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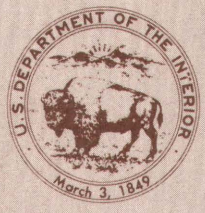
The Classical Chemical Analysis of Silicate Rocks—The Old and the New

GEOLOGICAL SURVEY BULLETIN 1547



The Classical Chemical Analysis of Silicate Rocks—The Old and the New

By HERBERT KIRSCHENBAUM

GEOLOGICAL SURVEY BULLETIN 1547

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THE CLASSICAL CHEMICAL ANALYSIS OF SILICATE ROCKS—THE OLD AND THE NEW

By HERBERT KIRSCHENBAUM

ABSTRACT

This bulletin describes perhaps the most accurate analytical methodology for determining the major constituents in silicate rocks and includes classical procedures modified mostly from Peck (1964) and Maxwell (1968) 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. Explanations are presented directly under varous steps of the procedures elaborating on the importance of that particular technique and how it affects the accuracy of the analysis. The flame photometer procedure for the determination of Na_2O and K_2O presented in this manual is as accurate and precise as the classical, yet time-consuming, J. Lawrence Smith procedure. Other time-consuming procedures such as those for H_2O^+, S, and CO_2 can also be replaced by newer instrumental techniques without sacrificing the accuracy and precision of the older methods. Data are presented in this Bulletin to bolster the statement that some of the new can replace some of the old and that these new instrumental techniques may prove to be the "classics" of tomorrow.

This bulletin supercedes Open-File Report 81-359, "A Manual of Modified Analytical Procedures for Conventional Rock Analysis," by Herbert Kirschenbaum.

INTRODUCTION

The data from the newly established Classical Rock Analysis Laboratory at the U.S. Geological Survey's (USGS) National Center in Reston, Va., must be directly comparable with data from the long-established USGS Conventional Rock Analysis Laboratory in Denver, Colo., so that geologists' interpretations of these analyses are not affected by analytical bias. This manual explains how the Reston laboratory obtains results comparable with those of Denver without the use of Denver's special equipment. Except for the flame photometer, equipment available to most laboratories is used in the Reston laboratory.

Any use of trade names and trademarks in this publication is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Analytical skills and methods should not be lost, even though instrumental analysis and the more rapid, but less accurate, analytical chemistry techniques are being widely used, and, as pointed out by Sanders (1977, p. 30), universities are paying less attention to classical analytical chemistry than in the past. 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 were being carefully evaluated by an experimental design in the form of a Youden Square to determine if there is a significant variation in data for constituents determined over extended intervals of several months. The study showed that this variation was not significant (Flanagan and Kirschenbaum, in press). Data gathered suggest that these procedures meet all criteria for reporting classical analyses (tables 1, 2).

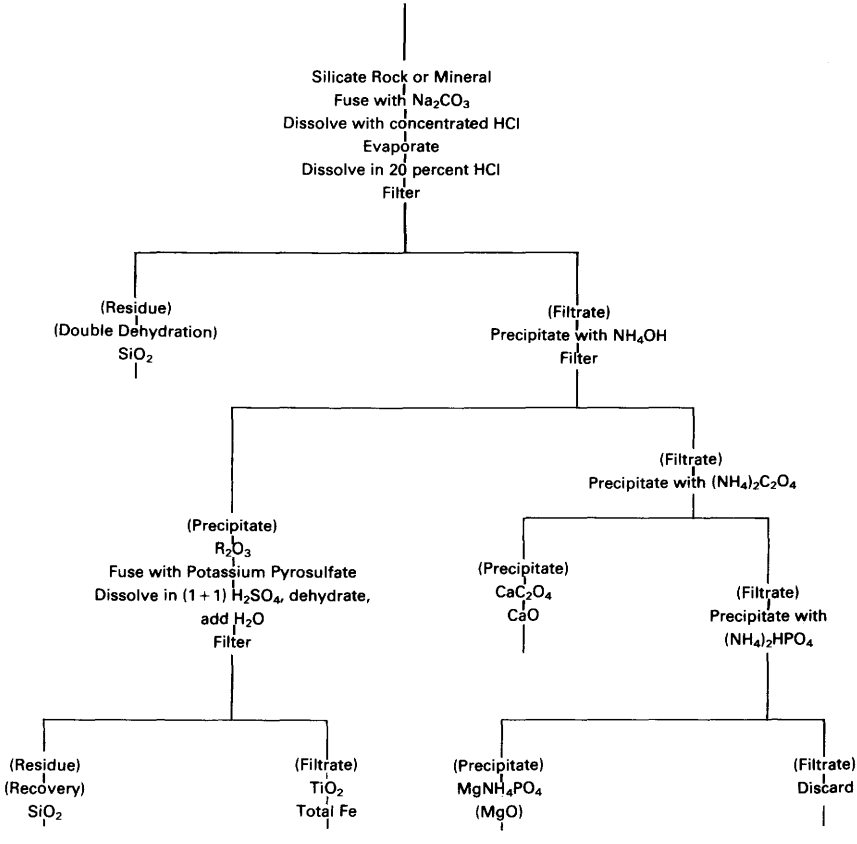


FIGURE 1.—An outline of procedures for the systematic classical rock analysis.

TABLE 1.—*Achievable limits of error in classical rock analysis*

[Classical chemistry summation of a total silicate analysis of constituents normally found: 99.50–100.25]

Constituent	Percentage
SiO_2	0.10
Al_2O_3	.15
CaO	.05
MgO	.05
Na_2O	.03
K_2O	.03
Total Fe	.08
FeO	.05
TiO_2	.03
P_2O_5	.03
MnO	.01
CO_2	.02
H_2O(+ or −)	.02

TABLE 2.—*Error standard deviations of the procedures*

Constituent	Error s.d.* (percent)
SiO_2	0.070
Al_2O_3	.15
Fe_2O_3†	.059
FeO	.046
MgO	.032
CaO	.020
Na_2O	.012
K_2O	.0039
H_2O^+	.041
H_2O^-	.0082
TiO_2	.0082
P_2O_5	.0091
MnO	.0022
CO_2‡	.005
Total Fe as Fe_2O_3	.056

*The error standard deviations are the square roots of the error mean squares for the 15 determinations in the analysis of variance for each constituent (Flanagan and Kirschenbaum, in press).
†Calculated from total Fe and FeO.
‡Acid evolution procedure (see section on "Critical Points—Carbon Dioxide.")

ACKNOWLEDGMENTS

I appreciate the suggestions of my fellow chemists, Lillie B. Jenkins and Joseph I. Dinnin, both now retired. Lillie B. Jenkins helped put the R_2O_3 determination into focus, and Joseph I. Dinnin aided in the digestion procedure for the flame photometric determinaton of Na_2O and K_2O.

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 Na_2CO_3 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, cause problems in a systematic analysis of silicate rocks. The peroxide may attack the platinum crucible, thus introducing excessive Pt into the systematic determinations.

SILICA

In the gravimetric determination of SiO_2, a thorough washing of the SiO_2 precipitate after the first and second dehydrations is critical to avoid low results. Therefore, I use fast-filtering (Whatman No. 41) paper for both filtrations. By following the recommended procedures, the washing of the precipitates will be easy, fast, and thorough. For rocks having a 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 rocks having a SiO_2 content of about 70 percent, less than 0.1 percent SiO_2 passes through the paper. All the SiO_2 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 simple to follow and gives excellent results. To avoid formation of $CaCO_3$ after the precipitation of the R_2O_3 group, it is important to filter as soon as possible after precipitation, keeping the solution warm on the steam bath during filtration. 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

Manganese is removed to prevent the precipitation of Mn with Mg. If Mn 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 SILICA

Potassium pyrosulfate (which is actually a mixture with potassium bisulfate, $KHSO_4$) is used to fuse the R_2O_3 precipitate for the determination of residual SiO_2. It is critical that the fusion cake be completely dissolved in (1+1) H_2SO_4. After dehydrating the SiO_2 by heating to fumes of SO_3, everything except SiO_2 must be dissolved. 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. For many years, the USGS' Denver Conventional Rock Analysis Laboratory has used the "Baker Instra-Analyzed" Reagent Potassium Pyrosulfate Acid-Flux Grade (catalog No. 1-2963) without experiencing dissolution problems, and it is used here successfully. Special care should also be observed in handling samples that contain high amounts of Ni and Cr. 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.

CALCIUM OXIDE

If Pt has become a contaminant in the analysis, it will interfere with the CaO determination by forming a Pt complex salt. The yellowish Pt 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 Pt complex remains on the filter paper and is discarded. In the determination of CaO, Sr will also precipitate. If the amount of SrO is not negligible, Sr must 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 Mg. 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 Mg and allows the solution to stand until precipitation is complete, the analyst avoids having to destroy the ammonium salts before the precipitation is made. Destroying the ammonium salts is not only 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 0.1 *N* Mohr's salt (ferrous ammonium sulfate) with 0.1000 *N* $K_2Cr_2O_7$. We varied the amounts of (1+1) H_2SO_4 and (1+1) H_3PO_4 and 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 Fe system by its formation of the ferric ion complex, $Fe(PO_4)_2^{3-}$, 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 Fe 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 Fe 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 Fe determination. Because a fresh H_2O_2 solution is required, a new solution should be prepared for each set of samples; that is, usually once a month. The working standards may be stored providing they are transferred to air-tight polyethylene containers comparing the absorbance value of one of these periodically with a freshly prepared standard. The spectrophotometer used is the Bausch and Lomb Spectronic 100 (fig. 2). 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

FIGURE 2.—Bausch and Lomb Spectronic 100.

may be diluted if necessary, and the absorbance reading of the unperoxidized solution will drop accordingly for the color correction. The concentration of standards suggested in the method is only a general guide. The standards for a sample should be adjusted to the expected sample percentages taking dilution factors into consideration.

