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A Review of Classical Silicate-Rock Analysis and Recommended Modifications of Classical Methods of Analysis

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By Lillie B. Jenkins

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United States Department of the Interior

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ABSTRACT

This work was undertaken to review current classical chemical methods, to define existing problems, and to suggest modifications to improve the accuracy and precision of classical chemistry. Problems that may arise in the analysis of silicate rocks are discussed, and detailed procedures are given for the determination of 13 constituents commonly present in silicate rocks.

The method for the determination of water is a simplification of the Penfield method and includes some modifications made by other authors. The detailed description of the method can easily be followed by inexperienced chemists who can thus obtain very accurate results. The equipment needed is simple and readily available.

A detailed discussion of the sample blank is given. The blank and the standard sample are used as controls for the analysis. A known amount of iron is added to the blank to ensure a precipitate in the blank of approximately the same size as the precipitate obtained in the sample.

Many possible errors that could be made in the determination of silica and that would lead to errors in the remaining determinations are presented, and precise directions are given on how to avoid these errors. If the methods recommended in many textbooks are followed as outlined, serious errors can be made. For example, heating the residue from the second dehydration of silica at 105°C to 110°C is the procedure commonly recommended in the literature. However, the well-known reaction

$$Pt^\circ + 4Fe^{3+} + 6Cl^- \rightarrow PtCl_6^{2-} + 4Fe^{2+}$$
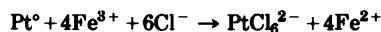
is greatly catalyzed when the residue is heated at 105°C, thereby introducing platinum into the analysis. Thus, the silica residue should not be heated above the temperature of the steam bath in order to avoid the introduction of platinum into the analysis. The complications encountered in the subsequent analysis when this precaution is not taken are discussed.

The necessity of removing platinum from solution with hydrogen sulfide prior to the determination of the ammonium hydroxide group has always been questionable. This step is elimi-

nated in this work because the introduction of platinum into the analysis is avoided when the steps outlined are followed.

The techniques outlined here eliminate the difficulties encountered in the precipitation of excess iron with ammonium hydroxide.

An excessive amount of ammonium salts can interfere with the precipitation of calcium and magnesium. These salts are easily and efficiently removed by the addition of nitric acid. Reprecipitating calcium oxide after dissolving the ignited calcium oxide precipitate ensures the removal of any magnesium that may have accompanied the calcium precipitate.

L. C. Peck (1964, U.S. Geological Survey Bulletin 1170) recommended that the filtrate from the calcium determination stand several days after the addition of dibasic ammonium phosphate and that the beakers be scratched in order to precipitate the magnesium ammonium phosphate. The procedure as outlined here eliminates these steps.

Calcium should be recovered from the magnesium pyrophosphate precipitate if the sample contains much magnesium and very little calcium.

The small amount of SiO_2 that escapes recovery by two dehydrations is customarily recovered from the R_2O_3 precipitate by fusion of the ignited oxides with $K_2S_2O_7$, dissolution of the cake in dilute H_2SO_4, and evaporation of the solution to fumes of SO_3. This procedure is recommended in this report with the following modifications:
1. A temperature of 600°C is set for the pyrosulfate fusion.
2. Platinum dishes are recommended for the dehydration of the residual silica rather than glass beakers.
3. The filtrate is made to a definite volume, and separate aliquots are taken for the determination of total iron and titanium.

For the ferrous iron determination, the sample is decomposed in a 100-ml platinum crucible, and the method used for calculating the percentage of iron in the sample is simple and direct.

The conditions for the precipitation of ammonium phosphomolybdate as reported in the literature are varied and indefinite. The method "The Determination of Phosphorus in Rocks Containing Vanadium" by R. B. Randolph and F. S. Grimaldi

(1953, U.S. Geological Survey Bulletin 992, p.49–55) was chosen for the precipitation of ammonium phosphomolybdate because it is a routine procedure for precipitating P_2O_5 in amounts from 0.1 mg to 2.0 mg with no changes in conditions or quantities or reagents. The precipitate is dissolved, and phosphorus is determined colorimetrically or gravimetrically as described.

Tests were made to determine the suitability of the IL 443 Flame Photometer for the quantitative determination of sodium and potassium in silicate rocks after determining a method of decomposition and a suitable solution for presentation of the sample to the flame. A 1-g sample is decomposed in order to ensure a representative sample. Complete decomposition is effected in a covered Teflon beaker with nitric, sulfuric, and hydrofluoric acid, and the sample is dissolved in hydrochloric acid. The standards are prepared with an internal standard, and the samples are closely bracketed with the standards when the readings are made.

Tests were made to determine the effect of various levels of sodium on the potassium determinations and the effect of various levels of potassium on the sodium determinations. No effects were observed. The accuracy of the data obtained and the simplicity of the method recommends its use even though the method is not classical.

INTRODUCTION

In order to determine which methods would be used in a newly created classical-analysis project devoted exclusively to a highly accurate and precise analysis of silicate rocks, a study was made of the methods published by Kolthoff and Sandell (1943), Hillebrand and others (1953), Shell (*in* Kolthoff and Elving, 1962), Peck (1964), Maxwell (1968), Bennett and Reed (1971), and others listed in the "Selected References." The project was created (1) to train chemists in classical analytical methods because of the progressively worsening
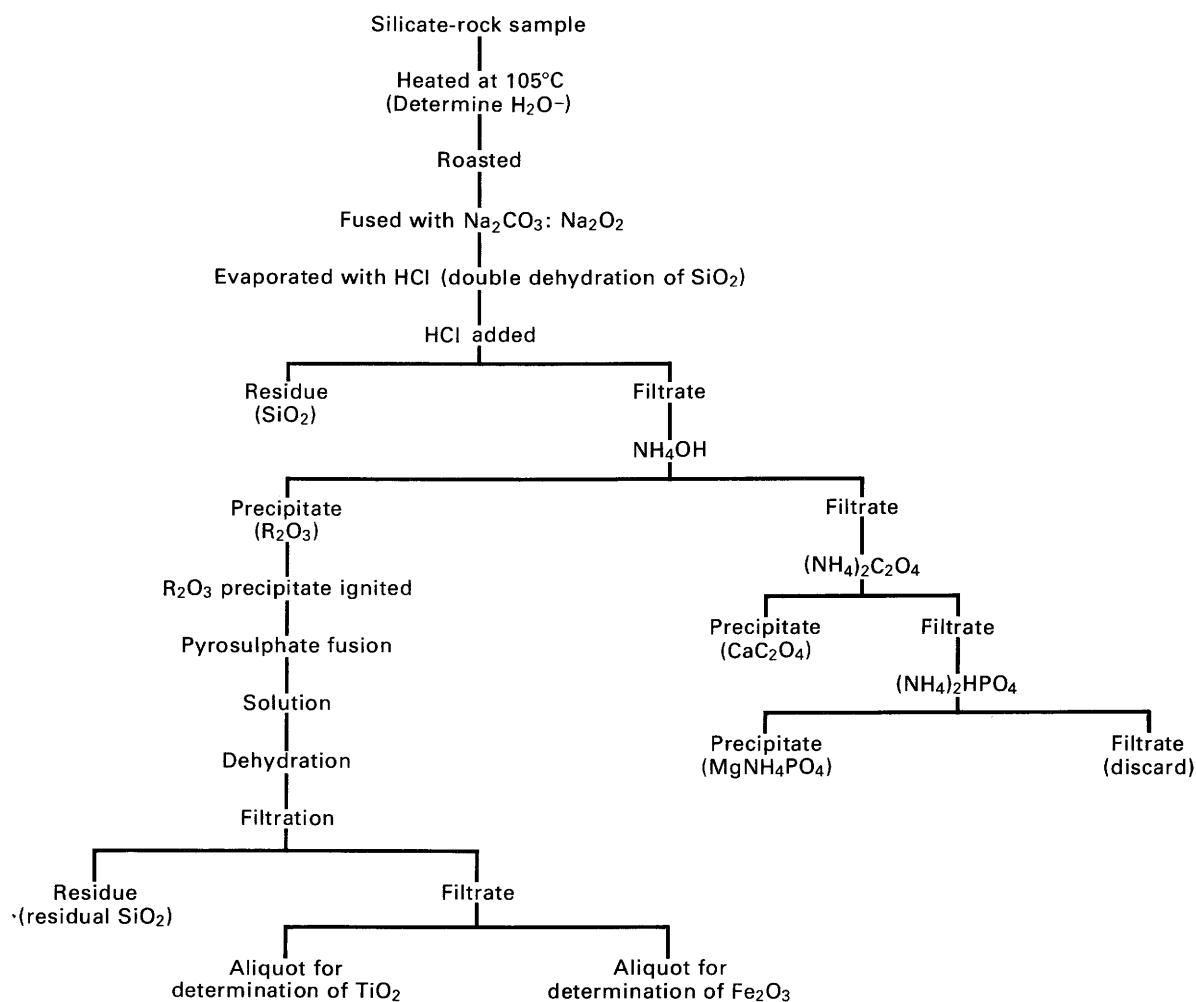
```
                    Silicate-rock sample
                            |
                    Heated at 105°C
                    (Determine H₂O⁻)
                            |
                        Roasted
                            |
                 Fused with Na₂CO₃: Na₂O₂
                            |
        Evaporated with HCl (double dehydration of SiO₂)
                            |
                        HCl added
                            |
         ┌──────────────────┴──────────────────┐
      Residue                              Filtrate
      (SiO₂)                                   |
                                            NH₄OH
                                               |
                            ┌──────────────────┴──────────┐
                       Precipitate                     Filtrate
                        (R₂O₃)                             |
                            |                         (NH₄)₂C₂O₄
                 R₂O₃ precipitate ignited                  |
                            |               ┌──────────────┴──────────┐
                  Pyrosulphate fusion   Precipitate             Filtrate
                            |            (CaC₂O₄)                   |
                        Solution                              (NH₄)₂HPO₄
                            |                                      |
                       Dehydration              ┌─────────────────┴────────────┐
                            |               Precipitate                    Filtrate
                       Filtration           (MgNH₄PO₄)                    (discard)
                            |
          ┌─────────────────┴────────────┐
       Residue                       Filtrate
     ·(residual SiO₂)                     |
                          ┌──────────────┴──────────────┐
                    Aliquot for                    Aliquot for
              determination of TiO₂          determination of Fe₂O₃
```

FIGURE 1.—Diagram for analysis of the sample after total water is determined on a 1-g sample.

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shortage of chemists trained in applied analytical chemistry by educational institutions and (2) to satisfy the demand for more classical analyses at the U.S. Geological Survey(USGS).

The procedures recommended are basically those described in the "Selected References," with some modifications. The discussions are given primarily to enable relatively inexperienced analysts to perform the analysis without difficulty and to eliminate some of the problems that more experienced analysts have encountered.

Methods are described for determining SiO_2, Al_2O_3, CaO, H_2O^+, H_2O^-, and MgO by gravimetric analysis; Fe_2O_3 and FeO by volumetric analysis; Na_2O and K_2O by flame photometric analysis; and TiO_2, P_2O_5, and MnO by spectrophotometric analysis. I recommend determining CO_2 by the widely accepted method of decomposing the sample with HCl and absorbing the carbon dioxide evolved into previously weighed absorption tubes. The CO_2 determination is not discussed further in this report as the special apparatus required and detailed procedures for the determination are given by Kolthoff and Sandell (1943, p. 385–389), Groves (1951, p. 110–114), Hillebrand and others (1953, p. 768–770), Peck (1964, p. 79–80), Maxwell (1968, p. 430–433), and Bennett and Reed (1971, p. 208–210).

The diagram for analysis of the sample after total water is determined is shown in figure 1.

TREATMENT OF THE SAMPLE

Ten to 20 g of a representative rock sample ground to pass a 100-mesh screen is usually required. Although an 8-g representative sample is adequate for a single determination of each constituent, more material is desirable to have a reserve for checking results and for use as a future reference material. A semiquantitative spectrographic analysis of the sample should be made in order to determine its approximate composition and the presence of any interfering constituents. The sample should be mixed well, then rolled and quartered on a piece of glazed paper with a demagnetized steel or plastic spatula. The quarters are then returned to the original sample bottle by use of the spatula. Pouring the sample causes a segregation of the particles and should be avoided. Four samples, a blank, and a standard sample can be analyzed conveniently and economically in each operation.

If sufficient sample is available, separate 1-g samples are used for the determination of total water ($H_2O^- H_2O^+$), P_2O_5 and MnO, Na_2O and K_2O, and FeO. Another 1-g sample is used for the determination of H_2O^-, SiO_2, Fe_2O_3, Al_2O_3, CaO, TiO_2, and MgO. Exactly 1 g of sample is weighed so that results can be calculated easily.

DETERMINATION OF TOTAL WATER

The water content of a silicate rock is divided into two parts: 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^+.

Percent total water =
$$\text{percent } H_2O^- + \text{percent } H_2O^+$$

The method of Penfield (1894) with some modifications is the method generally used for the determination of water in silicates. The sample mixed with a flux is fused in the enlarged end of a Penfield tube in order to expel the water into the upper part of the tube, which is cooled in an ice bath (figs. 2, 3). The fused bulb and sample are pulled off, and this end is sealed. A closely fitting glass rod is inserted into the tube, and the tube is stoppered and weighed. The tube is then dried and reweighed; the loss in weight is the weight of the total water in the sample.

Other volatile substances except carbon dioxide are retained by the flux. If carbon dioxide remains in the tube, the value for total water is high. I use Sandell's (1951) technique of conveniently displacing carbon dioxide from the tube by inserting a closely fitting glass rod into the tube just before it is stoppered. This technique eliminates the need for special equipment to drain CO_2 from the tube (Peck, 1964).

Maxwell (1968) used lead oxide as the flux. Shapiro (1975) used sodium tungstate. Peck (1964) stated that neither sodium tungstate, lead oxide, nor lead chromate is a satisfactory flux and recommended that a mixture of two parts lead oxide and one part lead chromate be used. Peck stated that this mixture is sufficiently reactive to decompose hornblende and that intumescence is not troublesome when this mixture is used in the analysis of samples containing carbon or carbon dioxide. I have found sodium tungstate to be a very satisfactory flux for the decomposition of silicate rocks.
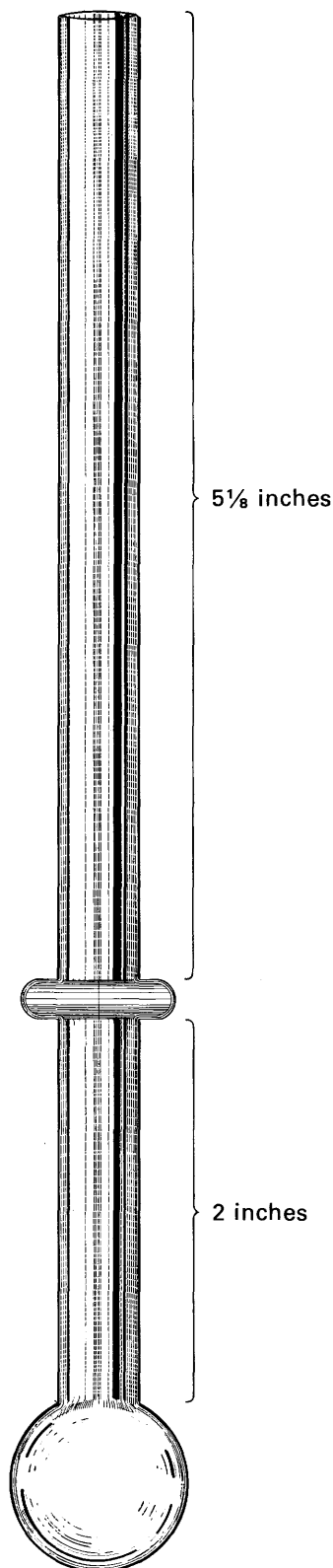
3

5⅛ inches

2 inches

FIGURE 2.—Penfield tube.

