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A MANUAL OF MODIFIED ANALYTICAL PROCEDURES

FOR CONVENTIONAL ROCK ANALYSIS

by

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OPEN-FILE REPORT

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By Herbert Kirschenbaum

ABSTRACT

This manual was written to establish the most accurate analytical methodology for determining the major constituents in silicate rocks. This report describes modified classical procedures for determining the amount of SiO_2, Al_2O_3, Fe_2O_3, FeO, CaO, MgO, H_2O^-, H_2O^+, TiO_2, P_2O_5, MnO, CO_2, and S in silicate rocks. In the determination of Na_2O and K_2O, the flame photometer is used. The flame photometer procedure presented in this manual is as accurate and precise as the classical, yet time-consuming, J. Lawrence Smith procedure for the alkalis. Explanations are presented directly under various steps of the procedures explaining the importance of that particular technique and how it affects the accuracy of the analysis.

INTRODUCTION

The data from the newly established classical chemistry laboratory at the U.S. Geological Survey's (USGS) National Center in Reston, Virginia, must be on a par with data from the long-established USGS Conventional Rock Analysis Laboratory in Denver, Colorado. Results of silicate-rock analyses performed at both laboratories should be comparable so that geologists' interpretations of these analyses are not affected by analytical bias. This manual explains how the Reston laboratory obtains results comparable with Denver's results without the use of Denver's special equipment. Except for the flame photometer, equipment available to most laboratories is used in the Reston laboratory.

Analytical skills and methods should not be lost even though instrumental analysis and the more rapid but less accurate analytical chemistry techniques are being used widely and, as pointed out by Sanders (1977, p. 30), universities are paying less attention to classical analytical chemistry than they used to do. The thoroughness of this manual will facilitate training chemists in total silicate-rock analysis. An outline of the classical analysis of silicate rocks is shown in figure 1.

The procedures described in this manual are being carefully evaluated by a Youden square experimental design to determine any between-groups variation for the techniques and to test the procedures statistically during several months. Data thus far gathered suggest that these procedures meet all criteria for reporting classical analyses (table 1).

Figure 1.--Systematic Classical Rock Procedures Outline Scheme:

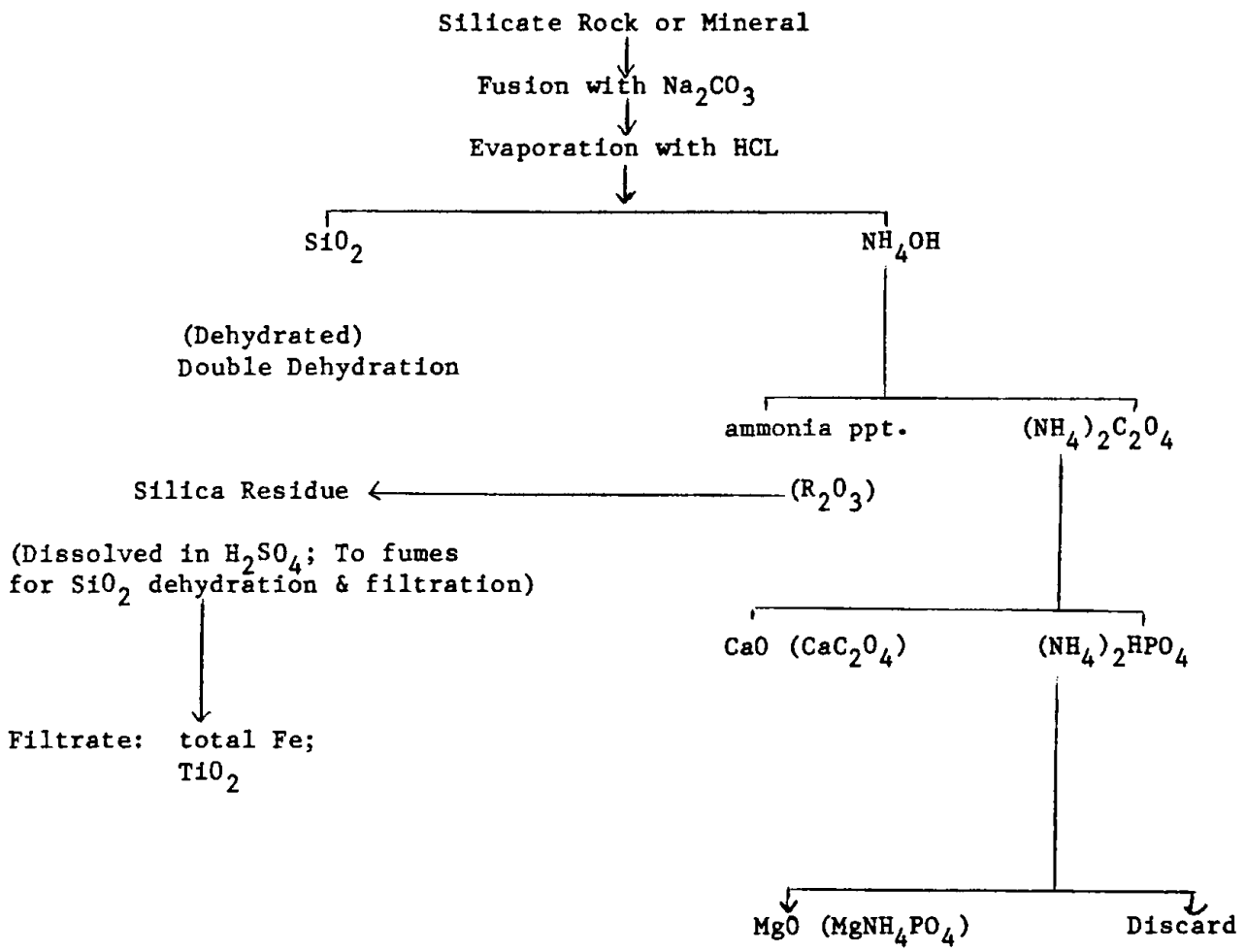


Table 1.--Desired classical chemistry precision (absolute error in percent)

SiO_2	0.10
Al_2O_3	0.15
CaO	0.05
MgO	0.05
Na_2O	0.03
K_2O	0.03
Total Fe	0.08
FeO	0.05
TiO_2	0.03
P_2O_5	0.03
MnO	0.01
CO_2	0.02
H_2O(+ or -)	0.02

Classical chemistry summation of a total silicate analysis of constituents normally found:

99.50 - 100.25

Acknowledgments

I appreciate the suggestions of co-working chemists, Lillie B. Jenkins and Joseph I. Dinnin. Lillie B. Jenkins helped put R_2O_3 determination into focus, and Joseph I. Dinnin aided in the digestion procedure for the flame photometric determination of Na_2O and K_2O. I also greatly appreciate the diligent review of this manual by Joseph I. Dinnin, Daniel R. Norton, and Brent P. Fabbi of the U.S. Geological Survey. I have incorporated the suggestions and advice of all three in this manual.

CRITICAL POINTS OF THE METHODS

Sample Decomposition

I have obtained excellent sample decomposition on 1 g of finely powdered silicate rock by fusing it with a total of 6 g of sodium carbonate at a temperature of 1,100°C in an electric furnace. The addition of a peroxide such as Na_2O_2 is unnecessary and may, in fact, even cause problems in a systematic analysis of silicate rocks. One such problem may be the peroxide attacking the platinum crucible and thus introducing excessive platinum into the systematic determinations.

Silica

In the gravimetric determination of silica, a thorough washing of the silica precipitate after the first and second dehydrations is critical in order to avoid low results. Therefore, I use fast filtering (Whatman #41) paper for both filtrations. The washing of the precipitates is easy, fast, and thorough. For rocks having an SiO_2 content of about 50 percent, the amount of SiO_2 that passes through the fast filtering paper after the second dehydration is about 0.3 percent. For rock having an SiO_2 content of about 70 percent, less than 0.1 percent SiO_2 passes through the paper. All the silica that passes into the filtrate is recovered in the gravimetric determination of residual SiO_2.

R_2O_3 Group

The method described in this manual for the determination of the R_2O_3 group is clear, is simple to follow, and gives excellent results. It is important to avoid formation of $CaCO_3$ after the precipitation of the R_2O_3 group, and this is achieved by keeping the precipitation beakers on the steam bath before and during filtration and by filtering as soon as possible. Excellent background reading can be found in Maxwell (1968, p. 345-348), Peck (1964, p. 26-30; 64-66), and Rieman and others (1951, p. 236-238).

Manganese Removal

The removal of manganese is necessary owing to the precipitation of manganese with magnesium. If manganese were not removed, corrections would have to be made for the coprecipitated manganous ammonium phosphate that is subsequently ignited to the pyrophosphate, $Mn_2P_2O_7$.

Residual SiO_2

Potassium pyrosulfate (a mixture of potassium pyrosulfate, $K_2S_2O_7$, and potassium bisulfate, $KHSO_4$) is used to fuse the R_2O_3 precipitate in the residual SiO_2 determination. It is critical that the fusion cake be completely dissolved in (1+1) H_2SO_4. After dehydrating the silica by heating to fumes of SO_3, everything except SiO_2 must be dissolved. I have found that not all brands of potassium pyrosulfate will yield a fusion cake that is easily and completely dissolved in this procedure. This difference in solubility is probably due to the variable composition of different brands of pyrosulfate.

Our Denver conventional rock analysis laboratory, for many years, has used the "Baker Instra-Analyzed" reagent, Potassium Pyrosulfate Acid-Flux Grade, Cat. #1-2963" without experiencing dissolution problems, and I have also used it without experiencing dissolution problems. Special care should also be observed in handling samples that contain high amounts of nickel and chromium. Under prolonged heating and high-temperature conditions, the sulfates of these elements form compounds that are difficult to dissolve. I have made a note of this in the "Recovery of Silica" section (p. 32).

Calcium Oxide

If platinum has become a contaminant in the analysis, it will interfere with the CaO determination by forming a platinum complex salt. The yellowish platinum complex will precipitate along with calcium oxalate, but it is easily removed during the CaO determination when the calcium oxalate is filtered and redissolved with hot 20 percent HCl. The insoluble platinum complex remains on the filter paper and is discarded. In the determination of CaO, strontium will also precipitate. If the amount of SrO is not negligible, strontium has to be determined on a separate sample, and the SrO correction must be made for the CaO figure (Groves, 1951, p. 60-63).

Magnesium Oxide

An accumulation of ammonium salts can retard the precipitation of small amounts of magnesium. By following Peck's (1964, p. 34) determination of MgO, in which he adds a large excess of ammonium phosphate in the first precipitation of magnesium and allows the solution to stand until precipitation is

complete, the analyst avoids having to destroy the ammonium salts before the precipitation is made. I am in complete agreement that the destruction of ammonium salts should be avoided. The procedure not only is time consuming but can cause splattering and thus result in losses.

Total Iron Oxide

Joseph I. Dinnin, formerly of the U.S. Geological Survey, and I made a study of the sharpest end point upon titrating 0.1N Mohr's salt (ferrous ammonium sulfate) with 0.1000N $K_2Cr_2O_7$. We varied the amounts of H_2SO_4 (1+1) and H_3PO_4 (1+1). We found that 40 ml (1+1) H_3PO_4 and 20 ml (1+1) H_2SO_4 produced the sharpest and clearest end point. H_2SO_4 and H_3PO_4 form colorless complexes with ferric ions whereas the free ferric ion and its chloride complex are yellow. In addition, H_3PO_4 lowers the reduction potential of the ferric-ferrous iron system by its formation of the ferric ion complex ($Fe(PO_4)_2^{\equiv}$), and the oxidation of the ferrous ion is thus facilitated. Therefore, H_3PO_4 produces a sharp color change at the equivalence point, and H_2SO_4 and H_3PO_4 keep the solution colorless to the end point and thus make the end point easy to detect (Kolthoff and others, 1969, p. 839-840).

Ferrous Iron

It is critical that ferrous iron does not become oxidized during the sample-digestion stage. If it is oxidized, low FeO results will be obtained. Experience will be the best teacher for the sample heating technique. This experience will be obtained by working with standard rocks of known FeO composition until accuracy is achieved.

Titanium Dioxide

The colorimetric determination of TiO_2 is made on the filtrate from the gravimetric SiO_2 recovery procedure and the fused residue after HF treatment of the same SiO_2 recovery procedure. The solution containing the filtrate and fused residue is made to a 100-ml volume in a volumetric flask. The total iron determination will also be made from this same solution and, therefore, all rinses in the course of the TiO_2 determination must be quantitative and must be saved for the total iron determination. The freshness of the H_2O_2 is critical, and I make up a fresh 6 percent H_2O_2 solution for each new run of samples; that is, usually once a month. The working standards may be stored providing they are transferred to polyethylene containers from the 100-ml glass volumetric containers. However, one of the standards of the kept lot should be checked periodically with a freshly made standard of the same concentration to see if the old and new give the same absorbance values. The spectrophotometer used is the Bausch and Lomb spectronic 100. I am a firm believer of close bracketing of samples by standards, and a sample reading should never be outside the range of the highest or lowest standard of the set of standards used. Samples may be diluted if necessary, and the absorbance reading of the unperoxidized solution will drop accordingly for the color correction. The concentration of standards written in the method is only a general guide. The concentration of standards used for a sample run should be close to the expected sample percentages and dilution factors should be taken into consideration.

