against a solution having a known iron content after this iron solution has been passed through the silver reductor.

Sodium diphenylamine sulfonate–0.2 percent. Dissolve 0.2 gram of sodium diphenylamine sulfonate in 100 ml of hot water.

Ammonium chloride–15 percent. Dissolve 300 grams of ammonium chloride in about 1 liter of water, and let the solution stand overnight; then filter it through a fine-porosity paper, and dilute it to 2 liters.

Potassium dichromate solution–5 percent. Dissolve 5 grams of potassium dichromate in 100 ml of water. Let the solution stand overnight, and filter it through a fine-porosity paper.

FERROUS OXIDE

Dissolving solution. Transfer 50 grams of boric acid to a 2-liter beaker; then add 1,500 ml of water, 175 ml of sulfuric acid, and 200 ml of phosphoric acid. Stir the solution and heat it on the water bath in order to dissolve the boric acid. Cool the solution, transfer it to a polyethylene storage bottle and dilute it to 2 liters.

Sodium diphenylamine sulfonate–0.2 percent. See "Total iron oxide," p. 85.

Potassium dichromate–0.06262N.—See "Total iron oxide," p. 85.

THE ALKALIS

Chloroplatinic acid (0.05 gram Pt per milliliter). Dissolve 25 grams of pure platinum sponge in aqua regia. Transfer the solution to a large evaporating dish, and evaporate it to a syrupy consistency on the water bath. Add 50 ml of water and 25 ml of hydrochloric acid; stir the solution, and again evaporate it to syrupy consistency. Repeat this last operation two more times. Dissolve the salts in water, and transfer the solution to a 400-ml beaker Saturate the solution with chlorine gas; heat it for several hours on the water bath, and filter it through a fine-porosity paper into a 500-ml volumetric flask. Wash the beaker and paper a few times with water; then dilute the filtrate to the mark and mix it. (The recovery of platinum from residues is discussed by Hillebrand and others, 1953, p. 43.)

Alcohol–80 percent. Add 300 ml of water to 1,500 ml of pure 95-percent ethyl alcohol.

MANGANESE AND PHOSPHORUS OXIDES

Boric acid–5 percent. Transfer 100 grams of boric acid to a 2-liter beaker; add about 1,900 ml of water, and heat the solution on the steam bath until the boric acid dissolves. Then let the solution stand overnight, and filter it through a fine-porosity paper into a reagent bottle. Dilute the solution to 2 liters.

Periodic acid–5 percent. Dissolve 25 grams of periodic acid in 300 ml of water. Let the solution stand overnight; filter it through a fine-porosity paper, and dilute the filtrate to 500 ml.

Stock manganese solution (1 ml=0.25 mg MnO). Dissolve 0.3872 grams of pure manganese metal in 300 ml of hot 1-to-9 nitric acid. Filter the solution through a fine-porosity paper into a 2-liter volumetric flask, and wash the beaker and paper with water. Dilute the solution to the mark, and mix it.

Standard manganese solution (1 ml=0.025 mg MnO). Pipet 50 ml of stock manganese solution into a 500-ml volumetric flask. Dilute this portion to about 200 ml; add 25 ml of nitric acid and 50 ml of 5-percent periodic acid solution, and wash down the inside of the flask with water. Immerse the flask in boiling water for 1 hour. Cool the solution to room temperature; dilute it to the mark, and mix it.

Standardization of the photometer for manganese oxide. Prepare, in 100-ml volumetric flasks, five solutions containing from 0.50 to 2.50 mg of manganese oxide in increments of 0.50 mg. Dilute each of the solutions to about 50 ml; add 20 ml of 1-to-1 nitric acid and 10 ml of 5-percent periodic acid solution to each. Then immerse all of the flasks in boiling water for 1 hour. Cool the solutions; dilute each to volume, and mix it. Make several transmittance measurements for each solution by following the technique described in the standard procedure for manganese oxide, and average the results obtained for each solution. Use the solution containing 2.50 mg of manganese oxide, which is the same as the standard manganese solution described above, to set the wavelengths for the photometer. From the average values, prepare transmittance tables that give the percent manganese oxide for each increment of 0.2 percent transmittance. Base the percentages of manganese oxide on a 0.25-gram sample in 50 ml of solution.

Ammonium nitrate–50 percent. Dissolve 1,000 grams of ammonium nitrate in about 1,000 ml of water, and heat the solution to dissolve the salts. Let the solution stand overnight. Filter it through a fine-porosity paper, and dilute it to 2 liters.

