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## RAPID ANALYSIS OF SILICATE ROCKS

By Leonard Shapiro and W. W. Brannock



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## ABSTRACT

Rapid methods are described for the determination of the major constituents in silicate rocks.  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are determined spectrophotometrically on aliquots of a solution prepared by fusion of the sample with  $\text{NaOH}$ . A molybdenum blue method is used for  $\text{SiO}_2$  and ferron is used in the determination of  $\text{Al}_2\text{O}_3$ . A second solution prepared by digestion of the sample with  $\text{HF}$  and  $\text{H}_2\text{SO}_4$  is used for the determination of  $\text{TiO}_2$ , total iron,  $\text{MnO}$  and  $\text{P}_2\text{O}_5$ , by spectrophotometric methods.  $\text{TiO}_2$  is determined as the peroxide, total iron as ferric chloride,  $\text{MnO}$  as permanganate, and  $\text{P}_2\text{O}_5$  as molybdivanadophosphoric acid. Additional aliquots of the solution prepared after digestion with  $\text{HF}$  plus  $\text{H}_2\text{SO}_4$  are used for the determination of  $\text{CaO}$  and  $\text{MgO}$  by titration methods, using versene. Another aliquot of the same solution is used for the determination of  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  by flame photometer.  $\text{FeO}$  is determined by titration with  $\text{K}_2\text{Cr}_2\text{O}_7$  after decomposition of the sample with  $\text{HF}$  and  $\text{H}_2\text{SO}_4$ . Loss on ignition is determined so that a summation may be obtained and used as an aid in checking the reliability of the results. A schedule for rapid complete analysis of silicate rocks in sets of eight samples is given. Results of rapid analysis of twelve synthetic mixtures prepared from National Bureau of Standards standard samples are compared with values based on those reported by the Bureau of Standards.



# RAPID ANALYSIS OF SILICATE ROCKS

## CONTENTS

|  | Page |   | Page |
|--|------|---|------|
| Abstract . . . . .                                 | ii   | Determination of $TiO_2$ . . . . .  | 9    |
| Introduction . . . . .                             | 2    | Determination of $F_2O_5$ . . . . .   | 10   |
| Special apparatus . . . . .                        | 3    | Determination of $MnO$ . . . . .  | 10   |
| Spectrophotometer . . . . .                        | 3    | Determination of $CaO$ . . . . .  | 11   |
| Flame photometer . . . . .                         | 3    | Determination of $MgO$ . . . . .  | 11   |
| Preparation of sample solutions . . . . .          | 5    | Determination of $K_2O$ and $Na_2O$ . . . . .                                     | 12   |
| Discussion . . . . .                               | 5    | Determination of $FeO$ . . . . .  | 13   |
| Reagents . . . . .                                 | 5    | Determination of loss on ignition . . . . .                                       | 14   |
| Solution A . . . . .                               | 7    | Experimental results . . . . .  | 14   |
| Solution B . . . . .                               | 7    | Suggested schedule for rapid analysis of<br>eight silicate rock samples . . . . . | 16   |
| Determination of $SiO_2$ . . . . .                 | 7    | References cited . . . . .  | 17   |
| Determination of $Al_2O_3$ . . . . .               | 8    |   |      |
| Determination of total iron as $Fe_2O_3$ . . . . . | 9    |   |      |

## ILLUSTRATIONS

|   | Page |
|---|------|
| Figure 1. Flow diagram for rapid analysis of silicate rocks . . . . . | 2    |
| 2. Test tube adaptor for the spectrophotometer . . . . .              | 4    |
| 3. Special glass atomizer for the flame photometer . . . . .          | 6    |

## TABLES

|  | Page |
|--|------|
| Table 1. Conversion of percent transmission (T) to absorbance (A) . . . . .                                    | 5    |
| 2. Percentage composition of National Bureau of Standards standard<br>samples in the mixture samples . . . . . | 14   |
| 3. Results obtained for National Bureau of Standards mixture samples . . . . .                                 | 15   |
| 4. Concentration ranges covered and deviations for National Bureau of Standards mixture<br>samples . . . . .   | 16   |

## INTRODUCTION

It is well known that chemical analysis of silicate rocks by classical methods is costly and time consuming. In order to increase the applicability and use of chemical analyses of silicate rocks, a program of research aimed at reducing the cost and the time required for analysis is being carried out in the Washington analytical laboratory of the U. S. Geological Survey.

As a first approach to this problem we have selected and developed procedures for the major constituents,  $SiO_2$ ,  $Al_2O_3$ , total iron as  $Fe_2O_3$ ,  $TiO_2$ ,  $MnO$ ,  $F_2O_5$ ,  $CaO$ ,  $MgO$ ,  $Na_2O$ , and  $K_2O$ . (See fig. 1.) The accuracy and precision of the results obtained by the methods described are less than that which would be expected to be obtained by competent analysts carefully using the classical or conventional methods.

Nevertheless, the rapid methods of analysis should be applicable to the analysis of a large number of samples which would ordinarily be analyzed by classical methods.

The methods described in this paper are rapid, simple, direct, and are less subjective than conventional methods. For these reasons it is easy to establish the reliability of the results obtained.

The rapid procedures can be easily learned and carried out by personnel with considerably less training than that required for analysis by classical methods. It is practicable for one person using the schedule suggested below, to analyze approximately sixteen silicate rock samples each five day week.

For the sake of simplicity, the procedures for preparation of sample solutions and for the various

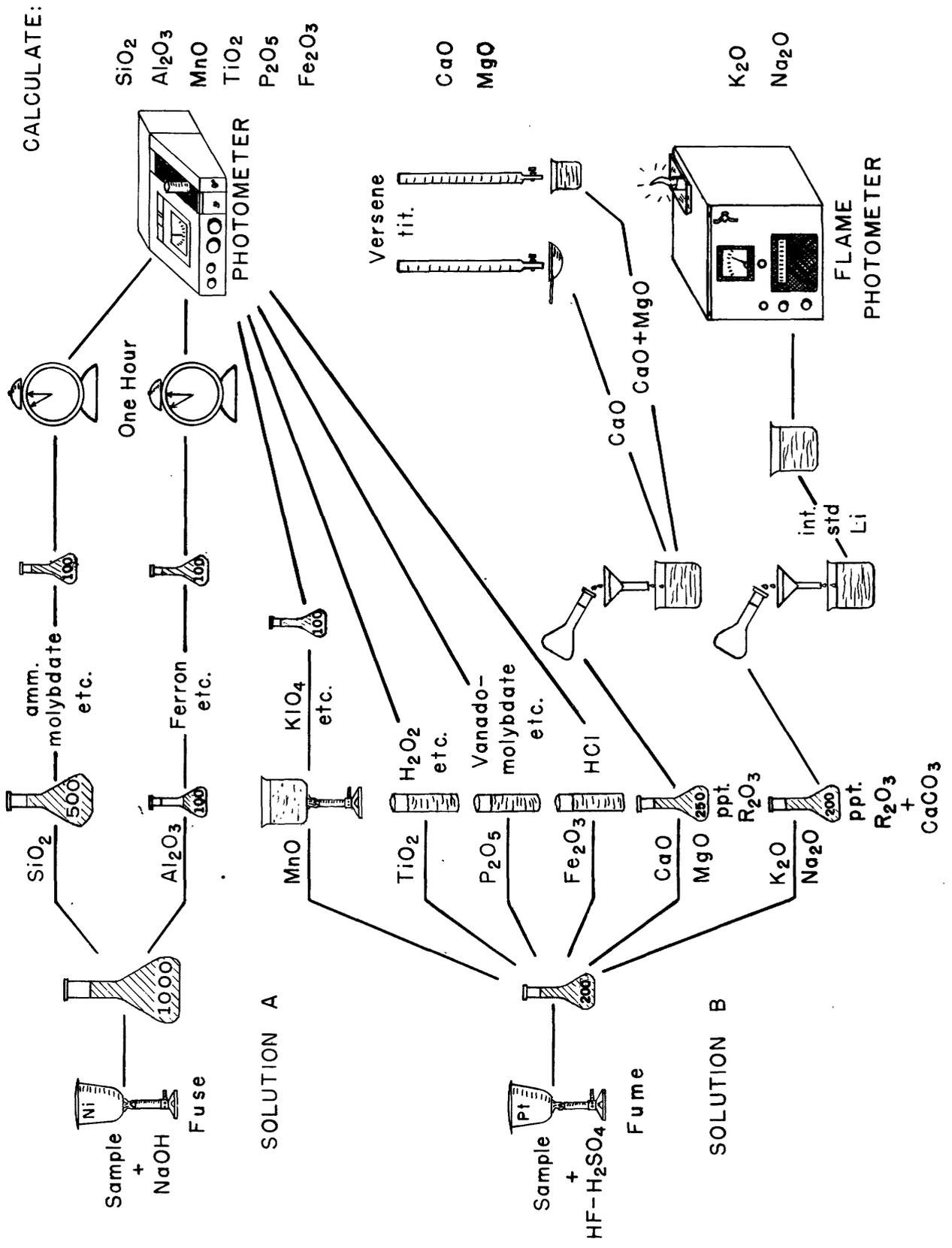


Figure 1.--Flow diagram for rapid analysis of silicate rocks.

determinations describe the analysis of a single sample. Large numbers of samples can be most efficiently analyzed in batches of six to twelve samples at a time. The actual number of samples per batch should be based on the amount of apparatus available. Unless specific instruction to the contrary is given, the operation described for each step in a procedure should be completed for all the samples in a batch before proceeding with subsequent steps.