APPARATUS

Penfield tube in tube support

Funnel—A long-stemmed funnel, which, when supported, will reach nearly to the bottom of the Penfield tube.

Capillary plug—A piece of Tygon[1] tubing about 1½ in long, one end of which fits snugly over the top of the Penfield tube and the other end of which has a capillary tube about 1¼ in long fitted into it.

Meker burner, safety glasses, propane-oxygen torch, timer

Displacement rod—Glass rod that fits snugly in the upper part of the Penfield tube. The length should be approximately the length of the tube minus the bulb.

REAGENT

Sodium tungstate—Heat several hundred grams of Na_2WO_4 overnight at 180°C in a drying oven. Allow to cool, grind to a fine powder, and store in an open container in the drying oven.

PROCEDURE

1. Determination of reagent blank.
2. Transfer 3 g of oven-dried Na_2WO_4 to a Penfield tube with the aid of a long-stemmed funnel. The funnel should extend well into the bulb of the tube.
3. Stopper the tube with a capillary plug and transfer the tube to the tube support in such a manner that the bulb end extends out of the tube support and the enlarged part of the tube is just inside.
4. Put on safety glasses.
5. Cover the upper part of the tube well with ice, and light the Meker burner.
6. Set the timer for 10 min and brush the flame around the tube for about 1 min.
7. Set the burner under the bulb of the Penfield tube and turn the tube slowly as the sample fuses.
8. Light the propane part of the torch; turn on the oxygen and adjust the flame to a fine point.

FIGURE 3.—Penfield tube in tube support.

9. Continue to heat the sample with the Meker burner until the 10 min have passed.
10. Remove the Meker burner and place the torch in the left hand and a pair of tongs in the right hand.
11. Place the tip of the torch in the middle of the extended tube, and pull off the bulb as the tube melts. Touch the torch to the end of the tube and seal it.
12. Turn off the oxygen.
13. Turn off the propane.
14. Carefully remove the tube from the ice bath; grasp with a piece of filter paper and gently blot it dry. DO NOT RUB. The development by friction of a charge of static electricity on the surface of the tube can cause a serious error.
15. Quickly remove the capillary plug from the tube and insert a displacement rod. Close the tube with a small cork.

16. Place the tube upright in a small beaker and allow it to stand in the balance room 30 min before weighing.
17. Weigh a 150-ml beaker and record its weight. Place the tube with the cork removed in the weighed beaker and record this weight. Replace the cork in the tube and let it stand another 30 min.
18. Repeat step 17 every 30 min until constant weight is obtained.
19. Remove the cork and reserve.
20. Set the tube upright in a beaker and place in an oven at a temperature of 105°–110°C overnight.
21. Replace the cork in the tube and set in the balance room for 30 min.
22. Remove the cork and weigh the tube. Repeat the weighings until constant weight is obtained.
23. The difference in the weight of the tube be-

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fore and after drying is the weight of total water in the blank (a).

24. Repeat this procedure with a 1-g sample and the 3 g of Na_2WO_4. The weight loss of the tube in grams is the weight of total water in the sample (b).

25. Calculate the percentage of water in the sample as follows:

Percent total water (H_2O^+ plus H_2O^-)
$$= 100 \times (b - a)/\text{sample weight in grams}$$

THE SAMPLE BLANK FOR THE MAIN PORTION

Although running blank and standard determinations is considered standard practice, analysts may not follow this practice unless asked to do so. No determination can be considered accurate unless a reliable blank has been determined and the results obtained in the analysis have been corrected accordingly (Bennett and Reed, 1971, p. 7; American Society for Testing Materials, 1950a,b).

Hillebrand and others (1953, p. 926) stated that a hot water bottle even of the best glass will afford weighable amounts of alkali to the water it holds. As Kolthoff and Sandell (1943, p. 287) stated:

> Errors arising from the impurities through the reagents and vessels, and sometimes from other sources, can be allowed for by running what is called a blank determination. In making a blank, the sample is omitted; otherwise the details of the procedure are followed exactly as far as possible. The same amount of reagent is added, the same volume of solution is employed, the same temperature is used in the operations, the same period of time is allowed for each step, and so on. The precipitate finally obtained is weighed, if the determination is a gravimetric one, and the amount found is deducted from the weight of precipitate given by the sample. The blank is best carried along simultaneously with the sample. Although the errors arising from the sources mentioned above are often greatly reduced by running a careful blank, they are not always entirely eliminated or even minimized, because the conditions in the determination itself cannot be exactly reproduced in the blank.

Because conditions in the determination cannot always be duplicated in the blank, the analyst must be able to evaluate a reliable blank. For example, a sodium carbonate-sodium peroxide flux, if used to decompose the sample, will attack the platinum crucible at a lower temperature than will the mixture of the flux and the sample. Therefore, the fusion of the flux used to prepare the blank should be made at a temperature no higher than 900°C or large amounts of platinum may be unnecessarily introduced into the analysis. An example of another problem related to blanks was given by Hillebrand and others (1953, p. 19–21): "a large iron or aluminum hydroxide precipitate will carry down all silica, arsenic, and antimony derived from the glassware, whereas the very much smaller precipitate obtained in the blank experiment may not."

Hillebrand and others (1953, p. 503) pointed out that one of the chief errors in a determination of Al_2O_3 in materials is that made by "misleading corrections for impurities derived from the reagents or through attack on the vessels used." They also said (Hillebrand and others, 1953, p. 682):

> Corrections for impurities derived from the reagents or by attack of the containing vessels are apt to be entirely misleading if made as in the usual fashion by carrying the reagents alone through the analysis. The reason for this lies chiefly in the size of the precipitate obtained in the analysis, as compared with that obtained with the reagents. The former carries down practically all of the silica that is introduced by the reagents, attack on glassware, or other causes; the latter carries down very little. This then leads to high results for silica and can be avoided by adding to the solution of the reagents approximately as much iron and aluminum as are contained in the sample under analysis.
>
> For example, in analyses of 0.5-g portions of bauxite, an average correction of less than 0.1 mg of silica was indicated by the reagents alone, and 0.9 mg when 0.25 g of alumina as pure aluminum chloride was added to the reagents. Corrections based on the analysis of the reagents alone would therefore have caused a plus error of 0.18 percent of silica.

In the procedure outlined in this report, a known amount of iron is added to the blank determination in order to increase the size of the precipitate obtained with the reagents to approximately the size of the precipitate obtained in the analysis of the samples.

REAGENTS

Standard iron solution (see page 22)
Hydrofluoric acid (48 percent)

PROCEDURE

Transfer a suitable aliquot of standard iron solution to a 300-ml platinum dish, add 10 ml of HF, and evaporate the solution to dryness.

Reserve this blank and use it in step 1 of "Removing the Melt from the Crucible" in the section "Determination of Silica in Samples Containing Less Than 2 Percent Fluorine."

DETERMINATION OF MOISTURE

A 1.000-g portion of the sample is added to a weighed platinum crucible; the crucible and its contents are weighed, heated in an oven having a temperature of 105°–110°C, cooled in a desiccator, and reweighed. The heating and weighing are repeated until constant weight is obtained. The sample is reserved for the determination of silica.

PROCEDURE

1. Obtain the weight of a covered 30-ml platinum crucible that has been cleaned by being fused with potassium pyrosulfate, washed with water, boiled in 1 + 1 HCl, washed with water again, and then heated at 1,200°C in an electric furnace until its weight is constant.
2. Transfer a 1.0000-g sample to this crucible, and record the weight of the covered crucible plus the sample.
3. Remove the cover from the crucible; replace it with a small piece of filter paper and place the platinum cover and the crucible and its contents in an oven at 105°–110°C for 1 h.
4. Remove crucible from oven. Replace the filter paper with the platinum lid, cool in desiccator, and weigh.
5. Repeat the heating at 105°–110°C as before until constant weight is obtained. A loss in weight of more than 5 mg indicates an hygroscopic sample, of which all portions to be used in the analysis of the major constituents should be weighed at one time.
6. Reserve this sample for the preparation of the main portion of the analysis as directed in the following procedures.
7. Calculate the percentage of moisture (H_2O^-) by multiplying the loss in weight in grams by 100.

ROASTING THE SAMPLE

Roasting the sample as described below oxidizes any reducing substances present in silicates that would attack the crucible during the fusion.

PROCEDURE

1. Support the covered platinum crucible, which contains the sample used for the moisture determination, on a clay or silica triangle over a burner and heat the crucible with a low flame to drive off combined water.
2. Increase the height of the flame until the bottom part of the crucible is dull red.
3. Move back the lid to permit the entrance of air and maintain the bottom of the crucible at a dull red for 5 min.
4. Cover the crucible and allow it to cool.
5. Reserve for fusion of the sample.

## DETERMINATION OF SILICA IN SAMPLES CONTAINING LESS THAN 2 PERCENT FLUORINE

For determination of silica in samples containing less than 2 percent fluorine, platinum crucibles are generally preferred to porcelain crucibles because removing the separated silica from porcelain crucibles is difficult. However, special care must be taken to prevent the introduction of an unnecessary amount of platinum into the analysis as it precipitates fractionally from solution when the solution is treated with ammonium hydroxide. The precipitation of platinum can cause serious difficulties in the subsequent steps of the analysis (Maxwell, 1968, p. 132, 365–366; Hillebrand and others, 1953, p. 341–343; Groves, 1951, p. 226). Platinum may be introduced by ferric chloride attacking the crucible.

The removal of platinum by precipitation with hydrogen sulfide is not a pleasant operation and can lead to other complications. Elements other than those of the hydrogen sulfide group may be precipitated by hydrogen sulfide in strong acid solution through the formation of mixed sulfides. Iron may be carried down to some extent, and, unless the precipitate is very small (which indicates the presence of platinum alone), the precipitate should be redissolved and the hydrogen sulfide precipitation should be repeated.

Rather than remove the platinum, the analyst should avoid introducing it by using a sodium carbonate-sodium peroxide fusion made in the electric furnace at 950°C for 20 min. This fusion effectively decomposes silicate rocks and does not attack the platinum crucible. The crucible should be weighed before and after fusions to verify that the loss of weight of the crucible is negligible. When

this procedure is followed, the platinum crucible can be used without worries about introducing platinum into the sample even if the sample is iron rich.

Hillebrand and others (1953), Shell (*in* Kolthoff and Elving, 1962), and Maxwell (1968) suggested that the residue from the second dehydration of silica be heated at 105°–110°C for 1 h. However, analysts in this laboratory have found that several milligrams of platinum are introduced into the analysis from the platinum dish if the residue from the HCl dehydration of silica in the platinum dish is heated at 105°–110°C, even if the residue contains little iron, and that the attack on the platinum dish increases as the iron content of the sample increases. Heating at 105°–110°C greatly catalyzes the reaction shown in the following equation:

$$Pt° + 4Fe^{3+} + 6Cl^- \rightarrow PtCl_6^{2-} + 4Fe^{2+}$$
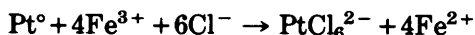
Once the solution in which platinum is present has been treated with ammonium hydroxide, it is apt to precipitate fractionally in subsequent operations involved in a complete analysis. It may show up as a yellowish- to greenish-gray deposit on the bottom of the beaker during evaporation following the separation of the R_2O_3 group or it may contaminate other precipitates. No problems were encountered when the residue from the silica dehydration was heated only to the temperature of the steam bath as recommended by Peck (1964, p. 23), and silica was completely recovered.

Potassium peroxide is added to the Na_2CO_3 used in the main fusion to ensure that iron in the sample is not reduced to the metallic state during the fusion.

Alcohol is added to the platinum dish containing the fused cake before HCl is added in order to reduce Mn (VI), which would react with HCl to form chlorine. The presence of manganese is indicated if the carbonate melt is green; the presence of chromium is indicated if it is yellow.

If the HF residue from the silica fluoridation weighs less than 5 mg, the R_2O_3 precipitate should be added to the crucible containing the small residue, as the introduction of platinum from a fusion of the residue could introduce a greater error than that made by weighing a small residue as R_2O_3. If the weight of the residue exceeds 5 mg, it must be added to the filtrate from the silica dehydrations before the R_2O_3 is precipitated. The solution of the HF residue can be effected for

many samples if a little warm 1 + 1 HCl is added to the crucible.

The residual silica must be recovered from the R_2O_3 precipitate and this value added to the silica value obtained by double dehydration in order to obtain an accurate silica value. The procedure for the recovery of residual SiO_2 follows the procedure for solution of the R_2O_3 precipitate.

PROCEDURES
FUSION OF SAMPLE

1. Weigh 4 g of anhydrous Na_2CO_3 and carefully add about 2 g of it to the cooled roasted sample.
2. Mix the sample and flux thoroughly with a short platinum stirring rod.
3. Add approximately 0.2 g Na_2O_2 and again mix thoroughly. Do not attempt to brush off the stirring rod. Tap it against the sides of the crucible and "rinse" it in the remainder of the flux.
4. Tap the crucible gently on the bench top to settle the fusion mixture and sprinkle the rest of the flux over the surface to provide a trap for decrepitating particles during the initial heating stages of the fusion step.
5. Place the crucible in an electric oven at a temperature of 400°–500°C and gradually increase the temperature of the furnace to 900°C.
6. Remove the crucible and immediately grasp it with a pair of Blair tongs; swirl over a Meker burner for about 1 min.
7. Remove the crucible cover and check the completeness of the fusion.
8. Set the crucible containing the reagent blank aside and return the crucible containing the sample to the furnace.
9. Increase the temperature of the furnace to 950°C and maintain this temperature for 20 min.