The colorimetric determination of MnO is performed by oxidizing manganese to permanganate with periodic acid and boiling in a nitric acid solution. The color is very stable, and this stability leads to precise and accurate results. A blank run along with the samples gives the same absorbance as the reference solution, distilled water. However, for the determination of phosphorus, sample blanks could contain an absorbance reading of about 0.01 to 0.02 Abs. (absorbance). Both the sample blank and the standard blank should be read against distilled water as the reference solution. The spectrophotometer used is the Bausch and Lomb spectronic 100. A critical point in these colorimetric determinations is that the 1-cm cells used should be a matched pair, and when filled by distilled water, they should give readings of no more than 0.002 Abs. difference when read against each other. Certain samples (pumices) may have a highly glassy structure, and the decomposition procedure for manganese and phosphorus oxides will not be sufficient to decompose all the silica. The undecomposed silica of these samples will retain titanium phosphate and iron, and total decomposition is necessary in order to report accurate P_2O_5 data. If a white residue is found on the filter paper after the sample solution is filtered into a 100-ml volumetric flask at the completion of the sample decomposition and digestion steps, perform the following procedure on the sample and a sample blank (Easton, 1972, p. 213-216).

1. Ignite paper and residue in a 25-ml platinum crucible under good oxidizing conditions by cracking the door of the electric furnace, thus allowing air to enter. Slowly bring temperature to 800°C.

2. When the paper is completely ignited, remove crucible from the furnace, cool, and add 0.5 g anhydrous Na_2CO_3. Fuse at 900°C for 30 min. Bring the temperature of the furnace to 1,000°C and fuse an additional 10 min.

3. Remove crucible from the furnace and allow to cool. Remove the cold cake to a 100-ml beaker and dissolve the soluble salts with 30 ml distilled water by heating on a steam bath, overnight if necessary. Filter through a Whatman #40 filter paper into a 50-ml beaker. Rinse the crucible and paper a few times with 1 percent Na_2CO_3.

4. Cover the beaker with a watch glass and carefully acidify the filtrate with (1+1) HNO_3. Add this solution to the previous main filtrate in the 100-ml volumetric flask, and dilute to volume with water.

Sodium and Potassium Oxides

Lithium is added to all calibrating standards and unknown samples used in the flame photometer determination of the alkalis, Na_2O and K_2O. The IL flame photometer 443 uses the internal standard as an index of sample concentration; thus, the volume proportion of lithium used as an internal standard must be kept constant. Any effects on the constituent to be measured will be similar to effects on the internal standard, and emission of the sample solution is measured as a ratio of the intensity of the emission exhibited by the sodium or potassium concentration and the intensity of the emission exhibited by the internal standard (Instrumentation Laboratory, Inc., 1977, p. 1-3). The sample must be fumed strongly in the $HF-HClO_4$ decomposition of Na_2O and K_2O. One way to determine that the sample is fuming strongly is to examine the color of the

fuming solution. The color of the solution will turn from clear to yellow when the samples have been fumed adequately. Because the flame fluctuates randomly, the data should be averaged between calibrations for the most accurate results.

Total H_2O (Penfield Method)

Two grams of sodium tungstate is used as a flux in the Penfield tube procedure for the determination of total water. The use of 2 g of sodium tungstate gives a water blank of about 0.10 ± 0.02 percent water. The sodium tungstate must initially be oven heated at 180°C to drive out the moisture, and the flux must be kept in an oven at 110°C when not in use to prevent moisture buildup. I like to subtract a "running blank" from the samples. A running blank is defined as the addition of cumulative blanks divided by the number of runs. For example, if the previous five blank runs were 0.10, 0.11, 0.10, 0.09, and 0.10 percent and the result presently found is 0.08 percent, the blank subtracted from the sample would be: 0.58 percent ÷ 6 = 0.097, or 0.10 percent. Running blanks give a more accurate figure to be subtracted from the sample, and they indicate slow trends, such as moisture buildup in the flux. Any large deviation of the daily blank from the previous average blank should be carefully checked.

Carbon Dioxide

The classic gravimetric procedure for the determination of CO_2 is well explained in the written procedure of this manual. However, for samples that contain less than 0.05 percent CO_2, an accurate and very fast procedure is as follows (Shapiro, 1975, p. 58-60):

1. Weigh 25 mg of sample on weighing paper, and transfer to a borosilicate test tube (10 x 75 mm) which has been modified by the addition of a bulge about 18 mm from the bottom of the tube. The bulge is made by heating the test tube over a Bunsen burner and pushing from within with a stiff wire having a small hook at one end (Shapiro, 1975, p. 12-13).

2. Add distilled H_2O until water level is 1/2 inch above extended bulge.

3. Bring to boil over flame and invert tube (extended bulge in downward position) to allow air bubbles to escape bulge.

4. Holding tube at 45^{o} angle, extended bulge upward, add 0.1 ml hot mixture of mercuric chloride and concentrated HCl (10 ml concentrated HCl mixed with 10 ml of decanted saturated mercuric chloride). Allow CO_2 bubbles to go up the extended bulge. The CO_2 bubble size is compared with the size of the CO_2 bubble given off by standard rocks of the same CO_2 range. The size of the bubble from a weighed 25 mg of W-1 represents a CO_2 content of 0.06 percent, and that from a weighed 25 mg of BCR represents a CO_2 content of 0.03 percent (Flanagan, 1976, p. 171). This fast acid-evolution procedure for samples containing less than 0.05 percent CO_2 is within the $\pm$ 0.02 percent precision of the gravimetric determination of CO_2.

Total Sulfur

In the determination of total sulfur, the barium sulfate precipitate must be free of chlorides. The coprecipitation of barium chloride will cause a positive error. Therefore, I test the final washing with silver nitrate to

make sure that chloride in the form of silver chloride is not present. Because the barium sulfate may dissolve and cause a negative error, the washing of the barium sulfate precipitate with water should not be excessive. The filter paper used for retaining the barium sulfate precipitate should be checked to see if it is introducing a positive error by leaving a significant residue upon ignition. This check is done by running procedural blanks through the determination. Once the analyst is satisfied that the paper does not yield a positive error (0.01 percent) when the percentage of sulfur is calculated, then blanks do not need to be run along with samples. I find it convenient to run seven samples and a BCR for each run. The percent sulfur of a BCR is 0.04 percent, and because the sulfur contents of most silicate rocks are less than 0.1 percent, a BCR is an excellent check to make sure that the reagents for the determination are reacting properly and that the analytical technique used is correct.

Oxygen Corrections

A correction for the oxygen equivalent of sulfur, fluorine, and chlorine must be applied when they are present as a sulfide, fluoride, and chloride (Maxwell, 1968, p. 235-236, 247, 250). When the amount of sulfur is small, and it is not practical to distinguish between individual sulfides such as pyrite and pyrrhotite, the correction factor for sulfur should be: S X 0.5. If the sulfide is known to be present as a pyrite, the correction factor is 0.374. If the sulfide is known to be present as pyrrhotite, the factor is 0.437. The correction factor for chloride is Cl X 0.22 and that for fluoride is F X 0.42. The oxygen corrections are subtracted from the summation total.

Determination of Moisture, H_2O^-

Procedure:

Before starting classical rock-analysis procedures, mix sample that has been ground to 100 mesh on tumblers for a minimum of 10 min, pour sample onto 6" x 6" glycine weighing paper, quarter it, and return it to bottle with a spatula.

1. Clean a 50-ml platinum crucible by fusing with potassium pyrosulfate, washing in hot HCl, and rinsing with distilled H_2O. Heat in a muffle furnace at 800°C for 10 min. Cool in desiccator for 30 min. Repeat until a constant weight, 0.2 mg, is obtained.

2. Transfer 1.0000 g sample to the weighed crucible.

3. Place the uncovered crucible in an oven, cover it with 7-cm diameter filter paper, and heat it at 105°-110°C for 1 hr. Transfer the crucible to a desiccator, cover, and allow it to cool for 30 min before weighing.

Calculation:

Loss in weight x 100 = percent H_2O^-.

Gravimetric Determination of Silica in Samples Containing <2 Percent Fluorine

If samples contain more than 2 percent F, low silica results would be obtained by using the procedure described below because the SiF_6^{2-} complex forms in acid solution and breaks down SiF_6^{2-} to the volatile SiF_4 at temperatures above 100°C.

Fusion with sodium carbonate method (Maxwell, 1968, p. 324-330):

1. Support the platinum crucible containing the 1.0000 g sample used for determining H_2O^-, covered, on a clay or silica triangle over a Bunsen burner, and heat the crucible with a low flame to drive off the combined water.

2. Increase the height of the flame until the bottom part of the crucible is a 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 in order to oxidize any reducing substances that may be present and that would otherwise attack the crucible during the fusion. Cover the crucible and allow it to cool.

4. Weigh 5 g of anhydrous Na_2CO_3 and add about 2 g of it to the cooled crucible. Mix the sample and flux thoroughly with a thin short length of glass rod; add another 2 g Na_2CO_3 and again mix thoroughly. Add the remainder of the Na_2CO_3 and mix, making sure that no clumps of Na_2CO_3 remain. Do not attempt to brush off the glass rod, tap it against the sides of the crucible, and "rinse" it in another weighed gram of Na_2CO_3. Tap the crucible gently on the bench top

to settle the fusion mixture and sprinkle the 1 g of Na_2CO_3 over the surface to provide a trap for splattering particles during the initial heating stages of the fusion steps.

5. Place the crucible in a silica tray in an electric furnace at a temperature of 400°C and gradually raise the temperature to 900°C. Keep at 900°C for 30 min before raising the temperature by additions of 50°C to 1,100°C. This gradual increase in temperature prevents splashing of melt. A temperature of 1,100°C insures decomposition of chromite and zircon.

6. Maintain sample at 1,100°C for 30 min.

7. Remove fused sample from furnace and allow it to cool.

8. Place crucible on a silica triangle and heat over a Meker burner (dull red heat) for 15 to 30 sec. Allow it to cool.

Note: The brief reheating of the cooled cake melts the layer adjacent to the crucible walls, and water is able to penetrate the space and loosen the cake in the crucible.

9. Add about 20 ml H_2O to the crucible, and with a glass stirring rod, apply gentle pressure to the cake to loosen it.

10. Transfer the cake to a 300-ml platinum dish. Wash the inside of the crucible, and catch the washings in the dish, but do not attempt to dislodge firmly adhering material. Wipe off the outside of the crucible and set it

aside. Should the cake not separate freely, place the water-filled crucible on the water bath and heat for 30 min.

Note: The color of the cooled melt may be significant; a green color may indicate the presence of manganate ion, which will react with HCl to release chlorine when the melt is dissolved in HCl and the chlorine will attack platinum. Therefore, a few milliliters of alcohol should always be added to the disintegrated melt before the addition of acid to reduce Mn (VI) to Mn (II).

11. Add 75 ml H_2O and 3 ml alcohol to the dish and cover it by a watch glass.

12. Insert the tip of a curved-stem funnel between the lip of the dish and the watch glass. Do not try to pulverize the cake as this may cause spillage. Add 5 ml HCl to the crucible and 20 ml HCl to a beaker. Pour HCl slowly from the beaker through the curved-stem funnel into the dish (make sure the dish is firmly covered by the watch glass) in portions small enough to avoid violent effervescence. Hold the crucible cover over the funnel and wash it with water; rub the cover with a rubber policeman that has been dipped into the acid contained in the crucible and again wash it with water. Scrub the inside of the crucible with a rubber policeman. Transfer the acid to the funnel; wash the policeman and the inside of the crucible with water, and catch the washings in the funnel. Wash funnel and funnel tip, and catch the washing in the large platinum dish.

13. Let the dish stand until most of the effervescence stops. Then pulverize the fused cake. Wash the underside of the cover glass, transfer the dish to the steam bath, and cover it quickly. When no more CO_2 is evolved, wash the underside of the cover glass again and wash down sides of the platinum dish, breaking up any lumps that remain.

Note: At this stage, any unattacked material will be either visible or detectable as a gritty residue. If more than a few particles are found, the sample should be discarded and the fusion repeated at a higher temperature.

14. Ignite the covered fusion crucible over a Meker burner until the crucible becomes red; while igniting the crucible, allow oxygen to enter it and note if it appears stained. If no stain, or very light stain appears on the crucible, place it in a muffle furnace at 800°C for 10 min and then in the desiccator for 30 min. Repeat until constant weight is achieved.

Note: If the crucible is much stained (most likely by Fe), add 10 ml (1:1) HCl to the crucible, cover it, and heat it on the water bath until the stain disappears. Rinse the solution into the platinum dish, and ignite crucible as before.