MANGANESE AND PHOSPHORUS OXIDES

The colorimetric determination of MnO is performed by oxidizing Mn to permanganate with periodic acid and boiling in a HNO_3 solution. The color is very stable, which leads to precise and accurate results. A blank run along with the samples should give the same absorbance as the reference solution, distilled H_2O. However, for the determination of P, 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 H_2O as the reference solution. The spectrophotometer used is the Bausch and Lomb Spectronic 100. It is important that the 1-cm cells used be a matched pair, and, when filled with distilled H_2O, the readings of the two cells

should differ by no more than 0.002 Abs. 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 SiO_2. The undecomposed SiO_2 of these samples will retain titanium phosphate and Fe, and total decomposition is necessary 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 partly opening 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 H_2O by heating on a steam bath, overnight if necessary. Filter through a Whatman No. 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 watchglass 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

Li 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 443 Flame Photometer (fig. 3) uses the internal standard as an index of sample concentration; thus, the volume proportion of Li 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 Na or K 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

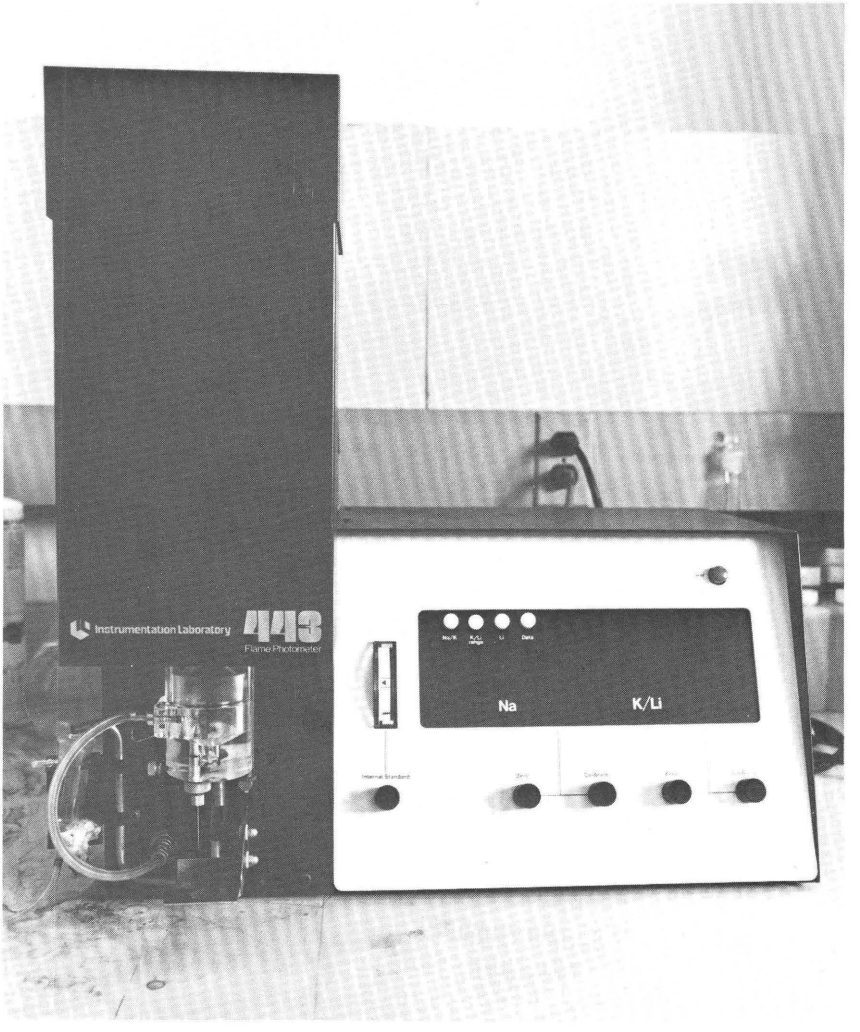


FIGURE 3.—IL 443 Flame Photometer.

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. Table 3 shows the accuracy and precision of the above procedures.

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 H_2O. The use of 2 g of sodium

TABLE 3.—*Accuracy and precision obtained during the training of three analysts in the use of the flame photometer procedure*

[Analyst 1—Nancy Skinner, USGS, 11-78; analyst 2—Zoe Hamlin, USGS, 2-81; analyst 3—V. K. Jain, Chief Analyst, Geology and Mining Department, Raipur, India, 6-81]

USGS Standard Reference Rock	Analyst 1	Analyst 2	Analyst 3	Reccommended value[1]
		Na_2O		
W-1	(1)2.20 (2)2.20	(1)2.18 (2)2.18	(1)2.18 (2)2.18	2.15
BCR-1	(1)3.28 (2)3.28	(1)3.27 (2)3.25	-- --	3.27
		K_2O		
W-1	(1)0.64 (2)0.64	(1)0.65 (2)0.65	(1)0.65 (2)0.65	.64
BCR-1	(1)1.70 (2)1.73	(1)1.71 (2)1.70	-- --	1.70

[1]Flanagan (1976, p. 171)

tungstate gives a H_2O blank of about 0.10 ± 0.02 percent H_2O. The sodium tungstate is heated at 180°C. to remove the moisture, and the flux must be kept in an oven at 110°C. when not in use to prevent moisture reabsorbance. I recommend subtracting an averaged blank from the samples. An averaged 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 $\div 6 = 0.097$, or 0.10 percent. Averaged blanks give a more accurate figure to be subtracted from the sample and indicate slow trends, such as moisture buildup in the flux. Any large deviation of the daily blank from the previous averaged blank should be carefully checked.

CARBON DIOXIDE

The classic gravimetric procedure for the determination of CO_2 is explained in the written procedure ("Gravimetric Determination of Carbon Dioxide by Acid Evolution") 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 sample on weighing paper and transfer to a borosilicate test tube (10 by 75 mm) which has been modified by the addition of a bulge about 10 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 with a small hook at one end (Shapiro, 1975, p. 12–13).

2. Add distilled H_2O until water level is 0.5 in 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 a 45° angle, extend bulge upward, add 0.1 mL *hot mixture* $HgCl_2$ and concentrated HCl (10 mL concentrated HCl mixed with 10 mL decanted saturated $MgCl_2$). Allow CO_2 bubbles to rise into 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–1 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 0.02-percent precision of the gravimetric determination of CO_2.

TOTAL SULFUR

In the determination of total S, the barium sulfate precipitate must be free of chlorides. The coprecipitation of barium chloride will cause a positive error. Therefore, the final washing of the barium sulfate precipitate must be tested with silver nitrate to ensure the absence of chlorides. 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 convinced that the paper does not contribute a significant error (0.01 percent) to the percentage of S, then these blanks no longer need to be run. I recommend running a BCR–1 standard along with each set of seven samples to check the reagents being used and the analytical technique.

OXYGEN CORRECTIONS

A correction for the O equivalent of S, F, and Cl must be applied when they are present as a sulfide, fluoride, and chloride (Maxwell, 1968, p. 235–236, 247, 250). When the amount of S is small and it is not practical to distinguish between individual sulfides such as pyrite and pyrrhotite, the correction factor for S

should be S×0.5. If the sulfide is known to be present as a pyrite, the correction factor if 0.374. If the sulfide is known to be present as pyrrhotite, the factor is 0.437. The correction factor for chloride is Cl×0.22 and that for fluoride is F×0.42. The oxygen corrections are subtracted from the summation total.

DETERMINATION OF CONSTITUENTS

DETERMINATION OF MOISTURE, H_2O^-

Procedure:

Before starting classical rock analysis procedures, the sample which has been ground to about 100 mesh must be well mixed using tumblers for a minimum of 10 min. Pour the sample onto 6-by 6-in glycine weighing paper, quarter it, and return it to the 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 within 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° to 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 (g)×100=percent H_2O^-.

GRAVIMETRIC DETERMINATON OF SILICA IN SAMPLES CONTAINING LESS THAN 2 PERCENT FLUORINE

If samples contain more than 2 percent F, low SiO_2 results would be obtained by using the procedure described below because the SiF_6^{2-} complex ion forms in acid solution and then becomes the volatile SiF_4 compound at temperatures above 100°C.

Fusion with Sodium Carbonate Procedure (Maxwell, 1968, p. 324–330):

1. Support the covered platinum crucible containing the 1.0000-g sample used for determining H_2O^- 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 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 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. Tap the glass rod against the sides of the crucible. Wipe the rod off in an additional gram of Na_2CO_3 which is then sprinkled over the surface to provide a trap for splattering particles during the initial heating stages of fusion. Tap the crucible gently on the bench top to settle the fusion mixture.
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 increments of 50° 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 furnace temperature at 1,100°C. for 30 min.
7. Remove the crucible containing the 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 H_2O 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 H_2O-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 Cl when the melt is dissolved in HCl and the Cl will attack Pt. Therefore, a few milliliters of ethyl 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 with a watchglass.
12. Insert the tip of a curved-stem funnel between the lip of the dish and the watchglass. Do not try to pulverize the cake because 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 watchglass) in portions small enough to avoid violent effervescence. Hold the crucible cover over the funnel and wash it with H_2O; clean the cover with a rubber policeman that has been dipped into the acid contained in the crucible and again wash it with H_2O. 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 H_2O and catch the washings in the funnel. Wash the funnel and funnel tip and catch the washing in the large platinum dish.
13. After most of the effervescence stops, 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, loosen the cover to allow O_2 to enter and note if the crucible 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 visibly stained (most likely by Fe), add 10 mL (1:1) HCl to the crucible, replace the cover, and heat the crucible on the H_2O bath until the stain disappears. Rinse the solution into the platinum dish and ignite the crucible as before.
15. Allow the solution in the platinum dish to evaporate to dryness on the steam bath. After the residue appears to be dry, it may be stirred with a glass rod. 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 dur-

ing this period, wash 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, so that possible dissolution of the SiO_2 may be avoided.

16. Prepare an 11-cm Whatman No. 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 SiO_2 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, using the same numbers as the platinum dishes. Wash the precipitate 15 times with hot 5 percent HCl. Pay particular attention to upper edges of the filter 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 watchglass over it. (This paper will later be added to the filter paper containing SiO_2 from a second dehydration and filtration.)

Note: A thorough washing of SiO_2 precipitate is very important. Appreciable amounts of Na, K, and alkaline earth metals not washed out of the precipitated SiO_2 may cause low results to be obtained for SiO_2 because they are first weighed as an alkaline silicate before HF treatment and as a sulfate after the HF decomposition.

17. The separated SiO_2 should be white but may be colored by hydrolyzed iron oxides (reddish) or by Pt (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 hr.
18. Add 50 mL 20 percent HCl and heat the solution for 30 min on the H_2O 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 Whatman No. 41 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 and 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 SiO_2 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. Open the furnace door slightly to allow air to enter for complete oxidation. Slowly raise the temperature of the furnace to 800°C. and leave until only a little C remains on the SiO_2 precipitate. Put the crucible cover in place and shut the furnace door, then gradually raise the temperature to 1,200°C. The precipitate should be white.
22. The precipitate is ignited at 1,200°C. for 30 min, cooled in a desiccator for 30 min, then weighed. Return the crucible to the furnace for a 20-min period and to the desiccator for a 30-min period, reweighing until constant weight is obtained (to within 0.0002 g). The final weight is the weight of the crucible and impure SiO_4.
23. Moisten the SiO_2 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 a hotplate just short of boiling until the solution is clear (about 5 min).
24. Partly remove 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: It is important to add (1+1) H_2SO_4 to obtain the true weight of SiO_2. After the SiO_2 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. Some Ti might 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 SiO_2.

Calculation:

Loss in weight (g) after HF addition$\times$100+SiO_2 recovered (g) from R_2O_3 group=percent SiO_2.

26. Add 0.5 g Na_2CO_3 to the residue, fuse the mixture in a furnace at 1,050°C. for 20 min, then cool, adding a little H_2O to wet the cake prior to adding (1+1) HCl dropwise and continuing until effervescence ceases. Then dissolve the cake completely in (1+1) HCl. Heat it on a hotplate 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 for 30 min). Reserve the crucible for the ignition of the R_2O_3 precipitate. This step is unnecessary if the residue is less than 9 mg (V. C. Smith, E. L. Brandt, and E. E. Engelman, USGS, oral commun., 1978), in which case the precipitate from R_2O_3 will be put directly into the crucible after SiO_2 HF treatment (step 25).