Solution of ammonium molybdate and ammonium nitrate. Dissolve 50 grams of ammonium molybdate in 200 ml of water. Let the solution stand overnight, and filter it through a fine-porosity paper into a 2-liter polyethylene bottle. Add 800 ml of 50-percent ammonium nitrate, and dilute the solution to 2 liters. Do not attempt to dissolve the two salts together—ammonium molybdate will not dissolve in ammonium nitrate solution.

Solution of ammonium vanadate and ammonium molybdate. Dissolve 5.000 grams of ammonium vanadate in 400 ml of hot water. Add 100 grams of ammonium molybdate, and stir the solution until the molybdate dissolves. Let the solution stand overnight; then filter it through a fine-porosity paper into a 2-liter volumetric flask. Wash the beaker and paper with water. Add 10 ml of ammonium hydroxide to the filtrate; dilute the solution to the mark, and mix it. Then transfer it to a polyethylene storage bottle.

Stock phosphorus solution (1 ml=0.25 mg P_2O_5). Dilute 2.2 ml of phosphoric acid to 200 ml. Determine the phosphorus pentoxide content of a 10-ml portion of this solution by precipitating phosphorus as magnesium-ammonium phosphate (Hillebrand and others, 1953, p. 702). Using a buret, transfer the amount of the solution containing 500 mg of phosphorus pentoxide to a 2-liter volumetric flask. Dilute this portion to the mark, and mix it.

Standardization of the photometer for phosphorus pentoxide. Prepare, in 100-ml volumetric flasks, six solutions containing from 0.00 to 2.50 mg of phosphorus pentoxide in increments of 0.50 mg. Dilute each solution to 60 ml, and add to each 8 ml of 1-to-1 nitric acid and 10 ml of ammonium molybdate-ammonium vanadate reagent. Dilute each solution to volume, and mix it. Measure the transmittancies of these solutions following the technique described in the standard procedure for phosphorus oxide (p. 78). Use the end members of the series, which are the same as the reference and low-standard solutions described in the procedure for phosphorus, to set the wavelength for the photometer. Make several transmittance readings for each solution in order to obtain an average value. Prepare a table giving the phosphorus pentoxide in percent for each increment of 0.2 percent transmittance. Base the percentage on a 0.25-gram sample in 100 ml of solution. In a similar manner, prepare another table for use at the longer wavelength for solutions containing from 2.50 to 5.00 mg of phosphorus pentoxide per 100 ml.

CARBON DIOXIDE

Anhydrous magnesium perchlorate. Sieve with a 35-mesh screen, and discard the fines.

Anhydrous copper sulfate (through 10 mesh onto 20 mesh). Make a paste by adding water to copper sulfate powder, and dehydrate this mixture by heating the paste overnight at 160°C. Grind the hard cake so formed by gentle pressure with a pestle in an agate mortar, and reserve the portion that passes a 10-mesh screen and is retained by a 20-mesh screen for use in the apparatus.

Loading the apparatus. Fill the left arm of the left-hand U-tube (fig. 11) with magnesium perchlorate and the right arm with sodium hydroxide-asbestos. Tap the tube with a policeman to compact these materials somewhat; then place a piece of cotton in each arm. Wipe the ground-glass joints clean, grease the stoppers, and put them in place. Add 5 ml of sulfuric acid to the bubbler, and grease the stopper generously before replacing it. Fill the left arm of the center U-tube with magnesium perchlorate. Fill the right arm to about one-third its height with anhydrous copper sulfate and the remainder of this arm with magnesium perchlorate. Put a plug of cotton in each arm. Wipe the joints clean; then grease the stoppers, and put them in place. In a similar manner fill the extreme right-hand tube with magnesium perchlorate.

Loading the absorbers. Place a layer of cotton in the bottom of the tube in order to cover the opening to the side tube. Half fill the absorber with magnesium perchlorate, and fill the remainder of the tube up to the stopper with sodium hydroxide-asbestos. Clean the ground-glass joint; grease the stopper, and replace it. Load two tubes in this manner. Use a third tube as a tare. Add glass beads to it until its weight is slightly less than that of the lighter of the two absorption tubes.

SULFUR

Barium chloride–10 percent. Dissolve 50 grams of barium chloride dihydrate in 400 ml of water. Let the solution stand overnight; filter it through a fine-textured paper, and dilute it to 500 ml.

Brom phenol blue indicator–0.1 percent. Wet 0.1 gram of brom phenol blue with one drop of ammonium hydroxide. Add 100 ml of water, and stir the solution until the indicator dissolves.

SULFUR TRIOXIDE

Barium chloride–10 percent. See "Sulfur."

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