15. Allow the solution in the platinum dish to evaporate to dryness on the steam bath. Stir the residue as the solution goes dry. The residue will be pale yellow to pale brown; a golden yellow indicates the presence of free HCl. As the drying continues, the residue will be nearly white. After this stage, dry for another hour. Add 50 ml 1:4 (20 percent) HCl; cover the dish and heat the solution for 30 min. Sometime during this period, sluice the salts on the

inside of the dish into the solution using 1:19 (5 percent) HCl, and stir until the NaCl crystals dissolve, (Peck, 1964, p. 63).

Note: This heating should not be prolonged, in order that as little as possible of the silica will be dissolved.

16. Prepare an 11-cm Whatman #41 filter paper in a 65-mm funnel, wash the paper once with hot 5 percent HCl, and decant the solution into a 250-ml beaker. Wash the residue once with hot 5 percent HCl. Stir the solution, and pour it quickly into the filter so that most of the silica is carried into the filter. Wash the rod with 5 percent HCl, scrub it with a policeman, wash it again, and place it in the beaker. Police the inside of the dish, and pour the wash solution into the paper. Wash the dish twice with 5 percent HCl and scrub the inside of the dish with a policeman each time before transferring the wash to the filter; wash off the policeman into the filter.

Note: At this point, number the funnels (same Nos. as platinum dishes). Wash the precipitate 15 times with hot 5 percent HCl. Pay particular attention to upper edges of paper-there should be no yellow (free of chloride). The solution should drain before the next wash is added. Lift the paper with platinum-tipped forceps to drain the funnel stem. Reserve the filter paper by putting a numbered watch glass over it. (This paper will later be added to the filter paper containing silica from a second dehydration and filtration).

Note: Importance of a thorough washing of silica precipitate: Appreciable amounts of Na, K, and alkaline earth metals if not washed out of the precipitated silica may cause low results to be obtained for silica because they are

first weighed as an alkaline silicate before HF treatment and as a sulfate after the HF decomposition.

17. The separated silica should be white but may be colored by hydrolyzed iron oxides (reddish) or by platinum (gray). Under normal conditions, these coloring agents will do no harm. Quantitatively transfer the contents of the beaker to the original platinum dish and again evaporate the contents to dryness, as described in step 15 above. Stir the residue as the solution goes dry; then continue heating the dry residue for 1 hour.

18. Add 50 ml 20 percent HCl and heat the solution for 30 min on the water bath. During this 30-min period, wash the salts on the inside of the dish with 5 percent HCl (Peck, 1964, p. 63).

19. Filter the solution through a 9-cm #41 Whatman filter paper (previously washed with hot 5 percent HCl) into a 400-ml beaker. DO NOT discard the filtrate (used for the determination of the R_2O_3 precipitate). Wash the stirring rod with 5 percent HCl, police the inside of the dish. Wash completely. Wash the precipitate on the paper 10 times with hot 5 percent HCl. Once again, no yellow should appear on the paper, and each solution should drain before the next wash is added. Be sure to wash thoroughly.

20. Fold the two papers containing the silica and put them in the weighed platinum crucible. Wipe out the insides of the funnels with a piece of filter paper and add it to the crucible.

21. Place the crucible in a cold electric muffle furnace with the crucible cover not quite in place. Slightly crack open the furnace door to allow air to enter for better oxidation. This will prevent graphites from forming from the burnt paper. Slowly raise temperature of furnace to 800°C and hold until only a little carbon is left on the silica precipitate. Put crucible cover in place and shut furnace door, then gradually raise temperature to 1,200°C. The precipitate should be white.

22. The precipitate is ignited at 1,200°C for 30 min. Put it in desiccator for 30 min and weigh. Return crucible to the furnace for 20 min and to the desiccator for 30-min periods until constant weight is obtained (to within .0002 g). The final weight is the weight of the impure silica.

23. Moisten the silica with 1 ml H_2O; then add six drops (1+1) H_2SO_4 and 10 ml HF, and replace the cover. Allow the crucible to stand 1 or 2 min to permit the initial reaction to take place. Heat the covered crucibles on hot plate just short of boiling 120°C (250°F) until the solution is clear (about 5 min).

24. Crack the crucible cover and increase the heat carefully to evaporate the solution to fumes of SO_3. Increase the heat until no more fumes can be seen. Cool the crucible and gently wipe the outer surface with a damp cloth to remove adhering material.

Note: Importance of adding (1+1) H_2SO_4 in obtaining true weight of SiO_2: After the silica precipitate has been strongly ignited, the principal contaminants will be present as the oxides TiO_2, Al_2O_3, and Fe_2O_3. In step 23 above,

HF causes the expulsion of Si as SiF_4, but if H_2SO_4 were not added, the contaminating metals would be left as fluorides after the residue ignition (Ti would be lost as TiF_4). H_2SO_4 forms sulfates with the contaminating metals. During later ignition, the sulfates are decomposed to oxides.

25. Ignite the covered crucible in an electric furnace at 800°C for 10 min. Cool, desiccate for 30 min, and weigh. The difference in weight is that of the pure silica.

Calculation: Loss in weight after HF addition x 100 + SiO_2 recovered from R_2O_3group = percent SiO_2.

26. Add 0.5 g Na_2CO_3 to the residue; fuse in furnace at 1,050°C for 20 min. Add a little H_2O and (1+1) HCl dropwise and continue until effervescence stops. Then dissolve cake completely in (1+1) HCl. Heat on hot plate if necessary. Quantitatively transfer the dissolved cake to the reserved filtrate from the SiO_2 determination. The crucible should be ignited at 800°C in the furnace and weighed to constant weight (ignite for 10 min; desiccate 30 min). Reserve the crucible for the ignition of the R_2O_3 precipitate. This step is unnecessary if residue <9 mg (V. Smith, E. Brandt, and E. Engelman, USGS, oral commun., 1978). If unnecessary, put precipitate from R_2O_3 directly into crucible after silica HF treatment (step 25).

Gravimetric Determination of Alumina by Difference Following Precipitation of R_2O_3 Group

1. Dilute the filtrate from the determination of silica to 200 ml. Add five drops of 0.1 percent brom cresol purple (pH 5.2-6.8) to the filtrate and put the beaker on top of the Meker burner, using tripod and asbestos mat. Allow the solution to heat and while stirring add pure NH_4OH stored in plastic bottle (Reagent grade NH_4OH contains silica) dropwise until a permanent precipitate forms. Allow precipitate to settle and check supernatant liquid to be certain the color is purple: add NH_4OH dropwise while heating until the solution is purple but just basic, and add two drops in excess. Remove beaker from burner, add 0.25 g dry filter pulp (S & S #289), stir and put on steam bath. This insures that the solution is kept hot until ready for filtering. Repeat above procedure with second sample, etc.

Note: The precipitate obtained from a hot solution is easily filterable. After the precipitation of the hydroxides of iron and aluminum, an ammoniacal solution slowly absorbs CO_2 from the air causing precipitation of $CaCO_3$. To avoid formation of $CaCO_3$, filter as soon as possible after precipitation and keep beakers heated on the steam bath before and during filtration.

2. Filter the hot solution through a 12.5-cm Whatman #40 filter paper into a 600-ml beaker. Filter rapidly, keeping bulk of precipitate in beaker until filtering is complete. Wash the inside of the beaker twice with hot 2 percent NH_4NO_3 solution and transfer washings to filter. Reserve washed precipitation beakers for later use.

Note: The precipitate must NOT be washed in H_2O--the hydrous aluminum oxide would be peptized and would run through the filter.

3. Wash precipitate 10 times with hot 2 percent NH_4NO_3, allowing the solution to drain each time. Take care during washings to wash the precipitate away from the edges of the paper. Reserve the filtrate.

4. In order to redissolve the R_2O_3 precipitate for the second precipitation, lift paper with platinum forceps and put into washed reserved beaker. Wash funnel with 5 percent HCl. Wash inside of beaker with 5 percent HCl. Put beaker on steam bath. Heat and stir. Add 1 ml (1+1) HCl and stir; add a second milliliter (1+1) HCl to dissolve the precipitate completely. Stir the filter paper in the acid solution, making certain that all the precipitate is dissolved. Using the stirring rod, shred the filter paper. Adjust the volume in the beaker to 150 ml.

5. Add 5 drops of brom cresol purple to the beaker. Boil over a Meker burner, and while stirring, add pure NH_4OH dropwise until precipitation is complete and the supernatant liquid is purple. Thus, the solution should be just basic and should contain 2 drops of NH_4OH in excess. Place the beaker on the steam bath while repeating the beginning of this step with another sample, etc.

Note: When two precipitations are made, separation from manganese (in amounts of as much as 20 mg) is substantially complete.

6. Filter the solution through a 12.5-cm Whatman #40 filter paper into the reserved 600-ml beaker containing the first filtrate. If beaker becomes full,

filter the remaining solution into a 400-ml beaker. Wash the inside of precipitation beaker twice with hot 2 percent NH_4NO_3 and add washings to the filter.

7. Wash the inside of the precipitation beaker with 5 percent HCl. Heat the solution on the steam bath for 5 min; wash down the sides of the beaker with 5 percent HCl and then with H_2O to wash down the acid. Add two drops of brom cresol purple and add pure NH_4OH dropwise until the solution turns purple. Heat the solution on the steam bath another 5 min. Pour the hot solution into the filter. Wash the beaker twice with 2 percent hot NH_4NO_3, adding washings to the filter. Thoroughly police beaker to transfer any remaining precipitate or film.

8. Wash precipitate 15 times with hot 2 percent NH_4NO_3. Cover the precipitate with wash solution each time, allowing full drainage.

9. Cover the funnel with a filter paper and allow the precipitate to dry partially overnight. Add (1+1) HCl dropwise to the combined filtrates until yellow; add two drops in excess and evaporate to a volume of 200 ml. Just neutralize the solution with NH_4OH and heat it below the boiling temperature for 15 min. If no precipitate is evident, reserve the solution for the next operation--the removal of manganese. If a precipitate is present, filter the solution through a 9-cm #40 Whatman paper. Wash the beaker three times with hot 2 percent NH_4NO_3 and transfer the washings to the filter. Wash the paper 10 times with the same solution. Fold the paper, and place it in the funnel containing the main part of the NH_4OH group precipitate. Reserve the filtrate for the next operation, the removal of manganese.

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

Note: The bulky precipitate should be partly dried or at least well drained, before being placed in the crucible; if not, the entrained liquid may boil and some precipitate may be lost by spurting.

11. Partly cover the crucible and place it in a cold electric muffle furnace. Allow the temperature to rise slowly to 800°C and, by cracking furnace door during the initial stages of the ignition, ensure that air has free access to the furnace. Burn off all carbon from paper.

12. Finally heat at just below 1,200°C (1,125°C) for 40 min.

Note: At 1,200°C, ferric oxide may be converted to magnetite. Below 1,100°C, the R_2O_3 precipitate may not be water free.

13. Cool in desiccator 30 min and weigh. Repeat ignition for 20-min periods until constant weight is obtained. Reserve the precipitate for the recovery of silica.

Calculation: wt. R_2O_3 x 100 = R_2O_3*

% R_2O_3- (% recovered SiO_2 + % total Fe (as Fe_2O_3) + % TiO_2 + % P_2O_5) = Al_2O_3

*weight of empty crucible used in calculation is the weight of the crucible after the pyrosulfate fusion in the Silica Recovery determination (after step 5, p. 32).

Note: Although the R_2O_3 group consists generally of Al_2O_3, P_2O_5, Fe_2O_3, TiO_2, and recovered SiO_2, other elements may be present. A preliminary spectrographic analysis of the sample is invaluable to determine whether such uncommon elements as chromium, vanadium, zirconium, the rare earths, and beryllium are present in macro-amounts.

Removal of Manganese

Procedure (Peck, 1964, p. 30-31, 66): 1. Evaporate the filtrate obtained in step 9, p. 27, to 100 ml; then add 1 ml 5 percent zirconyl chloride solution and 0.1 g of paper pulp.

Note: A solution of colloidal hydrated manganese dioxide filters slowly, and the precipitate passes through the finest paper. The zirconium solution forms a hydroxide gel that gathers the precipitate and makes this separation complete. The paper pulp prevents channeling when the precipitate is washed.

2. Make the solution ammoniacal and then just acid with (1+1) HCl. Add 1 g ammonium persulfate to oxidize the Mn to MnO_2. Stir the solution and heat for 20 min on the steam bath. Add 1 ml NH_4OH (make ammoniacal) and continue heating the solution for an additional 5 min.

Note: Mg but no Ca coprecipitates appreciably with the MNO_2. Coprecipitation of Mg is minimized if the precipitation is made from an acid solution, but the precipitation of MnO_2 is incomplete. Therefore, the precipitation is made in acid solution, heated, made ammoniacal, and heated again.

3. Stir the solution and filter it at once through a 9-cm Whatman #40 filter paper into a 400-ml beaker. Wash the inside of the precipitation beaker three times with a hot 2 percent ammonium nitrate solution and transfer the washings to the filter. Wash the precipitate on the paper 10 times with the same solution.

4. Discard the hydrated manganese dioxide and zirconium hydroxide precipitate, and reserve the filtrate for the determination of calcium.