GRAVIMETRIC DETERMINATION OF ALUMINA BY DIFFERENCE FOLLOWING PRECIPITATION OF THE R_2O_3 GROUP

1. Dilute the filtrate from the determination of SiO_2 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 over a Meker burner, using a tripod and asbestos mat. Allow the solution to heat and, while stirring, add pure NH_4OH stored in a plastic bottle (reagent-grade NH_4OH contains SiO_2) dropwise until a permanent precipitate forms. While heating, add NH_4OH dropwise until the solution is just purple. Allow the precipitate to settle and check the supernatant liquid to be certain the color is purple. Add two drops in excess. Remove the beaker from the burner, add 0.25 g dry filter pulp (S&S No. 289), stir, and put it on a steam bath to keep the solution hot until it is ready for filtering. Repeat the above procedure with second and succeeding samples.

   Note: The precipitate obtained from a hot solution is easily filterable. After the precipitation of the hydroxides of Fe and Al, an ammoniacal solution slowly absorbs CO_2 from the air causing precipitation of $CaCO_3$. To avoid the formation of $CaCO_3$, filter as

soon as possible after precipitation and keep the beakers heated on the steam bath before and during filtration.

2. Filter the hot solution through a 12.5-cm Whatman No. 40 filter paper into a 600-mL beaker. Filter rapidly, keeping the bulk of the precipitate in the beaker until filtering is complete. Wash the inside of the beaker twice with hot 2 percent NH_4NO_3 solution and transfer the washings to the filter. Reserve the washed precipitation beaker.

   Note: The precipitate must NOT be washed in H_2O—the hydrous Al_2O_3 would be peptized and would run through the filter.

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

4. Dissolve the R_2O_3 precipitate for the second precipitation by lifting the paper with platinum forceps and putting it into the washed reserved precipitation beaker. Wash the funnel with 5 percent HCl. Wash the inside of the beaker with 5 percent HCl. Put the beaker on the 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 with distilled H_2O to 150 mL.

5. Add five 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 just purple. Add two drops of NH_4OH in excess. Place the beaker on the steam bath while repeating the beginning of this step with the second and succeeding samples.

   Note: When two precipitations are made, the separation of Mn in amounts as much as 20 mg is substantially complete.

6. Filter the solution through a 12.5-cm Whatman No. 40 filter paper into the reserved 600-mL beaker containing the first filtrate. Wash the inside of the 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 hot 2 percent NH_4NO_3, adding washings to the filter. Thoroughly police the beaker to transfer any remaining precipitate or film.

8. Wash the precipitate 15 times with hot 2 percent NH_4NO_3. Cover the precipitate with wash solution each time, allowing complete drainage.
9. Cover the funnel with a filter paper and allow the precipitate to partially dry. Add (1+1) HCl dropwise to the combined filtrates until a yellow color forms; add two drops in excess and evaporate it to a volume of 200 mL. Just neutralize the solution with pure NH_4OH and heat it on the steam bath for 15 min. If no precipitate is evident, reserve the solution for the removal of manganese. If a precipitate is present, filter the solution through a 9-cm Whatman No. 40 filter 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 removal of manganese.
10. Without folding it, place the paper in the crucible containing the residue that was left after volatilization of the SiO_2 with HF. Wipe the inside of the funnel with a piece of filter paper dampened with H_2O and place it on the paper containing the precipitate. Fold in the sides of the paper, starting with the single thickness side, pushing the paper down into the crucible with the triple thickness side on top.

    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 partly opening the furnace door during the initial stages of the ignition, ensure that air has free access to the furnace. Burn off all the C from the paper.
12. Finally, heat it at 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 H_2O free.
13. Cool in a disiccator for 30 min and weigh. Repeat ignition for 20-min periods until constant weight is obtained. Reserve the precipitate for the recovery of SiO_2.

Calculation:

$$\text{wt. } R_2O_3 \text{ (g)} \times 100 = \%\ R_2O_3*$$

$$\%\ R_2O_3 - (\%\ \text{recovered } SiO_2 + \%\ \text{total Fe (as } Fe_2O_3) + \%\ TiO_2 + \%\ P_2O_5) = \%\ Al_2O_3$$

*Weight of the empty crucible used in calculation is the weight of the crucible after the pyrosulfate fusion in the SiO_2 recovery determination (after step 5, "Recovery of Silica").

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 elements as Cr, V, Zr, the rare earths, and Be are present in measureable amounts.

REMOVAL OF MANGANESE

Procedure (Peck, 1964, p. 30–31, 66):

1. Evaporate the filtrate obtained in step 9, "Gravimetric Determination of Alumina by Difference Following Precipitation of the R_2O_3 Group," to 100 mL; then add 1 mL 5 percent zirconyl chloride solution and 0.1 g of paper pulp.

   Note: A soluton of colloidal hydrated MnO_2 filters slowly and the precipitate passes through the finest paper. The Zr 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 2 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 not 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 No. 40 filter paper into a 400-mL beaker. Wash the inside of the precipitation beaker three times with a hot 2-percent NH_4NO_3 solution and transfer the washings to the filter. Wash the precipitate on the paper 10 times with the same solution.
4. Discard the hydrated MnO_2 and zirconium hydroxide precipitate and reserve the filtrate for the determination of Ca.

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 potassium pyrosulfate to the Vycor crucible and add 1 g potassium pyrosulfate to the platinum crucible.
3. Place the Vycor crucible (covered) in the muffle furnace at 700°C. Heat the R_2O_3 precipitate at 800°C. for 2 to 3 min or until fused. Check for specks of unfused matter when cooled.
4. Remove the Vycor crucible from the 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 (1+1) H_2SO_4 to the beaker and set it aside. Police the cover and add the washings to the beaker. Rotate the platinum crucible over a small flame until the pyrosulfate melts. Increase the heat until the 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 potassium pyrosulfate on the surface of the crucible cover to dissolve stains or adhering particles. Cool the crucible, add a little H_2O to its contents, and heat it on top of the steam bath for 5 min. Police the inside of the crucible, cover and transfer the 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 this until a constant weight is obtained. Reserve the 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 the SiO_2 determination was not fused with 0.5 g Na_2CO_3.
6. Cover the 250-mL beaker and heat it on the H_2O 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, dehydrating the SiO_2.
7. Cool the beaker and contents and dilute the solution to 75 mL with H_2O. Heat the beaker on the H_2O bath until everything dissolves except a fleecy residue of SiO_2.

   Note: Samples that contain high amounts of Ni and Cr 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 No. 40 filter paper into a 250-mL beaker. This author keeps the solution warm while filtering 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 Ti and total Fe_2O_3.

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 HF. Transfer the crucible to a 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. The loss in weight is the weight of SiO_2.
11. Add 1 g 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 Ti and total Fe. Evaporate the solution on the steam bath to less than 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 Whatman No. 40 filter paper into a 600-mL beaker. Wash the inside of the precipitation beaker with 0.1 percent ammonium oxalate solution and transfer the washings to the filter paper. 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. Wash the inside of the precipitation beaker with hot 20 percent HCl. Heat the solution in the precipitation beaker on a steam

bath. Pour the solution through the filter. Wash the inside of the beaker three times with hot 20 percent HCl and transfer the 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. While stirring, add NH_4OH dropwise 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 steam bath and let it stand 4 to 16 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 Whatman No. 40 filter paper into the beaker containing the first filtrate. Wash the beaker with 0.1-percent solution of ammonium oxalate and transfer the washings 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 Mg determination.
7. Fold the paper and place it in the platinum crucible that was reserved after the SiO_2 recovery determination.
8. Wipe the inside of the funnel with a piece of dampened 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 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, cooling, and weighing 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 the crucible with 5 percent HCl and rinse with distilled H_2O. Ignite the clean crucible at 800°C. in the furnace until constant weight and reserve for the determination of MgO.

Calculation:

wt. CaO (g)×100=percent CaO.

GRAVIMETRIC DETERMINATION OF MAGNESIUM OXIDE

Procedure (Peck, 1964, p. 68–69):

1. To the combined filtrates from the Ca determination, add 25 mL 20 percent dibasic ammonium phosphate. Add 40 mL NH_4OH, 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 No. 42 filter paper. Wash the inside of the beaker with 5 percent NH_4OH and pour the washings into the filter. Wash the paper three times with the same solution. Discard the filtrate and place a clean 150-mL beaker under the funnel.
3. Wash the inside of the precipitation beaker with enough 20 percent HCl to bring the precipitate into solution with stirring and washing if necessary. Pour the solution into the filter paper containing the Mg precipitate, wash the inside of the beaker three more times with 20 percent HCl, and transfer washings 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 more times with 5 percent HCl. Discard the paper.
4. Dilute the solution in the 150-mL beaker to 90 mL. (If the MgO is more than 20 percent, make the second precipitation from a volume of 200 mL.) Add 1 mL (1+19) H_3PO_4 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 1 min, add one drop of NH_4OH, and stir. Continue in this manner until 10 drops of NH_4OH have been added. Add an additional 10 mL NH_4OH. Stir the solution and let it stand overnight.
5. Filter the solution through a 9-cm Whatman No. 42 filter paper. Wash the inside of the beaker once with 5 percent NH_4OH and transfer the washings to the filter. Wash the stirring rod with NH_4OH solution and police the inside of the beaker. 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 NH_4NO_3 to the crucible reserved after the CaO determination. Fold the paper and place it in the crucible. Wipe the funnel with a piece of dampened 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 C 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 and subsequent loss of phosphorous. 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:

$$\text{wt. } Mg_2P_2O_7 \text{ (g)} \times 36.23 = \text{percent MgO.}$$

Conversion factors:

$$MgO \xleftarrow{\quad} \frac{0.6032}{1.6579} \xrightarrow{\quad} Mg$$

$$MgO \xleftarrow{\quad} \frac{2.7604}{0.3623} \xrightarrow{\quad} Mg_2P_2O_7$$

COLORIMETRIC DETERMINATION OF TITANIUM OXIDE

Working Standards:

To a 100-mL volumetric flask, add x mL of stock Ti solution:

$$\frac{x \text{ mL} \times 1000 \ \mu\text{g mL}^{-1}}{100 \text{ mL}} = 0.x \text{ percent } TiO_2/100 \text{ mL},$$

where $x = 2, 5, 10,$ and 12.

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

Procedure

1. Use the standard blank as a reference solution. Add the sample which does not contain the H_2O_2 solution to a 1-cm cell and fill to a 3.5-mL mark. Read at 410 nm. Then add 0.2 mL 6 percent H_2O_2 to the 1-cm cell containing the sample solution. Mix with a thin stirring rod and wash off the rod into the beaker containing the sample solution and rinses. Save all the rinsings and sample solution for the total Fe determination.
2. The standards containing H_2O_2 are read and discarded.
3. Determine the absorbance reading of the sample containing H_2O_2.
4. Subtract from this value the absorbance reading of the sample solution which contains no H_2O_2 (see note B below).
   The absorbance factor for each standard is given by

$$\frac{\text{percent } TiO_2}{\text{Abs.}} = \text{Abs. factor.}$$

   The percent TiO_2 in the sample is calculated by multiplying its corrected TiO_2 Abs. by the average of all the absorbance factors obtained from the standards.