### SPECIAL APPARATUS

Most of the apparatus used in the procedures described in this paper is usually available in laboratories making silicate rock analyses. In addition to commonplace items such as beakers, volumetric flasks, pyrex bottles, burets, pipets, funnels, analytical balance, and filter paper, several more specialized types of apparatus are needed, together with the spectrophotometer and flame photometer described below.

In the preparation of solutions for determination of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , the samples are fused in covered nickel crucibles of approximately 75 ml capacity.

In some procedures the use of polyethylene bottles or vycor beakers or flasks is advised for storing solutions, to avoid contamination which might result from use of ordinary glassware.

#### Spectrophotometer

All spectrophotometric measurements were made with a Beckman Model B Spectrophotometer. Nevertheless the methods can be readily adapted to use other good quality spectrophotometers. Only one phototube was employed for the measurements, all of which were made in the range, 320 to 700 m  $\mu$ .

To insure the stability of the source of illumination a storage battery is used. The amplifier circuit of the instrument is fed by a -c line current.

As it is desirable to measure colors of low intensity accurately, test tubes having a diameter of about 27.5 mm are used instead of tubes of smaller diameter which are more commonly used. The simple adaptor shown in figure 2 was built to support these tubes in the instrument. Care must be taken to insure that the adaptor is rigidly fixed in the spectrophotometer, as slight shifts in position cause large changes in the fraction of incident light reflected from the test-tube surface. The comparison tubes should be carefully matched using a colored solution, and marked so that they can always be placed in the carrier in the same position. A commercial adaptor which accommodates tubes of smaller diameter may be purchased for the instrument, but the adaptor described here in which comparison tubes with longer path length can be used is more satisfactory.

The spectrophotometer is operated as follows: Insert a comparison tube containing a reference blank solution in the tube adaptor. Set the wave-length selector to the desired wave length, the sensitivity switch to position 1, and open the phototube shutter. Adjust the meter to read 100 percent transmittance by varying the slit width. Then replace the comparison tube containing the reference-blank solution with one containing the sample solution. Open the shutter and observe the meter reading. If the reading is less than

31.5 percent, turn the sensitivity switch to the position which gives a reading greater than 31.5 percent and record the meter reading and sensitivity setting. Should the reading still be less than 31.5 percent after turning the sensitivity switch to position 4, the reading at position 4 is used.

For those determinations in which the spectrophotometer is used, percent transmittance readings are first converted to absorbance by interpolation of the values in table 1 which was derived by use of the equation:  $A = 2 - \log T$ . All calculations are then made with the absorbance values. Absorbance values are easier to use than percent transmittance values because, when Beers' Law is followed, the absorbance is proportional to the concentration of the constituent imparting the color to the solution being analyzed and percent transmittance is not.

#### Flame Photometer

The procedures described for the determination of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  have been worked out specifically for the Perkin-Elmer Model 52C flame photometer. Other types of flame photometers can be substituted for this instrument if the characteristics of the particular instruments are studied and specific procedures are devised.

When the Model 52C flame photometer is used it is set up as suggested in the instruction manual, except for several changes. A special glass atomizer shown in figure 3 is substituted for the atomizer furnished by the manufacturer and two pressure regulators are installed in series between the propane supply and the instrument.

The capillary aspirator type atomizer shown has certain advantages over the funnel-type atomizer when used with the flame photometer in the determination of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in silicate rocks. It atomizes solution into the flame at the relatively slow fixed rate of approximately 4 ml per minute so that a maximum of approximately 10 ml of each sample and standard solution is consumed for each complete determination. This atomizer draws solution up through the capillary intake tube from a small beaker. When the beaker is withdrawn the capillary tube empties in a moment. The outside of the tube can then be wiped clean with a piece of lintless tissue, another solution can be passed in, and almost immediately the capillary is flushed clean of the previous solution. There is no waiting for solutions to clear, and deliberate rinsing and flushing, needed in using the funnel type of atomizer, is unnecessary.

Two pressure regulators, installed in the gas line, give a more steady burner flame by reducing fluctuations in the gas pressure.

To start operation of the flame photometer for the determinations  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , first turn the electric switch on the panel of the instrument to the "on" position. Then adjust the air pressure to 10 lbs. in<sup>2</sup>, open the main valve on the propane tank, set the gas regulator which is nearest the main valve to 10 lbs in<sup>2</sup>, and allow propane to pass to the burner by opening the valve on the second regulator. Light the burner and adjust the pressure, using the second gas valve, so that the flame is steady and blue with small sharply

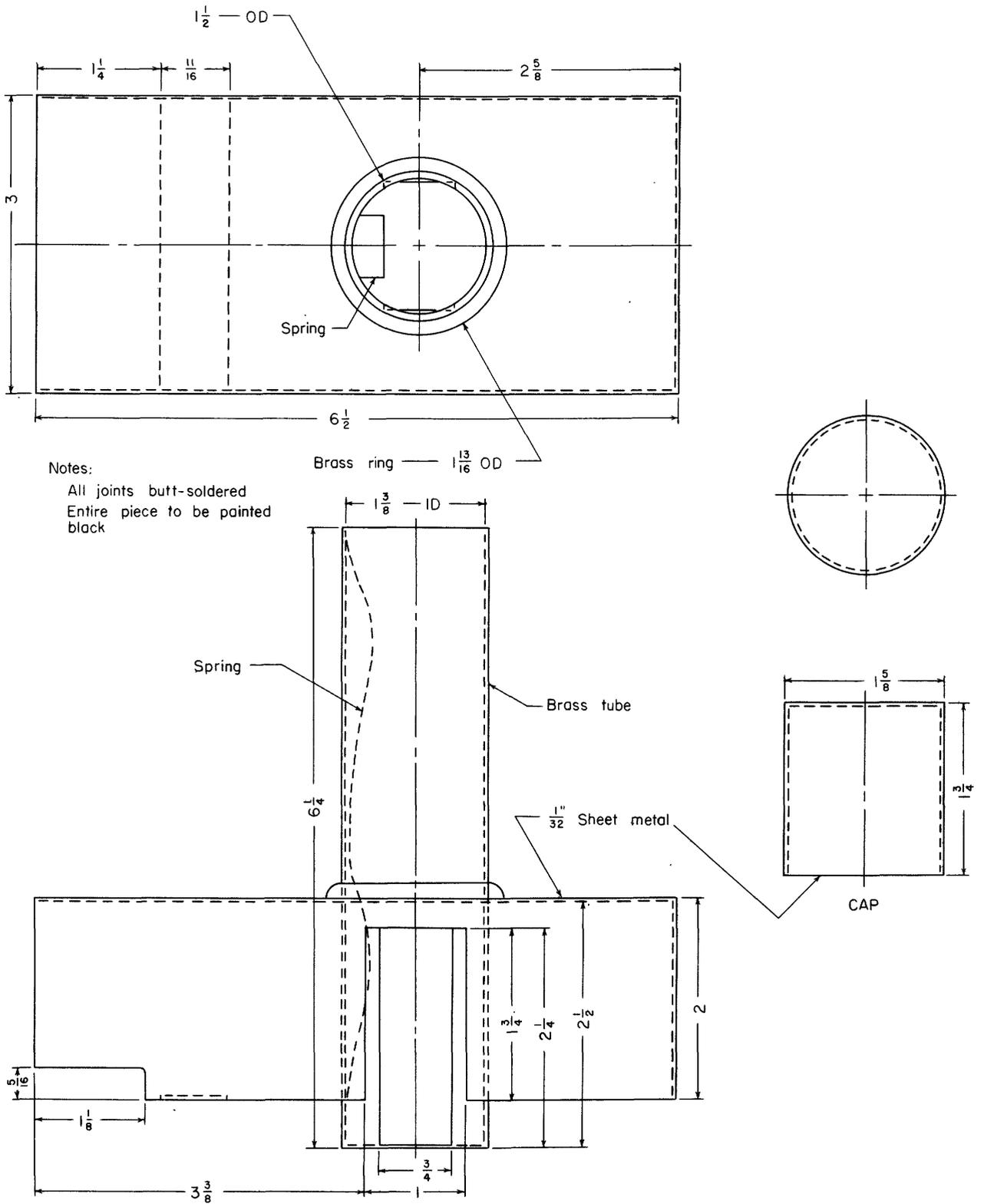


Figure 2. -- Test tube adaptor for the spectrophotometer.