10. Remove the crucible from the oven and immediately grasp it with a pair of Blair tongs.
11. Remove the cover and swirl the crucible over a Meker burner for about 1 min. Do not allow the flame to envelop the crucible, and do not allow the crucible bottom ever to come into contact with the blue cone of the burner flame.
12. Check for completeness of the fusion.
13. Replace the cover of the crucible and return it to the furnace.
14. Heat at 950°C for 10–15 min. If a preliminary semiquantitative spectrographic analysis indicated the presence of chromite or zircon, further heating at about 1,100°C is necessary to insure the decomposition of these minerals. Some platinum attack occurs if heating is prolonged at this temperature and should be avoided if possible.
15. Remove the crucible from the oven.
16. Grasp the crucible with a pair of Blair tongs and immediately rotate the crucible as it cools so that the contents will solidify around its walls.
17. Cover the crucible and allow it to cool.
18. Grasp the crucible with the Blair tongs and again heat it over the Meker burner for no more than 15 s at a dull red heat; remove it from the flame and allow it to cool to room temperature.

REMOVING THE MELT FROM THE CRUCIBLE

1. Gently strike the bench top with the crucible to loosen the melt from the crucible, and transfer the melt to a 300-ml platinum dish. Should the cake not separate freely and easily, add water and place the water-filled crucible on the steam bath and heat to loosen the cake.
2. Carefully transfer the contents of the crucible to the platinum dish and police the inside of the crucible to remove any adhering particles, adding all rinsings to the dish. If necessary, fill the crucible with water and digest overnight at room temperature.
3. Rinse the crucible with a few milliliters of 1+1 HCl and finally with water, transferring all washings to the platinum dish.
4. Police the crucible and its cover.
5. Heat the crucible at 1,200°C for 30 min. Cool in a desiccator and weigh.

6. Compare this weight with the weight of the crucible before the fusion was made in order to determine the attack of the fusion on the platinum.
7. Repeat the heating and cooling until the crucible is at constant weight.
8. Record this weight and reserve the crucible for the ignition of the dehydrated silica.
9. Add enough water to the platinum dish to make the volume about 75 ml. Add 10 ml of ethyl alcohol to the dish, cover it with a speedy-vap cover, and let the solution stand overnight or until cake has disintegrated.

DEHYDRATION OF SILICA

1. Bend the lower 1½ in of a funnel at about a 30° angle and support it in a filter stand.
2. Stir contents of the platinum dish and verify that the cake has disintegrated. Crush any lumps that may be left by exerting light pressure with a platinum stirring rod.
3. Set the dish under the funnel in such a manner that the end of the bent funnel stem is between the lip of the dish and the speedy-vap cover.
4. Pour 50 ml of 1+1 HCl into a graduated cylinder and add through the funnel into the dish in portions small enough to avoid violent effervescence.
5. Let the dish stand until most of the effervescence stops; then rinse the funnel with a little water, catching the rinsings in the dish.
6. Remove the funnel.
7. Wash the underside of the speedy-vap cover into the dish and replace it on the dish.
8. Set the dish on the steam bath and let the solution evaporate to apparent dryness.
9. Stir the residue as the solution goes dry.
10. Without further heating, remove the dish from the heat, cool, and add 10 ml of concentrated HCl.
11. Tilt the dish and allow the acid to wet all the residue and to run up the sides of the dish. After 1 or 2 min, add approximately 50 ml of water, washing down the sides of the dish and the stirring rod.
12. Cover the dish and heat on the steam bath for 5–10 min, stirring to dissolve all soluble salts.
13. Wash down the sides of the dish if necessary to keep the volume at approximately 50 ml.

14. Decant the solution through an 11-cm #40 filter paper that has been washed once with HCl (5 + 95).
15. Wash down the sides of the dish, stir the silica into the acid, and pour it quickly onto the filter.
16. Wash any remaining silica onto the filter with a stream of hot HCl (5 + 95).
17. Scrub the stirring rod and the inside of the dish with a rubber policeman; then wash with hot HCl (5 + 95) and pour the washings through the filter.
18. Wipe out the inside of the dish and the underside of the lip with a small piece of filter paper, and add it to the filter.
19. Finally wash the residue and paper 10 times with the hot HCl (5 + 95). Allow the solution to drain through each time before the next wash is added.
20. When all traces of yellow color have been removed, lift the paper and drain the funnel stem into the beaker.
21. Carefully fold the paper in the funnel with the aid of a small platinum stirring rod and place the paper in the weighed crucible reserved for the ignition of the silica.
22. Place the crucible in an oven at 105°–110°C to dry.
23. Rinse the funnel into the beaker; then quantitatively transfer the solution to the platinum dish.
24. Reserve the beaker for the filtrate from the second dehydration.
25. Again evaporate the filtrate to apparent dryness; then continue heating the dry residue for 1 h on the steam bath.
26. Cool and drench the residue with 10 ml of concentrated HCl. Wet the salts with the acid as before.
27. Add approximately 50 ml of water to the dish and continue with the digestion, decantation filtering and washing, catching the filtrate in the 400-ml beaker as before, except use 9-cm #40 filter paper for the filtration.
28. Lift the paper and wash the funnel stem into the beaker. Reserve the solution.
29. Carefully fold the paper in the funnel with the aid of a platinum stirring rod and add to the crucible containing the main silica precipitate.
30. Place the cover on the crucible in such a manner that the crucible is only partially covered, and place in a cold electric muffle furnace with the door partially open.
31. Allow the temperature of the furnace to rise slowly to 800°C and maintain the temperature of the furnace at 800°C until all carbon is completely consumed.
32. Finally, heat at 1,200°C until the weight remains constant. The weight of the crucible and the silica minus the weight of the crucible is the weight of the impure silica.
33. Cautiously wash down the crucible lid into the crucible with a few drops of water.
34. Wash down the sides of the crucible onto the silica.
35. Add six drops of dilute H_2SO_4 (1 + 1) and 10 ml of concentrated HF to the crucible and set on a steam bath and evaporate to about 1 ml.
36. Place the crucible and its contents on a hot plate and carefully evaporate until fumes of SO_3 cease.
37. Cautiously heat the crucible over a small flame until the residue is dry; then place the covered crucible in an electric furnace at 1,100°C for 15 min.
38. Cool in a desiccator and weigh.
39. Repeat steps 33–38 until the weight remains constant. The difference between this weight and the weight of the crucible plus the impure silica represents the amount of SiO_2 determined by double dehydration. To this amount of SiO_2 add the residual SiO_2 and calculate the percentage of SiO_2 by multiplying this weight by 100 and dividing by the weight of the sample.
40. Record the weight of the residue from the volatilization of the silica. If this weight is more than 5 mg, the sample probably contains large amounts of titanium or zirconium. In any case, the residue should be examined visually to determine if it is more than a reddish-brown stain on the bottom of the crucible.
41. If the weight of the HF residue is less than 5 mg, reserve the crucible and its contents for the ignition of the R_2O_3 precipitate.
42. If the weight of the residue is more than 5 mg, add a few milliliters of warm 1 + 1 HCl to the crucible and digest for a few minutes at room temperature.
43. Transfer the solution to the filtrate reserved for the R_2O_3 precipitation.
44. If the residue is not dissolved in the warm

HCl (1 + 1), filter it into the main solution, and burn off the residue.

45. Add about 1 g of Na_2CO_3 to the crucible and fuse the residue in an electric furnace at 950°C for 20 min.
46. Add a little water to the melt and transfer the solution to the filtrate reserved from the double dehydration of silica.
47. Reserve this solution for the precipitation of the ammonium hydroxide group.
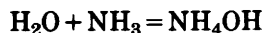
DETERMINATION OF THE R_2O_3 GROUP

A total of 10 to 15 ml of HCl in a volume of 200 ml is necessary to ensure that enough NH_4Cl will be formed when the HCl is neutralized with NH_4OH to prevent the coprecipitation of magnesium with the R_2O_3 group. Iron, aluminum, and the like can be quantitatively separated from manganese by precipitation with NH_4OH in boiling solution, provided the solution is boiled for no more than 2 min after careful adjustment of the alkalinity and is then immediately filtered. If contamination of the R_2O_3 by the introduction of platinum is indicated, the ignited R_2O_3 precipitate may be fused with Na_2CO_3 at 950°C and the R_2O_3 reprecipitated.

REAGENTS

Bromocresol purple indicator (0.1 percent)—Wet 0.5 g of bromocresol purple with a few milliliters of NH_4OH and dilute to 500 ml with water. Add just enough 1 + 1 HCl to make acid.

NH_4NO_3 wash solution (2 percent)—Add one drop of bromocresol purple and 20 g of NH_4NO_3 to 1 L of hot water; then add NH_4OH until the solution is just alkaline.

NH_4OH—Add 500 ml of water to a 1-L polyethylene bottle, set in an ice bath, and add NH_3 gas until the volume increases to 1 L.

$$H_2O + NH_3 = NH_4OH$$

HCl—(1 + 1 and concentrated)

PROCEDURES

PRECIPITATION OF THE R_2O_3 GROUP

1. Heat the solution reserved for precipitation of the R_2O_3 group, which should be about 200 ml in volume and contain about 15 ml of HCl, to incipient boiling.
2. Remove from the heat and add NH_4OH slowly to the hot solution by pouring NH_4OH from a graduate cylinder until a precipitate that just fails to redissolve begins to form.
3. Add about two drops of bromocresol indicator to the solution and continue the addition of NH_4OH dropwise while stirring until the solution is purple. The presence of much iron will make recognition of the endpoint difficult. Test for completeness of neutralization during the dropwise addition of NH_4OH by tilting the beaker slightly and noting the color of the solution as a drop of ammonia or a drop of indicator strikes the surface.
4. Add two drops of 1 + 1 HCl to the solution, which should be just acid, and bring it to a vigorous boil.
5. Boil 1 min while stirring.
6. Remove the beaker from the heat and add one or two drops of NH_4OH.
7. Confirm that the solution is purple; then place the beaker on the steam bath and let the precipitate settle for no more than 5 min.
8. Immediately filter the hot solution through an 11-cm #40 paper into a 600-ml beaker.
9. Transfer the precipitate to the paper and wash once with the hot 2-percent NH_4NO_3 wash solution.
10. Wash the beaker and the precipitate four more times with the 2-percent NH_4NO_3 wash solution.
11. Lift the filter paper just enough to allow the liquid in the stem of the funnel to drain into the 600-ml beaker.
12. Add a few drops of concentrated HCl to the solution and reserve for the filtrate from the second precipitation of the R_2O_3 group.
13. Remove the bulk of the precipitate from the filter paper with a stirring rod, and place the precipitate and the rod in the beaker used from the first R_2O_3 precipitation.
14. Pipet 5 ml of hot 1 + 1 HCl around the sides of this beaker.
15. Rub the lip of the beaker with a small piece of filter paper and a drop of acid, and add the paper to the funnel containing the main precipitate.
16. Place the beaker under the funnel and pipet 5 ml of hot 1 + 1 HCl around the top edge of the filter paper and slowly over the precipi-

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tate, allowing it to run through the funnel into the beaker.

17. Pipet 5 ml of hot water over the precipitate in the same manner.

18. With a small platinum stirring rod, lift the fold of the filter paper and dissolve the precipitate from the paper into the beaker with four more 5-ml portions of hot $1+1$ HCl and hot water.

19. Finally, wash the paper thoroughly with water, allowing the washings to drain into the beaker.

20. Remove the filter paper and reserve.

21. Rinse the funnel into the beaker and dilute the solution to about 150 ml.

22. Heat the solution just short of boiling.

23. Add about 1 ml of indicator and slowly add NH_4OH from a graduate cylinder to the hot solution until a precipitate begins to form.

24. Add NH_4OH dropwise and precipitate the R_2O_3 group as described above.

25. Add the reserved filter paper and macerate it.

26. Add NH_4OH dropwise, if necessary, to ensure that the solution is just basic.

27. Add $1+1$ HCl dropwise until the solution is just acid.

28. Bring the solution to a rapid boil, boil 1 min, then set on the steam bath.

29. Add NH_4OH dropwise until the solution is just purple; then let it stand on the steam bath for no more than 5 min.

30. Confirm that the endpoint has been reached and filter the hot solution through an 11-cm #40 filter paper into the 600-ml beaker containing the first filtrate.

31. Quantitatively transfer the precipitate to the paper with the aid of a small piece of filter paper, the wash solution, and a policeman.

32. Wash the beaker and the precipitate four times with hot 2-percent NH_4NO_3 wash solution.

33. Drain the funnel.

34. Cover the precipitate with a watch glass and let it air dry; then transfer the paper and the precipitate to the previously weighed platinum crucible containing the HF residue from the silica determinations and reserve for the precipitate obtained from the recovery of R_2O_3 from the beaker.

35. Make the filtrate just acid to HCl and evaporate to about 100 ml.

36. Rinse the face of the watch glass used to cover the beaker with a few milliliters of $1+1$ HCl, catching the washings in the beaker.

37. Rinse down the sides of the beaker with a few milliliters of HCl and reserve for the recovery of R_2O_3 from the beaker.

RECOVERY OF R_2O_3 FROM THE BEAKER

1. Dilute the solution reserved for the recovery of R_2O_3 to about 100 ml.

2. Heat just short of boiling and add one or two drops of bromocresol purple indicator.

3. Add NH_4OH dropwise until the solution just turns purple; then add HCl dropwise until the solution is just acid.

4. Bring the solution to a rapid boil and boil 1 min.

5. Remove from the heat and add NH_4OH dropwise until the solution is just purple.

6. Digest on the steam bath no longer than 5 min.

7. Add a little paper pulp, and filter through a 9-cm #40 filter paper into the 600-ml beaker containing the main portion of the filtrate from the R_2O_3 precipitation.

8. Wash the beaker and the precipitate with 2-percent NH_4NO_3 wash solution as described in the procedure for the precipitation of the R_2O_3 group, quantitatively transferring the precipitate to the papers.

9. Add the papers and precipitate to the main R_2O_3 precipitate and reserve.

10. Rinse the funnels into the 600-ml beaker containing the filtrate.

11. Make the solution just acid with $1+1$ HCl and heat just short of boiling.

12. Evaporate the solution to about 150 ml; then make just ammoniacal.

13. Digest on the steam bath, and if any precipitate appears, filter as before and add to the main R_2O_3 precipitate.

14. If no precipitate appears, proceed with the ignition of R_2O_3 precipitate and the removal of ammonium salts from the filtrate.

IGNITION OF R_2O_3 PRECIPITATE

1. Place the cover on the crucible in such a manner that the crucible is only partially covered and place in a cold electric muffle furnace and leave the door partially open.

2. Allow the temperature of the furnace to rise slowly to 800°C and ensure that air has free access to the furnace during the initial stages of the ignition. At no time should the paper be allowed to burst into flames.
3. Maintain the temperature of the furnace at 800°C until all carbon is completely consumed. Keep the lid of the crucible displaced during the heating to prevent reduction of iron.
4. Finally, heat at 1,150°C to constant weight.
5. If the HF residue from the silica determination was less than 5 mg and the R_2O_3 precipitate has been added to the crucible containing this residue, subtract the weight of the crucible before determining silica from the weight of the crucible plus the R_2O_3 to determine the weight of the R_2O_3. If the HF residue has been fused and added to the solution before precipitating the R_2O_3 group, subtract the weight of the crucible after the fusion from the weight of the crucible plus the R_2O_3 in order to obtain the weight of the R_2O_3.