Note (Sandell, 1959): A. The yellow anionic complex that Ti 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 Ti 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.

TITRIMETRIC DETERMINATION OF TOTAL IRON OXIDE BY USE OF A SILVER REDUCTOR

Procedure (Peck, 1964, p. 72)

1. Stir 15 mL NH_4OH into the solution that was reserved in a 250-mL beaker after the determination of Ti. Cover the beaker with a ribbed cover glass and evaporate on the steam bath to a volume of 75 mL. Cool the solution; add two drops of 5 percent $K_2Cr_2O_7$

and stir. If the solution does not become distinctly more yellow, evaporate it further and retest from time to time by the addition of $K_2Cr_2O_7$ two drops at a time. When the dichromate color persists, add 25 mL 15 percent ammonium chloride and adjust volume to 100 mL.

Note: A. Chloride ions must be present to precipitate Ag ions as they form, or the ferric ion reduction is incomplete. B. Before the solution is passed through the reductor, the acid concentration is reduced by the addition of NH_4OH. Acid stronger than 1 *N* attacks the Ag, and the H_2 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 Fe 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 Ag_2O. Stir the column with a long glass rod. Wash the column with 200 mL H_2O. Test the washings with pH paper to make certain the column is washed free of NH_4OH. Wash the column with 200 mL 5 percent HCl.

2. Drain the reductor (fig. 4) until the level of the liquid is about 0.125 in above the Ag. Add 40 mL (1+1) H_3PO_4 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 tips into the acid. Transfer about half the Fe solution to the reservoir. Fully open the stopcock on the reductor and, as the solution drains, transfer the remainder of the Fe solution to the reservoir. Let the solution drain until its level is about 0.125 in above the Ag. Lift the reductor as the volume of the effluent increases, keeping 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 Ag, repeating 5 more times. Add 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 four drops of 0.2 percent sodium diphenylamine sulfonate and titrate with 0.06262 *N* $K_2Cr_2O_7$ using a magnetic stirrer (a distinct purple color should last 30 sec).

Calculations:

$$\text{Percent total Fe (as } Fe_2O_3) = \frac{\text{mL } K_2Cr_2O_7}{2},$$

or

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

$$= \text{percent total Fe as } Fe_2O_3.$$

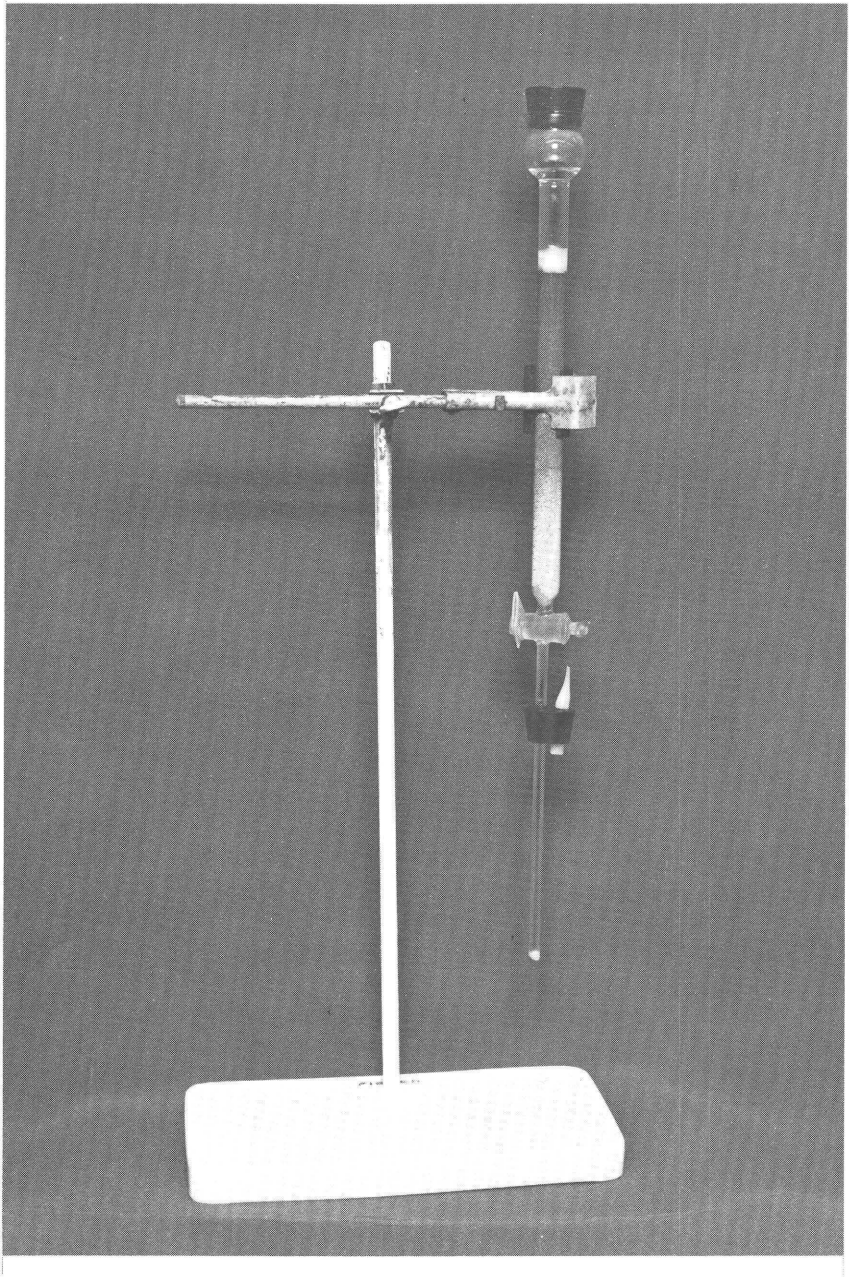


FIGURE 4.—Silver reductor.

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

TITRIMETRIC DETERMINATION OF TOTAL IRON OXIDE AS FE_2O_3 ON A SEPARATE PORTION OF THE SAMPLE

On occasion, such as a check on the efficiency of the silver reductor by analyzing USGS standard reference rocks for total Fe_2O_3 or due to spoilage of a sample so that the Fe determination cannot be analyzed from the original weighed sample, it became necessary to determine total Fe on a separate portion of sample. Thus, we had to develop a decomposition procedure for silicate rocks whose matrix is similar to that of the original sample before proceeding to step 2, "Titrimetric Determination of Total Iron Oxide By Use of a Silver Reductor."

The following sample decomposition procedure allows portions of a separate sample to be put through the silver reductor and has proven to be bias-free in the determination of total Fe:

1. Weigh 1.0000 g sample and transfer it to a 100-mL Teflon beaker.
2. Mix 10 mL HF and 10 mL H_2SO_4 in a 30-mL Teflon beaker.
3. Using a dropper, add the mixed acid slowly to the sample in the 100-mL Teflon beaker.
4. Cover the Teflon beaker and digest the contents in a boiling water bath overnight.
5. Remove the cover and evaporate the HF on a hotplate by bringing to dense white fumes for 10 min.
6. If the silicate rock is a basalt or dolerite, treat the dissolved sample in the following manner:
   A. Add 20 mL distilled H_2O in small portions, stirring continuously with a stirring rod.
   B. Add 10 mL concentrated HCl and digest overnight in a boiling water bath.

C. Transfer the contents of the Teflon beaker to a 250-mL glass beaker with distilled water. Cover the beaker with a watch glass and heat on a hot plate.
D. Add 5 mL HCl and continue heating until the sulfates go into solution.
E. Fill it to 100-mL volume with distilled H_2O.
F. Proceed to step 2, "Titrimetric Determination of Total Iron Oxide By Use of a Silver Reductor," for the determination of total Fe_2O_3.

7. If the silicate rock is a peridotite or dunite (samples containing a high Cr content) follow this procedure:

   After step 6B of the decomposition procedure, decant contents of the Teflon beaker in a 250-mL glass beaker. Transfer the residue in the Teflon beaker to a 20-mL glass beaker. Add 2 mL of a one to one by volume solution of H_2SO_4 and H_3PO_4 and take to fumes to dissolve residue. Transfer it with distilled H_2O to the 250-mL beaker containing the decanted solution. Add 5 mL concentrated HCl, cover the beaker, and heat it on a hotplate until complete dissolution. Cool the contents and continue with step 6E.

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 with 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; and cover the crucible and allow it 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 and 5 mL HF. Place the covered crucible with sample on a silica triangle suspended firmly over a Bunsen burner with 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 warming 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 because hot concentrated H_2SO_4 oxidizes the ferrous Fe.
5. To 250 mL H_2O in a 600-mL beaker, add 50 mL 5 percent boric acid, 5 mL H_2SO_4, and 10 mL H_3PO_4 and mix well.

6. At the conclusion of the 10-min 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 of 0.2 percent sodium diphenylamine sulfonate to the beaker and titrate with 0.06262 *N* $K_2Cr_2O_7$.

Calculation:

$$\text{mL } K_2Cr_2O_7 \times 0.9 = \text{percent FeO},$$

or

$$\frac{\text{mL titrant} \times N}{1{,}000} \times \frac{71.85}{1} \times \frac{100}{\text{Sample wt.}} = \text{percent FeO}$$

and, percent Fe_2O_3=percent total Fe as Fe_2O_3-(percent FeO×1.1113).

COLORIMETRIC DETERMINATION OF MANGANESE AND PHOSPHORUS OXIDES

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

Because HNO_3 and HF, the acids used in the decomposition of samples, contain P, a blank must be run with the samples during decomposition. Distilled H_2O is used as a reference solution when determining P_2O_5 and MnO for samples, blanks, and standards.

1. Transfer 1 g sample to a 100-mL platinum dish or Teflon beaker and moisten it with H_2O. Add 10 mL HNO_3. After the effervescence has ceased, add 10 mL HF. Cover and digest on a steam bath for 1 hr. Evaporate it on a hotplate to near dryness. Cool, add 5 mL HNO_3, add 5 mL HF, and mix. Evaporate it to dryness on the hotplate.
2. Cool, add 20 mL (1+1) HNO_3, and evaporate it to dryness. Heat the contents of the dish 30 min after the residue appears to be dry.
3. Cool and add 40 mL (1+1) HNO_3 and 10 mL 5 percent boric acid. The boric acid ties up residual HF, thus protecting the glassware.
4. Cover and digest contents in a boiling H_2O 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 Mn will go into solution.

5. Filter it through a 7-cm Whatman No. 40 filter paper into a 100-mL volumetric flask and police the dish with H_2O containing a few drops of HNO_3.
6. Wash the 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, Cr interferes with the colorimetric determination of Mn.
7. Dilute it to a 100-mL volume and mix.