Table 1.--Conversion of percent transmission (*T*) to absorbance (*A*).

| <i>T</i> | <i>A</i> | <i>T</i> | <i>A</i> | <i>T</i> | <i>A</i> | <i>T</i> | <i>A</i> |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 30.0     | 0.523    | 50.0     | 0.301    | 70.0     | 0.155    | 90.0     | 0.046    |
| 30.5     | .516     | 50.5     | .297     | 70.5     | .152     | 90.5     | .043     |
| 31.0     | .509     | 51.0     | .292     | 71.0     | .149     | 91.0     | .041     |
| 31.5     | .502     | 51.5     | .288     | 71.5     | .146     | 91.5     | .039     |
| 32.0     | .495     | 52.0     | .284     | 72.0     | .143     | 92.0     | .036     |
| 32.5     | .488     | 52.5     | .280     | 72.5     | .140     | 92.5     | .034     |
| 33.0     | .482     | 53.0     | .276     | 73.0     | .137     | 93.0     | .032     |
| 33.5     | .475     | 53.5     | .272     | 73.5     | .134     | 93.5     | .029     |
| 34.0     | .469     | 54.0     | .268     | 74.0     | .131     | 94.0     | .027     |
| 34.5     | .462     | 54.5     | .264     | 74.5     | .128     | 94.5     | .025     |
| 35.0     | .456     | 55.0     | .260     | 75.0     | .125     | 95.0     | .022     |
| 35.5     | .450     | 55.5     | .256     | 75.5     | .122     | 95.5     | .020     |
| 36.0     | .444     | 56.0     | .252     | 76.0     | .119     | 96.0     | .018     |
| 36.5     | .438     | 56.5     | .248     | 76.5     | .116     | 96.5     | .016     |
| 37.0     | .432     | 57.0     | .244     | 77.0     | .114     | 97.0     | .013     |
| 37.5     | .426     | 57.5     | .240     | 77.5     | .111     | 97.5     | .011     |
| 38.0     | .420     | 58.0     | .237     | 78.0     | .108     | 98.0     | .009     |
| 38.5     | .415     | 58.5     | .233     | 78.5     | .105     | 98.5     | .007     |
| 39.0     | .409     | 59.0     | .229     | 79.0     | .102     | 99.0     | .004     |
| 39.5     | .403     | 59.5     | .226     | 79.5     | .100     | 99.5     | .002     |
| 40.0     | .398     | 60.0     | .222     | 80.0     | .097     |          |          |
| 40.5     | .393     | 60.5     | .218     | 80.5     | .094     |          |          |
| 41.0     | .387     | 61.0     | .215     | 81.0     | .092     |          |          |
| 41.5     | .382     | 61.5     | .211     | 81.5     | .089     |          |          |
| 42.0     | .377     | 62.0     | .208     | 82.0     | .086     |          |          |
| 42.5     | .372     | 62.5     | .204     | 82.5     | .084     |          |          |
| 43.0     | .367     | 63.0     | .201     | 83.0     | .081     |          |          |
| 43.5     | .362     | 63.5     | .197     | 83.5     | .078     |          |          |
| 44.0     | .357     | 64.0     | .194     | 84.0     | .076     |          |          |
| 44.5     | .352     | 64.5     | .190     | 84.5     | .073     |          |          |
| 45.0     | .347     | 65.0     | .187     | 85.0     | .071     |          |          |
| 45.5     | .342     | 65.5     | .184     | 85.5     | .068     |          |          |
| 46.0     | .337     | 66.0     | .180     | 86.0     | .066     |          |          |
| 46.5     | .333     | 66.5     | .177     | 86.5     | .063     |          |          |
| 47.0     | .328     | 67.0     | .174     | 87.0     | .060     |          |          |
| 47.5     | .323     | 67.5     | .171     | 87.5     | .058     |          |          |
| 48.0     | .319     | 68.0     | .168     | 88.0     | .056     |          |          |
| 48.5     | .314     | 68.5     | .164     | 88.5     | .053     |          |          |
| 49.0     | .310     | 69.0     | .161     | 89.0     | .051     |          |          |
| 49.5     | .305     | 69.5     | .158     | 89.5     | .049     |          |          |

defined bright blue inner cones, which do not jump irregularly from the burner grid. The burner chimney should be shifted until the flame passes up through its center. The instrument is then allowed to warm up for about 30 min before readings are taken.

#### PREPARATION OF SAMPLE SOLUTIONS

##### Discussion

The major part of the analysis is made on two solutions which are designated solution *A* and solution *B*. (See fig. 1.) Solution *A* is used in the determination of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. It is prepared by fusing 0.1000 g of the sample, with NaOH in a nickel crucible. In this way complete decomposition of the sample is obtained very quickly at a comparatively low temperature. The nickel crucible is only slightly attacked, and the nickel taken into solution does not interfere with the subsequent determination of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

Solution *B* is used in the determinations of TiO<sub>2</sub>, total iron, MnO, P<sub>2</sub>O<sub>5</sub>, Mg, CaO, Na<sub>2</sub>O, and

K<sub>2</sub>O. To prepare this solution, a 1.000 g sample is digested, with HF and H<sub>2</sub>SO<sub>4</sub> in a large platinum crucible, overnight, on a steambath. HF is removed by heating until copious fumes of SO<sub>3</sub> are given off, and the residue is dissolved in water and made to volume.

To minimize contamination from glass, the aliquots of solution *B* used for determining Na<sub>2</sub>O and K<sub>2</sub>O, should be withdrawn immediately after preparation of the solution. Na<sub>2</sub>O and K<sub>2</sub>O should then be determined immediately, or the aliquots should be stored in plastic, vycor, or platinum containers.

##### Reagents

NaOH, pellets, A.C.S. grade. Store in plastic bottle to prevent contamination that might result from attack on the glass of the reagent bottle when pellets absorb moisture from the air.

HF, 48 percent

H<sub>2</sub>SO<sub>4</sub>, 1+1

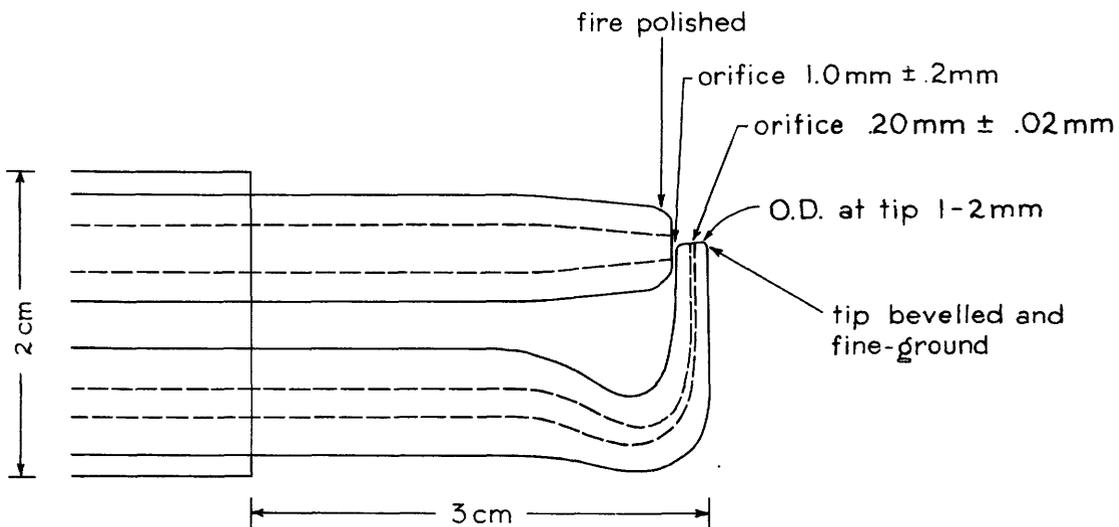
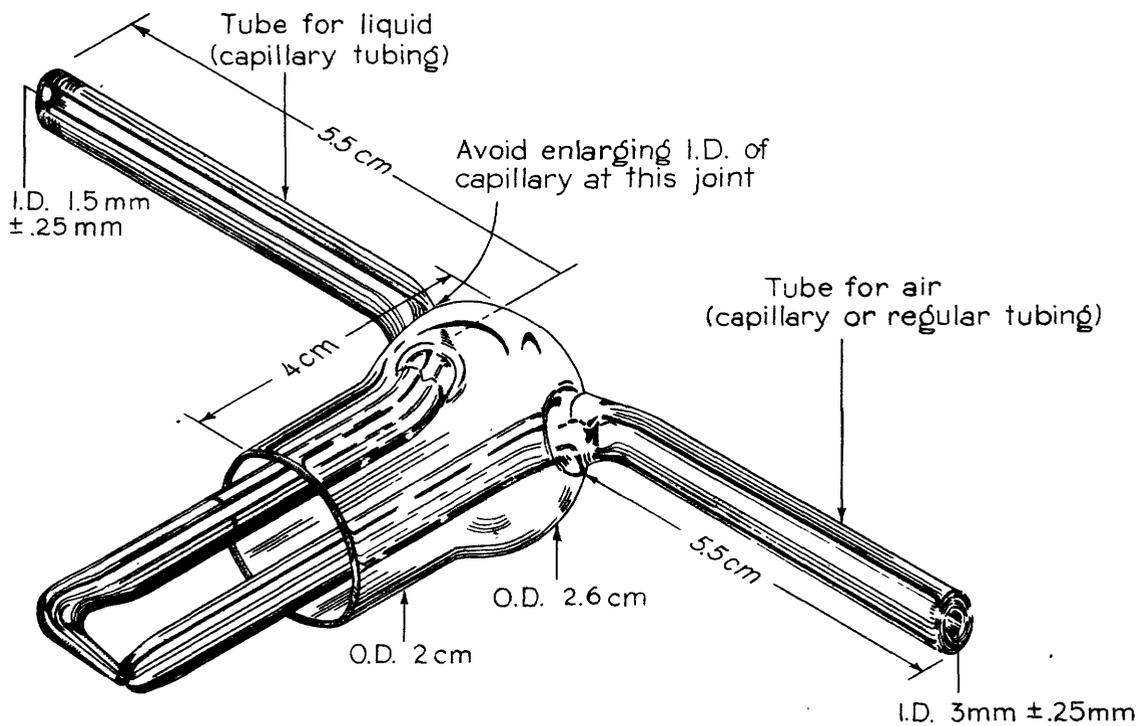


Figure 3.--Special glass atomizer for the flame photometer.