Recovery of Silica

Procedure (Peck, 1964, p. 69-70; Maxwell, 1968, p. 348-350):

1. Place a 30-ml Vycor crucible upside down over the platinum crucible containing the ammonium hydroxide precipitate. Invert the two crucibles together so that the precipitate falls into the Vycor crucible. Tap the bottom of the platinum crucible and hold it in place for a few seconds to allow dust to

settle. Use a brush to loosen the precipitate from the platinum crucible into the Vycor crucible. Do not attempt to dislodge firmly adhered material.

Caution: The ignited residue is easily blown out of the crucible.

2. Add 7 g of potassium pyrosulfate to the Vycor crucible, and add 1 g of potassium pyrosulfate to the platinum crucible.

3. Place Vycor crucible (covered) in muffle furnace at 700°C. Fuse the R_2O_3 precipitates at 800°C for 2-3 min or until fused. Check for specks of unfused matter when cooled.

4. Remove the Vycor crucible from furnace, cool, add water to cover its contents, and heat it on top of the steam bath for 5 min. Police the inside of the crucible to loosen the cake, and transfer the contents to a 250-ml beaker. Add 20 ml of (1+1) H_2SO_4 to beaker and set it aside. Police cover and add to beaker. Rotate the platinum crucible over a small flame until the pyrosulfate melts. Increase heat until crucible is dull red and fumes of SO_3 appear. Continue heating long enough to dissolve the small amount of precipitate left in the crucible. Place a small piece of $K_2S_2O_7$ on the surface of the crucible cover to dissolve stains or adhering particles. Cool crucible, add a little water to its contents, and heat it on top of the steam bath for 5 min. Police inside of crucible and cover, and transfer contents to the 250-ml beaker containing (1+1) H_2SO_4 and the fusion cake from the Vycor crucible.

5. Ignite the platinum crucible at 800°C in an electric furnace for 10 min. Cool for 30 min in a desiccator. Repeat until constant weight is obtained. Reserve crucible for CaO determination or SiO_2 recovery, depending on the determination that is completed first. The weight of the crucible is used in the calculation of percent R_2O_3 if the residue from silica determination was not fused with 0.5 g Na_2O_3.

6. Cover the 250-ml beaker and heat on water bath until the contents have dissolved, then uncover it and evaporate the contents on a hotplate to moderate fumes of SO_3. Continue fuming for 15 min (heating to fumes dehydrates the silica).

7. Cool the beaker and contents and dilute the solution to 75 ml with water. Heat beaker on water bath until everything dissolves except a fleecy residue of silica.

Note: Samples that contain high amounts of nickel and chromium form sulfates that are difficult to dissolve. All heating should be carried to fumes of the acid but heating should not be prolonged and should not be at a high temperature (Hillebrand and others, 1953, p. 678).

8. Filter the warm solution through a 9-cm Whatman #40 filter paper into a 250-ml beaker. This author keeps the solution warm while filtering in order to prevent salts from crystallizing. Wash and police stirring rod and beaker well with 1 percent H_2SO_4. Wash precipitate on the paper 10 times with 1 percent H_2SO_4 and drain the funnel stem. Reserve the filtrate for the determination of titanium and total iron oxide.

9. Transfer the paper to the crucible that was cleaned after the determination of CaO. Burn off the paper in an electric muffle furnace at low temperature. Finally, ignite the precipitate for 10 min at 1,000°C; cool and weigh.

10. Treat the small residue, which should be white, with a drop of (1+1) H_2SO_4 and 1 or 2 ml of HF. Transfer crucible to hotplate and heat until fumes of SO_3 appear. Continue heating until all the H_2SO_4 is expelled. Place the covered crucible in an electric furnace at 1,000°C for 10 min; allow to cool in a desiccator for 30 min and weigh to obtain weight of silica.

11. Add 1 g of potassium pyrosulfate to the crucible and fuse over a flame to dissolve the small remaining residue. Cool the crucible; add water, and heat it on the steam bath for 5 min. Transfer the contents of the crucible to the 250-ml beaker containing the solution that is reserved for the determination of titanium and total iron. Evaporate the solution on the steam bath below a volume of 100 ml. Quantitatively transfer the solution to a 100-ml volumetric flask. Fill to volume with distilled H_2O.

Ignite the crucible, cool it in a desiccator, weigh and reserve it for use in the CaO determination if CaO is not already determined, or reserve it for the MgO determination.

Gravimetric Determination of Calcium Oxide

Procedure (Peck, 1964, p. 67-68): 1. Heat the solution reserved after Mn removal on a steam bath to incipient boiling. DO NOT BOIL. Add 30 ml 10

percent oxalic acid solution--rapidly at first, then slowly if a precipitate forms.

2. Add five drops of 0.1 percent brom cresol purple indicator and then add NH_4OH dropwise while stirring until the solution turns purple. Add 1 ml NH_4OH (in excess). Stir the solution, remove it from the steam bath, and let it stand at room temperature overnight.

3. Filter the solution through a 9-cm #40 Whatman filter paper into a 600-ml beaker, retaining as much of the precipitate in the original beaker as possible. Wash down the inside of the precipitation beaker with 0.1 percent ammonium oxalate solution, and transfer wash to the filter. Wash the paper three times with the ammonium oxalate solution. Replace the beaker containing the filtrate with a 150-ml beaker. Reserve the filtrate.

4. This author washes the inside of the precipitation beaker with hot 20 percent HCl. Heat the solution in the beaker on a steam bath or hotplate, and if necessary, add (1+1) HCl to bring the precipitate into solution. Pour the solution through the filter. Wash the inside of the beaker three times with hot 20 percent HCl, and transfer washings to the filter. If calcium oxalate can be seen on the paper, dissolve this precipitate with small portions of hot 20 percent HCl from the wash bottle. When no more precipitate is visible, wash the paper five times with hot 5 percent HCl, making sure all areas are reached including inside flap. Discard the paper.

5. Dilute the solution in the 150-ml beaker to 90 ml. Add two drops of 0.1 percent brom cresol purple indicator, and heat the solution to incipient

boiling. Add NH_4OH dropwise while stirring until the solution turns purple. Add 10 ml 10 percent oxalic acid solution and again neutralize the solution by dropwise addition of NH_4OH. Add 1 ml NH_4OH in excess. Remove the solution from the burner, and let it stand at least 4 hr.

Note: If the CaO content of the sample exceeds 20 percent, make the second precipitation from a volume of 200 ml.

6. Filter the solution through a 9-cm #40 Whatman paper into the beaker containing the first filtrate. Wash the beaker with 0.1 percent solution of ammonium oxalate, and transfer the wash to the filter. Scrub the stirring rod with a policeman, wash the rod, and lay it aside. Scrub the inside of the beaker with a policeman, and pour the wash solution in the filter. Wash and police beaker, transferring the washings to the filter. Wash precipitate on the paper five times with the oxalate solution. Lift paper to drain the funnel stem. Reserve the filtrate for the magnesium determination.

7. Fold the paper and place it in the platinum crucible that was reserved after the silica recovery determination.

8. Wipe the inside of the funnel with a piece of damp filter paper, and place the paper in the crucible. Partly cover the crucible, and starting the furnace cold, burn off the paper at a low temperature (450°C). Leave the door of the furnace slightly cracked open. Heat the crucible at 1,000°C for 30 min

while crucible is covered tightly and the furnace door is shut. Cool for 30 min in desiccator and weigh rapidly. Reheat at 1,000°C for 15 min; cool for 30 min, and weigh rapidly. Continue the heating until constant weight is obtained.

Note: The ignited CaO precipitate will absorb H_2O and CO_2 and thus introduce a positive error (as large as 0.1 percent) if weighing is not rapid.

9. Discard the precipitate. Wash and dry crucible (rinse crucible with (1+1) HCl and heat if necessary). Ignite crucible at 800°C in furnace until constant weight, and reserve for the determination of MgO.

Calculation: wt. CaO x 100 = percent CaO

Gravimetric Determination of Magnesium Oxide

Procedure (Peck, 1964, p. 68-69): 1. To the combined filtrates from the calcium determination, add 25 ml of 20 percent dibasic ammonium phosphate. Add 40 ml of ammonium hydroxide, stir, and let the solution stand overnight. Stir occasionally the next day, and let the solution stand an additional night. If no precipitate forms after the first night, let the solution stand two additional nights, and during the intervening days, stir the solution occasionally and scratch the bottom of the beaker.

2. Filter the solution through an 11-cm Whatman #42 filter paper. Wash the inside of the beaker with 5 percent ammonium hydroxide, and pour the wash into the filter. Wash the paper three times with the same solution; then fold

back the paper to drain the funnel stem. Discard the filtrate and place a clean 150-ml beaker under the funnel.

3. This author washes the inside of the precipitation beaker with 20 percent HCl, and stirs to bring the precipitate into solution. Warm the covered beaker on a steam bath or hotplate. Add more acid if the precipitate does not dissolve completely. Pour the solution through the filter, wash the inside of the beaker three more times with 20 percent HCl, and transfer washes to the filter. Dissolve any precipitate remaining on the paper with small amounts of acid from the wash bottle. Finally, wash the paper five times with 20 percent HCl and five times with 5 percent HCl. Discard the paper.

4. Dilute the solution in the 150-ml beaker to 90 ml. Add 1 ml (1+19) phosphoric acid and two drops of brom cresol purple. Add NH_4OH by drops until a permanent precipitate forms or until the solution turns purple, whichever takes place first. Let the solution stand for about a minute; add one drop of NH_4OH, and stir. Continue in this manner until 10 drops of NH_4OH have been added. Add 10 ml of NH_4OH. Stir the solution and let it stand overnight.

Note: If the MgO > 20 percent, make the second precipitation from a volume of 200 ml.

Note: Failure to get a precipitate of the proper composition is the most serious source of error. Upon ignition, the following salts will decompose (Rieman and others, 1951, p. 338):

1. No error: $2MgNH_4PO_4$ --------> $Mg_2P_2O_7+2NH_3+H_2O$

2. Proper composition but low end value due to solubility of $MgHPO_4$: $2MgHPO_4$ -----> $Mg_2P_2O_7+H_2O$

3. Negative error: $Mg_3(PO_4)_2$ -----> $Mg_3(PO_4)_2$

4. Negative error: $Mg(OH)_2$ -----> $MgO+H_2O$

5. Positive error: $2Mg(NH_4)_4\ (PO_4)_2$ -----> $2Mg(PO_3)+8NH_3+4H_2O$

a. Because magnesium pyrophosphate ($Mg_2P_2O_7$) is the only suitable form for the gravimetric determination of magnesium, any of the above-listed salts except $MgNH_4PO_4$ will cause an error.

b. Because of the complicated equilibria, pure magnesium ammonium phosphate cannot be obtained on the first precipitation. As the conditions of the second precipitation can be adequately controlled, the second precipitate should be pure.

c. Precipitation of compounds other than magnesium ammonium phosphate may result if precipitation is not begun from an acid solution that is slowly made alkaline.

d. Some precipitate may be lost if too much washing is performed or if NH_3 is not present in the wash solution.

5. Filter the solution through a 9-cm Whatman #42 paper. Wash the inside of the beaker once with 5 percent NH_4OH, and transfer the wash to the filter. Wash the stirring rod with NH_4OH solution and use a policeman. Police the inside of the beaker. Transfer wash to the filter and wash loose precipitate into the paper. Wash and police until precipitate is completely transferred. Wash the precipitate on the paper three times with 5 percent NH_4OH. Drain funnel stem and discard the filtrate.

6. Add 0.5 g ammonium nitrate to the crucible reserved after the CaO determination. Fold the paper and place it in the crucible. Wipe the funnel with a piece of damp filter paper, and place it in the crucible.

7. Place the crucible, with the cover drawn back slightly, in a cold electric muffle furnace; allow the temperature to rise to about 450°C, and maintain this temperature until all the carbon is burned off and the residue is grayish-white. Do not allow the crucible to become even a dull red before this stage is reached, and at no time allow the contents of the crucible to catch fire.

Note: Slow charring and careful ignition below 900°C prevent reduction (loss of P). Under careful ignition, a gray precipitate, which introduces only a negligible error, is usually obtained. P will be lost by volatilization of P_2O_5 if the precipitate is ignited above 1,100°C.

8. Heat the covered crucible and contents at approximately 1,100°C for 30 min; cool in a desiccator for 30 min and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$. Repeat until constant weight is obtained.

Calculation: wt. $Mg_2P_2O_7$ x 36.23 = percent MgO

Conversion factors:

$$\underset{MgO}{1.6579} \overset{0.6032}{\rightleftharpoons} Mg$$

$$\underset{MgO}{0.3623} \overset{2.7604}{\rightleftharpoons} Mg_2P_2O_7$$

Colorimetric Determination of Titanium Dioxide

Reagents and Standards

1. 6 percent H_2O_2 - Dilute 10 ml of 30 percent H_2O_2 to 50 ml and transfer the solution to a polyethylene bottle having a tight sealing cap. Make a fresh solution each month (Peck, 1964, p. 84).

2. 20 percent potassium pyrosulfate - Dissolve 400 g of potassium pyrosulfate in 1,800 ml H_2O. Let solution stand overnight. Filter through Whatman #42 filter paper and dilute to 2 liters.