Determination of Manganese Oxide (Maxwell, 1968, p. 388)

1. Pipet a 25-mL aliquot of the sample to a 50-mL volumetric flask.
2. For each 50 mL of final volume, add 10 mL concentrated HNO_3 and 5 mL 1 percent potassium periodate solution. Wash the inside of the flask with water, swirl to mix, and immerse the flask in a boiling H_2O bath for 2 hr or until the magenta color development is complete.
3. Cool it and add 2.5 mL (1+1) H_3PO_4 for each 50 mL volume. Dilute it 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):

$$\frac{0.1 \text{ mg}}{\text{mL}} \times \frac{x \text{ mL}}{\text{diluted to 50 mL}} = 0.0002 \times x \text{ percent MnO},$$

where $x = 3$, 4, 5, and 10.

Add 10 mL HNO_3 and 5 mL 1 percent potassium periodate and put it in a boiling H_2O bath for 2 hr or until the magenta color development is complete. Cool it and add 2.5 mL (1+1) H_3PO_4. Dilute to 50 mL and mix. Measure absorbance at 525 nm.

Note (Peck, 1964, p. 45–47): A. A high HNO_3 concentration assures the complete solution of titanium phosphate and gives the correct acidity for the determination of both Mn and P in portions of the filtrate. B. Mn is oxidized to permanganate by boiling it in a 20-percent HNO_3 solution containing potassium periodate. The oxidized solution is very stable. C. Fe is decolorized by the addition of H_3PO_4 and does not interfere with the colorimetric determination of Mn.

Calculation:

Because the sample concentration os 0.005 g/mL,

$\frac{1.00\text{ g}}{100\text{ mL}} \times \frac{25\text{ mL}}{50\text{ mL}} = \frac{0.005\text{ g}}{\text{mL}}$, the sample dilution factor is 200.

The absorbance factor for each standard is $\frac{\text{percent MnO.}}{\text{Abs.}}$

The percent MnO in the sample is calculated by multiplying its absorbance by the average of all the absorbance factors obtained for the standards and by the sample dilution factor (above).

DETERMINATION OF PHOSPHORUS OXIDE (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 it for 15 min on the steam bath.
3. Add 25 mL 2.5 percent ammonium molybdate and 20 percent NH_4NO_3 solution. Stir the solution frequently while heating for an additional 15 min. Let the solution stand at room temperature overnight.

   Note: The heating in steps 2 and 3 is necessary to ensure the complete precipitation of ammonium phosphomolybdate.
4. Prewash a 7-cm Whatman No. 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 the inside of the beaker twice with the wash solution of NH_4NO_3 in 1 percent HNO_3 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 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 washings to the filter. Dissolve any yellow precipitate left on the paper with small portions of NH_4OH; then wash the paper five times and discard. The final volume of the NH_4OH should not exceed 25 mL.

   Note: Before its determination, P is separated from diverse ions by precipitating it as ammonium phosphomolybdate. If separation is not done (1) colored ions (Fe, Cr) interfere with the absorbance, (2)

F decreases the intensity of the color by forming a complex with Mo, and (3) SiO_2 forms a colored complex with the reagent.

7. Pipet 5 mL HNO_3, 10 mL 0.25 percent ammonium vanadate solution, and 20 mL 5 percent ammonium molybdate in that order. Dilute it to volume (100 mL) and mix. Allow it to stand for 30 min. Measure it at 460 nm in a 1-cm cell against distilled H_2O. Read the vanadium molybdophosphate complex (Maxwell, 1968, p. 392).

Standards (P_2O_5):

$$\frac{1.00 \text{ mg}}{\text{mL}} \times \frac{x \text{ mL}}{100 \text{ mL}} = 0.001 \times x \text{ percent } P_2O_5,$$

where $x = 0.5$, 1.0, 2.0, and 4.0.

Add 5 mL concentrated HNO_3 to each and dilute it to 50 mL with H_2O. Pipet into each flask 10 mL ammonium vanadate and 20 mL ammonium molybdate (5 percent). Make up a reagent blank with the above concentration of reagents in a 100-mL volumetric flask. Dilute each solution to 100 mL. Mix and allow to stand 30 min. Measure at 460 nm in a 1-cm cell against distilled water.

Calculation:

Because the sample concentration is 0.0025 g/mL,

$$\frac{1.00 \text{ g}}{100 \text{ mL}} \times \frac{25 \text{ mL}}{100 \text{ mL}} = \frac{0.0025 \text{ g}}{\text{mL}}, \text{ the sample dilution factor is 400.}$$

The absorbance factor for each standard is $\frac{\text{percent } P_2O_5}{\text{Abs.}}$

The percent P_2O_5 in the sample is calculated by multiplying its absorbance by the average of all the absorbance factors obtained from the standards and by the sample dilution factor (above).

DETERMINATION OF SODIUM AND POTASSIUM USING THE IL 443 FLAME PHOTOMETER

Decomposition

1. Weigh 0.2500 g sample and transfer it to a 100-mL Teflon beaker. Wet sample with a small amount of distilled H_2O. Add 10 mL HF and 5 mL $HClO_4$.
2. Digest it overnight (covered) in a boiling H_2O bath.

3. Remove the cover and heat it to fume strongly for 10 min.
4. Cool, dilute with distilled H_2O, and transfer it to a 250-mL volumetric flask. Pipet 25 mL 2,000 ppm Li_2O and fill it to the 250-mL mark with H_2O.
5. A blank containing reagants only should be run along with the samples.

Note: These solutions cannot be used with the original equipment of the IL 443, specifically the plastic atomizer assembly, because the 2 percent $HClO_4$ attacks the plastic well. The accessory assembly must be used.

Recrystallization of Sodium and Potassium Chloride

1. Prepare a saturated solution of the salts.
2. Filter the solution through a Whatman No. 40 filter paper.
3. Reprecipitate it with HCl.
4. Filter the solution through a (coarse- or medium-) sintered funnel (Buchner flask).
5. Dry it overnight at 110°C.
6. Pulverize it by using a mortar and pestle.
7. Transfer the solution to a Vycor crucible and heat it in a muffle furnace at 600°C. to drive off all trapped H_2O (3 hr).

Working Standards

From 1,000 ppm stock solution of each Na_2O and K_2O standard:

Milliliter	Concentration Na_2O+K_2O (ppm)	Percent (equivalent to sample percent) 0.25 g diluted to 250 mL
0.0	0	Blank used to zero the IL 443.
1.0	4	.4 (used to calibrate the IL 443).
2.0	8	.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

To the working standards, add 25 mL 2,000 ppm Li_2O and 5 mL $HClO_4$. Fill the flask to the 250-mL mark with distilled H_2O and transfer it to a tightly capped polyethylene bottle.

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.

$$x = \left[\left(\frac{x_2 - x_1}{y_2 - y_1} \right) \times (y - y_1) + x_1 \right]$$

Calculation:

In general,

$$\text{percent } M_2O = \frac{x}{10^6} \times \text{volume} \times \frac{100}{\text{Sample wt.}}.$$

For a 0.25-g sample diluted to 250 mL,

$$\text{percent } M_2O = \frac{x\ \mu g}{mL} \times \frac{1}{10^6} \times 250 \text{ mL} \times \frac{100}{0.25 \text{ g}} = \frac{x}{10}.$$

Calculation by interpolation is recommended.

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 dried sodium tungstate flux to the Penfield tube through an elongated stem open bulb-top funnel. Mix the sample and flux it by rotating the closed bulb end of the Penfield tube. Run a blank with the flux only. Add the capillary plug to the open end of the tube. Put the tube through the ice-bath apparatus (figs. 5, 6).
2. Decompose the sample (mixed with the flux) by heating it slowly at first with a Meker burner for 10 min and decompose the blanks by heating them for 5 min. Keep rotating the tube to prevent caking on one side of the bulb.
3. Use an oxypropane torch to heat the area just below the bulb area of the Penfield tube to sever the bulb containing the decomposed sample from the tube. Allow it to cool at least 1 min. Remove it from the ice-bath apparatus. Remove the capillary plug.

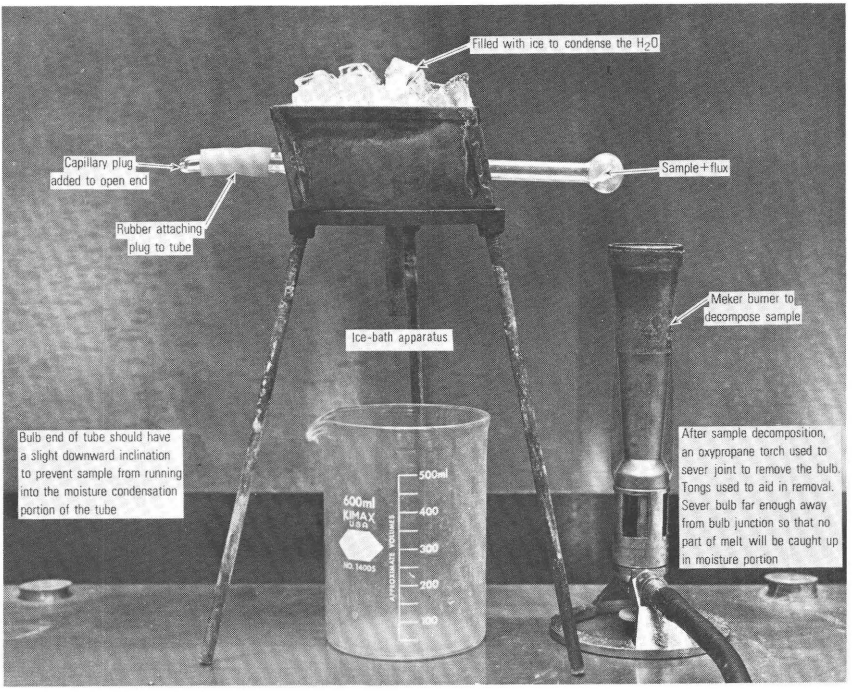


FIGURE 5.—Apparatus for the Penfield method of determining total H_2O.

4. Add the cork stopper to the open end of the tube to prevent moisture from escaping. Put the tube next to the balance for 20 to 30 min so that the tube reaches equilibrium. Weigh the tube without the cork to obtain the weight of the tube plus moisture.
5. Heat the uncorked tube at 110°C. in an oven a minimum of 2 hr to remove moisture.
6. Put the tube in a desiccator for 30 min and weigh it to obtain the weight of the tube minus moisture.

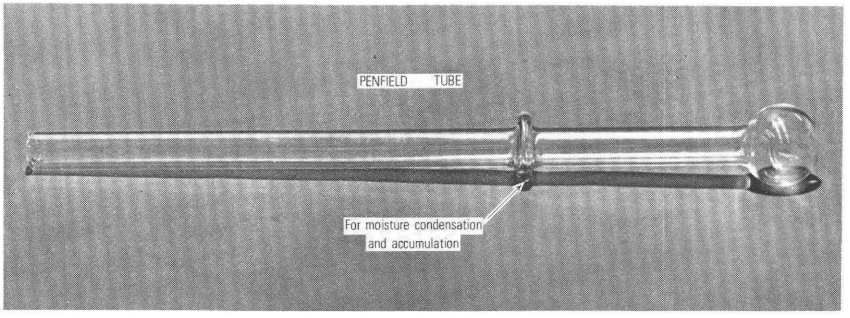
Calculation:

$$\text{percent total } H_2O = [(\text{weight of the tube} + \text{moisture}) - (\text{weight of the tube} - \text{moisture}) - \text{blank}] \times 100.$$

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

THE DETERMINATION OF H_2O^+ BY AN ELEMENTAL ANALYZER

The H_2O^+ contents of silicate rocks can be determined in a much simpler fashion than the Penfield method with an elemental analyzer.