Percent R_2O_3 = (weight R_2O_3 in grams/sample weight in grams) × 100

6. Reserve the R_2O_3 precipitate for the determination of residual SiO_2, TiO_2, and total iron as Fe_2O_3.

REMOVAL OF AMMONIUM SALTS

The method of J. Lawrence Smith is used in this laboratory to remove ammonium salts. By this operation, which requires no attention, 100 g of ammonium chloride can be separated as easily and safely as 1 g from a few milligrams of alkalies, magnesium, or the alkaline earths. Maxwell (1968) suggested that the NH_4 salts be removed by this method. Peck (1964) did not recommend the removal of NH_4 salts. Hillebrand and others (1953, p. 622–623) stated that the correct amount of ammonium chloride to have present is a problem; a large excess reduces the precipitation of magnesium and barium but at the same time retards the precipitation of calcium and more especially of strontium. They stated that no removal of ammonium salts is necessary unless special operations have introduced excessive amounts.

I recommend that the ammonium salts be removed before calcium is precipitated because excess salts interfere with the precipitation of calcium and because the removal of ammonium salts

is an operation that requires very little of the chemist's time.

HCl
HNO_3 (concentrated)
Bromocresol purple indicator (0.1 percent)

PROCEDURE

1. Add 3–4 drops of bromocresol purple indicator to the filtrate from the R_2O_3 precipitation, make just acid with 1 + 1 HCl, and evaporate to about 100 ml.
2. Cover with a speedy-vap glass, cautiously add 50 ml of concentrated HNO_3, and evaporate to dryness in the steam bath.
3. Rinse the cover and sides of the beaker with water and dilute to 100 ml.
4. Heat the solution on the steam bath.
5. If insoluble salts appear, repeat the addition of concentrated HNO_3 and the evaporation until a clear solution of about 100 ml volume is obtained.
6. Make the solution just ammoniacal, then just acid to 1 + 1 HCl and continue with the procedure for the removal of manganese by ammonium persulfate.

REMOVAL OF MANGANESE BY AMMONIUM PERSULFATE

After the double precipitation of the ammonia precipitate as described above, most, if not all, of the manganese will be in the filtrate and will be precipitated with calcium and magnesium if it is not removed before the determination of these elements. This manganese must then be determined and the magnesium and calcium values corrected for its presence.

The separation of manganese with ammonium persulfate in the presence of zirconyl hydroxide (Peck and Smith, 1961) is a simple and rapid method for the quantitative removal of manganese and should be used routinely before proceeding with the determination of calcium.

REAGENTS

$ZrCl_2$ solution (5 percent)—Dissolve 25 g of $ZrCl_2 \cdot 8H_2O$ in 200 ml of water containing 5 ml of 1 + 1 HCl. Let the solution stand over-

night. Filter it through a #42 paper or its equivalent into a 500-ml volumetric flask and dilute to volume.

HCl (1 + 1)

NH₄OH (concentrated)

Ammonium persulfate

NH₄NO₃ (2 percent)—Dissolve 20 g of NH₄NO₃ in 1 L of water and heat just short of boiling. Add one or two drops of bromocresol purple and NH₄OH dropwise until solution just turns purple.

PROCEDURE

1. To the solution reserved after the removal of ammonium salts, which should have a volume of 100 ml, add 1 ml of the 5-percent $ZrCl_2$ solution and a little paper pulp.
2. Make the solution just ammoniacal to bromocresol purple, then just acid with 1 + 1 HCl.
3. Add 1 g of ammonium persulfate.
4. Stir the solution and heat it for 20 min on the steam bath.
5. Add 1 ml concentrated NH₄OH and continue heating the solution for another 5 min.
6. Stir the solution and filter it at once through a #40 paper into a 400-ml beaker.
7. Wash the inside of the beaker three times with the hot 2-percent NH₄NO₃ solution, and transfer the washings to the filter.
8. Wash the precipitate on the paper 10 times with the wash solution.
9. Discard the precipitate.
10. Make the filtrate just acid to HCl and reserve for the determination of calcium.
11. Clean the glassware used for the removal of manganese with a dilute nitric acid solution containing hydrogen peroxide.

GRAVIMETRIC DETERMINATION OF CALCIUM OXIDE

Calcium is precipitated as calcium oxalate by adding ammonium oxalate to the hot hydrochloric acid solution from which all the other elements, save the alkali metals, magnesium, and the other alkaline earth metals, have been removed and neutralizing with ammonium hydroxide.

The alkali metals are removed by double precipitation of the oxalate. Small amounts of barium as are usually found in rocks are usually removed when double precipitations are made. Strontium is nearly completely precipitated with calcium. If the calcium value needs to be corrected for the presence of strontium and barium, a separation can be made by the nitric acid method described by Kolthoff and Sandell (1943, p. 746).

Maxwell (1968, p. 366) stated that "Any platinum which separates with the calcium oxalate will be reduced to platinum during the ignition and can be removed by dissolving the ignited oxide and reprecipitating the calcium; the direct solution and reprecipitation of the calcium oxalate will not suffice."

Magnesium is the most common contaminant of calcium oxalate. When calcium is in excess, it is usually separated from magnesium by double precipitation with ammonium oxalate. Satisfactory separations can be made if the amount of magnesium equals or is in moderate excess over that of calcium. Where an extremely accurate determination of a very small amount of calcium is desired, especially in the presence of much magnesium, the magnesium pyrophosphate precipitate must be analyzed for its calcium pyrophosphate content.

The weight of the CaO recovered from the magnesium pyrophosphate precipitate is added to the weight of CaO found by double precipitation with $(NH_4)_2C_2O_4$.

REAGENTS

Ammonium oxalate (6 percent)—Dissolve 60 g of $(NH_4)_2C_2O_4$ in 1 L of hot water. Filter the solution into a 1-L flask.

Ammonium oxalate (0.1 percent)—Take 16.67 ml of 6-percent ammonium oxalate solution and dilute to 1 L

Bromocresol purple indicator (0.1 percent)

HCl (concentrated, 5 percent, and 1 + 1)

NH₄OH (1 + 1)

HNO₃ (concentrated)

PROCEDURE

1. Add a few drops of bromocresol purple indicator to the filtrate from the manganese removal and make it just acid to HCl.
2. Add 5 ml of concentrated HCl in excess, and while it is boiling vigorously, slowly add 50 ml of the 6-percent ammonium oxalate solution.
3. Set the beaker on the steam bath and add (1 + 1) NH₄OH dropwise while stirring until

the solution just turns purple; then add about 1 ml in excess.

4. Digest at room temperature overnight.
5. Filter the solution through a 9-cm #42 filter paper into a 600-ml beaker, retaining as much of the precipitate in the original beaker as possible.
6. Wash the precipitate in the beaker two or three times with cold 0.1-percent ammonium oxalate solution and pour the washings onto the filter.
7. Wash the precipitate on the paper two or three times with the 0.1-percent ammonium oxalate wash solution.
8. Remove the 600-ml beakers from the funnel and acidify the filtrate with a few drops of $1+1$ HCl.
9. Reserve for the filtrate from the second precipitation of calcium.
10. Place a 250-ml beaker under the funnel.
11. Pipet about 10 ml of hot HCl $(1+1)$ down the sides of the beaker.
12. Pour the solution through the filter into the 250-ml beaker.
13. Wash the beaker thoroughly with hot 5-percent HCl and finally with hot water, pouring all washings through the filter into the 250-ml beaker.
14. Lift the fold of the paper with a small platinum rod and wash the paper with the hot 5-percent HCl solution and finally with water. The final volume should be aproximately 100 ml.
15. Transfer the paper to a weighed platinum crucible and reserve for the second calcium precipitate.
16. Rinse the funnel into the solution with water. Add two or three drops of bromocresol purple to the beaker containing the dissolved calcium oxalate, place it on a steam bath, and heat just short of boiling.
17. Add $1+1$ NH$_4$OH dropwise until the solution just turns purple; then make just acid with HCl $(1+1)$.
18. Set the beaker on a wire gauze over a Meker burner and bring the solution to a vigorous boil while stirring.
19. Add 10 ml of 6-percent ammonium oxalate to the boiling solution while continuing to stir.
20. Set the beaker on a steam bath and add $1+1$ NH$_4$OH dropwise until the solution just turns purple.

21. Add 1 ml of $1+1$ NH$_4$OH in excess and keep the solution at room temperature overnight.
22. Filter through a #42 9-cm paper into the beaker containing the filtrate from the first precipitation of calcium.
23. Transfer the precipitate quantitatively to the paper with the aid of a policeman and the cold 0.1-percent ammonium oxalate wash solution.
24. Wash the precipitate and paper moderately, then fold the paper over the precipitate and add it to the crucible containing the paper reserved from the first calcium precipitation.
25. Reserve the 250-ml beakers for the precipitation of calcium oxalate after dissolving the ignited precipitate.
26. Place the crucible in a cold electric furnace.
27. Allow the temperature of the furnace to increase gradually to 800°C in order to char the paper slowly. Do not increase the temperature of the furnace above 800°C until the carbon has been consumed.
28. Finally, ignite the precipitate at 1,150°C for 30 min; cool and weigh.
29. Repeat the heating and cooling until constant weight is obtained.
30. Acidify the filtrate with a few drops of $1+1$ HCl and evaporate it to about 100 ml. If ammonia salts fall out of solution, remove them as before except add only 10 ml of concentrated HNO$_3$ before evaporating the solution to dryness.
31. Reserve the filtrate for the determination of magnesium.
32. Add a few milliliters of water cautiously to the ignited precipitate and then cautiously add 10 ml of HCl $(1+1)$.
33. Transfer the solution to a 250-ml beaker and precipitate the calcium oxalate as before.
34. Allow the solution to stand overnight, filter, wash, and ignite as before.

If the weight of the precipitate obtained in step 34 is the same as the weight of the precipitate before redissolving, calculate the percentage of CaO by multiplying the weight of CaO, in grams, by 100 and dividing by the weight of the sample. If the weight of CaO is less than that after the first ignition, the precipitate should be redissolved and reprecipitated until the weight of the precipitate remains constant.

Check the magnesium ammonium phosphate precipitate for the presence of calcium as directed in the procedure for the determination of magne-

sium and correct the calcium value to include any calcium found in that precipitate.

GRAVIMETRIC DETERMINATION OF MAGNESIUM

Magnesium is precipitated as magnesium ammonium phosphate, ignited to magnesium pyrophosphate, and weighed as such.

$$(2MgNH_4PO_4) \rightarrow Mg_2P_2O_7 + 2NH_3 + H_2O$$

Two precipitations are always made. An excess of ammonium phosphate is added to the first precipitation to ensure quantitative precipitation of magnesium. In the reprecipitation, the excess of reagent is limited to the small amount required to reduce the solubility of the precipitate, thereby limiting the coprecipitation of other substances. An additional precipitation is made on the filtrate in order to verify that the precipitations have been complete.

The precipitate is finally washed with ammonium nitrate wash solution to aid in the ignition of the precipitate. Special care must be taken in burning off the filter paper containing the magnesium ammonium phosphate precipitate. Rapid ignition at a high temperature usually leaves unburned carbon which remains even after prolonged heating. The phosphate can be reduced by strong heating in the presence of carbon, causing damage to the crucible. The paper is slowly burned off in an electric furnace at as low a temperature as possible before gradually raising the temperature to 1,100°C in an electric furnace. At this temperature, the precipitate can usually be heated to constant weight without decomposition.

REAGENTS

$(NH_4)_2HPO_4$—Dissolve 50 g of $(NH_4)_2HPO_4$ in 200 ml of water and filter.

NH_4OH (1 + 1, 10 percent, and concentrated)

NH_4NO_3 wash solution—Dissolve 200 g of NH_4NO_3 in water, add 200 ml of concentrated NH_4OH, and dilute to 1 L

Bromocresol purple indicator (0.1 percent)

HCl (1:20)

PROCEDURE

1. Place the filtrate from the calcium determination, which should have a volume of about 225 ml and should be just acid to HCl, in an ice bath and cool to about 10°C.

2. Add 15 ml of $(NH_4)_2HPO_4$ solution (25 percent) and one or two drops of bromocresol purple indicator to the cold solution.

4. Continue the stirring for several minutes and add a 10-percent excess of concentrated NH_4OH.

5. Set the solution aside for at least 8 h in a cool atmosphere.

6. Filter the solution through an 11-cm #42 paper into a 400-ml beaker. The bulk of the precipitate should be kept in the beaker.

7. Wash the beaker and precipitate moderately with 10-percent NH_4OH wash solution and pour the washings through the filter, adding all washings through the funnel into the filtrate.

8. Evaporate the filtrate to about 100 ml and reserve for the second filtration.

9. Set a 250-ml beaker under the funnel and dissolve the magnesium ammonium phosphate into the beaker with alternate 5-ml portions of 1:20 HCl and hot water pipeted around the sides of the beaker and poured through the funnel into the 250-ml beaker.

10. Continue to dissolve the magnesium ammonium phosphate in the beaker and on the paper in this manner until it has been quantitatively transferred to the 250-ml beaker. The volume of the solution should be about 100 ml.

11. Transfer the filter paper to a weighed platinum crucible containing about 0.5 g of ammonium nitrate, char the paper, and slowly burn off the carbon at as low a temperature as possible with free access of air.

12. Reserve for the main portion of the precipitate.

13. Cool the solution to about 10°C; pipet 1 ml of the $(NH_4)_2HPO_4$ into the solution.

14. Add one or two drops of bromocresol purple indicator and then add 1 + 1 NH_4OH dropwise while stirring constantly until the solution just turns purple.

15. Continue the stirring as in the first precipitation while adding enough 1 + 1 NH_4OH to make a 5-percent solution by volume.

16. Allow the solution to stand overnight and filter on an 11-cm #42 paper, quantitatively transferring the precipitate to the paper and washing moderately with the cold 10-percent NH_4OH solution.

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17. Catch the filtrate and washings in the beaker containing the filtrate from the first magnesium precipitation.
18. Finally, wash the precipitate on the filter with two 10-ml portions of the NH_4NO_3 wash solution; then transfer it to the platinum crucible containing the residue from the first magnesium precipitation.
19. Evaporate the filtrate to about 200 ml and reserve for the final recovery of magnesium.
20. Set the crucible in a cold electric furnace and slowly dry and char the paper without inflaming. Do not allow the temperature of the furnace to exceed 450°C until the paper is consumed.
21. Allow the temperature of the furnace to reach 800°C gradually and maintain this temperature until the precipitate is a light gray.
22. Finally ignite the precipitate at 1,100°C to constant weight.
23. Cool the filtrate reserved from the previous precipitation of magnesium to about 10°C, make just acid to HCl, and then add 15 ml of $(NH_4)_2HPO_4$ solution (25 percent) and one or two drops of bromocresol purple indicator.
24. Add $1+1$ NH_4OH dropwise while stirring constantly until the solution just turns purple.
25. Continue the stirring for several minutes and add a 10-percent excess of concentrated NH_4OH.
26. Set the solution aside for at least 8 h in a cool atmosphere.