3. Stock titanium solution (1 ml = 1 mg TiO_2) - Transfer 1.013 g of NBS (U.S. National Bureau of Standards) TiO_2 #154, dried at 105°C to a 250-ml Erlenmeyer flask. Add 10 g ammonium sulfate and 25 ml concentrated H_2SO_4. Place a short-stemmed glass funnel in the neck of the flask. Put flask on hotplate, and stir using magnetic stirrer until dissolved (near boiling). The

acid should become translucent. When the solution is cool, transfer it to a 1-liter beaker containing 500-ml water. Let solution stand overnight; then filter it thorough a Whatman #42 filter paper into a 1-liter volume flask. Wash the beaker and paper with 5 percent H_2SO_4. Dilute to mark and mix well.

Alternate dissolution: Transfer 1.013 g #154 NBS TiO_2, and 10 g potassium pyrosulfate to Vycor crucible, cover, and fuse. Quantitatively transfer fused cake to 600-ml beaker containing 200 ml 10 percent H_2SO_4. Heat to near boiling; stir using magnetic stirrer until contents are dissolved.

Working standards:

1. $$\frac{2 \text{ ml of } 1{,}000 \frac{\mu g}{ml}}{100 \text{ ml}} = 0.2 \text{ percent } TiO_2 \text{ per } 100 \text{ ml}$$

2. $$\frac{5 \text{ ml} \times 1{,}000 \frac{\mu g}{ml}}{100 \text{ ml}} = 0.5 \text{ percent per } 100 \text{ ml}$$

3. $$\frac{10 \text{ ml} \times 1{,}000 \frac{\mu g}{ml}}{100 \text{ ml}} = 1.0 \text{ percent per } 100 \text{ ml}$$

4. $$\frac{12 \text{ ml} \times 1{,}000 \frac{\mu g}{ml}}{100 \text{ ml}} = 1.2 \text{ percent per } 100 \text{ ml}$$

To each flask, add 1) 40 ml 20 percent potassium pyrosulfate solution and 2) 10 ml (1+1) H_2SO_4. Dilute each solution to volume and mix. Make a standard blank containing 40 ml of 20 percent potassium pyrosulfate and 10 ml (1+1) H_2SO_4 in a 100-ml volumetric flask. Fill to volume with distilled H_2O and mix. Use this reagent blank to zero spectrophotometer.

Procedure

1. Use the standard blank as reference solution. First read the unperoxidized sample at 410 nm in a 1-cm cell. Then add 0.2 ml of 6 percent H_2O_2 to the 1-cm cell containing the sample solution. Mix with thin stirring rod, wash off rod in beaker containing the sample solution and rinses. Save all rinses and sample solution for the total Fe determination.

2. The peroxidized standards are read and discarded.

3. Determine absorbance reading of the peroxidized solution.

4. Subtract from this value the absorbance reading for the unperoxidized solution (see note b below).

Example: Absorbance reading peroxidized solution = 1.072

Absorbance reading unperoxidized solution = 0.133

TiO_2 absorbance = 0.939

Average absorbance factor from standards:

$$\frac{\text{(average percentage of } TiO_2\text{)}}{\text{Average Abs.}} = 1.165$$

Therefore: .939 x 1.165 = 1.09 percent TiO_2

Note (Sandell, 1959): a. The yellow anionic complex that titanium forms with H_2O_2 is thought to be $TiO_2\ (SO_4)_2{+2}$ or possibly $Ti(H_2O_2)^{+4}$. b. The intensity of the colored solution increases as temperature increases (the increase is due largely to the change in intensity of the ferric sulfate, rather than to a change in intensity of the titanium complex), and all measurements should be made at the same temperature. c. For the color to reach full intensity, the solution must contain at least 5 percent H_2SO_4, but larger amounts do no harm.

Titrimetric Determination of Total Iron Oxide by use of a Silver Reductor

Procedure (Peck, 1964, p. 72)

1. Stir 15 ml of ammonium hydroxide into the solution that was reserved in a 250-ml beaker after the determination of titanium. Cover the beaker with a raised watch glass and evaporate on the steam bath to a volume of 75 ml. Cool the solution; add two drops of 5 percent potassium dichromate, and

stir. If the solution does not become distinctly more yellow, evaporate it further and retest from time to time by the addition of potassium dichromate. When the dichromate color persists, add 25 ml of 15 percent chloride and adjust volume to 100 ml.

Note: a. Chloride ions must be present in order to precipitate silver ions as they form; otherwise, ferric ion reduction is incomplete.

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

c. H_2O_2, if not previously removed, passes through the reductor and reoxidizes ferrous iron in the effluent. The solution is, therefore, heated and tested with $K_2Cr_2O_7$.

d. To reactivate the reductor: 100 ml H_2O + 100 ml (1+1) NH_4OH dissolves the silver oxide. Stir the column with a long glass rod. Wash column with 200 ml H_2O. Test with ph paper to make certain the column is washed free of NH_4OH. Wash column with 5 percent HCl.

2. Drain the reductor until the level of the liquid is about 1/8 inch above the silver. Add 40 ml (1 to 1) phosphoric acid and 10 ml (1+1) H_2SO_4 to a clean 600-ml beaker, and lower the reductor into the beaker until the delivery tube dips into the acid. Transfer about half the iron solution to

the reservoir. Fully open the stopcock on the reductor, and as the solution drains, transfer the remainder of the iron solution to the reservoir. Let the solution drain until its level is about 1/8 inch above the silver. Lift the reductor as the volume of the effluent increases, but keep the tip of the delivery tube below the level of the liquid.

3. Wash the inside of the reservoir with a small amount of 5 percent HCl and allow the solution to drain until its level is a little above the silver. Repeat 5 times. Add more 5 percent HCl and continue draining until the volume of the solution in the beaker is almost 300 ml. Close the stopcock, and lift the delivery tube clear of the liquid. Wash the tip of the delivery tube with water; then continue draining the reductor until the volume of the effluent is 300 ml.

4. Add 4 drops of 0.2 percent sodium diphenylamine sulfonate and titrate with 0.06262 N potassium dichromate using magnetic stirrer (a distinct purple color should last 30 sec).

Calculations:

A. Percent total iron (as Fe_2O_3) =

$$\frac{\text{ml titrant} \times N}{1{,}000} \times \frac{159.68}{2} \times \frac{100}{\text{Sample Wt. (g)}} =$$

(1 g sample) $\frac{\text{ml} \times 0.1 \text{ (normality)} \times 79.84}{10}$ or ml X .7984

if using 0.06262 N $K_2C_2O_7$ and 1 g sample: $\frac{\text{ml } K_2Cr_2O_7}{2}$ = percent Fe_2O_3 (total Fe)

B. Percent Fe_2O_3 = percent total Fe (as Fe_2O_3) - (percent FeO x 1.1113)

Errors (Rieman and others, 1951, p. 185, 205-206, 322):

1. Diphenylamine sulfonic acid indicator, like other diphenylamine indicators, is not very stable in the presence of excess oxidant, and care must be taken not to allow this indicator to remain in contact with the oxidant for too long a period. Diphenylamine indicators are especially unstable in the titration of the dichromate with ferrous ion.

2. More than 0.3 ml of diphenylamine sulfonic acid indicator causes an appreciable titration error.

3. Upon reduction, the dichromate yields chromic (III) ion whose green color tends to obscure the color change of indicators. Error is usually negligible. Hence color change at the end point proceeds from blue-green to a grayish tinge to a purple. The titration should be conducted dropwise when the gray tinge is noted, because the oxidation of the indicator is somewhat slow.

Titrimetric Determination of Ferrous Iron

Procedure (Maxwell, 1968, p. 417): 1. Weigh 0.5000 g sample and transfer it quantitatively to a 100-ml platinum crucible having a tightly fitting cover.

2. Add 1 ml H_2O and swirl to distribute sample over the bottom to prevent caking; add two or three drops of (1+1) H_2SO_4 to decompose any carbonate compounds present; cover and allow to stand until all reaction has ceased.

3. To 10 ml H_2O in a 50-ml Teflon beaker, add 5 ml H_2SO_4 (concentrated) and 5 ml HF. Place the covered crucible with sample on a silica triangle suspended firmly over a Bunsen burner having a low flame. Slide the cover to one side, quickly add the hot acid mixture from the Teflon beaker, replace the cover and immediately begin brushing the sides and cover of the crucible with the flame of a second burner until the contents are boiling and steam escapes.

4. Adjust the height of the flame of the first burner so that the contents of the crucible boil gently and continue heating for 10 min. The heating should not be prolonged (use a timer), nor should the temperature be high enough to evaporate the water to the point that the hot concentrated H_2SO_4 oxidizes the ferrous iron.

5. To 200 ml H_2O in a 600-ml beaker, add 50 ml 5 percent boric acid, 5 ml concentrated H_2SO_4 , and 10 ml 85 percent H_3PO_4, and mix well.

6. At the conclusion of the heating period, submerge the crucible below the surface of the acid solution in the 600-ml beaker. Never allow more than the platinum of the tongs to touch the acid solution. Immediately dislodge the cover from the crucible with a stirring rod and stir to mix the contents of the crucible and beaker. Make sure that all soluble material has dissolved. Remove and rinse the crucible and cover.

7. Add four drops 0.2 percent sodium diphenylamine sulfonate to the beaker and titrate with $K_2Cr_2O_7$.

Calculation: If N of $K_2Cr_2O_7$ is 0.06262, then ml $K_2Cr_2O_7$ x 0.9 = percent FeO. If N of $K_2Cr_2O_7$ is 0.1000, then ml $K_2Cr_2O_7$ x 1.437 = percent FeO. These conversion factors were calculated from:

$$\text{percent FeO} = \frac{\text{ml titrant X N}}{1{,}000} \times \frac{71.85}{1} \times \frac{100}{\text{sample weight} = 0.5\text{ g}}$$

Colorimetric Determination of MnO and P_2O_5

Decomposition of Sample (Maxwell, 1968, p. 384-385)

Because the acids HNO_3 and HF used in the decomposition of samples contain P, a blank must be run with the samples during decomposition. Samples, blank, and standards are read against distilled water as the reference solution in the colorimetric determination of P_2O_5 and MnO.

1. Transfer 1 g sample to a 100-ml platinum dish or Teflon beaker, moisten with a squirt of water, and swirl beaker to get all particles in contact with the water. Add 10 ml concentrated HNO_3; when any effervescence has ceased, add 10 ml HF (concentration = 48 percent). Cover and digest on steam bath for 1 hr. Evaporate on hotplate to near drying. Cool, add 5 ml HNO_3, add 5 ml HF, and mix. Evaporate to dryness on the hotplate.

2. Cool, add 20 ml (1+1) HNO_3, and again evaporate to dryness. Heat contents of the dish 30 min after the salts appear to be dry.

3. Cool, add 20 ml (1+1) HNO_3 and 10 ml 5 percent boric acid (saturated). The boric acid protects glassware from attack by residual HF.

4. Cover and digest contents in a boiling water bath or on a hotplate overnight. Digestion and solution should be complete. If a brown precipitate is observed (MnO_2), add a few grains of sodium sulfite and stir; the MnO_2 will be reduced, and the manganese will go into solution.

5. Filter through a 7-cm Whatman #40 filter paper into a 100-ml volumetric flask, and police dish with water containing a few drops of HNO_3.

6. Wash dish and paper several times with this solution.

Note: Chromite is one of the minerals that is not dissolved by the HF-HNO_3 mixture and is thus filtered off. If not filtered, chromium interferes with the colorimetric determination of Mn.

7. Dilute to 100 ml volume and mix.

Determination of MnO (Maxwell, 1968, p. 388)

1. Pipet a 25-ml aliquot of sample to a 50-ml volumetric flask.

2. For each 50 ml of final volume, add 10 ml concentrated HNO_3 and 5 ml of 1 percent potassium periodate solution. Wash down inside of the flask with

water, swirl to mix, and immerse the flask in a boiling water bath for 2 hr or until color development is complete.

3. Cool, and add 2.5 ml of dilute (1+1) H_3PO_4 for each 50 ml volume. Dilute to mark, mix, and measure the absorbance of the complex at 525 nm in a 1-cm cell using distilled H_2O as a reference blank.

Standards (MnO)

0.1 mg:

$$X \frac{\text{ml}}{\text{diluted to 50 ml}} \quad \frac{3 \text{ ml}}{} = 0.0006 \text{ percent MnO}$$

$$X \frac{4}{50} = 0.0008 \text{ percent MnO}$$

$$X \frac{5}{50} = 0.001 \text{ percent MnO}$$

$$X \frac{10}{50} = 0.002 \text{ percent MnO}$$

Add 10 ml concentrated HNO_3, 5 ml 1 percent potassium periodate, and put in boiling water bath for 2 hr or until color development is complete. Cool, add 2.5 ml (1+1) H_3PO_4. Read at 525 nm on spectrophotometer.

Note: (Peck, 1964, p. 45-47): a. A high nitric acid concentration assures complete solution of titanium phosphate and gives the correct acidity for the determination of both manganese and phosphorus in portions of the filtrate.

b. Manganese is oxidized to permanganate by boiling it in a 20 percent nitric acid solution containing potassium periodate. The oxidized solution is very stable.

c. Iron is decolorized by the addition of phosphoric acid and does not interfere with the coloimetric determination of manganese.