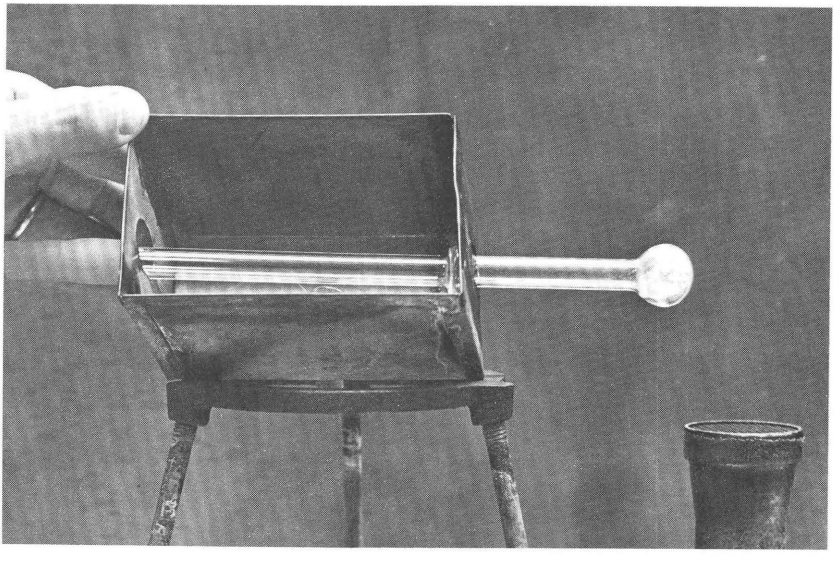


FIGURE 6.—Penfield tube.

The Rock Analysis Project, USGS, Reston, Va., employs the Perkin-Elmer Model 240 (fig. 7) and the Model 240B (automated) (fig. 8) C,H,N Elemental Analyzer. C, H, and N contents are analyzed by detecting and measuring their combustion products, CO_2, H_2O, and N. The combustion products are then analyzed automatically in a self-integrating, steady-state, thermal conductivity analyzer. Results are recorded in a bar-graph form on a 0- to 1-mv recorder. A pure O_2 supply is required for sample combustion, and He is used to carry the combustion products from the combustion train through the analytical system to the atmosphere. Three pairs of thermal conductivity cells, in series, are used to detect H_2O, CO_2, and N. For H_2O, a magnesium perchlorate trap between the first pair of cells absorbs H_2O from the gas mixture

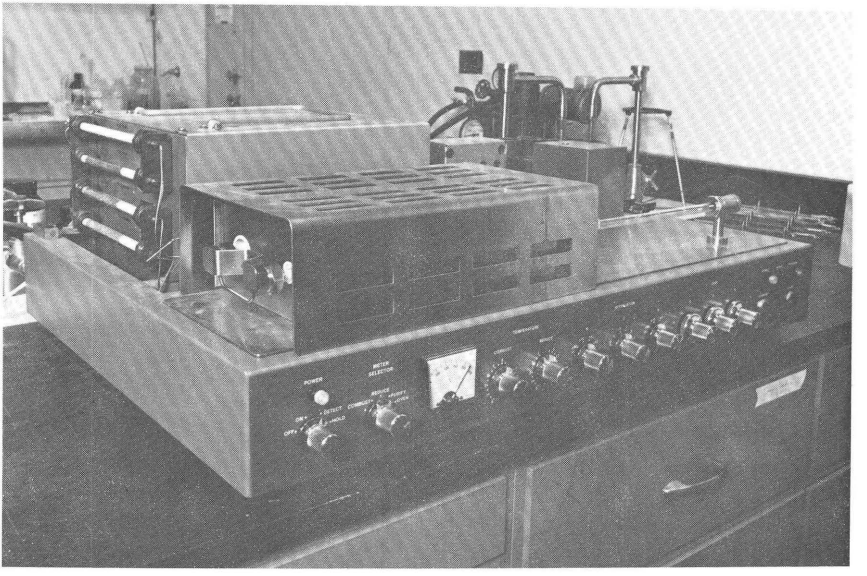


FIGURE 7.—PE Elemental Analyzer, Model 240.

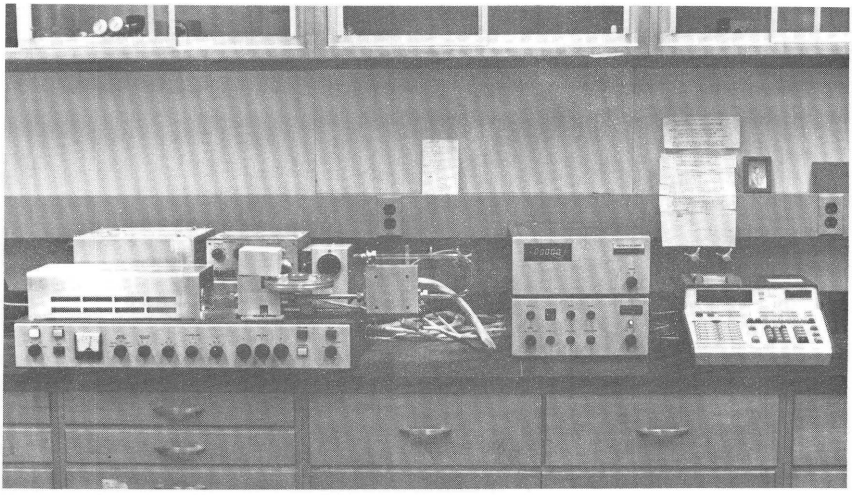


FIGURE 8.—PE Elemental Analyzer, Model 240B, with autoanalyzer.

before it enters the second cell so that the signal obtained is proportional to the amount of H_2O removed. Analysis time is approximately 13 min (Perkin-Elmer Corporation, 1974).

Samples to be determined for H_2O^+ are dried overnight in an oven at 105° to 110°C. If the drying step is not undertaken, some of the

hygroscopic H_2O may be removed by the He passing over the sample prior to combustion, and the remaining H_2O^- may be included in the determination of H_2O^+. Also, the determination of total H_2O may prove to yield erroneous data due to the loss of some H_2O^-. Therefore, it is best to remove all the H_2O^- by drying in an oven to determine the H_2O^+ on the sample. A comparison of total H_2O determined by the classical Penfield method and the sum of H_2O^+ determined by the elemental analyzer and H_2O^- removed at 105°C. is shown in table 4. Table 5 shows a comparison between the recommended H_2O^+ values and those obtained on the Model 240 and Model 240B Elemental Analyzers. The sample sizes ranged from 15 to 20 mg and were weighed on a microbalance (fig. 9). It is important to note that if there is a large amount of H_2O^- in the sample, an appropriate correction has to be made for the sample weight taken in the H_2O^+ determination.

GRAVIMETRIC DETERMINATION OF CARBON DIOXIDE BY ACID EVOLUTION

Principle of method:

Air carries the CO_2 liberated by the addition of acid through a series of absorbents[1] 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.

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

1. Replace the "weighed absorbers" with a bridge.
2. Open all valves except the condenser valve and vacuum valve.
3. Start H_2O running through the condenser.
4. With the aid of a powder funnel, add 5.0000 g silicate sample (or 1.0000 g carbonate sample) to the generating flask. Wash the powder adhering to the funnel into the flask and adjust the volume of water in the flask to 25 mL.
5. Open the vacuum valve slowly to start a stream of air through the system (fig. 10). Observe the rate of flow at the H_2SO_4 bubbler. Swirl the flask to make a slurry of the powder. Put the flask

[1]Absorbents:

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

TABLE 4.—*Comparison of Penfield method and elemental analyzer*

[From table 1, Skinner and others (1981, p. 4]

Unknown sample No.	Rock type	(1) H_2O^-	(2) H_2O^+ by elemental analyzer	(3) Total H_2O Col (1)+ Col (2)	Total H_2O Penfield method
1	Basalt with biotite[1] ----	0.17	0.86	1.03	1.01, 1.01
2	Basalt ------	.75	2.46, 2.46, 2.58	3.21, 3.21, 3.33	3.31, 3.25, 3.35, 3.34
3	Biotite[1] -----	.10	3.88, 3.84	3.98, 3.94	3.66, 3.99, 4.10
4	PCC-1 -----	.33	4.78, 4.90, 4.69	5.11, 5.23, 5.02	5.11, 5.15, 5.16
5	Granite -----	.39	.86, .86, .93	1.25, 1.25, 1.32	1.35, 1.36
6	-----do-----	.01	.17, .16, .18	.18, .17, .19	.17, .20,
7	____[2] with pyroxene --	.05	1.31, 1.37, 1.37	1.36, 1.42, 1.42	1.61, 1.62
8	Dacite ------	.25	1.03, 1.02, 1.06	1.28, 1.27, 1.31	1.30
9	Hornblende gabbro ----	.05	.56, .55, .57	.61, .60, .62	.73
10	Rhyolite ----	.02	.29, .29, .30	.31, .31, .32	.60

[1]Vandadium pentoxide used as a flux to ensure total decomposition of the sample.

[2]Rock name not given.

TABLE 5.—*Comparison of recommended H_2O^+ values and those obtained on Model 240 and Model 240B elemental analyzers*

[Sample sizes ranged from 15 to 20 mg. Project Monthly Report — January 21 to February 20, 1979; project no. 9770-00446; Rock Analysis Project, Reston, project leader, Floyd W. Brown]

USGS standard rocks	H_2O^+ recommended	Averages obtained using Model 240	Values obtained with Model 240B with autosampler	Averages for Model 240B	Percent relative deviation
PCC-1---	4.70	4.72(4)	4.74, 4.75, 4.57, 4.63, 4.71, 4.68	4.68	1.1
BCR-1---	.77	.81(5)	.73, .77, .78, –, –, –	.76	2.6
SDC-1---	1.50	1.74(3)	1.77, 1.81, 1.81, 1.78, 1.80, –	1.79	.89
STM-1 --	1.40	1.52(3)	1.50, 1.54, 1.57, 1.53, 1.50, –	1.53	1.4
BHVO-1-	.19	.14(2)	.11, .14, .13, .10, –, –	.12	12.5
G-1-----	.34	.30(2)	.31, .32, .32, .33, –, –	.32	1.6

in place on the apparatus. Continue drawing the air through the system for 10 min at the rate of three bubbles per second.