### Solution A

1. Weigh accurately 0.1000 g of sample, ground to pass a 100 mesh screen. Transfer to a nickel crucible of approximately 75 ml capacity.
2. Add 10 pellets (approximately 1.5g) of NaOH.
3. Cover the crucible and heat to dull red for 3 to 5 min. Remove from the heat and swirl the melt around the sides of the crucible. Allow to cool.
4. Add approximately 50 ml of distilled water and allow to stand at least 15 to 20 min, stirring occasionally with a platinum rod.
5. Transfer the contents of the crucible to a 600 ml beaker containing approximately 400 ml of distilled water and 6 ml of HCl. Scrub the crucible with a rubber policeman and wash any remaining solution or residue into the beaker.
6. Transfer the solution to a 1 liter volumetric flask, make up to volume with distilled water and mix well.

### Solution B

1. Transfer a 1.000 g sample to a platinum crucible of approximately 100 ml capacity.
2. Add 10 ml of 1+1 H<sub>2</sub>SO<sub>4</sub>.
3. Add approximately 20 ml of HF.
4. Cover the crucible and digest overnight on a steambath.
5. Remove the cover, rinse and allow the crucible to heat on the steambath until the volume of the solution is reduced to approximately 5 ml.
6. Place the crucible over an electric heater or gas burner and heat until strong SO<sub>3</sub> fumes evolve.
7. Allow the crucible and contents to cool.
8. Fill the crucible with distilled water.
9. Cover the crucible and digest on the steam-bath until the residue dissolves. If a residue remains after digesting for approximately one-half hour, transfer solution and residue to a 400 ml vycor beaker and boil gently for 10-15 min. If a small amount of insoluble material still remains, it may be barium sulfate, zircon, or possibly tourmaline. This may be filtered off and discarded, because BaO and ZrO<sub>2</sub> are not determined. Tourmaline is found, but rarely in more than trivial quantities.
10. Transfer the solution to a 200 ml volumetric flask, make up to volume and mix well.
11. Immediately withdraw 50 ml of the solution with a pipet and transfer to a 200 ml volumetric flask if K<sub>2</sub>O and Na<sub>2</sub>O can be determined the same day or, if K<sub>2</sub>O and Na<sub>2</sub>O cannot be determined the same day, transfer the aliquot to a plastic, platinum, or vycor container to eliminate the possibility of alkali contamination from the container.

### DETERMINATION OF SiO<sub>2</sub>

In the determination of SiO<sub>2</sub> (Bunting, 1944) the yellow silicomolybdate complex is reduced to molybdenum blue and the transmission of light is measured at 650 m mu. As silica is the predominant constituent in silicate rocks, relatively more precise values are desired for SiO<sub>2</sub> than for the constituents present in lower concentrations. For this reason sample weighing, volume measurements, and spectrophotometer readings must be made very carefully.

#### REAGENTS

Ammonium molybdate reagent solution: Dissolve 75 g. ammonium molybdate in 750 ml of water. Add 100 ml of 1+1 H<sub>2</sub>SO<sub>4</sub> and make up to one liter volume. Store in a plastic bottle.

Tartaric acid solution, 10 percent: Water solution stored in a plastic bottle, 500 ml.

Reducing solution: Dissolve 7 g of sodium sulfite in water. Add 1.5 g of 1-amino-2-naphthol-4-sulfonic acid and stir until dissolved. Dissolve 90 g of sodium bisulfite in 800 ml of water and add this solution to the solution above and mix.

Reference standard solution: A solution is prepared by the method described above under "Preparation of sample solution, Solution A" using the National Bureau of Standards standard sample no. 70 or no. 99. The nickel crucible should be carefully cleaned with dilute HCl before use to remove any iron which may have been left on the crucible from the previous fusion. The standard solution should be stored in a plastic bottle and should be prepared fresh if more than one week old.

#### PROCEDURE

1. Withdraw 50 ml of sample solution A, and 50 ml of the reference standard, with a pipet, and transfer each aliquot to separate 500 ml volumetric flasks. Make the solutions up to volume with distilled water and mix well.
2. Withdraw 50 ml of each solution from step 1 with a pipet and transfer to separate 100 ml volumetric flasks.
3. Add approximately 50 ml of distilled water to another 100 ml flask to be used for preparation of the reagent blank solution.
4. Add 1 ml of the ammonium molybdate reagent to each flask, swirling the flasks during the additions. Mix well and allow to stand for 10 min.
5. Add 4 ml of the tartaric acid solution, swirling the flasks while adding.
6. Add 1 ml of the reductant solution while swirling the flasks, make to volume, mix well, and allow to stand at least 30 min.
7. Determine the percent transmission for each solution at 650 m mu using the reagent blank solution as the reference blank solution.

## CALCULATIONS

1. Convert each of the values obtained for percent transmission to absorbance using table 1.

2. Compute the factor:

$$\frac{\text{Percent SiO}_2 \text{ of comparison standard}}{\text{absorbance of comparison standard}} = \text{Factor}$$

3. Compute percent SiO<sub>2</sub> in samples:

$$\text{Factor} \times \text{absorbance of sample solution} = \text{Percent SiO}_2$$

## DETERMINATION OF Al<sub>2</sub>O<sub>3</sub>

Al<sub>2</sub>O<sub>3</sub> is determined by measuring the transmission of light, at 370 m mu of the complex of aluminum with ferron (8-hydroxy-7-iodo-5-quinoline sulfonic acid, (Davenport, 1949).

Iron and titanium also form complexes with ferron which affect the absorbance at 370 m mu. The effects are proportional to their respective concentrations and are additive so it is possible to apply corrections for them. The correction for TiO<sub>2</sub> is based on the concentration of TiO<sub>2</sub> in the sample as determined in the section "Determination of TiO<sub>2</sub>". The correction for iron is based on the determination of the effect of the iron actually present in the solution used in the determination of Al<sub>2</sub>O<sub>3</sub>. This is necessary because of the partial retention of iron by the nickel crucible used for the NaOH fusion. The effect of the iron actually present in the solution can readily be determined because it is the only common ion complexed by ferron which has appreciable absorbance at 600 m mu and the relationship of concentration of iron to absorbance is linear at both 370 m mu and 600 m mu.

## REAGENTS

Ferron (8-hydroxy-7-iodo-5-quinoline sulfonic acid) solution, .2 percent: water solution, 1000 ml.

Ammonium acetate solution, 10 percent: water solution, 1000 ml.

HCl, 1+9 solution:

Standard Fe solution: Prepare a solution in which 1 ml contains 0.01 mg of Fe<sub>2</sub>O<sub>3</sub> by diluting 10 ml, of the standard iron solution, Fe<sub>2</sub>O<sub>3</sub> = 0.5 mg/ml described under "Determination of total iron as Fe<sub>2</sub>O<sub>3</sub>, Reagents", to 500 ml with water.

Standard TiO<sub>2</sub> solution: Dilute 10 ml of the standard TiO<sub>2</sub> solution described under "Determination of TiO<sub>2</sub>, Reagents" to 500 ml with water. The TiO<sub>2</sub> concentration is equivalent to that of a solution prepared from sample containing 2 percent TiO<sub>2</sub> when the procedure below is followed.

Reference standard solution: The "reference standard solution", prepared for the "Determination of SiO<sub>2</sub>" and described under "Reagents", is used.

## PROCEDURE

1. Transfer 10 ml of solution A, 10 ml of the reference standard solution, and 10 ml of the standard Fe<sub>2</sub>O<sub>3</sub> solution to separate 100 ml volumetric flasks.

For the first set of samples, and occasionally thereafter, 10 ml of the standard TiO<sub>2</sub> solution is also carried through the procedure.

2. Dilute the solutions in the flasks to approximately 70 ml. Add approximately 70 ml of distilled water to another 100 ml volumetric flask to be used for the preparation of a reagent blank solution.

3. Add 1 ml of HCl (1+9) to each flask and mix.

4. Add 10 ml of the ammonium acetate solution to each flask while swirling the flask.

5. Finally, add 10 ml of the ferron solution while swirling the flask. Make up to volume, mix well, and allow the solutions to stand at least 1 hr.