If any precipitate is observed, it should be filtered, redissolved, reprecipitated, and ignited to constant weight. This weight is added to the weight of the main precipitate.

Calculate the percentage of MgO as follows:

Percent $MgO = $ (weight $Mg_2P_2O_7$
$\times 0.3622$/sample weight in grams) $\times 100$

Reserve the ignited precipitate for the recovery of calcium in the magnesium pyrophosphate precipitate if this step is deemed necessary, and correct the magnesium value obtained as directed if any calcium is found to be present.

RECOVERY OF CALCIUM FROM
THE MAGNESIUM PYROPHOSPHATE PRECIPITATE

Calcium was found in the magnesium pyrophosphate precipitate of standard samples PCC-1 and DTS-1. The accepted MgO value of PCC-1 is 43.18 percent, and that of DTS-1 is 49.80 percent. The accepted value for CaO content of PCC-1 is 0.51 percent and that for DTS-1 is 0.15 percent. In both samples, all the CaO was found in the magnesium pyrophosphate precipitate. The method used here is based on one that was devised by Hillebrand for the recovery from the magnesium pyrophosphate precipitate of the small amount of calcium that escapes precipitation as oxalate. The method as described by Hillebrand and others (1953, p. 613) and Maxwell (1968, p. 367) omits the usual precipitation with oxalate, and calcium is precipitated as phosphate along with the magnesium and is recovered from the magnesium ammonium phosphate precipitate as described below.

When several samples of varying MgO and CaO content are run routinely, it is convenient to precipitate the calcium with oxalate in all the samples and to recover the calcium in the magnesium pyrophosphate precipitate only for those samples containing very small amounts of calcium oxide and large amounts of magnesium.

REAGENTS

H_2SO_4 $(1+1)$
Ethyl alcohol
Ammonium oxalate (6 percent)
Water-alcohol wash solution (15:70)
HNO_3 (concentrated)
HCl (5 percent)
Bromocresol purple indicator (0.1 percent)

PROCEDURE

1. Transfer the ignited and weighed magnesium ammonium phosphate precipitate to a 250-ml beaker.
2. Add H_2SO_4 $(1+1)$ slowly by pipet to dissolve the precipitate, avoiding more than approximately 0.5 ml in excess. If the precipitate dissolves with difficulty, add 1–2 ml concentrated HNO_3, boil, and then evaporate to fumes of SO_3. Cool.
3. Dissolve the residue in the minimum amount of water and add 70 ml of ethyl alcohol for each 15 ml of solution.
4. Mix thoroughly and let stand overnight.
5. Filter through a 9-cm #42 filter paper, quantitatively transferring the precipitate to the paper.

6. Wash moderately with the water-alcohol wash solution.
7. Dissolve the precipitate into a 250-ml beaker with hot 5-percent HCl.
8. Lift the fold of the paper with a small platinum rod and wash the paper and funnel with 5-percent HCl and finally with water.
9. Dilute the solution to about 100 ml.
10. Add two or three drops of bromocresol purple to the solution.
11. Heat just short of boiling and precipitate calcium with ammonium oxalate as described in the procedure for the gravimetric determination of calcium.
12. Ignite the precipitate to constant weight.
13. Add this weight to the weight of calcium oxide previously found and correct the weight of $Mg_2P_2O_7$ for coprecipitated calcium by subtracting the weight of $Ca_3(PO_4)_2$ equivalent to the CaO recovered from the $Mg_2P_2O_7$ precipitate.

$$\text{CaO} \underset{0.5424}{\overset{1.8438}{\rightleftharpoons}} \text{Ca}_3(\text{PO}_4)_2$$

SOLUTION OF THE R_2O_3 PRECIPITATE AND THE DETERMINATION OF RESIDUAL SILICA

Many tests have been made and reported in the literature showing that silica is not completely recovered in two dehydrations. Various methods have been suggested for the recovery of this silica. Usually the ignited R_2O_3 is dissolved in potassium pyrosulfate, sulfuric acid is added, and the silica is recovered by dehydration. Total iron and titanium are determined on the filtrate.

Dissolved platinum interferes in the determination of total iron; therefore, the fusion of the main portion of the precipitate is made in a vycor crucible, and the platinum crucible is cleaned by a short fusion at as low a temperature as possible.

Fusion of the R_2O_3 can be effected efficiently in vycor crucibles at a relatively low temperature. However, I found that when vycor crucibles containing 7 g of potassium pyrosulfate were heated over a Meker burner, cleaned, and reweighed four times, they consistently weighed 2 mg less after each fusion. Fusions made in vycor crucibles in an electric furnace at 600°C showed no loss of weight.

The pyrosulfate fusion of the ignited R_2O_3 precipitate is next transferred to a beaker or to a platinum dish, sulfuric acid is added, and after the cake is dissolved, the solution is brought to fumes of SO_3 to dehydrate the silica. When the silica was fumed in Pyrex beakers, visual observation indicated attack of the beakers. Therefore, the use of platinum dishes is recommended for the dehydration of the residual silica.

The ignited precipitate must be heated finally at a temperature of 1,150°C–1,200°C until constant weight is obtained, and the treatment with sulfuric acid and hydrogen flouride to volatilize the silica must be repeated until constant weight is obtained.

REAGENTS

$K_2S_2O_7$—In our laboratory, we have obtained good results by using Bakers Instra-analyzed acid—flux grade.
H_2SO_4 (1 + 1)
HF (concentrated

PROCEDURE

1. Weigh 6 g of $K_2S_2O_7$ and carefully transfer 3 g of it to the crucible containing the ignited R_2O_3 residue.
2. Stir with a platinum rod to mix.
3. Working over a sheet of powder paper, place a 30-ml vycor crucible upside down over the platinum crucible, rinse the stirring rod in the flux, and transfer the contents of the platinum crucible to the vycor crucible.
4. Add 1 g of $K_2S_2O_7$ to the platinum crucible. Rinse the platinum rod in the $K_2S_2O_7$.
5. Place the cover on the vycor crucible and place in an electric furnace at 400°C.
6. Gradually increase the temperature of the furnace to 700°C for another 30 min.
7. Set the vycor crucible and its contents on a triangle supported by a tripod and placed over a small flame.
8. Gradually increase the temperature until SO_3 fumes just begin.
9. Grasp the crucible with the Blair tongs and swirl over the flame for 1 or 2 min.
10. Verify that the fusion is complete and set the crucible aside to cool.
11. Place the platinum crucible in a furnace at a temperature of 600°C for 5 min; then swirl over a small flame for about 30 s. Do not heat the crucible above a dull red.
12. Cool.

13. Wash the cover into the crucible and digest the crucible and its contents on the steam bath until the melt disintegrates.
14. Quantitatively transfer the contents of the crucible to a 75-ml platinum dish and evaporate on the steam bath.
15. Heat the platinum crucible at 1,150°C for about 15 min. Cool and weigh.
16. Compare this weight with the weight of the empty crucible before igniting the R_2O_3 precipitate.
17. The loss in weight should not exceed more than a few tenths of a milligram as the solution for determining iron should be platinum free.
18. Wash the top of the vycor crucible into the vycor beaker with a little water.
19. Set the crucible on the steam bath until the melt has dislodged from the crucible; then quantitatively transfer the melt and the solution to the 75-ml platinum dish.
20. Add enough water to make the volume 50–60 ml and heat on the steam bath until the melt has dissolved.
21. Transfer the platinum dish and its contents to a hot plate and evaporate to about 40 ml.
22. Carefully pipet 20 ml of $1+1$ H_2SO_4 into the dish and continue the evaporation.
23. Finally increase the surface temperature of the hot plate to about 350°C.
24. Bring the solution to fumes of SO_3 with occasional stirring.
25. Fume for about 10 min; then remove from the heat and cool.
26. Dilute the solution to about 70 ml, set on the steam bath, and digest until only a fleecy residue of silica remains. Add water as necessary to keep the volume of the solution about 70 ml.
27. Cool the solution and filter through a 9-cm #42 paper into a 100-ml volumetric flask.
28. Quantitatively transfer the precipitate to the filter with the aid of a small piece of paper and a policeman.
29. Wash the precipitate and paper with a few milliliters of water; then transfer to a weighed platinum crucible.
30. Reserve the filtrate.
31. Carefully ash the paper in the crucible.
32. Finally, ignite the precipitate at 1,200°C until constant weight is obtained.
33. Add one or two drops of $1+1$ H_2SO_4 and

about 5 ml of concentrated HF to the crucible and volatilize the silica.
34. Repeat the volatilization and ignition until constant weight is obtained.
35. The weight of residual silica equals the weight of the crucible plus the silica minus the weight of the crucible plus the residue.
36. Add 1 g of $K_2S_2O_7$ to the residue from the volatilization of the residual silica and fuse in an electric furnace at 600°C.
37. Cool.
38. Add a little water to the melt and digest on the steam bath until dissolved.
39. Filter into the 100-ml volumetric flask containing the main solution from the residual silica.
40. Make the filtrate to volume and reserve for the determination of total iron and titanium.

DETERMINATION OF TITANIUM OXIDE ON THE SOLUTION OF THE R_2O_3 GROUP

Peck (1964) recommended that titanium be determined on a portion of the solution of the R_2O_3 precipitate. The transmittance of a portion of the sample is measured, hydrogen peroxide is added to the cell, and the transmittance is measured again.

The amount of titanium oxide equivalent to the transmittance of the unperoxidized solution is subtracted from the equivalent of the transmittance of the peroxidized solution in order to obtain the correct value for titanium oxide. The solution in the cell and the rinsings are reserved and combined with the remainder of the R_2O_3 solution and, after evaporation to reduce the volume and to expel hydrogen peroxide, are used for the determination of total iron.

Maxwell (1968, p. 423) recommended that total iron be determined by use of the solution from the ferrous iron determination and stated that if the sulfuric acid solution of the pyrosulfate fusion of the R_2O_3 group residue is used for the colorimetric determination of TiO_2, the solution should be evaporated to a small volume to expel all hydrogen peroxide, that H_2S should be passed through the solution to remove platinum, and that the solution should be evaporated to expel all traces of H_2S before the titration of the iron.

Kolthoff and Sandell (1943) determined titanium on the solution remaining after the titration of iron with permanganate.

Scheffer (*in* Kolthoff and Elving, 1961) determined titanium on a separate sample. Hillebrand and others (1953, p. 581) stated, "In rock analyses, the test is usually made after the volumetric determination of iron in the sulfuric acid solution of the pyrosulfate fusion of the weighed ammonia precipitate." Titanium and iron are determined in our laboratory on separate aliquots of the sulfuric acid solution of the R_2O_3 precipitate. This procedure has proven to be convenient and accurate. Platinum need not be removed prior to the iron titration as only a negligible amount of platinum will be introduced into the analysis if the precautions mentioned above are observed.

Because 3-percent hydrogen peroxide deteriorates rapidly, it is prepared from the very stable 30-percent peroxide as needed. Beer's law was observed for solutions containing as much as 0.2 mg TiO_2 per milliliter.

Chromium, vanadium, and iron interfere in the colorimetric determination of titanium because of the color of their solutions and may be present in the R_2O_3 residue to such an extent that a correction is necessary. This correction is made by subtracting the reading of an aliquot of the sample without hydrogen peroxide from the reading obtained for another aliquot to which hydrogen peroxide is added.

All readings are made at the same room temperature to eliminate the effect of temperature on the color intensity.

REAGENTS

Standard TiO_2 solution (1 ml = 1.00 mg TiO_2)—Weigh 1.013 g of U.S. National Bureau of Standards sample No. 154 (TiO_2 98.7 percent) that has been dried overnight in an oven at a temperature of 105°–110°C, and transfer it to a 400-ml beaker. Add a magnetic stirring bar and 100 ml of concentrated H_2SO_4 to the beaker. Set the beaker and its contents on a magnetic stirring hot plate (such as Fisher Thermix) and bring the solution to a constant boil while stirring. Continue the heating and stirring until the solution is complete. Cool, then rapidly pour it into about 500 ml of water and allow it to stand at room temperature overnight.

Filter the solution through a 11-cm #42 filter paper into a 1-L flask and wash the beaker and the paper with water. Place the

paper in a vycor crucible. Slowly char the paper and carefully burn off the resulting carbon. Add 1 g of $K_2S_2O_7$ to the crucible and fuse the residue in an electric furnace at 700°C for 30 min. Cool the melt, add a few milliliters of the TiO_2 solution to dissolve the melt, transfer it to the flask, and make to volume.

$K_2S_2O_7$ solution (16 percent)—Dissolve 80 g of $K_2S_2O_7$ in about 400 ml of hot water. Cool to room temperature and filter into a 500-ml volumetric flask. Wash the beaker and paper moderately with water and dilute the solution to 500 ml.

H_2O_2 (3 percent)—Pipet 2.5 ml of 30-percent H_2O_2 and transfer it to a 25-ml volumetric flask and dilute to volume. Prepare just before using.

H_2SO_4 (1 + 1)

H_2SO_4 (1 + 1)

PROCEDURE

This procedure is to be followed as outlined if the solution of the R_2O_3 precipitate contains 8 g of $K_2S_2O_7$ and is 10 percent in H_2SO_4. Adjust the $K_2S_2O_7$ and H_2SO_4 content of the standards if other than these amounts are used.

1. Pipet two 20-ml aliquots of the solution of the R_2O_3 precipitate and transfer each to a separate 25-ml volumetric flask lettered A or B.
2. Dilute the sample in flask A to 25 ml with water.
3. Reserve flask B.
4. Prepare a series of standard solutions containing 0, 0.10, 0.50, 1.00, 2.00, 3.00, and 5.00 ml of standard TiO_2 solution (1 ml = 1 mg TiO_2) in 25-ml volumetric flasks; each flask should contain 4 ml of 1 + 1 H_2SO_4 and 10 ml of 16-percent solution of $K_2S_2O_7$.
5. Dilute these solutions to about 20 ml; then add 1.25 ml of 3-percent H_2O_2 solution to each flask and to flask B, which contains an aliquot of the sample.
6. Dilute the solutions to 25 ml and mix thoroughly.
7. Arrange the standards and the sample in flask B in order of the intensity of the color of the solutions.
8. Measure the absorbance of each solution in a 1-cm cell in this order, using distilled water as a reference solution and measuring the absorbance of the solutions in flask A.

9. Correct the absorbance reading of solution B for any color given to the solution by interfering elements by subtracting the absorbance reading of solution A from the absorbance reading of solution B.