6. During the 10-min period, weigh the CO_2-absorption tube. Open the stopcock of each tube momentarily before placing it on the balance pan.
7. Close the vacuum valve and valves adjacent to the bridge and replace the bridge with the CO_2 absorber. Open all the valves and

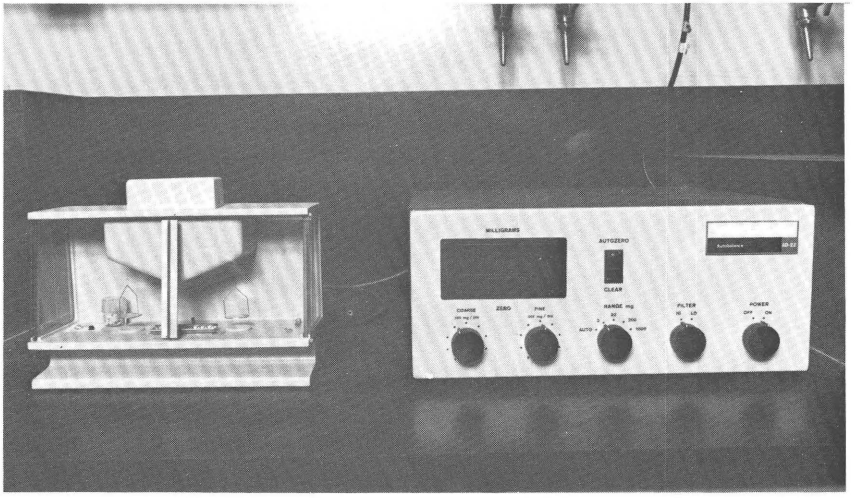


FIGURE 9.—Electromagnetic Ultramicrobalance, Model PE AD2Z, used for weighing H_2O samples.

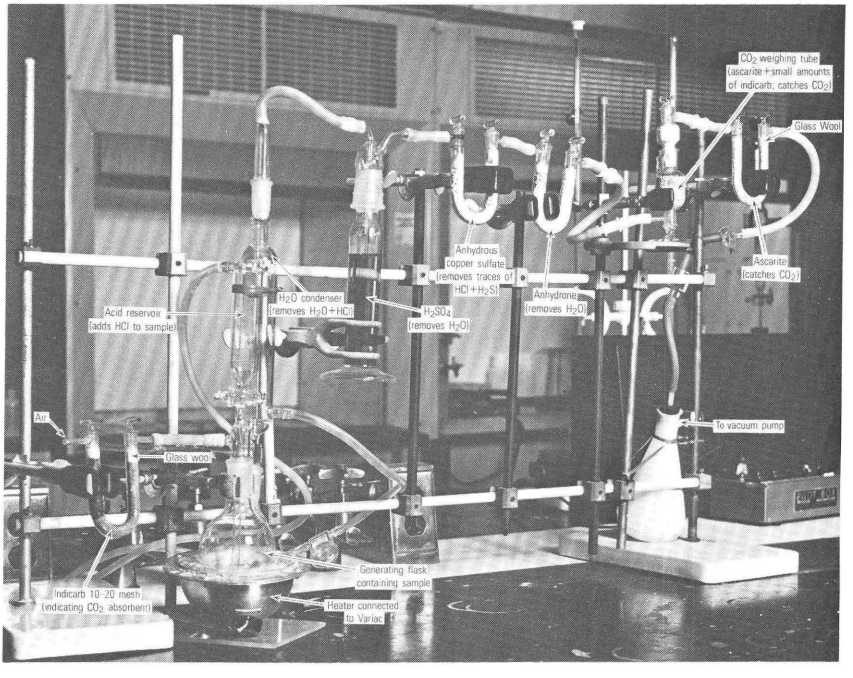


FIGURE 10.—Apparatus for gravimetric determination of carbon dioxide by acid evolution.

adjust the 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 the vacuum valve. Check for leaks indicated by bubbles or H_2SO_4 rising in the tube. If there is no leak, open the 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 the vacuum valve.
10. Heat the H_2O in the generating flask almost to boiling. 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 airflow and bring the solution in the flask to a gentle boil. Continue boiling gently for 2 min. Slow the air flow to about three bubbles per second and continue drawing the air through the system at this rate for 20 min.
12. Close the vacuum valve and valves adjacent to CO_2-absorption tube (containing CO_2 sample) and immediately open the generator valve to relieve the pressure; close the absorbent-tube valve. Remove the absorption tube (CO_2 weighing tube in fig. 10) from the system and put it in the balance room.
13. After 1 hr, weigh it, opening the valve of the tube momentarily before placing it on the balance pan.
14. Clean the generator flask using H_2O, wash solution (5 percent NH_4OH), and brom cresol purple indicator to make sure all the acid is rinsed out.

Calculation:

wt. absorption tube (g) after acid evolution − wt. of absorption tube (g) before acid evolution ÷ sample wt. (g) × 100 = percent CO_2.

DETERMINATION OF INORGANIC CARBON WITH THE CO_2 COULOMETER

A sample is treated with acid in a CO_2 coulometer apparatus (fig. 11). The subsequently evolved CO_2 is transferred to the CO_2 coulometer cell which is filled with an aqueous medium containing ethanolamine and a colorimetric indicator, thymolphthalein. When gas is passed through the solution, CO_2 is quantitatively absorbed and is converted to a strong titratable acid, hydroxyethylcarbamic acid by the ethanolamine. The coulometer electrically generates base to titrate the released acid to a photometric end point. Electronic scaling within the coulometer converts the number of coulombs to a digital readout of micrograms of C.

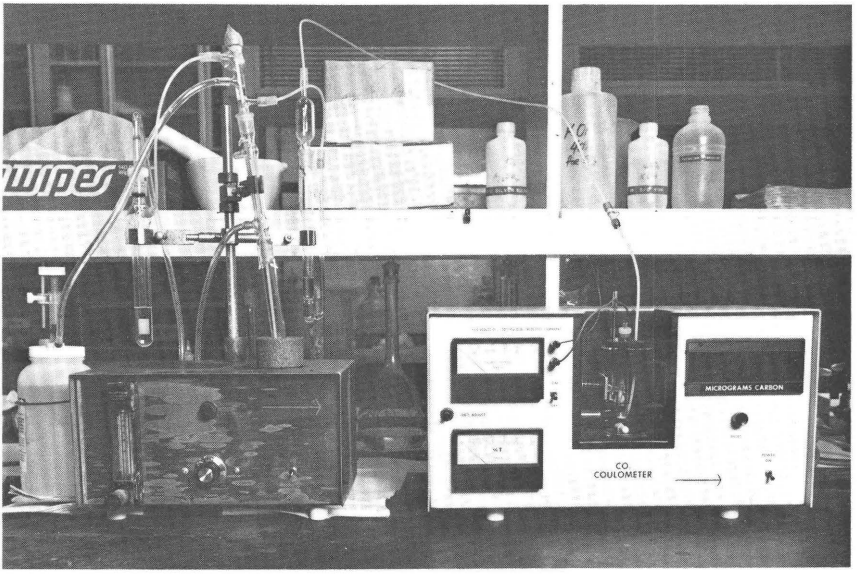


FIGURE 11.—Coulometer apparatus for determining carbon dioxide.

The coulometric process is not an empirical technique and gives results in basic theoretical units as does the classic gravimetric method. Therefore, chemical or sample calibration is not required as in other instrumental methods such as infrared and thermal conductivity (Coulometrics, Inc., 1978, p. 1).

Norton and Engleman (1980) have adopted the CO_2 coulometer method in the USGS Denver laboratory to replace the standard reference method based on gravimetric analysis. They claim excellent agreement and reproducibility (table 6) for all samples in the range of 0.00 to 2.00 percent CO_2. They studied sample dispersion, rate of flow of carrier gas, rate of heating, and reproducibility of end point. Norton and Engleman use the following sample sizes: 1 g powdered sample for the 0- to 1-percent range of CO_2; 0.2 g for the 1- to 5-percent range; 0.1 g for the 5- to 10-percent range; and 0.02 g for the range greater than 10 percent. Samples in the range of 0.2 to 1 g are weighed on an analytical balance and transferred to the sample tube using a powder funnel. Samples weighing 0.1 g and less are weighed on a microbalance in a porcelain boat, and the container with the sample is transferred to the sample tube. Interferences from H_2S, SO_2, NO_2, Cl_2, and halogen acids are reported to be absorbed by the silver sulfate solution that Norton and Engleman selected.

TABLE 6.—*Comparison of carbon dioxide data between the coulometric and gravimetric methods*
[From Norton and Engleman (1980), table 1]

Sample No.	Type	Coulometric method	Gravimetric method
D103336	Andesite	0.00, 0.00	0.00
W186955D	Tuff	.00	.00
W186957	------ do ------	.00	.00
W186758	------ do ------	.01	.00
D103921	Rhyolite	.00	.00
D103972	Basalt	.01, .01	.01
D104041	------ do ------	.01	.01
D104045	Andesite	.00	.01
D103937	Dolomite (?)	.01	.01
D103938	Gabbro	.01	.01
D103939	Websterite	.01	.01
D103932	Tholeite	.02, .02	.02
D102433	Basalt	.02, .02, .02, .02	.02
D103211	Granodiorite	.04, .04	.05
D103201	Gneiss	.09, .09	.09
D103619	Basalt	.13, .12, .13, .13	.15
D103275	Syenite	.19, .19	.20
D103997	Rhyolite	.25, .25	.25
D102715	Peridotite	.30, .31, .29, .29	.30
D103315	Basalt	.32, .33, .33, .33	.34
D102343	Spilite	2.01	2.02

Calculation:

$$\text{percent } CO_2 = \frac{CO_2\ (\mu g) - \text{blank}}{\text{Sample wt. (g)}} \times 10^{-4}$$

DETERMINATION OF TOTAL SULFUR

The S in most silicate rocks is very low (0.1 percent or less) and is usually in the form of a sulfide such as pyrite or pyrrhotite.

Procedure (Peck, 1964, p. 82):

1. Transfer 1.0000 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 S (see Hillebrand and others, 1953, p. 712–714). B. When S 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 provides a means for removing elements such as Fe and the alkaline earths but introduces a large amount of alkali salts into the solution.
3. Fuse at 1,100°C. in an electric furnace for 30 min, starting the furnace cold.
4. Remove the samples from the furnace, allow them to cool, heat the crucibles over the Meker for 30 sec, and allow crucibles 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 it on a steam bath for 30 min. Discard the acid and wash out the crucible. Weigh the 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. Cover the beaker and heat it on the steam bath overnight. Break up all lumps with a flat-ended stirring rod.
7. Filter through a 9-cm S&S Blue No. 589 filter paper into a 400-mL beaker. Wash the inside of the beaker three times with 1 percent Na_2CO_3 and transfer the washings 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 a dropper, add and stir in (1+1) HCl until the solution becomes yellow; then add 2 mL more (1+1) HCl.

   Note: The final solution should contain only a small excess of HCl

because the solubility of $BaSO_4$ increases as acid concentration increases (Maxwell, 1968, p. 236).

10. Cover it and heat it on a steam bath for 30 min and pipet dropwise 5 mL 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 $BaSO_4$ 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 No. 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 0.1 *M* silver nitrate to be sure that the filter paper is free of chlorides. Discard the filtrate.
13. Char off the paper in the weighed platinum crucible, keeping the crucible below red heat (550°C.).