6. Transfer 50 ml of each solution to comparison tubes and determine percent transmission at 370 m mu, using the reagent blank solution as the reference blank.

7. Determine percent transmission at 600 m mu for each solution, except the reference standard solution and the solution containing the standard TiO<sub>2</sub>, using the reagent blank solution as the reference blank.

## CALCULATIONS

1. Convert all the readings for percent transmission to absorbance using table 1.

2. Calculate the factor for the iron correction:

$$\frac{\text{absorbance of standard Fe}_2\text{O}_3 \text{ at } 370 \text{ m mu}}{\text{absorbance of standard Fe}_2\text{O}_3 \text{ at } 600 \text{ m mu}} = \text{Fe}_2\text{O}_3 \text{ correction factor.}$$

3. Calculate the corrections for iron effect:

$$\text{The iron correction} = \text{Fe}_2\text{O}_3 \text{ correction factor} \times \text{absorbance of sample solution at } 600 \text{ m mu} = \text{absorbance at } 370 \text{ m mu due to iron.}$$

4. Calculate the correction factor for TiO<sub>2</sub>, if standard TiO<sub>2</sub> solution was run:

$$\frac{2.00}{\text{absorbance of standard TiO}_2 \text{ solution at } 370 \text{ m mu}} = \text{factor for TiO}_2$$

5. Calculate the corrections for TiO<sub>2</sub> effect using the factor (step 4) or use the factor previously determined:

$$\text{TiO}_2 \text{ correction} = \frac{\text{concentration of TiO}_2 \text{ in sample solution}}{\text{factor}}$$

6. Subtract the sum of the Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> corrections from the absorbance values obtained for the sample solution at 370 m mu.

7. Calculate the factor for Al<sub>2</sub>O<sub>3</sub>:

$$\frac{\text{Concentration Al}_2\text{O}_3 \text{ in reference standard}}{\text{absorbance at } 370 \text{ m mu}} = \text{factor}$$

8. Calculate percent Al<sub>2</sub>O<sub>3</sub>

$$\text{factor} \times \text{corrected absorbance (step 7)} = \text{percent Al}_2\text{O}_3$$

9. Should the Al<sub>2</sub>O<sub>3</sub> be greater than 25 percent, the determination should be repeated using 5 ml of solution A and calculations should be made accordingly.

## DETERMINATION OF TOTAL IRON AS $\text{Fe}_2\text{O}_3$

Total iron is determined by measuring the transmission of light at 440 m  $\mu$  of the yellow ferric chloride complex in 1+1 HCl (Pinsl, 1944). The color intensity is appreciably affected by temperature and acid concentration. Errors due to these effects can be satisfactorily controlled by running standard solutions of ferric iron simultaneously with each set of sample solutions and using aliquots of the same 1+1 HCl for both sample and standard solutions. The procedure is very simple and rapid.

### REAGENTS

1+1 HCl: Mix 1 liter of HCl and 1 liter of distilled water and allow to come to room temperature before using.

Standard iron solution,  $\text{Fe}_2\text{O}_3 = 0.5 \text{ mg/ml}$ : Weigh 0.699 g of pure iron wire. Dissolve in 50 ml of 1+1 HCl. Add 50 ml of  $\text{H}_2\text{SO}_4$ . Evaporate and heat to fumes of  $\text{SO}_3$ , adding approximately 1 ml of  $\text{HNO}_3$  as the fuming point is approached. Cool, dilute to 200 ml, and heat until solution is clear. Cool and make up to 2 liters with distilled water. The iron concentration in this standard is equal to that of a solution prepared as directed under "Preparation of sample solution, Solution B" from a sample containing 10 percent total iron as  $\text{Fe}_2\text{O}_3$ .

Standard iron solution,  $\text{Fe}_2\text{O}_3 = 0.25 \text{ mg/ml}$ : Make 500 ml of the standard iron solution containing 0.5 mg  $\text{Fe}_2\text{O}_3/\text{ml}$  to 1 liter with 2.5 percent  $\text{H}_2\text{SO}_4$ . The iron concentration in this standard is equal to that of a solution prepared as directed under "Preparation of sample solution, Solution B" from a sample containing 5 percent total iron as  $\text{Fe}_2\text{O}_3$ .

### PROCEDURE

1. Add exactly 25 ml of the 1+1 HCl to a comparison tube for the sample, to two tubes for standards, and to another tube for the reagent blank solution.
2. Add 5 ml of solution B to one of the tubes containing the 1+1 HCl and mix well.
3. Add 5 ml of standard iron solution,  $\text{Fe}_2\text{O}_3 = 0.5 \text{ mg/ml}$  and 5 ml of standard iron solution,  $\text{Fe}_2\text{O}_3 = 0.25 \text{ mg/ml}$  to tubes containing the 1+1 HCl and mix well.
4. Add 5 ml of distilled water to another of the tubes containing 1+1 HCl. This will be the reagent blank solution.
5. Determine the percent transmission at 440 m  $\mu$  for the sample and standard solutions using the reagent blank as the reference blank solution.

### CALCULATIONS

1. Convert the readings obtained for percent transmission to absorbance using table 1.

### CALCULATIONS--Continued.

2. Compute a factor for each standard solution:

$$\frac{10}{\text{absorbance of standard, } (\text{Fe}_2\text{O}_3 = 0.5 \text{ mg/ml})} = \text{factor}$$

$$\frac{5}{\text{absorbance of standard, } (\text{Fe}_2\text{O}_3 = 0.25 \text{ mg/ml})} = \text{factor}$$

3. Compute percent total iron as  $\text{Fe}_2\text{O}_3$  using the average of the factors (step 2) for the factor:

Factor X absorbance of sample solution = percent total iron as  $\text{Fe}_2\text{O}_3$ .

If percent  $\text{Fe}_2\text{O}_3$  in the sample is desired it is calculated in the usual way by subtracting the  $\text{Fe}_2\text{O}_3$  equivalent of FeO (separately determined) from percent total iron as  $\text{Fe}_2\text{O}_3$ .

## DETERMINATION OF $\text{TiO}_2$

$\text{TiO}_2$  is determined by an adaptation of the well-known peroxide procedure. It is common practice in conventional procedures to determine  $\text{TiO}_2$  on the  $\text{R}_2\text{O}_3$  group precipitate. In the method described here the determination is made without separations by developing the yellow titanium peroxide on an aliquot of a solution of the original sample and measuring the transmission of light at 400 m  $\mu$ .

### REAGENTS

$\text{TiO}_2$  reagent solution: Add 100 ml 1+1  $\text{H}_2\text{SO}_4$ , 100 ml  $\text{H}_3\text{PO}_4$ , and 100 ml of 30 percent  $\text{H}_2\text{O}_2$  to 700 ml of water, mix and store in a brown bottle.

Standard  $\text{TiO}_2$  solution: Weigh 0.1013 g of National Bureau of Standards standard titanium dioxide no. 154 in a small platinum crucible. Add 1 g of sodium bisulfate and fuse. Allow to cool and place crucible in a beaker containing 50 ml of 1+1  $\text{H}_2\text{SO}_4$ . Heat until melt completely dissolves. Cool and make the solution to 1 liter, with distilled water, in a volumetric flask. Store in a 1 liter glass-stoppered bottle. The  $\text{TiO}_2$  concentration is equal to 0.1 mg per ml or to that of a solution prepared as directed under "Preparation of sample solution Solution B", from a sample containing 2.00 percent  $\text{TiO}_2$ .

### PROCEDURE

1. Transfer a 15 ml aliquot of solution B to a comparison tube. A 15 ml aliquot of the standard  $\text{TiO}_2$  solution is run with the first set of sample solutions and occasionally thereafter to determine the factor for

$$\frac{\text{Percent } \text{TiO}_2}{\text{absorbance}}$$

2. Transfer 15 ml of distilled water to a comparison tube for use in preparing a reagent blank solution.
3. Add 15 ml of  $\text{TiO}_2$  reagent solution to each tube and mix well.

4. Determine the percent transmission of each solution at 400 m mu, using the reagent blank solution as the reference solution.

#### CALCULATIONS

1. Convert each of the values for percent transmission to absorbance using table 1.
2. Compute the factor if a standard solution was run:
 
$$\frac{2.00}{\text{absorbance of standard solution}} = \text{factor}$$
3. Compute percent  $\text{TiO}_2$  using the factor calculated (step 2) or use the factor as previously determined:

$$\text{factor} \times \text{absorbance of sample solution} = \text{percent TiO}_2$$

#### DETERMINATION OF $\text{P}_2\text{O}_5$

$\text{P}_2\text{O}_5$  is determined by measuring the light transmitted, at 430 m mu, by the yellow molybdivanod-phosphoric acid complex (Kitson and Mellon, 1944). The simplest conventional procedures involve precipitation as phosphomolybdate, filtration, and either titrating or drying and weighing the precipitate. The procedure employed here, which is much simpler, requires only the mixing of reagent and sample solutions and determination of percent transmission.

#### REAGENTS

$\text{P}_2\text{O}_5$  reagent solution: Dissolve 1.25 g of ammonium metavanadate in 400 ml of 1+1  $\text{HNO}_3$ . Dissolve 50 g of ammonium molybdate in 400 ml of water. Mix the solutions and make up to a liter volume with distilled water.