10. Prepare a curve from the absorbance reading of the standards and obtain the weight of TiO_2 measured from this curve.

11. Calculate the percentage of TiO_2 in the sample as follows:

Percent TiO_2 = [weight of TiO_2 in aliquot/ weight of sample in aliquot (=200 mg)] × 100

Percent TiO_2 = weight of TiO_2 in aliquot/2

DETERMINATION OF TOTAL IRON ON THE SOLUTION OF THE R_2O_3 GROUP

An aliquot of the solution of the R_2O_3 group is used for the determination of total iron. The method is essentially that recommended by Peck (1964) except that the solution from the titanium determination is not reserved and evaporated, and the necessity of removing hydrogen peroxide is thereby eliminated.

APPARATUS AND REAGENTS

Silver reductor (fig. 4)—A Jones-Blair reductor by Kimax (Kimble No. 39000) or Sargent-Welch (No. S-72227) filled with a 1:1 ratio by volume of electrodeposited and copper-reduced silver (Dinnin, 1960, p. 295–296; Kolthoff and Belcher, 1957, p. 12–16).

A 10-ml micro-buret

Standard $K_2Cr_2O_7$ solution (0.1 N)—Weigh 9.810 g of primary standard grade $K_2Cr_2O_7$ into a weighing bottle. Record the weight of the bottle plus the reagent. Place the bottle and its contents in an oven at 105°–110°C and dry for 2 h. Cool in a desiccator and weigh. Repeat the heating (at 105°–110°C) and cooling until constant weight is obtained. With the aid of a small funnel, wash the contents of the weighing bottle into a 2-L volumetric flask. Dry the weighing bottle in the oven, cool, and reweigh to obtain the true weight of the $K_2Cr_2O_7$ used. Add about 1 L of water to the flask and mix to dissolve the reagent; then dilute to volume with water and mix thoroughly. Standardize against standard iron solution.

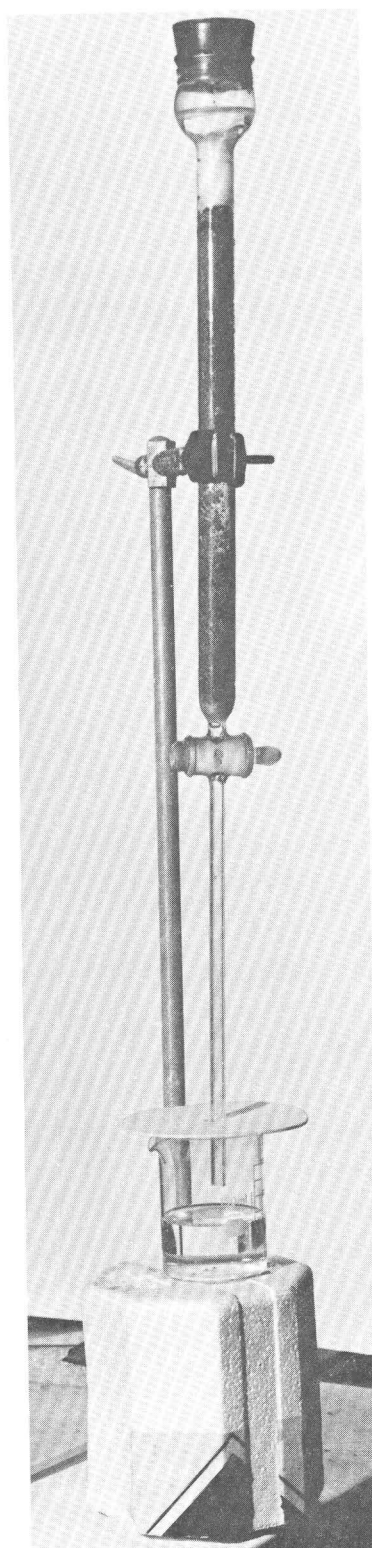Stannous chloride solution—Dissolve 5 g of

FIGURE 4.—Silver reductor.

SnCl$_2$·H$_2$O in 10 ml of HCl and dilute to 100 ml. Add scraps of iron-free granulated tin and boil until the solution is clear. Keep the solution in a closed dropping bottle containing metallic tin.

NH$_4$Cl solution (15 percent)—Dissolve 300 g of NH$_4$Cl in water, filter, and dilute to 2 L.

Standard Fe$_2$O$_3$ solution—Transfer 1.2815 g of standard sample Sibley iron ore (U.S. National Bureau of Standards standard sample #27) that has been previously dried in an oven for 2 h to a previously weighed weighing bottle. Record the weight of the bottle and its contents.

Place the bottle and its contents in an oven at 105°–110°C and repeat the heating and weighing to constant weight.

Quantitatively transfer the iron ore to a 250-ml beaker with the aid of 10 ml of concentrated HCl. Add 40 ml more concentrated HCl to the beaker, cover the beaker, and digest the solution just short of boiling for about 30 min. If the iron ore has not completely dissolved, add a little of the stannous chloride dropwise, and continue the digestion until all the dark particles have dissolved.

Dilute the solution to about 100 ml with water and add 3 ml of bromine water to destroy any excess SnCl$_2$; then boil vigorously to destroy the bromine water; Cool and filter into a 250-ml volumetric flask, wash the paper moderately with water, ash the paper, treat with a little concentrated HCl, then evaporate to dryness and fuse the residue with about 0.5 g of Na$_2$CO$_3$. Dissolve the melt in a little water, transfer to the volumetric flask, and make to volume.

Sodium diphenylamine sulfonate (0.2 percent)—Dissolve 0.2 g of sodium diphenylamine sulfonate in 100 ml of hot water.

HCl (1 + 1 and 5 percent)

NH$_4$OH (1 + 1)

H$_3$PO$_4$ (1 + 1)

PROCEDURE

1. To a series of 250-ml beakers, add aliquots of standard Fe$_2$O$_3$ solution to make solutions containing 0–100 mg of Fe$_2$O$_3$. Dilute to 50 ml.

2. Add aqueous 1 + 1 NH$_4$OH while stirring until a precipitate that does not dissolve just begins to form; then add 1 + 1 HCl dropwise to just dissolve the precipitate.

3. Add 25 ml of 15-percent NH$_4$Cl solution to adjust the volume of the solution to 100 ml.

4. Pour 500 ml of 5-percent HCl through the reductor and allow the solution to drain until the level is about ⅛ in above the silver.

5. Add 20 ml of 1 + 1 H$_3$PO$_4$ to a clean 600-ml beaker and lower the reductor into the beaker until the delivery tube dips into the acid.

6. Transfer about half the iron solution to the reservoir.

7. Fully open the stopcock on the reductor, and as the solution drains, transfer the remainder of the iron solution to the reservoir and let the solution drain until its level is about ⅛ in above the silver.

8. Lift the reductor as the volume of the effluent increases, but keep the tip of the delivery tube below the level of the liquid.

9. Wash the inside of the reservoir with a small amount of 5-percent of HCl and continue draining until the volume of the solution in the beaker is almost 300 ml.

10. Close the stopcock and lift the delivery tube clear of the liquid.

11. Wash the tip of the delivery tube with water.

12. Add two or three drops of 0.2-percent solution of sodium diphenylamine sulfonate to the solution and immediately titrate with standard K$_2$Cr$_2$O$_7$ solution, while stirring, until the purple color caused by the addition of one drop of titrant disappears slowly.

13. Wash down the inside of the beaker with a fine stream of water; then continue adding the K$_2$Cr$_2$O$_7$ solution in fractional drops while stirring the solution until a distinct purple color forms that persists for at least 30 s.

14. Calculate the normality of the solution as follows:

Normality of K$_2$Cr$_2$O$_7$ solution

$$= \frac{\text{mg of Fe}_2\text{O}_3 \text{ titrated by 1 ml of } 0.1N \text{ K}_2\text{Cr}_2\text{O}_7 \text{ (7.985 mg)}}{\text{mg Fe}_2\text{O}_3 \text{ (mg Fe}_2\text{O}_3 \text{ in standard sample) titrated by the K}_2\text{Cr}_2\text{O}_7 \text{ used}}$$

15. Transfer 10 ml of the solution of the R$_2$O$_3$ precipitate that was reserved for the iron determination to a 250-ml beaker and proceed as directed in steps 1–3 above.

16. Calculate the percentage of total iron in the sample as follows:

Percent total iron as Fe_2O_3
$$= (M \times N \times 79.34/\text{sample weight} \text{ in milligrams}) \times 100$$

where

$M =$ milliliters of $K_2Cr_2O_7$
$N =$ normality of the $K_2Cr_2O_7$
$79.34 =$ iron equivalent $159.68/2$

DETERMINATION OF FERROUS IRON

The Cooke method (1867) of decomposing the sample in a hydrofluoric-sulfuric acid mixture in the absence of air and titrating the ferrous iron in the solution with permanganate has been studied and modified by many investigators. Because of the rapid oxidation of ferrous sulfate in the presence of hydrofluoric acid, air must be removed before hydrofluoric acid is added to the sample and must be excluded thereafter

Pratt (1894) simplified the method by eliminating the Cooke apparatus and using a large platinum crucible fitted with a perforated cover for the introduction of carbon dioxide into the crucible containing the mineral powder and boiling sulfuric and hydrofluoric acids.

Hillebrand and others (1953, p. 915) used carbon dioxide only at the start and depended on the steam of the boiling solution to exclude air. They recommended the use of a 100-ml platinum crucible for the decomposition of the sample.

Barnebey (1915) suggested the use of potassium dichromate for the titrant and the addition of boric acid to stabilize the ferrous iron against the action of the air during the titration with potassium ferricyanide and also to avoid a large displacement of the observed endpoint in the presence of hydrofluoric acid.

Knop (1924) worked out the details for the use of diphenylamine as an internal indicator for this reaction. Sarver (1927) recommended the use of dichromate together with diphenylamine as an internal indicator.

Kolthoff and Sandell (1943) described a simple procedure for the determination of ferrous iron in which carbon dioxide is not used during the decomposition. The sulfuric acid is heated nearly to boiling before the hydrofluoric acid is added. The steam from the boiling sulfuric acid excludes the air from the crucible. This method has been found satisfactory for most silicates. A 100-ml platinum crucible is used for the decomposition, and the crucible and its contents are then immersed beneath the surface of a sulfuric-boric acid solution; the ferrous iron is titrated with a standard solution of $K_2Cr_2O_7$ and diphenlyamine sulfonic acid is used as an indicator.

Research on the problems associated with the determination of ferrous iron has been extensive. Many of the problems that may arise in analyzing unusual samples have been discussed by Hillebrand and others (1953), Maxwell (1968), and Peck (1964).

APPARATUS AND REAGENTS

Platinum crucible of 100-ml capacity
Blair-type tongs made of nichrome, the handle bent at an angle of $90°$
Timer
Surface thermometer
H_3BO_3 solution, 5 percent (saturated)
Barium diphenylamine sulfonate indicator (0.2 percent)
H_2SO_4 (1+1)
HF (concentrated)
H_3PO_4 (concentrated)
Standard $K_2Cr_2O_7$ solution (see p. 21)

PROCEDURE

1. Weigh 0.500 g of sample into a 100-ml platinum crucible having a tightly fitting cover.
2. Disperse the sample in about 5 ml of water and add two or three drops of 1+1 H_2SO_4 to decompose any carbonate materials present.
3. Cover the crucible and allow it to stand until all reaction has ceased.
4. Add 10 ml of 1+1 H_2SO_4 to a plastic graduate cylinder, and add 5 ml of concentrated HF to another plastic graduate cylinder.
5. Set the crucible on a hot plate that has a surface temperature of about 400°C.
6. Pour the 5 ml of HF into the graduate cylinder containing the 10 ml of 1+1 H_2SO_4 slightly displace the crucible lid, and quickly and carefully add the H_2SO_4-HF solution to the crucible.
7. Replace the cover on the crucible and boil the sample gently for 10 min.
8. During this 10 min, add 10 ml of concentrated H_3PO_4 to a 600-ml beaker containing 200 ml of water, 50 ml of saturated H_3BO_3 solution, and 35 ml of 1+1 H_2SO_4 and place the beaker near the crucible.

9. Grasp the crucible with the Blair-type tongs, and while pressing the top of the crucible with a glass rod, immerse the crucible in the H_3BO_3 solution.
10. Remove the tongs and turn the crucible on its side.
11. Swirl it to allow its contents to go into the solution.
12. Remove the crucible with the aid of a glass rod and wash particles clinging to it into the solution with the aid of a little water.
13. Add four or five drops of 0.2-percent barium diphenylamine sulfonate indicator and titrate with standard $K_2Cr_2O_7$ solution until the purple color caused by the addition of one drop of $K_2Cr_2O_7$ fades slowly.
14. Wash down the inside of the beaker and continue the titration by adding fractional drops of $K_2Cr_2O_7$ until a purple color forms that lasts for 30 s.
15. Calculate the percentage of FeO as follows:
Percent FeO $= (M \times N \times 71.85 \times 100/$
          sample weight in milligrams$) \times 100$
where
M = milliliters of $K_2Cr_2O_7$ solution used
N = normality of $K_2Cr_2O_7$
71.85 = iron equivalent

DETERMINATION OF Al₂O₃

Aluminum is one of the elements precipitated by ammonium hydroxide from the filtrate reserved from the double dehydrations of silica. This precipitate is commonly called the R_2O_3 group, and the weight of aluminum oxide is obtained by deducting the weight of the other elements from the total weight of the group.

The total iron and the TiO_2 (determined on the solution of the dissolved precipitate), the P_2O_5 and the residual silica are elements other than aluminum usually found in the R_2O_3 precipitate of a silicate when the suggested procedure is followed.

If present in the sample, zirconium, chromium, vanadium, the rare earths, beryllium, and members of the H_2S group will be precipitated also and must be determined and subtracted from the total weight of the oxides or they will be counted as Al_2O_3. However, most silicate rocks contain only negligible amounts of these elements, and they are not determined in routine analyses.

Calculations:
Percent Al_2O_3 = percent R_2O_3 − percent total Fe
          as Fe_2O_3 − percent P_2O_5 − percent TiO_2

PREPARATION OF THE SOLUTION FOR THE DETERMINATION OF MANGANESE AND PHOSPHORUS

A nitric acid solution free of carbon compounds, chlorides, silica, and fluorine is prepared for the determination of manganese and of phosphorous. Soluble organic matter, if present, would interfere with the determination of manganese by reducing permanganate. Mineral acids other than nitric will interfere in the precipitation of ammonium phosphomolybdate. Therefore, the decomposition of the sample is effected by nitric and hydrofluoric acid, and silicic acid is removed by dehydration. Boric acid is added to complex any remaining fluoride. The small residue is fused with sodium carbonate, the melt is leached with water to extract the phosphate, and the solution is filtered into the main portion of the sample. The solution is made to volume, and separate aliquots are taken for the determination of manganese and phosphorous.