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

14. When the paper has become completely charred, raise the temperature until the crucible is dull red and burn off the carbon. When the residue is white, ignite it at 900°C. for 15 min.
15. Remove the crucible from the furnace, cool, and add one drop of (1+1) H_2SO_4 and 2 mL HF. Heat it on hotplate until the H_2SO_4 is expelled. Ignite the crucible at 900°C. in an electric furnace for 15 min. Cool it in a desiccator and weigh it to constant weight by returning the crucible to the furnace, then to the desiccator, and reweighing.

    Note: The ignited residue is treated with HF and H_2SO_4 to remove any SiO_2 that was carried down with the precipitate.

Calculation:

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

DETERMINATION OF SULFUR USING A SULFUR ANALYZER

Our laboratory uses the LECO SC-132 (fig. 12) Sulfur Analyzer for the determination of S. In the classical scheme of silicate rock analysis, it is important to have reliable data in the range of 0.00 to 0.10 percent total S. The LECO SC-132 is currently operating reliably at these low levels (table 7) and is replacing the classical gravimetric $BaSO_4$ procedure.

Combustion of the samples takes place in an O_2 atmosphere where the S is oxidized to SO_2. Moisture and dust are removed by tubes containing quartz wool and anhydrone. Our laboratory uses tubes packed with anhydrone coarser than 20 mesh. Using only the coarser particles of anhydrone allows ease of gas flow through the tubes. The SO_2 gas is then measured by a solid-state infrared detector. The analysis time is about 120 sec. The accuracy is ± 1 percent of the S content, and the sensitivity is 0.001 percent (LECO Corporation, 1980, p. 3).

The procedure used in our laboratory for low-level S content in silicate rock samples is as follows. Before running samples, the instrument is calibrated with a low-level LECO coal (<1 percent S) standard, and blanks are run until the baseline of the SC-132 gives a consistent readout.

FIGURE 12.—LECO SC-132 Sulfur Analyzer.

1. Press the GAS key.
2. Weigh the 200-mg silicate rock sample.
3. Press the ENTER key to enter the sample weight.
4. Add three scoops (0.25 g each) of reagent-grade V_2O_5 flux and mix with the sample.
5. Add another scoop of V_2O_5 to cover the sample. The total amount of V_2O_5 flux is 1 g.
6. Press the ANALYZE key and wait 2 min before loading the boat containing the sample and flux into the furnace.
7. Load the furnace and press the ANALYZE key at the same time.

The operating temperature is 1,371°C. The 1 g of reagent-grade V_2O_5 flux we use contains about 10 ppm S. Therefore, because the total S recorded by the instrument includes S from both the 0.200-g sample and 1 g of flux, a blank correction of 50 (that is, five times the S content of V_2O_5) must be subtracted.

TABLE 7.—*Comparison of low-level sulfur using the sulfur analyzer (LECO) and gravimetric methods*
[Analyst—H. Kirschenbaum]

Sample	Percent sulfur	
	LECO	Gravimetric
1	0.005	0.00
2	.048	.04
3	< .005	.00
4	.015	.02
5	< .005	.00
6	.014	.012
7	.014	.02
8	.021	.012

REAGENTS

SILICA

1. Sodium carbonate, anhydrous powder.
2. Ethyl alcohol.
3. Hydrochloric acid (concentrated).
4. Hydrochloric acid (20 percent).
5. Hydrochloric acid (5 percent).
6. Sulfuric acid (1+1).
7. Hydrofluoric acid (concentrated).

R_2O_3 GROUP

1. Ammonium hydroxide. Add 500 mL distilled H_2O to a 1-L 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). Weight 0.1 g brom cresol purple. Stir it with distilled H_2O until it is dissolved and dilute to 100 mL volume.
3. Ammonium nitrate (2 percent). Weigh 20 g of NH_4NO_3 into a 2-L beaker, add distilled H_2O until it is dissolved and dilute it to 1,000 mL.
4. Hydrochloric acid (5 percent).
5. Hydrochloric acid (1+1).

REMOVAL OF MANGANESE

1. Zirconyl chloride (5 percent). Dissolve 25 g zirconyl chloride (octahydrate) in about 200 mL H_2O containing 5 mL 12 *N* HCl. Allow the solution to stand overnight. Filter it through a Whatman No. 42 filter paper into a 500-mL volumetric flask and dilute it to volume.
2. Ammonium persulfate, crystal.
3. Ammonium nitrate (2 percent). Weigh 20 g NH_4NO_3 into a 1-L beaker, add distilled H_2O until it is dissolved, and dilute it to 1,000 mL.

SILICA RESIDUE

1. "Baker Instra-Analyzed" Reagent Potassium Pyrosulfate Acid-Flux Grade (catalog No. 1-2963). The author specifically recommends this reagent for best results in the dissolution of the pyrosulfate fusion cake.
2. Sulfuric acid (1+1).
3. Sulfuric acid (1 percent). Dilute 10 mL H_2SO_4 to 1 L with distilled H_2O.

CALCIUM OXIDE

1. Oxalic acid (10 percent). Add 100 g oxalic acid to 900 mL hot distilled H_2O; let the solution stand overnight. Filter it through Whatman No. 42 filter paper and dilute it to 1 L.

2. Ammonium oxalate (0.1 percent). Dissolve 1 g ammonium oxalate in distilled water and dilute to 1 L.
3. Hydrochloric acid (20 percent).
4. Hydrochloric acid (5 percent).

MAGNESIUM OXIDE

1. Ammonium phosphate, dibasic (20 percent). Dissolve 200 g in 800 mL distilled H_2O. Let the solution stand overnight. Filter it through a Whatman No. 42 filter paper and dilute it to 1 L.
2. Ammonium hydroxide (5 percent).
3. Hydrochloric acid (5 percent).
4. Phosphoric acid (1+19).

TITANIUM DIOXIDE

Colorimetric determination of titanium dioxide:

1. Hydrogen peroxide (6 percent). Dilute 10 ml 30 percent H_2O_2 to 50 mL and transfer the solution to a polyethylene bottle with a tight-sealing cap. Make a fresh solution each month (Peck, 1964, p. 84).
2. Potassium pyrosulfate (20 percent). Dissolve 400 g potassium pyrosulfate in 1,800 mL H_2O. Let the solution stand overnight. Filter it through a Whatman No. 42 filter paper and dilute it to 2 L in a volumetric flask.
3. Stock titanium solution (1 mL=1 mg TiO_2). Transfer 1.013 g NBS (U.S. National Bureau of Standards) TiO_2 No. 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 the flask on a hotplate and stir it using a magnetic stirrer until it is dissolved (near boiling). The solution should become translucent. When the solution is cool, transfer it to a 1-L beaker containing 500 mL H_2O. Let the solution stand overnight; then filter it through a Whatman No. 42 filter paper into a 1-L volumetric flask. Wash the beaker and paper with 5 percent H_2SO_4. Dilute it to mark and mix it well.

TOTAL IRON OXIDE

1. Potassium dichromate (5 percent). Dissolve 5 g $K_2Cr_2O_7$ in 100 mL H_2O. Filter it through a Whatman No. 42 filter paper.

2. Sodium diphenylamine sulfonate (0.2 percent). Dissolve 0.2 g in 100 mL hot H_2O.
3. Potassium dichromate (0.06262 *N*). Add 1,000 mL H_2O to a 2-L volumetric flask. Weigh 6.141 g and transfer it to the flask. Swirl it until the $K_2Cr_2O_7$ dissolves. Dilute it to the 2-L mark and mix.

   Potassium dichromate (0.1 *N*). Weigh 4.9035 g $K_2Cr_2O_7$ for each liter of solution.

   For 2 L, weight 9.8070 g. Before use, dry $K_2Cr_2O_7$ for 2 hr at 110°C.
4. Silver (granular). Granular Ag is needed for the Walden Silver Reductor. For instructions on loading the reductor, see Peck (1964, p. 85).
5. Ammonium chloride (15 percent). Dissolve 150 g ammonium chloride in 500 mL distilled H_2O and dilute it to 1 L.

FERROUS IRON

1. Boric acid solution, saturated (5 percent). Dissolve it by stirring 100 g boric acid in 1 L hot H_2O; cool and dilute it to 2 L.
2. Sodium diphenylamine sulfonate (0.2 percent). Dissolve 0.2 g in 100 mL hot H_2O.
3. Potassium dichromate (0.06262 *N*). See the 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 N, cool, transfer it to a 500-mL volumetric flask, and make it to volume. To make the working MnO standard at 0.1 mg/mL, add 10 mL stock solution to a 100-mL volumetric flask, add 2 mL concentrated HNO_3, and dilute it 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-L volumetric flask and dilute it to 1 L.
3. Phosphoric acid (1+1).

PHOSPHORUS PENTOXIDE

1. Ammonium nitrate (50 percent). Dissolve 1,000 g NH_4NO_3 in 1 L H_2O while heating the solution. Dilute it to 2 L (filter if solution is not clear).

2. Ammonium molybdate (2.5 percent) and ammonium nitrate (20 percent). 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 it to 200 mL.
3. Ammonium nitrate (2 percent) in nitric acid (1 percent). Dissolve 20 g NH_4NO_3 in 1 L 1 percent HNO_3 (10 mL HNO_3/1 L H_2O).
4. Ammonium molybdate (5 percent). Dissolve 50 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 500 mL warm H_2O. Let it stand overnight. Filter it through Whatman No. 42 filter paper. Dilute it to 1 L and store it in a polyethylene bottle.
5. Ammonium vanadate (0.25 percent). Dissolve 2.5 g NH_4VO_3 in 500 mL hot H_2O, cool, and add 20 mL concentrated HNO_3. Let it stand for several hours. Filter it if it is not clear and dilute it to 1 L. Store it in glass bottle.
6. Standard phosphate solution 1 mg/mL P_2O_5. Dissolve 0.959 g of KH_2PO_4 (recrystallized and dried at 110°C.) in H_2O and dilute it to 500 mL. Store it in a tightly capped polyethylene bottle.

SODIUM AND POTASSIUM OXIDES

Standards (Stock Solutions):

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

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

Li_2O (20,000 ppm=20.0 mg/mL). In a 1-L volumetric flask, dissolve 56.76 g LiCl. Store it in a tightly capped 2-L polyethylene bottle.

Working Li_2O internal standard.

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

(Pipet 25 mL of 2,000 ppm standard into each of the 250-mL flasks.)

TOTAL H_2O (PENFIELD METHOD)

Flux. Sodium tungstate, anhydrous powder, $Na_2WO_4\cdot 2H_2O$. Heat the

sodium tungstate and anhydrous powder at 180°C. in an oven overnight to drive out moisture. Keep the flux in the oven at 110°C. when not in use to prevent moisture buildup.

TOTAL SULFUR

1. Barium chloride (10 percent). Dissolve 50 g barium chloride dihydrate in 400 mL H_2O. Let the solution stand overnight. Filter it and dilute it 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 it until dissolved.
3. Silver nitrate (0.1 *M*). Dissolve 3.4 g of silver nitrate in 200 mL of distilled H_2O.

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