Standard  $\text{P}_2\text{O}_5$  solution: Weigh 0.0849 g of National Bureau of Standards standard phosphate rock sample no. 120. Transfer to a 150 ml beaker and add 25 ml of 1+1  $\text{HNO}_3$ . Digest on a steam-bath until solution is essentially complete. Cool and make up to 1 liter volume in a volumetric flask. Store in a glass-stoppered bottle. The concentration of  $\text{P}_2\text{O}_5$  is equal to that of a solution prepared, as directed under "Preparation of sample solution, Solution B," from a sample containing 50 percent  $\text{P}_2\text{O}_5$ .

#### PROCEDURE

1. Transfer a 25 ml aliquot of sample solution B to a comparison tube. A 25 ml aliquot of the standard  $\text{P}_2\text{O}_5$  solution is run with the first set of sample solutions and occasionally thereafter to determine the factor for

$$\frac{\text{Percent P}_2\text{O}_5}{\text{absorbance}}$$

2. Transfer 25 ml of water to a comparison tube. The resulting solution, after being treated the same as the sample solutions, will be used as a reference blank solution.

3. Add 10 ml of reagent solution to each comparison tube, swirling the tube during the addition. Mix and allow to stand for at least five minutes.

4. Determine the percent transmission, at 430 m mu, for each solution using the reagent blank solution as the reference blank solution.

#### CALCULATIONS

1. Convert the readings for percent transmission to absorbance using table 1.
2. Compute a factor if the standard solution was run:
 
$$\frac{0.50}{\text{absorbance of standard solution}} = \text{factor}$$
3. Compute percent  $\text{P}_2\text{O}_5$  using the factor calculated above (step 2) or use the factor previously determined:

$$\text{factor} \times \text{absorbance} = \text{percent P}_2\text{O}_5$$

#### DETERMINATION OF MnO

MnO is determined by measuring the light transmitted at 525 m mu, by an aliquot of sample solution in which the manganese has been oxidized to permanganate with  $\text{KIO}_4$ .

#### REAGENTS

$\text{H}_2\text{SO}_4$  1+9,  $\text{H}_3\text{PO}_4$ ,  $\text{KIO}_4$ .

Standard MnO solution: Weigh 0.0552 g of National Bureau of Standards standard manganese ore no. 25b. Transfer to a 250 ml beaker and add 25 ml of 1+1  $\text{HNO}_3$  and 2 to 3 ml of 3 percent  $\text{H}_2\text{O}_2$ . Digest on a steam-bath until no black residue remains. Cool and add 50 ml of  $\text{H}_2\text{SO}_4$ . Evaporate and continue heating until fumes of  $\text{SO}_3$  evolve. Cool and dilute to approximately 200 ml volume. Cool and make up to 2 liter volume. Store a liter of the solution in a glass stoppered bottle. The MnO concentration is equal to that of a solution prepared as directed under "Preparation of sample solution solution B" from a sample containing 0.50 percent MnO.

#### PROCEDURE

Transfer a 20 ml aliquot of solution B to a 100 ml beaker. For the first set of determinations and occasionally thereafter 20 ml of the standard MnO solution is run with the sample solutions to determine the factor

$$\frac{\text{percent MnO}}{\text{absorbance}}$$

2. Add 25 ml of 1+9  $\text{H}_2\text{SO}_4$ .
3. Add 0.5 ml  $\text{H}_3\text{PO}_4$ .
4. Add approximately 0.2 g of  $\text{KIO}_4$ .
5. Heat the solutions and keep at near boiling temperature for at least 10 min.

6. Cool the solutions to room temperature in a water bath.

7. Transfer the solutions to 100 ml volumetric flasks, make up to volume, and mix well.

8. Determine the percent transmission for each solution at 525 m  $\mu$ , using water as the reference.

#### CALCULATIONS

1. Convert each of the values for percent transmission to absorbance using table 1 above.

2. Compute the factor if a standard was run:

$$\frac{0.50}{\text{absorbance of standard solution}} = \text{factor}$$

3. Compute percent MnO using the factor calculated (step 2), or use the factor as previously determined:

$$\text{factor} \times \text{absorbance of sample solution} = \text{percent MnO.}$$

#### DETERMINATION OF CaO

CaO is determined by titration with sodium versenate solution (disodium ethylenediamine tetraacetate) using murexide (ammonium purpurate) as an indicator (Betz and Noll, 1950). Iron and aluminum in appreciable quantities interfere with the determination and must be removed.

#### REAGENTS

NaOH, 10 percent: 500 ml water solution stored in a plastic bottle.

Murexide or ammonium purpurate reagent: A small scoop which holds approximately 0.2 g of indicator is used for measuring the reagent.

Standard CaCl<sub>2</sub> solution: Weigh 0.8925 of dry CaCO<sub>3</sub>. Transfer to a 150 ml beaker. Add 50 ml of water and then add dilute HCl slowly until all of the CaCO<sub>3</sub> is dissolved. Boil for a few minutes. Cool and transfer to 1 liter volumetric flask and make up to volume. One ml contains CaCl<sub>2</sub> equivalent to 0.5 mg CaO.

Standard versenate solution: Weigh 2.5 g of disodium ethylenediamine tetraacetate and 0.1 g MgCl<sub>2</sub> · 6H<sub>2</sub>O. Dissolve in 2 liters of distilled water. Standardize the versenate solution by titrating several 10 ml aliquots of the standard CaCl<sub>2</sub> solution using the procedure described below. (Steps 6 and 7.)

#### PROCEDURE

1. Transfer a 50 ml aliquot of solution B to a 250 ml beaker.

2. Dilute to approximately 200 ml with distilled water.

3. Insert the electrodes of a pH meter and add NH<sub>4</sub>OH (1+1) dropwise from a buret until the meter reads pH 4.8 to 5.1.

4. Wash the contents of the beaker into a 250 ml volumetric flask. Do not police the beaker. Make to volume and mix.

5. Pour the contents of the flask through a dry filter paper, in a dry funnel, into a dry beaker using Whatman no. 40 12.5 cm paper. Filter approximately 200 ml of the solution. The filtrate is used for both CaO and MgO determinations.

6. Transfer 50 ml aliquots from the beaker to 2 porcelain 350 ml casseroles. Into a 150 ml beaker place approximately 100 ml of water, 10 ml of 10 percent NaOH and 2 scoops (0.4g) calcium indicator. Transfer 50 ml of this mixture to each of the 2 casseroles, with a graduate.

7. Titrate as follows: Use two 50 ml burets side by side filled with standard versenate solution. A daylight fluorescent lamp supported over the casseroles is a good source of illumination. Add the versenate solution to one casserole, which serves as the color reference, until the end point is clearly passed. The color does not change beyond the end point so the solution in the second casserole can now be titrated carefully to match the color of the first. The second titration is recorded.

#### CALCULATIONS

1. Calculate the percent CaO:

$$\text{Volume of titration (ml)} \times \text{CaO equivalent (mg CaO per ml versenate)} \times 2 = \text{percent CaO.}$$

#### DETERMINATION OF MgO

MgO is determined by titration with sodium versenate solution using Eriochrome Black T (Betz and Noll, 1950). By this method the total calcium plus magnesium is titrated and MgO is calculated after subtracting the volume of sodium versenate solution equivalent to the calcium.

#### REAGENTS

Eriochrome Black T reagent: Water solution, 0.1 g of the pure dye in 50 ml. This solution should be prepared fresh each day.

Titration buffer solution: Dissolve 70g of NH<sub>4</sub>Cl in 600 ml of concentrated NH<sub>4</sub>OH and dilute to 1 liter with distilled water.

Standard sodium versenate solution: Titrate 10 ml of the standard calcium chloride described under "Determination of CaO, Reagents" with the standard sodium versenate solution also described under "Determination of CaO, Reagents" using the Eriochrome Black T reagent, by the method described below. Compute the CaO equivalent per ml of solution. Titrate 25 ml of the standard MgCl<sub>2</sub> solution described below with the same standard sodium versenate solution by the method described below. Calculate the MgO equivalent per ml of solution.

Standard MgCl<sub>2</sub> solution: Weigh 0.1206 pure magnesium ribbon. Dissolve in a few ml of dilute HCl in

a beaker. Evaporate to dryness. Dissolve in distilled water and make up to 2 liters in a volumetric flask. Store in a pyrex bottle. One ml contains  $MgCl_2$  equivalent to 0.1mg MgO.

#### PROCEDURE

1. Transfer a 50 ml aliquot of the solution from which  $R_2O_3$  has been removed ("Determination of CaO, step 5") to a 400 ml beaker.
2. Add approximately 250 ml of distilled water.
3. Add 10 ml of the titration buffer solution.
4. Add 0.5 ml of Eriochrome Black T indicator.
5. Titrate with standard sodium versenate until the red color of the solution changes to blue. A titration illuminator and electric stirrer as described under apparatus are very helpful in this titration.