Calculation: Because the concentration of MnO is 0.005 g/ml $\left(\frac{1.00\ g}{100\ ml} \times \frac{25\ ml}{50\ ml} = \frac{0.005\ g}{ml}\right)$, the sample dilution factor is 200.

The average absorbance factor is written: $\frac{\text{average percent MnO}}{\text{average Abs.}}$.

Therefore, percent MnO = $\frac{\text{average percent MnO}}{\text{average Abs.}}$ x sample absorbance x 200

Determination of P_2O_5 (Peck, 1964, p. 78)

Procedure: 1. Pipet a 25-ml aliquot from the 100-ml volumetric flask (used for the determination of MnO and P_2O_5) into a 100-ml beaker.

2. Heat for 15 min on the steam bath.

Note: Ammonium phosphomolybdate precipitated from a hot solution insures complete precipitation especially when the solution will be heated for an additional 15 min (see step 3 below).

3. Add 25 ml 2.5 percent ammonium molybdate and 20 percent ammonium nitrate solution. Stir the solution frequently while heating for an additional 15 min. Let the solution stand at room temperature overnight.

4. Prewash a 7-cm Whatman #42 filter paper three times with 5 percent NH_4OH and once with 2 percent ammonium nitrate in 1 percent HNO_3.

Note: The paper may contain enough extractable coloring matter to cause an error of 0.005 percent and, therefore, must be prewashed.

5. Decant the solution through the filter into a 150-ml beaker. Wash down the inside of the beaker twice with the wash solution of ammonium nitrate in 1 percent nitric acid, and transfer the washings to the filter; then wash the paper five times with the same solution. Drain the funnel stem and discard the filtrate.

6. Place a 100-ml volumetric flask under the funnel. Wash down the inside of the beaker with 5 percent NH_4OH and stir until precipitate dissolves. Transfer this solution to the filter; then wash the inside of the beaker three times with 5 percent NH_4OH, and transfer the washes to the filter. Dissolve any yellow precipitate left on the paper with small portions of NH_4OH; then completely wash the paper five times and discard it. The final volume of the NH_4OH should not exceed 25 ml.

Note: Before its determination, phosphorus is separated from diverse ions by precipitating it as ammonium phosphomolybdate. If separation is not done 1) colored ions (iron, chromium) interfere with the absorbance;

2) fluorine decreases the intensity of the color by forming a complex with molybdenum, and 3) silica forms a colored complex with the reagent.

7. Add 5 ml concentrated HNO_3. Nitric acid must be added before ammonium molybdate or ammonium vanadate. Add by pipet 10 ml ammonium vanadate solution and 20 ml 5 percent ammonium molybdate in that order. Mix, dilute to volume (100 ml), and mix. Allow to stand for 30 min. Measure at 460 nm in a 1-cm cell against distilled water. Read the vanadium molybdiphosphate complex (Maxwell, 1968, p. 392).

Standards:

$$1.00 \frac{\text{mg } P_2O_5}{\text{ml}} \times \frac{0.5 \text{ ml}}{100 \text{ ml}} = 0.0005 \text{ percent } P_2O_5$$

$$1.00 \frac{\text{mg } P_2O_5}{\text{ml}} \times \frac{1.00 \text{ ml}}{100 \text{ ml}} = 0.001 \text{ percent } P_2O_5$$

$$1.00 \frac{\text{mg } P_2O_5}{\text{ml}} \times \frac{2.00 \text{ ml}}{100 \text{ ml}} = 0.002 \text{ percent } P_2O_5$$

$$1.00 \frac{\text{mg } P_2O_5}{\text{ml}} \times \frac{4.00 \text{ ml}}{100 \text{ ml}} = 0.004 \text{ percent } P_2O_5$$

1. Add 5 ml concentrated HNO_3 to each sample and standard.

2. Dilute to 50 ml with H_2O.

3. Pipet 10 ml ammonium vanadate.

4. Pipet 20 ml ammonium molybdate (5 percent).

5. Make up a reagent blank with above concentration of reagents in a 100-ml volumetric flask.

6. Dilute to 100 ml.

7. Mix, allow to stand 30 min.

8. Measure at 460 nm in a 1-cm cell against distilled water.

Calculation: Because the concentration of P_2O_5 is 0.0025 g/ml $\left(\frac{1.00\ g}{100\ ml} \times \frac{25\ ml}{100\ ml} = 0.0025\ g/ml\right)$, the sample dilution factor is 400.

Therefore, percent $P_2O_5 = \frac{\text{average percent } P_2O_5}{\text{average Abs.}} \times \text{sample absorbance} \times 400.$

Determination of Sodium and Potassium by use of an

IL 443 Flame Photometer

Decomposition

1. Weigh 0.2500 g of sample and transfer to a 100-ml Teflon beaker. Squirt with distilled H_2O to just wet sample. Add 10 ml HF and 5 ml $HClO_4$.

2. Digest overnight (covered) in a boiling water bath.

3. Remove cover and evaporate to a concentrated acid. Evaporate until the solution fumes. Fume strongly for 10 min.

4. Cool, dilute with H_2O, transfer to a 250-ml volumetric flask. Pipet 25 ml of 2,000 ppm Li_2O and fill to 250-ml mark.

5. A blank containing reagents and no sample should be run along with samples.

Note: This solution cannot be used with original equipment of the IL 443, specifically, the plastic atomizer assembly, because the 2 percent $HClO_4$ attacks the plastic well. Accessory assembly must be ordered.

Recrystallization of NaCl and KCl

1. Prepare a saturated solution of the salts.

2. Filter through Whatman #40 filter paper.

3. Reprecipitate with concentrated HCl.

4. Filter through (coarse or medium) sintered funnel (Buchner flask).

5. Dry overnight at 110°C.

6. Pulverize by using mortar and pestle.

7. Transfer to Vycor crucible and heat in muffle furnace at 600°C to drive off all imbibed water (3 hr).

Standards (Stock Solutions)

Na_2O (1,000 ppm = 1.0 mg/ml): In a 1-liter volumetric flask, dissolve 1.8860 g NaCl dried at 105°C. Store in tightly capped polyethylene bottle.

K_2O (1,000 ppm = 1.0 mg/ml): In a 1-liter volumetric flask, dissolve 1.5830 g KCl dried at 105°C. Store in tightly capped polyethylene bottle.

Li_2O (20,000 ppm = 20.0 mg/ml): In a 1-liter volumetric flask, dissolve 56.76 g LiCl to obtain a stock solution containing 20,000 ppm Li_2O. Store in tightly capped 2-liter polyethylene bottle.

Working Li_2O internal standard

$$20{,}000 \frac{\mu g\ Li_2O}{ml} \times \frac{200\ ml}{2{,}000\ ml} = 2{,}000\ ppm\ Li_2O$$

If 200 ppm Li_2O is needed in each of the standard, blank, and sample flasks, pipet 25 ml of 2,000 ppm standard into the 250-ml flasks.

Working Standards

Working standards should be diluted to 250 ml and stored in plastic containers. From 1,000 ppm stock solution:

ml (Na_2O and K_2O)	Concentration in ppm	Percent (equivalent to sample percent) 0.25 g diluted to 250 ml
1.0	4	0.4 (calibrates the IL 443)
2.0	8	0.8
4.0	16	1.6
6.0	24	2.4
8.0	32	3.2
10.0	40	4.0
12.0	48	4.8
0.0	0	Blank used to zero the IL 443

To the working standards, add 25 ml of 2,000 ppm Li_2O and 5 ml $HClO_4$. Fill the flask to 250-ml mark with distilled H_2O.

Calibration by Interpolation (Maxwell, 1968, p. 407)

x = concentration of alkali metal (M_2O) in sample

y = scale reading for sample

x_1 = concentration of M_2O in low standard

y_1 = scale reading for low standard

x_2 = concentration of M_2O in high standard

y_2 = scale reading for high standard

$$x = \left[\left(\frac{X_2 - X_1}{Y_2 - Y_1}\right) \times (Y - Y_1)\right] + X_1$$

Calculation: In general, percent M_2O = $\frac{X}{10^6}$ X volume X $\frac{100}{\text{sample wt.}}$

For a 0.25-g sample diluted to 250 ml:

$$\text{percent } M_2O = X \frac{\text{ug}}{\text{ml}} \times \frac{1}{10^6} \times 250 \text{ ml} \times \frac{100}{0.25 \text{ g}} = \frac{X}{10}$$

Note: The most accurate results are obtained by interpolation calculations.

Determination of Total H_2O by the Penfield Method

Procedure (Hillebrand and others, 1953, p. 827-828): 1. Add 1.0000 g sample and 2 g sodium tungstate flux to Penfield tube through an elongated stem, open bulb-top funnel. Mix sample and flux by twirling closed bulb end of Penfield tube. Run a blank with flux only. Add capillary plug to open end of tube. Put tube through ice-bath apparatus (figs. 2,3).

2. Decompose sample (mixed with the flux) by heating with Meker burner for 10 min and decompose blanks by heating for 5 min. Decompose samples and blanks slowly at first so that volatile elements will not escape with H_2O. Keep rotating tube to prevent caking on one side of the bulb.

3. Use an oxypropropane torch to heat just below bulb area of Penfield tube to sever the bulb containing decomposed sample from the tube. Allow to cool at least 1 min. Remove from ice-bath apparatus. Remove capillary plug.

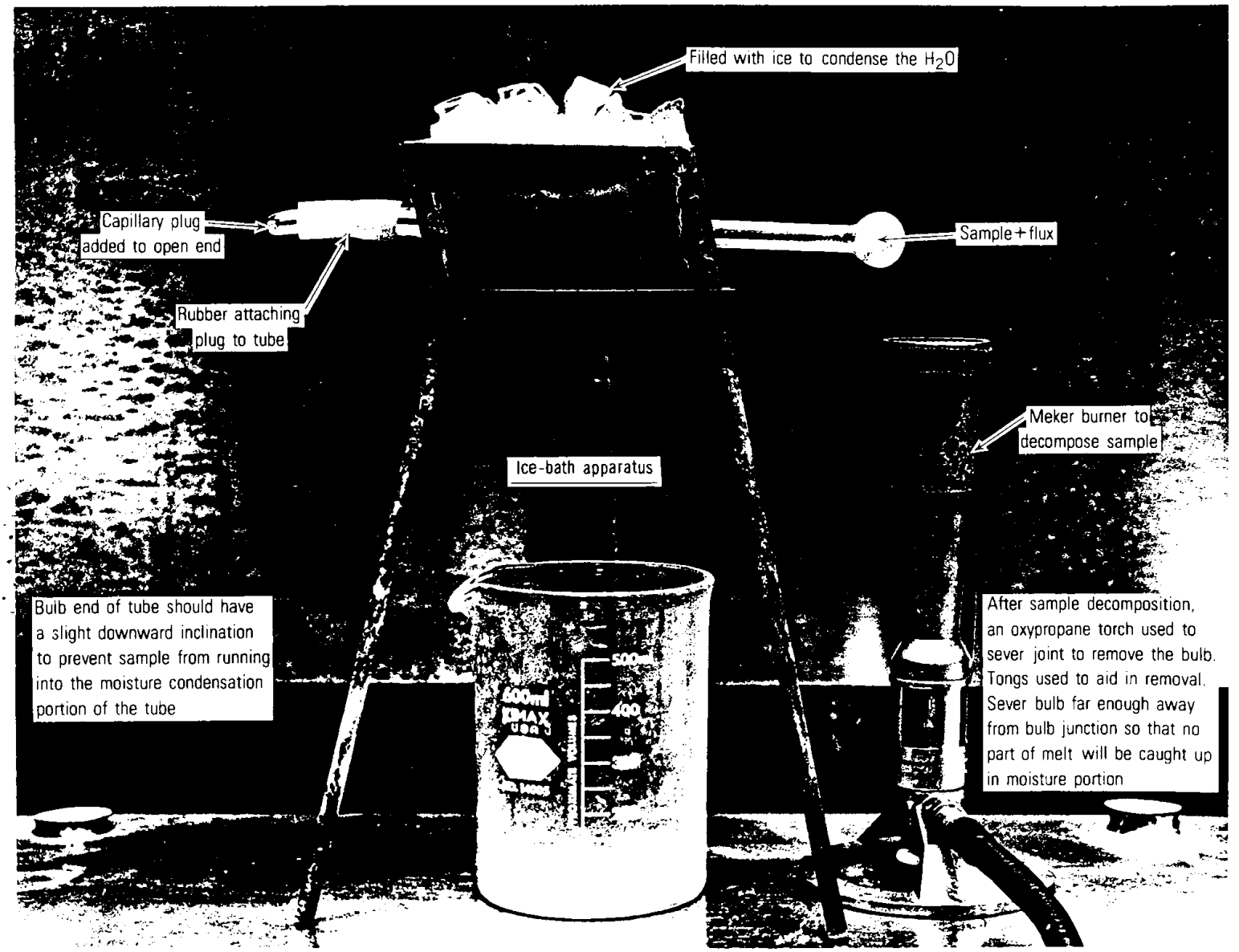
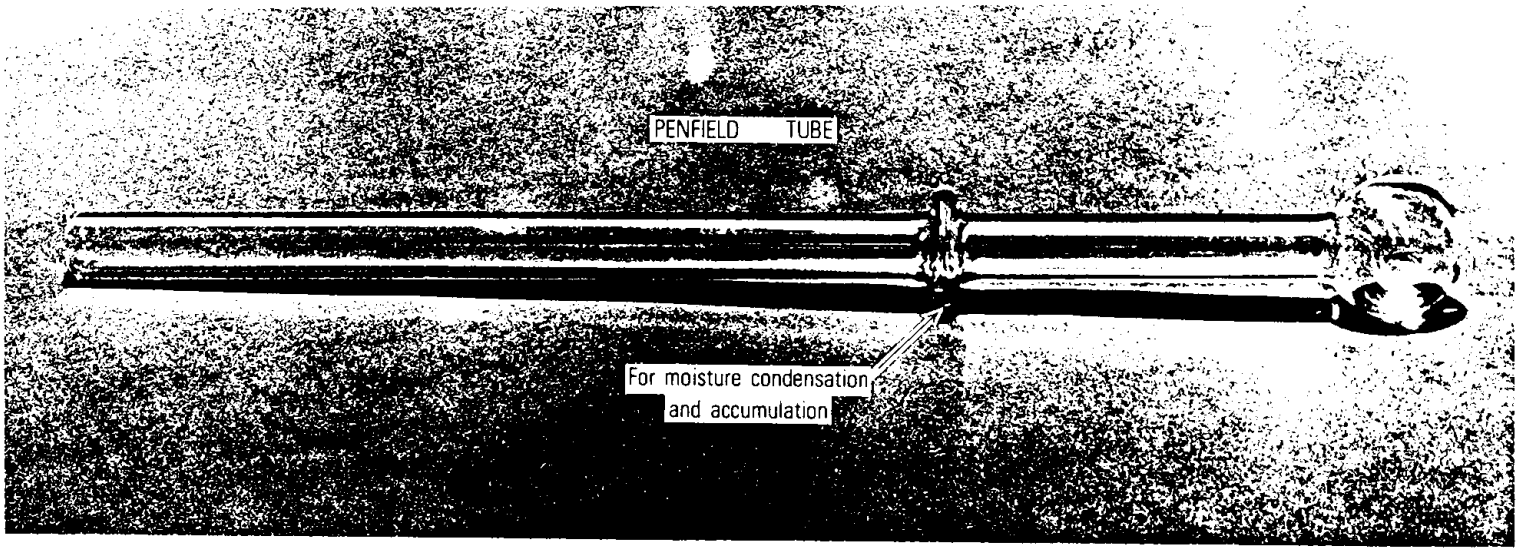