REAGENTS

HNO_3 (concentrated)
HNO_3 (1 + 1) that has been boiled and cooled to remove oxides of nitrogen
HF (concentrated)
H_3BO_3 (5 percent)
Sodium sulfite
Na_2CO_3

PROCEDURE

1. Weigh 1 g of the sample and transfer it to a platinum evaporating dish (75 to 100-ml capacity).
2. Cover the dish with a platinum cover and set it on a triangle over a low flame.
3. Gradually increase the flame until the bottom of the dish is red.
4. Partially open the dish and continue the heating for 5 min.
5. Allow the dish to cool; then swirl the powder in a few milliliters of water, breaking up any lumps with a platinum stirring rod.
6. Set the dish on a steam bath and add 20 ml

of concentrated HNO_3 and 20 ml of concentrated HF to it.

7. Stir the solution with a platinum rod and let it evaporate to dryness.
8. Wet the dried salts by washing down the sides of the dish with a little water; then add 10 ml of concentrated HNO_3 followed by 10 ml of HF.
9. Repeat the evaporation to dryness.
10. Add 10 ml of concentrated HNO_3 to the dish.
11. Wash the salts down into the acid with a little water; then evaporate the solution to dryness.
12. Repeat the addition of concentrated HNO_3 and the evaporation to dryness.
13. Heat the solution for an additional 30 min on the steam bath after the salts appear to be dry.
14. Cool.
15. Add 40 ml of $1+1$ HNO_3 that has been previously boiled and cooled to remove oxides of nitrogen.
16. Add 20 ml of 5-percent H_3BO_3 solution to the dish.
17. Cover and digest for 2 h on the steam bath.
18. Stir the solution occasionally, and if a brown insoluble precipitate persists, add a few crystals of sodium sulfite to reduce the manganese and render a clear solution.
19. Spread a thin film of stopcock grease on the underlip of the platinum dish, add a little paper pulp, and filter through a 9-cm #40 paper into a 100-ml volumetric flask.
20. Wash the dish and the paper with a little water.
21. Police the platinum dish with the aid of a small piece of filter paper.
22. Add the paper to the funnel; then carefully char the papers in a small platinum crucible.
23. Burn off the carbon and fuse the residue with about 0.5 g of Na_2CO_3.
24. Leach the melt with a few milliliters of water, add a few milliliters of the main solution to the crucible, and filter into the volumetric flask.
25. Wash the crucible and the filter four or five times with water.
26. Discard the filter paper and make the solution to volume and mix.
27. Transfer a 25-ml aliquot of the solution to a 50-ml volumetric flask and reserve for the colorimetric determination of manganese.
28. Transfer a 50-ml aliquot of the solution to a 50-ml beaker and reserve for the determination of phosphorous.
29. Reserve the remaining solution for determining whether there is any interference in the manganese determination caused by the presence of any elements that form colored solutions.

DETERMINATION OF MANGANESE

The colorimetric method for determining manganese as described by Willard and Greathouse (1917) is essentially the accepted method for determining small amounts of manganese (Maxwell, 1968; Hillebrand and others, 1953; Kolthoff and Sandell, 1943; Peck, 1964). It is based upon the oxidation of manganese to permanganate and the comparison of the color of the solution with that of standard solutions containing known amounts of manganese present as permanganate. The oxidation is effected in a hot acid solution using potassium periodate as the oxidizing agent. Phosphoric acid is added to complex ferric iron and to prevent the precipitation of manganese compounds and ferric periodate. The solutions can be heated conveniently by immersing the volumetric flask (which is supported by a test-tube holder) in a boiling water bath (Peck, 1964, p. 77).

REAGENTS

Standard manganese solution A (1 ml = 1 mg MnO)—Transfer 0.6754 g of manganese ore (U.S. National Bureau of Standards sample 25c) that has been dried for 2 h at 120°C to a 250-ml beaker. Add 20 ml of $1+1$ HNO_3 and digest on the steam bath until no dark residue remains. Bring to a vigorous boil to expel the oxides of nitrogen; cool and filter into a 500-ml volumetric flask. Wash the beaker and paper moderately with water. Ash the paper and fuse the residue with about 0.5 g of anhydrous Na_2CO_3. Leach the cake with water and add to the flask containing the main portion of the solution. Dilute to volume and mix thoroughly.

Standard manganese solution B (1 ml = 0.1 mg MnO)—Transfer a 25-ml aliquot of solution A to a 250-ml volumetric flask, add 10 ml of $1+1$ HNO_3 and dilute to volume.

KIO_4 solution (1 percent)—Weigh 5 g of potassium periodate (KIO_4) into a 400-ml beaker. Add

about 100 ml of $1+1$ HNO_3 and digest on the steam bath until the salts dissolve; then transfer the solution to a 500-ml volumetric flask, cool, dilute to volume, and mix.

H_3PO_4 $(1+1)$

HNO_3 (concentrated)

1. Add 0-, 0.1-, 0.5-, 1.0-, 1.5-, and 2-mg portions of standard manganese solution B to a series of 50-ml volumetric flasks and add 10 ml of concentrated HNO_3 and 10 ml of KIO_4 solution.
2. Wash down the inside of each flask with a few milliliters of water and mix the solution.
3. To the 25-ml aliquot of the sample that was reserved for the determination of manganese, add 5 ml of concentrated HNO_3 and 10 ml of KIO_4 solution.
4. Wash down the inside of the flask with a few milliliters of water and mix the solutions.

   Continue the procedure for samples and standards as follows:
5. Slip the second ring of the steam bath cover over the neck of the volumetric flask; fasten a test-tube clamp to the upper part of the neck and insert the flask into the boiling bath in such a manner that the upper part of the flask extends above the surface of the steam bath as the clamp rests on the top of the steam bath.
6. Heat the solution for 1 h or until heating ceases to cause color changes.
7. Cool the solution and add 5 ml of $1+1$ H_3PO_4
8. Make to volume with water and mix well.
9. Arrange the solutions according to the depth of the color. Starting with the lightest in color, measure the absorbance at 525 Mm in a 1-cm cell, using distilled water as a reference blank.
10. Measure the absorbance of the original sample solution obtained in step 29 of "Preparation of the Solution for the Determination of Manganese and Phosphorous," using distilled water as a reference blank, and correct the absorbance readings of the samples by subtracting this reading divided by two, from the absorbance reading of the sample. Make a calibration curve from the absorbance readings of the standards and determine the

number of milligrams of MnO in the sample aliquot from this curve.

Percent MnO = (milligrams of MnO/milligrams of sample) $\times$ 100

= (milligrams of MnO/250)

DETERMINATION OF PHOSPHOROUS

Phosphorus is first separated from interfering elements by precipitation as ammonium phosphomolybdate (Peck, 1964). The precipitate is dissolved in ammonium hydroxide, and phosphorus is determined gravimetrically after its precipitation as magnesium ammonium phosphate or colorimetrically by the molybdovanadophosphoric acid method (Kitson and Mellon, 1944, p. 379). The molybdovanadophosphoric acid method is considered to be the most specific spectrophotometric method for the determination of phosphorus. When an excess of a molybdate solution is added to an acidified solution of a vanadate and an orthophosphate, a yellow hue forms, which presumably indicates the presence of molybdovanadophosphoric acid.

Mission (1908) first proposed using this reaction as a basis for a colorimetric method of determining phosphorus in steel. Kitson and Mellon (1944) made a spectrophotometric study of the method and recommended its use for measuring phosphorus colorimetrically. Some of the extensive literature on the nature of the complex and the best conditions for its formation is discussed below.

Phosphorus must be present as the orthophosphate, and as it is usually present in this form in silicate rocks, the analyst need only put the sample into solution before adding the acid, vanadate, and molybdate for the color to appear. However, as other elements also form a colored complex, their interference must be eliminated.

The conditions for the precipitation of ammonium phosphomolybdate as reported in the literature are varied and indefinite. The temperature at which the precipitation is made and the amount of ammonium molybdate and the amount of HNO_3 needed greatly influence the completeness of the precipitation and the composition of the precipitate.

Randolph and Grimaldi (1953) described a routine procedure for the determination of P_2O_5 in amounts from 0.1 mg to 2.0 g that requires no changes in conditions or quantities of reagents. Results reported for standard samples and phos-

phate rocks indicate that the molybdate precipitate is of constant composition, and the P_2O_5 is determined gravimetrically from the weight of the molybdate precipitate.

Workers in this laboratory have found that the values obtained for P_2O_5 when the ammonium phosphomolybdate was dried at 100°C were slightly higher than the values obtained when the precipitate was ignited to $P_2O_5 \cdot 24\ MoO_3$ at 480°C. The values obtained for P_2O_5 in each of these methods were higher than the accepted values that were obtained when the ammonium phosphomolybdate was redissolved and P_2O_5 was determined either colorimetrically or gravimetrically.

The conditions described here for the precipitation of ammonium phosphomolybdate are bascially those recommended by Randolph and Grimaldi (1953). Formic acid is not added to routine determinations as only small amounts of vanadium are expected to be present in silicate rocks.

The P_2O_5 content of the sample is determined colorimetrically when it is less than 0.8 percent and gravimetrically, after precipitation as magnesium ammonium phosphate, when it is greater than 0.8 percent. The colorimetric method may be used for samples containing more than 0.8 percent P_2O_5 if the ammoniacal solution of the ammonium phosphomolybdate is made to volume and phosphorus is determined on an aliquot containing less than 4 mg of P_2O_5 in 100 ml. If more than 4 mg of P_2O_5 is present in the ammoniacal solution used for the colorimetric determination of phosphorus, a precipitate that will not redissolve will form when the solution is made acid.

Procedures involving a wide variety of conditions for the formation of the yellow complex have been recommended. Nitric acid must be added first; then vanadate and molybdate are added separately or as one reagent containing both chemicals (Barton, 1948).

The concentrations of nitric acid recommended range from 0.04 to 1.0 N (Rieman and Beukenkamp, *in* Kolthoff and Elving, 1961). Kitson and Mellon (1944, p. 379) stated that the optimum amount of acid is 10 ml of nitric acid (1:2) in 100 ml volume (0.5 N). Peck (1964) recommended a 0.48 N solution, and Maxwell used a 0.6 N nitric acid solution. Kitson and Mellon (1944) and Maxwell (1968) recommended using 10 ml of 0.25-percent ammonium vanadate solution and 20 ml of ammonium molybdate solution added separately.

Peck (1964) recommended using 10 ml of 0.25-percent ammonium vanadate solution and 10 ml of ammonium molybdate solution added as one reagent containing both chemicals. The conditions for the color formation described in the "Procedure" below are those recommended by Peck (1964).

REAGENTS

H_3PO_4 (85 percent)—Analytical grade.

Ammonium molybdate solution—Dissolve 160 g of ammonium molybdate ($[NH_4]_4Mo_7O_{24} \cdot 4H_2O$) in 900 ml of hot water. Cool and filter.

NH_4NO_3 wash solution—Dissolve 20 g of NH_4NO_3 in about 1 L of $1 + 99\ HNO_3$.

NH_4OH solution (5 percent and $1 + 1$)

Magnesium mixture—Dissolve 50 g of $MgCl_2 \cdot 6H_2O$ and 100 g of NH_4Cl in 500 ml of water. Add one drop of bromocresol purple indicator (0.1 percent); then make the solution slightly alkaline with NH_4OH and allow it to stand at least 12 h. Filter, acidify with HCl, and dilute to 1 L.

Citric acid solution (35 percent)—Dissolve 35 g of citric acid ($C_6H_8O_7$) in 100 ml of water.

Ammonium Vanadate and ammonium molybdate solution—Dissolve 5.000 g of ammonium vanadate in 400 ml of hot water. Add 100 g of ammonium molybdate, and stir the solution until the molybdate dissolves. Let the solution stand overnight; then filter it into a 2-L volumetric flask. Wash the beaker and paper with water. Add 10 ml of concentrated NH_4OH to the filtrate; dilute the solution to volume and mix it. Store in a polyethylene bottle.

Bromocresol purple indicator (0.1 percent)

HNO_3 (concentrated and $1 + 1$)

HCl (5 percent and $1 + 1$)

$N_2H_4O_3$ (2 percent)

PROCEDURE

STANDARDIZATION OF THE PHOSPHORUS SOLUTION

A. Precipitation of phosphorus as ammonium phosphomolybdate

1. Dilute 2.2 ml of 85-percent H_3PO_4 to 200 ml. This is phosphorus standard solution A.

2. To two series of four 150-ml beakers, pipet 0, 2.0, 5.0, and 10.0 ml of phosphorus standard solution A and dilute to about 10 ml.

3. Add two or three drops of bromocresol purple, then $1+1$ NH$_4$OH until the solution just turns purple.
4. Dilute to 40 ml.
5. Add 8 g of NH$_4$NO$_3$ (solid) and warm on the steam bath until it dissolves.
6. Set the beakers in a water bath and keep at a temperature of about 60°C.
7. Add 15 ml of concentrated HNO$_3$ and immediately add 45 ml of the ammonium molybdate solution slowly while stirring.
8. Add water, if necessary, to make the total volume 100 ml and let stand at room temperature until the precipitate settles.

B. **Gravimetric determination of phosphorus as magnesium ammonium phosphate**
1. Decant the solutions from which phosphorus was precipitated as ammonium phosphomolybdate through a 9-cm #42 filter paper that has been washed with 5-percent NH$_4$OH wash solution.
2. Wash the precipitate left in the beaker several times with the NH$_4$NO$_3$ wash solution, pouring the washings through the filter.
3. Wipe the underlip of the beaker with a small piece of filter paper and expel the wash solution from the stem of the funnel.
4. Discard the filtrate.
5. Wash down the inside of the beaker with the 5-percent NH$_4$OH solution and stir to dissolve the precipitate.
6. Set the beaker under the funnel and dissolve the precipitate from the paper into the beaker by washing over the precipitate and around the upper edges of the filter paper with several small portions of the 5-percent NH$_4$OH solution until no yellow color remains.
7. Wash the paper three times with small portions of water, twice with 5-percent HCl, and finally three times with water.
8. Discard the filter paper and wash the funnel into the beaker.
9. Add $1+1$ HCl dropwise to the solution until it is just acid to bromocresol purple; then add to it 1 ml of 35-percent citric acid to hold traces of iron, if any, in solution.
10. Cool the solution to about 10°C in an ice bath.
11. Add 10 ml of the magnesium mixture and then, while stirring constantly, add $1+1$ NH$_4$OH drop by drop until the solution is just alkaline to bromocresol purple.
12. Continue the stirring for several minutes, then add a 10 percent by volume excess of concentrated NH$_4$OH.
13. Set the solution aside for at least 8 h; then filter through an 11-cm #42 paper and wash it a few times with the 5-percent NH$_4$OH wash solution.
14. Dissolve the precipitate into the original beaker by pipeting 5-ml portions of $1+1$ HCl over the precipitate and around the upper edges of the filter paper using about 25 ml of $1+1$ HCl in all.
15. Wash the filter paper thoroughly with 5-percent HCl solution and finally with water.
16. Dilute the solution to 50–100 ml.
17. Cool to about 10°C, add 2 ml of magnesium mixture; then while stirring constantly, add $1+1$ NH$_4$OH slowly to the solution as in step 11 above.
18. Allow the mixture to stand overnight and filter on an 11-cm #42 paper, quantitatively transferring the precipitate to the paper and washing moderately with cold 5-percent NH$_4$OH wash solution.
19. Finally, wash the precipitate on the filter with two 10-ml portions of 5-percent NH$_4$OH wash solution.
20. Transfer the precipitate to a weighed platinum crucible, slowly char the paper, and carefully burn off the resulting carbon in an electric furnace.
21. Allow the temperature of the furnace to reach 800°C gradually, and maintain this temperature until the Mg$_2$P$_2$O$_7$ precipitate is white.
22. Finally, ignite the precipitate at 1,050°C to constant weight.
23. Obtain the average weight of Mg$_2$P$_2$O$_7$ in 1 ml of phosphorus standard solution A. Multiply this value by 0.6379 (molecular ratio of P$_2$O$_5$ to Mg$_2$P$_2$O$_7$) to obtain the weight of P$_2$O$_5$ in 1 ml of standard solution A.
24. Transfer a suitable aliquot of solution A to a 1-L volumetric flask to make phosphorus standard solution B (1 ml $= 0.20$ mg P$_2$O$_s$). Dilute to volume and mix.