#### CALCULATIONS

1. To obtain the volume of standard versenate consumed by the CaO for the sample solution, multiply the ratio of the CaO equivalent obtained for the versenate solution using murexide indicator ("Determination of CaO, Reagents, Standard versenate solution") to the CaO equivalent for the same versenate solution when Eriochrome Black T indicator was used ("Determination of MgO, Standard versenate solution") by the volume of versenate used in the determination of CaO in the sample ("Determination of CaO", step 4):

$$\frac{\text{CaO equivalent with Murexide}}{\text{CaO equivalent with Eriochrome Black T}} \times \text{sample titration with murexide} = \frac{\text{volume of versenate consumed by CaO in sample solution}}{\text{volume of versenate consumed by MgO}}$$

2. Calculate the volume of versenate consumed by MgO:

$$(\text{sample titration, Eriochrome Black T indicator}) - (\text{volume of versenate consumed by CaO}) = \text{volume of versenate consumed by MgO}$$

3. Calculate percent MgO in samples:

$$\frac{\text{volume of versenate consumed by MgO} \times \text{MgO equivalent (mg MgO per ml versenate} \times 2)}{\text{ml versenate} \times 2} = \text{percent MgO}$$

#### DETERMINATION OF $K_2O$ AND $Na_2O$

$K_2O$  and  $Na_2O$  are determined by a flame photometer method in which lithium is used as an internal standard (Brannock and Berthold, U. S. Geol. Survey Bull., in press). Iron, aluminum, and calcium, which affect the results, are removed before introduction of the internal standard.

The use of an internal standard reduces the effect on results for  $K_2O$  and  $Na_2O$  due to differences in concentration of dissolved salts and differences in viscosity between standard and sample solutions as well as reducing deviations in readings brought about by changes in the character of the flame resulting from small variations in air and gas pressures.

Satisfactory results for the alkalis are obtained by comparing each sample solution with two standard solutions--one in which the concentration of the alkali being determined is higher than in the sample solution and the other in which it is lower. The concentration interval of the standard solutions used is relatively small and as a result the relationship between concentration of  $K_2O$  or  $Na_2O$  in the standard and sample solutions is essentially linear.

#### REAGENTS

$K_2SO_4$ ,  $Na_2SO_4$ ,  $Li_2SO_4$ ,  $(NH_4)_2SO_4$ , all A. C. S. grade.

Stock solution of  $K_2SO_4$  containing 1.156 g of dry  $K_2SO_4/1$  which is equivalent to 0.25 g  $K_2O/400$  ml. Prepare 2 liters.

Stock solution of  $Na_2SO_4$  containing 1.432 g of dry  $Na_2SO_4/1$  which is equivalent to 0.25 g  $Na_2O/400$  ml. Prepare 2 liters.

Stock solution of  $Li_2SO_4$  containing 15.84 g of  $Li_2SO_4/1$  which is equivalent to 2000 ppm lithium concentration. Prepare 8 liters or more.

Standard solutions equivalent to .5, 1, 2, 4, 6, 8, 10 and 12 percent  $K_2O$  respectively each containing 100 ppm lithium and 2 percent  $(NH_4)_2SO_4$  are prepared by diluting 5, 10, 20, 30, 40, 60, 80, 120 ml of stock solution of  $K_2SO_4$  plus 50 ml of stock  $Li_2SO_4$  and 20 g of  $(NH_4)_2SO_4$ , in each, to 1 liter with distilled water in a volumetric flask.

Standard solutions of similar concentrations to those for  $K_2O$  are prepared, for  $Na_2O$ , in the same way using the stock  $Na_2SO_4$  solution and the stock  $Li_2SO_4$  solution.

Internal standard solution in which the concentration of lithium is 200 ppm is prepared by diluting 200 ml of the stock solution of  $Li_2SO_4$  to 2 liters with distilled water.

Solution of  $(NH_4)_2SO_4$ , 25 percent, prepared by dissolving 480 g of  $(NH_4)_2SO_4$  and making up to 2 liters with distilled water.

#### PROCEDURE

1. Light the burner of the flame photometer and adjust the flame as described under special apparatus, Flame photometer.

2. Turn the electric switch on the panel of the flame photometer to the "on" position.

3. Transfer 50 ml of solution B above to a 200 ml volumetric flask.

4. Add 20 ml of 25 percent ammonium sulfate solution to the flask and dilute to 150 to 175 ml with distilled water.

5. Add  $NH_4OH$  (alkali free) to the solution in the flask until a slight excess is present as indicated by the color change of a small piece of litmus paper.

6. Then add approximately 1 ml of freshly prepared concentrated ammonium carbonate solution.

7. Make the solution up to 200 ml with distilled water and mix well.

8. Filter 75 to 100 ml of the solution through dry 12.5 cm Whatman no. 40 dry filter, in a dry funnel, into a dry pyrex bottle or beaker.

9. Withdraw 50 ml of the filtrate with a pipet and mix with 50 ml of lithium sulfate solution, containing 200 ppm lithium, in a pyrex beaker or bottle. The solution is now ready for determination of  $K_2O$  and  $Na_2O$  by the flame photometer.

10. If the approximate concentration of potassium in the sample solution can be estimated, omit steps 10-13 and proceed with step 14. If the approximate concentration of potassium in the sample solution cannot be estimated, pour 15 to 20 ml of standard potassium sulfate solution, in which the potassium sulfate concentration is equivalent to 12 percent  $K_2O$ , into a 30 ml beaker. Place the beaker, containing the standard solution, in position on the beaker stand so that the atomizer inlet tube is immersed in the solution. As the solution atomizes into the flame set the element selector to the position of maximum response for potassium.

11. With the same solution (step 10) atomizing into the flame set the internal standard dial to approximately 95 and adjust the coarse and fine gain controls so that the meter reads 50. Remove the beaker containing the standard solution and with no solution atomizing set the meter to read 50 with the zero adjusting knob. Replace the beaker with the same standard solution and while the solution atomizes adjust the internal standard dial so that the meter reads exactly 50. Record the setting of the internal standard dial. Remove the beaker and wipe the outside of the liquid inlet tube of the atomizer with a clean lintless facial tissue.

12. Put 15 to 20 ml of the sample solution (step 9) in a 30 ml beaker and place in position so that it atomizes into the flame. Adjust the internal standard dial so that the meter reads exactly 50. Remove the beaker, wipe the atomizer tube with a tissue and record the setting of the internal standard dial.

13. Assume the recorded readings to be proportional to concentration of potassium in standard and sample solutions and calculate the approximate concentration of potassium as  $K_2O$ .

14. Repeat step 11 for the sample solution using the standard solution with the nearest higher concentration to the estimated concentration of potassium in the sample solution.

15. Repeat step 12.

16. Repeat step 12 using the standard solution with the nearest lower potassium concentration to the estimated concentration of potassium, in the sample solution, instead of the sample solution.

17. With the same solution (step 16) atomizing, shift the position of the internal standard dial and then

reset it so that the meter again reads 50. Record the setting of the internal standard dial, remove the beaker and solution and wipe the atomizer tube.

18. Repeat step 12.

19. Repeat step 12 using the higher standard instead of the sample solution.

20.  $Na_2O$  is determined on a portion of the same sample solution which was used for the determination of  $K_2O$  (step 10). The element selector is set to the position of maximum response for sodium and the  $Na_2O$  is determined in the same way as  $K_2O$ .

#### CALCULATIONS

1. The two-point equation below is used to calculate the concentration of  $K_2O$  and  $Na_2O$  in the sample solution after averaging the readings obtained for each standard and the sample solution.

$$x = \frac{y - y_1}{y_2 - y_1} (x_2 - x_1) - x_1$$

x = concentration of  $K_2O$  in the sample solution

y = dial reading for the sample solution

$x_1$  = concentration of  $K_2O$  in the lower standard solution

$y_1$  = dial reading for the lower standard solution

$x_2$  = concentration of  $K_2O$  in the higher standard solution

$y_2$  = dial reading for the higher standard solution

#### DETERMINATION OF $FeO$

Ferrous iron is determined by the conventional titrimetric method using standard dichromate solution with diphenylamine sulfonic acid as the indicator. When decomposition is carried out on batches of approximately eight samples simultaneously the time consumption per sample is small.

#### REAGENTS

$H_2SO_4$ , 48 percent HF,  $K_2Cr_2O_7$ , all A. C. S. grade.

$H_2SO_4$  1+3

Diphenylamine sulfonate indicator: Dissolve 0.2g of sodium diphenylamine sulfonate in 1 liter of water. Add 1 liter of 85 percent  $H_3PO_4$  and mix well.

Standard dichromate solution: Weigh 2.808 g of dry National Bureau of Standards potassium dichromate or other pure dry potassium dichromate and make up to 2 liters in a volumetric flask. 1 ml = 2.000 mg  $FeO$ .

#### PROCEDURE

1. Weigh 0.5000g of sample and place in platinum crucible of approximately 100 ml volume.

2. Add 20 ml of 1+3  $H_2SO_4$  to the crucible, cover and carefully bring to a boil over a gas burner or an electric heater.