Figure 2. Apparatus for the Penfield method of determining total H_2O.



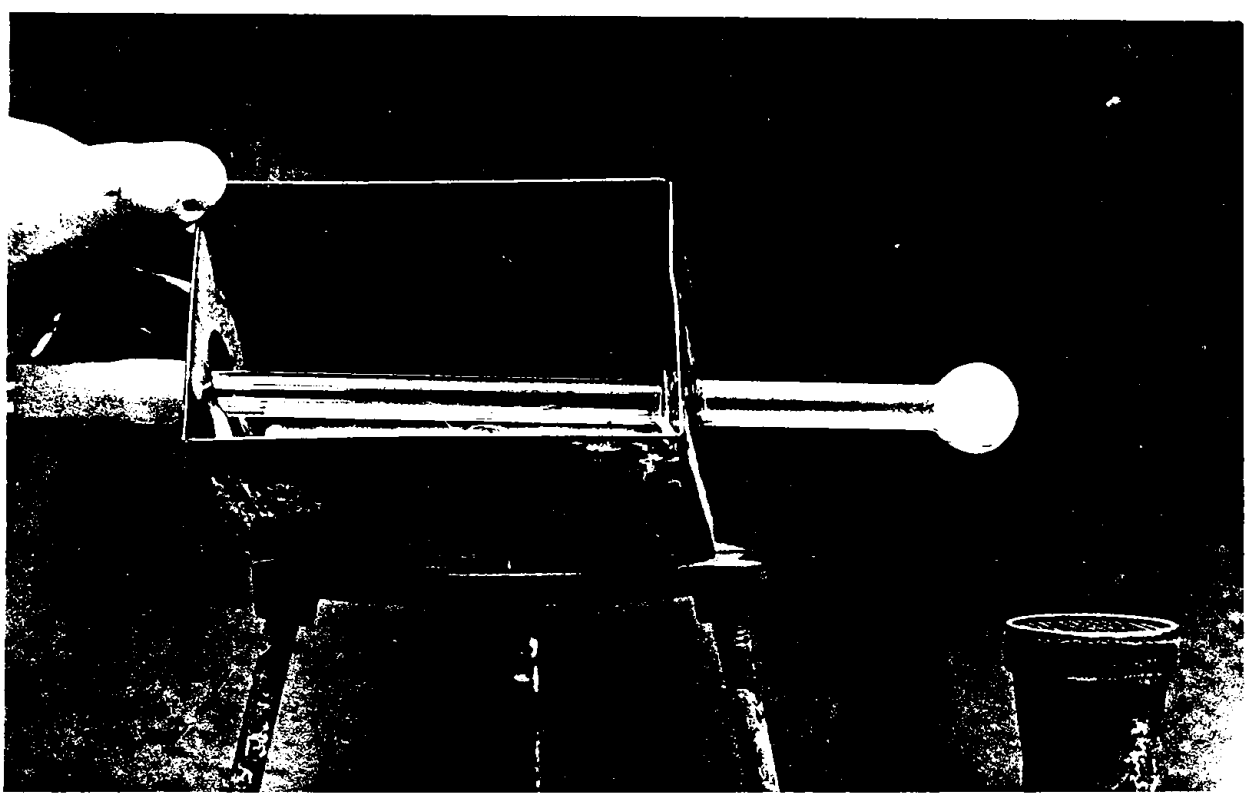


Figure 3. Penfield tube.

4. Add cork stoppers to open end of tube to prevent moisture escaping. Put tube in balance room and keep next to balance at least 20 min (20-30 min) so that the tubes come to equilibrium. Before weighing tube, remove cork so that the weight of the tube plus moisture is obtained.

5. Heat uncorked tube at 110°C in an oven a minimum of 2 hr to evaporate off the water.

6. Put tube in desiccator for 30 min and weigh to obtain the weight of the tube minus moisture.

Calculation: Subtract the blank. The difference in weight is the weight of moisture in 1 g sample x 100 = percent total H_2O.

percent total H_2O - percent H_2O^- = percent H_2O^+

Gravimetric determination of CO_2 by Acid Evolution

Principle of method: Air carries the CO_2 liberated by addition of acid through a series of absorbents* that remove interfering substances and finally into the weighed absorbers that remove CO_2.

Note: The water is heated before the addition of the acid because if all the acid is added to the cold solution, the violent evolution of CO_2 when the solution is heated may cause the solution to back up into the U-tube containing solid reagents.

*Absorbents:

1. H_2O condenser - removes H_2O and HCl.
2. Ascarite (sodium hydrate asbestos absorbent) - catches CO_2.
3. Magnesium perchlorate (anhydrome) - removes H_2O.
4. Anhydrous copper sulfate in pumice - removes traces of HCl and H_2S.
5. H_2SO_4 - removes H_2O.

Operating CO_2 apparatus (Peck, 1964, p. 79-80):

1. Replace "weighed absorbers" with bridge.

2. Open all valves except condenser valve and vacuum valve.

3. Start H_2O running through condenser.

4. With aid of powder funnel, add 5.000 g of a silicate sample (or 1 g of a carbonate sample) to the generating flask. Wash powder adhering to the funnel into the flask, and adjust the volume of water in the flask to 25 ml.

5. Open vacuum valve slowly to start a stream of air through the system (fig. 4). Observe the rate of flow at the H_2SO_4 bubbler. Swirl flask to make a slurry of the powder. Put flask in place on apparatus. Continue drawing air through the system for 10 min at the rate of three bubbles/second.

6. During the 10-min period, weigh CO_2-absorption tube. Open stopcock of each tube momentarily before placing it on the balance pan.

7. Close vacuum valve and valves adjacent to the bridge and replace the bridge with the CO_2 absorber. Open all valves and adjust vacuum valve so that a stream of air flows rapidly through the system.

8. Test for leaks in the system: Close the first (air) valve; wait a few seconds, and close vacuum valve. Check for leaks indicated by bubbles or H_2SO_4 rising in tube. If no leak, open air valve (first valve) to release the vacuum.

9. Add 25 ml (1+1) HCl to the acid reservoir. Start a moderate flow of air through the system by opening vacuum valve.

10. Heat the water in the generating flask almost to boiling. (On Variac, set to 100 to heat; reduce to 75 to continue heating). Slow the rate of air flow and add acid (few drops at first) in small portions. Leave a little acid in the reservoir so that air will not be admitted through it.

11. Increase the air flow, and bring the solution in the flask to a gentle boil. Continue boiling gently for 2 min. Slow down the flow of air to about three bubbles/second, and continue drawing air through the system at this rate for 20 min.

12. Close vacuum valve and valves adjacent to CO_2-absorption tube (containing CO_2 sample) and immedicately open generator valve to relieve pressure; close absorbent-tube valve. Remove absorption tube (CO_2 weighing tube in fig. 4) from system and put in balance room.

13. After 1 hr, weigh. Open the valve of tube momentarily before placing on balance pan.

14. Clean generator flask using H_2O, wash solution (5 percent NH_4OH), and indicator to make sure all the acid is rinsed out.

15. Calculation: wt. absorption tube after acid evolution minus wt. of absorption tube before acid evolution ÷ sample wt. x 100 = percent CO_2.

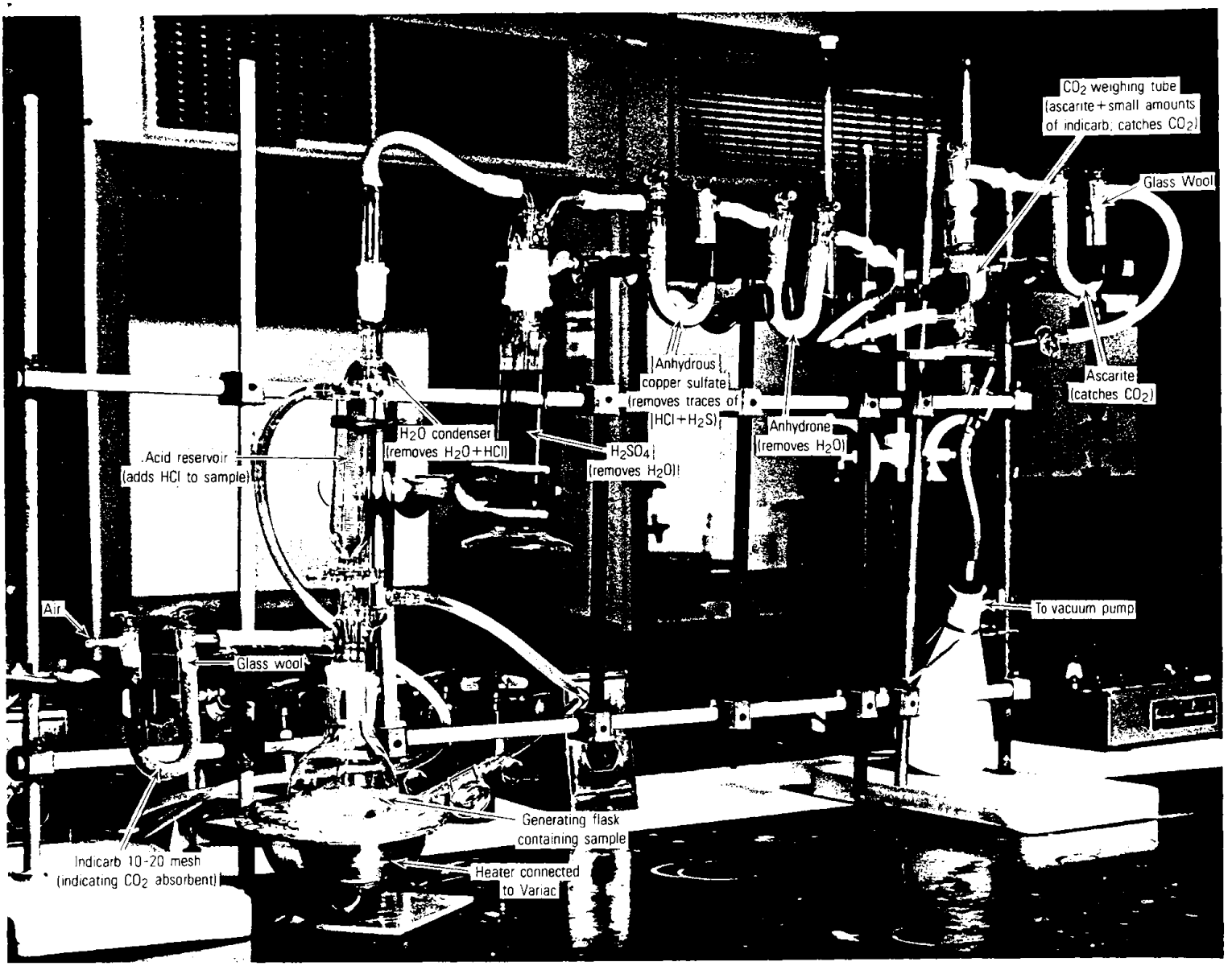


Figure 4. Apparatus for gravimetric determination of CO_2 by acid evolution.