A. The gravimetric method

1. Transfer to a 150-ml beaker an aliquot of standard solution B that contains 4 mg of P_2O_5 and dilute to about 40 ml.
2. Add about 40 ml of water to another beaker.
3. To these solutions and to each of the sample solutions reserved for the determination of phosphorus, add two or three drops of bromocresol purple, then $1+1$ NH_4OH until the solution just turns purple.
4. Add 8 g of NH_4NO_3 (solid) and continue with the precipitation of phosphorus as ammonium phosphomolybdate as directed above in steps 5–8 of section "A. Precipitation of Phosphorus as Ammonium Phosphomolybdate."
5. Visually determine whether the volume of the ammonium phosphomolybdate precipitate in any of the samples exceeds the volume of the precipitate in the 4-mg standard.
6. Colorimetrically determine the P_2O_5 content of one blank and of all the samples having a precipitate smaller than the precipitate in the 4-mg standard.
7. Determine the P_2O_5 content of one blank and of any samples having a precipitate larger than the precipitate formed in the 4-mg standard by the gravimetric method described above in section "B. Gravimetric Determination of Phosphorus as Magnesium Ammonium Phosphate."
8. Correct the weight of the $Mg_2P_2O_7$ found in the sample for the weight of $Mg_2P_2O_7$ found in the blank and calculate the percent of P_2O_5 as follows:

$$\text{Percent } P_2O_5 = W \times 63.79/S$$

where

W = milligrams of $Mg_2P_2O_7$
S = milligrams of sample used, and
63.79 = molecular ratio of P_2O_5 to $Mg_2P_2O_7$ (0.6379) multiplied by 100.

B. The colorimetric method

1. Decant the solutions from which ammonium phosphomolybdate was precipitated through a 9-cm #42 paper.

2. Wash the precipitate left in the beaker several times with the NH_4NO_3 wash solution and transfer the washings to the filter.
3. Wipe the underlip of the beaker with a small piece of filter paper and add the paper to the funnel.
4. Expel the wash solution from the stem of the funnel.
5. Discard the filtrate.
6. Place a 100-ml volumetric flask under the funnel.
7. Wash down the inside of the beaker with a few milliliters of 5-percent NH_4OH solution.
8. Transfer this solution to the filter.
9. Continue to dissolve all the yellow precipitate from the beaker and the filter with small portions of 5-percent NH_4OH solution. The total volume of the NH_4OH solution should not exceed 25 ml.
10. Finally, wash the paper with water and wash the funnel into the flask, keeping the volume below 60 ml.
11. Remove the flasks and add $1+1$ HNO_3 to just neutralize the solutions.
12. Dilute those samples containing more another 100-ml volumetric flask and dian appropriate aliquot and transfer it to lute to about 60 ml. Reserve.
13. To a series of 100-ml volumetric flasks, pipet 0, 1, 2, 5, 10, 15, and 20 ml of phosphorus standard solution B and dilute to about 50 ml.
14. Add 8 ml of $1+1$ HNO_3 to each of the samples, the reagent blank, and the standard solutions; then add 10 ml of ammonium vanadate-ammonium molybdate solution to each and mix.
15. Dilute each solution to volume and mix thoroughly.
16. After 30 min, measure the absorbance of the molybdovanadophosphoric acid complex at 460 Mm in a 1-cm cell; use the reagent blank as the reference.
17. Prepare a calibration curve from the absorbance readings of the standards and determine the weight of the P_2O_5 in the sample solution from this curve. This weight divided by the weight of the sample in the solution $\times 100$ is the percentage of P_2O_5 in the sample.

The IL443 Flame Photometer is used for the quantitative determination of sodium and potassium after the silicate rock is decomposed and dissolved in hydrochloric acid. The accuracy of the data obtained and the simplicity of operation of this instrument recommend its use for determination of sodium and potassium in silicate rocks, even though this method is not classical. Such design features as ratioed internal standard operation, high ionization-suppressant concentration, and low flame temperature contribute to the accuracy of the instrument.

A constant 15 M solution of lithium is added to all samples and standards as an internal standard. The samples are closely bracketed with the standards when the readings are made, and the sample solutions are read at least twice; an average reading is used for calculating the number of milligrams of sodium and potassium in the solution. If the second reading is made from a second aliquot containing a different amount of the sample solution, possible interferences from elements in the sample can be detected.

A 1-g sample is decomposed in a Teflon beaker with nitric acid, sulfuric acid, and hydrofluoric acid and is dissolved in hydrochloric acid.

Tests were made to determine the effect of various levels of sodium on the potassium determination and the effect of various levels of potassium on the sodium determinations. No effects were observed.

Determinations made on different size samples of a group of silicate rocks gave no indication of interferences from other elements present in the sample. Solutions containing from 2 to 10 percent HCl gave identical readings; however, there was some indication of attack on the atomizer bowl when solutions of higher acidity were aspirated. In our laboratory, a 4-percent HCl solution is presented for aspiration.

APPARATUS

Laboratory flame photometer IL443 having gold-plated connections for the aspirator bowl.

Teflon beakers--Design of Teflon vessel for decomposition of rock samples by Shapiro (1959).

400-ml vycor or other pure silicon beakers

30-ml plastic beakers--use for aspirating samples

Plastic or Teflon stirring rods

Potassium stock solution (1 ml = 1 mg K₂O)--Dissolve 1.583 of KCl in about 50 ml of water and dilute to 1 L. Transfer the solution to a 1-L plastic bottle for storage.

Sodium stock solution (1 ml = 1 mg Na₂O)--Dissolve 1.886 g of reagent-grade NaCl in a little water and dilute to 1 L. Transfer the solution to a 1-L plastic bottle for storage.

H₂SO₄ (1 + 1)

HF (concentrated)

HNO₃ (1 + 1)

HCl (1:2)

Lithium stock solution (10 ml = 10.41 mg Li)--Dissolve 6.360 g of LiCl in a little water and dilute to 1 L. Transfer the solution to a 1-L plastic bottle for storage.

PROCEDURE

DECOMPOSITION OF THE SAMPLE

1. Transfer a 1-g sample to a Teflon beaker and disperse with a little water.
2. Add 10 ml of 1 + 1 H₂SO₄ to the beaker and immerse in the steam bath.
3. Add 10 ml of concentrated HF and then 10 ml of 1 + 1 HNO₃.
4. Cover the beaker and digest the contents for 6-8 h.
5. Remove the cover and wash material adhering to it into the beaker. Continue the evaporation on the steam bath until the volume of the solution is about 5 ml.
6. Set the uncovered beaker on a hot plate that has a surface temperature of 470° - 500°C and heat until fumes of SO₃ cease.
7. Cool.
8. Add 120 ml of 1:2 HCl to a 400-ml vycor beaker.
9. Transfer about 20 ml of this HCl to the Teflon beaker and transfer the contents of the Teflon beaker to the vycor beaker with the aid of a little water and a Teflon policeman.
10. Bring the solution to a vigorous boil and boil about 3 min. A clear solution should be obtained; if it is not, filter, ignite the residue, and treat with HF and H₂SO₄ as in steps 2 and 3 above. Dissolve the residue in a portion of the main solution and add to that of the main portion of the sample.

11. Transfer this solution to a 200-ml volumetric flask. Make to volume with water and then transfer it to a dry polyethylene bottle.
12. Pipet 20 ml of this solution and transfer it to a 100-ml volumetric flask. Add 10 ml of lithium solution (10 ml = 10.41 mg Li). Make to volume, then transfer to a plastic bottle.
13. Reserve.

PREPARATION OF STANDARD SOLUTIONS

1. Add volumes of standard solutions equal to 0, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 mg each of Na_2O and K_2O to a series of 100-ml volumetric flasks.
2. Add 8 ml of 1 + 1 HCl to each flask.
3. Add 10 ml of lithium solution (10 ml = 10.41 mg Li)
4. Make to volume and transfer to plastic bottles. Reserve.
5. Following the procedures outlined under "Section Six--Operation" of the instruction manual for the flame photometer (Instrumentation Laboratory, Inc., 1977), aspirate the standards and record the readings.
6. Aspirate the sample solution.
7. Select the standard solution having the nearest lower concentration of potassium and sodium and the standard solution having the nearest higher concentration of potassium and sodium and bracket the reading of the sample solution.
8. Calculate the milligrams of K_2O and the milligrams of Na_2O in the solution from the following equation.

$$[U \, mg = (Ru - Rls)(mgHs - mgLs/Rhs - Rls) + mgLs]$$

where

U mg = milligrams of K_2O or Na_2O found in the sample solution,

Ru = reading for sample solution

Rls = reading for lower standard

mgHs = milligrams of K_2O or Na_2O in the higher standard

mgLs = milligrams of K_2O or Na_2O in the lower standard

Rhs = reading for higher standard

Rls = reading for lower standard

Percent Na_2O or K_2O in the sample = [U mg (for the sample) − U mg (for the blank)/mg sample in the solution] × 100

SUMMATION OF ANALYTICAL RESULTS

The 13 constituents for which the procedures are given and CO_2 are the constituents usually determined in a routine rock analysis. The results are customarily reported in terms of percent of oxides in the air-dried sample.

Kolthoff and Sandell (1943, p. 283) stated that careful analysts usually aim to obtain an accuracy corresponding to an error of one part per thousand in the determination of a constituent occurring in relatively large amounts in a sample. They submitted the following table to show the degree of accuracy expected for smaller amounts of constituents. The digit expected to vary is represented by X.

Percentage constituent in sample	Permissible variation in percent
1.00	$0.0X$
0.1	$0.0X$-$0.00X$
0.01	$0.00X$
0.001	$0.00X$-$0.000X$

Maxwell (1968, p. 18 - 35) discussed precision and accuracy and gave an extensive list of references.

A good analysis will usually give a summation that is very close to 100 percent. Hillebrand and others (1953, p. 802) said "Given the purest obtainable reagents, an ample supply of platinum, facilities for working, and a reasonably clean labo-

TABLE 1. *Comparison of results (in percent) obtained in this laboratory by the methods recommended in this work and recommended averages from Flanagan (1976, p. 171)*

[For each sample, the first row of results is from Flanagan (1976), and the second row of results contains values obtained in this laboratory]

Sample	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	Total	Total Fe as Fe_2O_3
G-2_____	69.11	15.40	1.08	1.45	0.76	1.94	4.07	4.51	0.55	0.11	0.50	0.14	0.034	0.08	99.73	2.65
	69.24	15.44	1.05	1.40	.71	1.94	4.13	4.55	.58	.06	.46	.14	.036	.10	99.84	2.61
G-1_____	72.64	14.04	.87	.96	.38	1.39	3.32	5.48	.34	.06	.26	.09	.03	.07	99.93	1.94
	72.28	14.32	.80	.95	.50	1.41	3.36	5.51	.34	.06	.29	.07	.02	.06	99.97	1.86
GSP-1____	67.38	15.25	1.77	2.31	.96	2.02	2.80	5.53	.57	.12	.66	.28	.042	.15	99.84	4.33
	67.30	15.18	1.74	2.30	1.12	2.06	2.76	5.48	.59	.10	.65	.29	.04	.14	99.75	4.30
DTS-1____	40.50	.24	1.21	7.23	49.80	0.15	0.007	.0012	.46	.06	.013	.002	.11	.08	99.86	8.64
	40.56	.68	.75	7.25	49.60	0.29	<0.01	.006	.45	.07	0	.005	.11	.08	99.86	8.81
AGV-1___	59.00	17.25	4.51	2.05	1.53	4.90	4.26	2.89	.81	1.03	1.04	.49	.097	.05	99.91	6.76
	59.17	16.98	4.58	2.00	1.52	4.89	4.20	2.92	.78	.97	1.08	.49	.11	.06	99.75	6.80
W-1_____	52.64	15.00	1.40	8.72	6.62	10.96	2.15	.64	.53	.16	1.07	.14	.17	.06	100.26	11.09
	52.50	14.47	1.79	8.68	6.59	10.90	2.18	.63	.57	.14	1.08	.10	.16	.08	99.87	11.44
BCR-1___	54.50	13.61	3.69	8.80	3.46	6.92	3.27	1.70	.77	.80	2.20	.36	.18	.03	100.28	13.40
	54.43	13.59	3.48	8.81	3.51	6.90	3.24	1.68	.78	.79	2.24	.32	.18	.04	99.99	13.27

ratory, there is usually little excuse for failure on the part of a competent chemist to reach a summation within the limits 99.75 and 100.50.

"If the analysis has to be made in other vessels than those of platinum and careful blank determinations are not carried along, a higher limit than 100.50 is certainly called for, but it is extremely doubtful if a lower one than 99.75 should be accepted."

Peck (1964, p. 10) considered 99.50 to 100.25 acceptable. The summations for the summary values for eight USGS rocks listed by Flanagan (1976, p. 171) range from 99.73 to 100.28. Kolthoff and Sandell (1943, p. 262 - 298), Groves (1951, p. 224 - 236), Hillebrand and others (1953, p. 802 - 806), and Maxwell (1968, p. 14 - 15 and p. 18 - 35) discussed summation of analytical results and possible errors in the analysis and listed many references on these subjects.

Values listed by Flanagan (1976, p. 171) as recommended averages obtained from a compilation of values obtained for USGS standards by analysts worldwide and the values obtained in this laboratory by the methods recommended here are listed in table 1.

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