Determination of Total Sulfur

The sulfur content of most silicate rocks is very low (0.1 percent), and the sulfur is usually in the form of a sulfide such as pyrite (FeS_2) or pyrrhotite (Fe_7S_8).

Procedure (Peck, 1964, p. 82): 1. Transfer a 1.000-g sample to a 25-ml platinum crucible.

2. Add 0.2 g KNO_3 and 5 g Na_2CO_3 in two 2-g portions to the crucible, and mix the powder and flux each time. Rinse the stirring rod in the remaining 1 g and spread the Na_2CO_3 over the top of the mixture.

Notes: a. Usually, 0.2 g KNO_3 is sufficient to oxidize the sulfides to sulfates, but if samples contain a large amount of sulfides, 0.2 g may not be sufficient, and the KNO_3 may have to be increased. If FeS_2 is greater than 2 percent, use another method to determine for total sulfur (see Hillebrand and others, 1953, p. 712-714).

b. When sulfide is present only as a sulfide, the sample must be fused with an oxidizing flux such as a mixture of Na_2CO_3 and KNO_3. This fusing results in the oxidation of sulfide to sulfate. The fusion method removes elements such as iron and the alkaline earths, but introduces a large amount of alkali salts into solution.

3. Fuse at 1,100°C in an electric furnace for 30 min; start the furnace cold.

4. Remove samples from furnace; allow to cool; heat crucibles over Meker for 30 sec and allow to cool again.

5. Transfer the cake to a 150-ml beaker. Scrub the crucible with a policeman and transfer any loose material to the beaker with H_2O. Add a few milliliters of HCl to the platinum crucible and heat on a steam bath for 30 min. Discard the acid and wash out the crucible. Weigh crucible to constant weight.

6. Add 2 ml ethyl alcohol (reduces and precipitates any Mn dissolved as manganate) to the beaker and adjust the volume of the solution to 60 ml by adding H_2O as needed. Heat the solution on the steam bath until the sodium carbonate is extracted from the cake; break up lumps with a flat-ended stirring rod.

7. Filter through a 9-cm #589 S+S Blue filter paper into a 400-ml beaker. Wash the inside of the beaker three times with 1 percent Na_2CO_3 and transfer washes to the filter. Wash the residue on the paper five times with 1 percent Na_2CO_3 solution.

8. Dilute this filtrate to 200 ml and cautiously add 7 ml HCl dropwise while stirring constantly.

Note: The volume is brought up to 200 ml both to minimize the tendency of $BaSO_4$ to absorb other ions and to minimize the precipitation of any SiO_2 present (Maxwell, 1968, p. 236).

9. Add five drops brom phenol blue indicator, and then using dropper, add and stir in (1+1) HCl until solution becomes yellow; then add 2 ml more (1+1) HCl.

Note: The final solution should contain only a small excess of HCl (approximately 0.05N) because the solubility of $BaSO_4$ increases as acid concentration increases (Maxwell, 1968, p. 236).

10. Heat on steam bath for 30 min and pipet dropwise 5 ml of 10 percent $BaCl_2$ solution; stir the solution and heat it on the steam bath for 2 hr. Stir occasionally during this period. Let the solution stand at room temperature overnight.

Note: The precipitation should be made at the boiling point to minimize the tendency of barium sulfate to supersaturate (Maxwell, 1968, p. 237). The precipitate and solution should be digested hot before filtration and should be allowed to stand for several hours to reduce the amount of coprecipitation that will take place (Maxwell, 1968, p. 237).

11. Filter the solution through a 7-cm Whatman #42 filter paper into a clean 150-ml beaker. Discard portions of the filtrate if they are clear but refilter any portion that is turbid.

12. Transfer the precipitate to the paper with H_2O; then wash the paper 10 times with H_2O. After 10 washings with H_2O, test another wash (in a clean 20-ml beaker) with drops of 0.1M $AgNO_3$ to be sure that the filter paper is free of chlorides. Discard filtrate.

13. Burn off the paper in the weighed platinum crucible and keep the crucible below red heat (550°C).

Note: Ignition of the precipitate must be done with care. Because $BaSO_4$ is easily reduced by carbon, there must be no flame during the burning of the paper, which should be done at a low temperature (<600°C) under oxidizing conditions (crack furnace door). In the presence of either Si or Fe, the precipitate must not be heated too strongly, i.e., 1,000°C, or some decomposition will take place (Maxwell, 1968, p. 237).

14. When the paper has become completely charred, raise temperature until crucible is dull red, and burn off carbon. When residue is white, ignite at 900°C for 15 min.

15. Remove crucible from furnace, cool, and add one drop of (1+1) H_2SO_4 and 2 ml HF. Heat on hotplate until H_2SO_4 is expelled. Ignite crucible at 900°C in electric furnace for 15 min. Cool in desiccator and weigh to constant weight by returning crucible to furnace and desiccator.

Note: The ignited residue is treated with HF and H_2SO_4 to correct for any silica that was carried down with the precipitate.

Calculation: $\frac{\text{M.W. of S}}{\text{M.W. of } BaSO_4}$ = factor = .137 where M.W. = molecular weight

percent S = wt. $BaSO_4$ x 13.7

REAGENTS

Silica

1. Sodium carbonate, anhydrous powder.
2. Ethyl alcohol.
3. HCl (concentrated).
4. HCl (20 percent)
5. HCl (5 percent).
6. H_2SO_4 (1+1)
7. HF (concentrated).

R_2O_3 Group

1. Ammonium hydroxide. Add 500 ml distilled water to a 1-liter polyethylene bottle. Place the bottle in an ice bath, and bubble ammonia into the water until the volume is 1,000 ml.

2. Brom cresol purple indicator, 0.1 percent. Weigh 0.1 g brom cresol purple. Stir with distilled water until dissolved and dilute to 100 ml volume.

3. Ammonium nitrate, 2 percent. Weigh 20 g of ammonium nitrate into a 2-liter beaker, add distilled water until dissolved, and dilute to 1,000 ml.

4. HCl (5 percent).

5. HCl (1+1).

Removal of Manganese

1. Zirconyl chloride, 5 percent. Dissolve 25 g of zirconium chloride (octahydrate) in about 200 ml H_2O containing 5 ml 12N HCl. Allow the solution to stand overnight. Filter through a #42 Whatman filter paper into a 500-ml volumetric flask and dilute to volume.

2. Ammonium persulfate, crystal.

3. Ammonium nitrate 2 percent. Weigh 20 grams of ammonium nitrate into a 1-liter beaker, add distilled water until dissolved, and dilute to 1,000 ml.

SiO_2 Residue

1. "Baker Insta-Analyzed" Reagent Potassium Pyrosulfate Acid-Flux Grade, Cat. #1-2963. The author specifically recommends this reagent for best results in the dissolution of the pyrosulfate fusion cake.

2. H_2SO_4 (1+1).

3. H_2SO_4 (1 percent). Dilute 10 ml H_2SO_4 to 1 liter with distilled H_2O.

Calcium Oxide

1. Oxalic acid (10 percent). Add 100 g of oxalic acid to 900 ml hot distilled water; let the solution stand overnight. Filter through #42 Whatman filter paper and dilute to 1 liter.

2. Ammonium oxalate (0.1 percent). Dissolve 1 g of ammonium oxalate in distilled water and dilute to 1 liter.

3. HCl (20 percent).

4. HCl (5 percent).

Magnesium Oxide

1. Ammonium phosphate, dibasic (20 percent). Dissolve 200 g in 800 ml distilled water. Let the solution stand overnight. Filter through Whatman #42 filter paper and dilute to 1 liter.

2. Ammonium hydroxide (5 percent).

3. HCl (5 percent).

4. Phosphoric acid (1+19).

Titanium dioxide

See "Procedure" section under "Colorimetric Determination of Titanium Oxide" (p. 40).

Total Iron Oxide

1. $K_2Cr_2O_7$, 5 percent. Dissolve 5 g $K_2Cr_2O_7$ in 100 ml H_2O. Filter through Whatman #42 filter paper.

2. Sodium diphenylamine sulfonate, 0.2 percent. Dissolve 0.2 g in 100 ml hot water.

3. Potassium dichromate 0.06262 N. Add 1,000 ml H_2O to a 2-liter volumetric flask. Weigh 6.141 g and transfer to flask. Swirl until the potassium dichromate dissolves. Dilute to 2-liter mark and mix.

Potassium dichromate, 0.1N. Weigh 4.9035 g for each liter of solution.

For 2 liters, weigh 9.8070 g. Before use, dry $K_2Cr_2O_7$ for 2 hr at 110°C.

4. Silver (granular). Granular silver is needed for the Walden Silver Reductor. For instructions on loading the reductor, see Peck (1964, p. 85).

Ferrous Iron

1. 5 percent boric acid solution, saturated. Dissolve by stirring 100 g of boric acid in 1 liter of hot water; cool, and dilute to 2 liters.

2. Sodium diphenylamine sulfonate, 0.2 percent. Dissolve 0.2 g in 100 ml hot water.

3. Potassium dichromate, 0.06262N. See above section on "Total Iron Oxide."

Manganese Oxide

1. Manganese stock solution, 1 mg/ml MnO. Dissolve 0.3872 g pure Mn metal in 20 ml hot (1+1) HNO_3. Boil out oxides of nitrogen, cool, transfer to a 500-ml volumetric flask, and make to volume. To make the working MnO standard at 0.1 mg/ml, add 10 ml of stock solution to a 100-ml, volumetric flask add 2 ml concentrated HNO_3, and dilute to volume.

2. Potassium periodate solution (1 percent). Dissolve 10 g potassium periodate in 200 ml (1+1) HNO_3 while warming the solution. Transfer to a 1-liter volumetric flask and dilute to 1-liter.

3. H_3PO_4 (1+1).

Phosphorus Pentoxide

1. 50 percent NH_4NO_3. Dissolve 1.000 g NH_4NO_3 in 1 liter H_2O while heating the solution. Dilute to 2 liters (filter if solution is not clear).

2. 2.5 percent ammonium molybdate and 20 percent NH_4NO_3. The molybdate of the 2.5 percent ammonium molybdate and 20 percent NH_4NO_3 drops out of the solution after standing for weeks. Therefore, a fresh solution should be made up before each run of P_2O_5. For a six-sample run; 200 ml is needed. Therefore, dissolve 5 g ammonium molybdate in 20 ml H_2O. Add 80 ml 50 percent NH_4NO_3. Dilute to 200 ml.

3. 2 percent ammonium nitrate in 1 percent HNO_3. 20 g NH_4NO_3 dissolved in 1 liter 1 percent HNO_3 (10 ml HNO_3/1 liter H_2O).

4. Ammonium molybdate (5 percent). Dissolve 50 g $(NH_4)_6\ Mo_7O_{24}\cdot 4\ H_2O$ in 500 ml warm H_2O. Let stand overnight. Filter through Whatman #42 filter paper. Dilute to 1 liter and store in polyethylene bottle.

5. Ammonium metavanadate (0.25 percent). Dissolve 2.5 g NH_4VO_3 in 500 ml hot water, cool, and add 20 ml concentrated HNO_3. Let stand for several hours. Filter if not clear, and dilute to 1 liter. Store in glass bottle.

6. Standard phosphate solution ($\frac{1.00\ mg\ P_2O_5}{ml}$). Dissolve 0.959 g of KH_2PO_4 (recrystallized and dried at 110°C) in water and dilute to 500 ml. Store in tightly capped polyethylene bottle.

Sodium and Potassium Oxides

See "Determination of Sodium and Potassium" section (p. 50-53).

Total H_2O (Penfield method)

Flux: Sodium tungstate, anhydrous powder, $Na_2WO_4\cdot 2H_2O$. Heat sodium tungstate, anhydrous powder at 180°C in oven overnight to drive out moisture. Keep flux in oven at 110°C when not in use to prevent moisture buildup.

Carbon Dioxide

See "Gravimetric Determination of CO_2 by Acid Evolution" section (p. 62-65).

1. Barium chloride (10 percent). Dissolve 50 g barium chloride dihydrate in 400 ml H_2O. Let solution stand overnight. Filter and dilute to 500 ml.

2. Brom phenol blue (0.1 percent). Wet 0.1 g brom phenol blue with a drop of NH_4OH. Add 100 ml H_2O and stir until dissolved.

3. 0.1M silver nitrate. Dissolve 3.4 g of silver nitrate in 200 ml of distilled water.

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