3. Add 5 to 8 ml of HF. Cover and bring to a boil. Boil gently for 15 min.

4. While the solution in the crucible is boiling add 400 ml of water and approximately 10 g of boric acid to an 800 ml beaker. Stir the liquid in the beaker to aid in solution of the boric acid.

5. After the solution in the crucible has boiled for 15 min, remove the crucible from the heat with tongs, hold the cover on the crucible with a stirring rod, and immediately immerse the covered crucible and contents in the boric acid solution. The crucible should be kept covered after immersion, until just prior to the titration.

6. Add 10 ml of the indicator solution and titrate the solution with standard dichromate solution to a purple end-point which persists for 20 to 30 sec.

#### CALCULATIONS

1. Compute percent FeO in the sample:

$$\frac{\text{ml dichromate} \times 2.000}{500} \times 100 =$$

$$\text{ml dichromate} \times 4 = \text{Percent FeO}$$

#### DETERMINATION OF LOSS ON IGNITION

The results obtained for loss on ignition can be used, after applying corrections for the oxidation of divalent iron, for estimating the amount of CO<sub>2</sub> plus H<sub>2</sub>O in the samples. Divalent iron is not always completely oxidized so, when the sample contains appreciable FeO, the value for CO<sub>2</sub> plus H<sub>2</sub>O may be in error.

#### PROCEDURE

1. Ignite, cool, and weigh a platinum or porcelain crucible of 20-30 ml capacity.
2. Add approximately 1 g of sample and weigh the crucible plus sample.
3. Heat over a low burner flame at first and gradually bring to full heat of the burner.
4. Heat at full heat of a Fisher burner for 1 hr or transfer to a muffle furnace and heat for 1 hr at 1000 C.
5. Allow the crucible and contents to cool in a desiccator.
6. Weigh the crucible and contents.

#### CALCULATIONS

1. Calculate the percent loss on ignition:

$$\frac{\text{Loss in weight}}{\text{sample weight}} \times 100 = \text{Percent loss on ignition.}$$

#### EXPERIMENTAL RESULTS

The methods described have been tested by analyzing twelve synthetic samples prepared by mixing selected National Bureau of Standards standard samples. The mixed samples have been prepared to include as nearly as possible the ranges of concentrations, of the above mentioned constituents, which might be expected to be found in typical silicate rocks. In table 2 is shown the percentage of each of

Table 2.--Percentage composition of National Bureau of Standards (N.B.S.) standard samples in the mixture samples.

| National Bureau of Standards sample no. | A  | B  | C  | D  | E  | F  | G  | H  | I  | J  | K  | L  |
|---|----|----|----|----|----|----|----|----|----|----|----|----|
| Quartz                                  |    |    |    | 38 |    |    |    |    | 50 |    |    |    |
| 1a Limestone                            |    |    |    |    |    |    |    | 30 |    |    |    |    |
| 26 Crescent iron ore                    |    |    | 10 | 14 | 19 | 9  | 5  | 7  |    |    |    |    |
| 69 Bauxite                              | 33 | 49 | 29 |    |    |    |    |    |    |    |    |    |
| 70 Feldspar                             | 33 |    | 50 |    |    | 66 | 55 |    |    |    |    |    |
| 88 Dolomite                             | 33 |    | 10 |    | 9  | 19 | 37 |    |    |    |    |    |
| 97 Clay                                 |    |    |    |    |    |    |    |    |    |    | 50 |    |
| 98 Clay                                 |    |    |    |    |    |    |    |    | 50 | 50 |    | 50 |
| 99 Feldspar                             |    | 49 |    | 47 | 65 |    |    | 59 |    |    |    | 50 |
| 102 Silica brick                        |    |    |    |    |    |    |    |    |    | 50 | 50 |    |
| 120 Phosphate rock                      | 1  | 2  | 1  | 1  | 7  | 6  | 3  | 4  |    |    |    |    |

Table 3.--Results obtained for National Bureau of Standards (N.B.S.) mixture samples

|                                  | A    |       |       | B    |       |       | C    |       |      |
|----------------------------------|------|-------|-------|------|-------|-------|------|-------|------|
|                                  | NBS  | Rapid |       | NBS  | Rapid |       | NBS  | Rapid |      |
| SiO <sub>2</sub>                 | 24.3 | 24.6  | 24.7  | 36.9 | 36.9  | 36.5  | 35.5 | 36.2  | 35.5 |
| Al <sub>2</sub> O <sub>3</sub>   | 24.2 | 24.3  | 24.2  | 36.4 | 36.6  | 36.8  | 25.4 | 25.0  | 24.6 |
| Fe <sub>2</sub> O <sub>3</sub> * | 1.9  | 1.7   | 1.9   | 2.8  | 2.8   | 2.8   | 10.0 | 10.1  | 9.9  |
| TiO <sub>2</sub>                 | 1.0  | .90   | .97   | 1.5  | 1.3   | 1.3   | .92  | .88   | .85  |
| MnO                              | .18  | .17   | .18   | .27  | .27   | .27   | .16  | .18   | .17  |
| P <sub>2</sub> O <sub>5</sub>    | .27  | .25   | .27   | .81  | .78   | .73   | .40  | .41   | .42  |
| CaO                              | 10.5 | 10.4  | 10.5  | 1.2  | 1.3   | 1.4   | 3.8  | 3.9   | 3.7  |
| MgO                              | 7.1  | 7.0   | 7.0   | .04  | .02   | .00   | 2.5  | 2.3   | 2.5  |
| Na <sub>2</sub> O                | .87  | .77   | .81   | 5.4  | 5.2   | 5.4   | 1.2  | 1.1   | 1.2  |
| K <sub>2</sub> O                 | 4.2  | 4.1   | 4.2   | .24  | .23   | .28   | 6.2  | 6.2   | 6.3  |
| Ignition loss                    |      | 26.0  | 26.0  |      | 14.6  | 14.6  |      | 14.1  | 14.1 |
|                                  |      | 100.2 | 100.7 |      | 100.0 | 100.1 |      | 100.4 | 99.2 |

|                                  | D    |       |       | E    |       |       | F    |       |       |
|----------------------------------|------|-------|-------|------|-------|-------|------|-------|-------|
|                                  | NBS  | Rapid |       | NBS  | Rapid |       | NBS  | Rapid |       |
| SiO <sub>2</sub>                 | 71.2 | 70.8  | 71.5  | 46.4 | 46.7  | 46.4  | 45.0 | 44.8  | 45.3  |
| Al <sub>2</sub> O <sub>3</sub>   | 9.2  | 9.3   | 9.6   | 12.7 | 12.3  | 12.8  | 12.1 | 11.8  | 12.4  |
| Fe <sub>2</sub> O <sub>3</sub> * | 12.0 | 12.0  | 12.0  | 15.8 | 15.7  | 15.6  | 8.0  | 7.9   | 8.0   |
| TiO <sub>2</sub>                 | .02  | .06   | .04   | .03  | .06   | .06   | .01  | .04   | .03   |
| MnO                              | --   | .02   | .02   | --   | .03   | .03   | --   | .02   | .02   |
| P <sub>2</sub> O <sub>5</sub>    | .25  | .30   | .28   | 2.4  | 2.4   | 2.5   | 2.0  | 2.0   | 2.0   |
| CaO                              | .77  | .87   | .96   | 6.8  | 6.9   | 6.9   | 8.8  | 8.8   | 9.0   |
| MgO                              | .49  | .50   | .51   | 2.7  | 2.5   | 2.5   | 4.4  | 4.3   | 4.3   |
| Na <sub>2</sub> O                | 5.1  | 5.0   | 5.0   | 7.0  | 6.9   | 7.0   | 1.6  | 1.5   | 1.6   |
| K <sub>2</sub> O                 | .19  | .21   | .25   | .28  | .30   | .31   | 8.3  | 8.4   | 8.4   |
| Ignition loss                    |      | 1.1   | 1.1   |      | 6.0   | 6.0   |      | 9.7   | 9.7   |
|                                  |      | 100.0 | 101.0 |      | 99.8  | 100.1 |      | 99.3  | 100.8 |

|                                  | G    |       |       | H    |       |       | I    |       |      |
|----------------------------------|------|-------|-------|------|-------|-------|------|-------|------|
|                                  | NBS  | Rapid |       | NBS  | Rapid |       | NBS  | Rapid |      |
| SiO <sub>2</sub>                 | 37.6 | 37.4  | 36.8  | 45.6 | 45.5  | 45.9  | 79.6 | 79.0  | 78.9 |
| Al <sub>2</sub> O <sub>3</sub>   | 10.1 | 10.3  | 10.2  | 12.7 | 13.0  | 13.2  | 12.8 | 12.7  | 12.4 |
| Fe <sub>2</sub> O <sub>3</sub> * | 4.0  | 4.1   | 4.0   | 6.4  | 6.6   | 6.2   | 1.0  | 1.0   | .96  |
| TiO <sub>2</sub>                 | .01  | .02   | .01   | .06  | .09   | .09   | .72  | .75   | .80  |
| MnO                              | .00  | .01   | .01   | --   | .03   | .03   | .00  | .01   | --   |
| P <sub>2</sub> O <sub>5</sub>    | .99  | 1.0   | .96   | 1.5  | 1.5   | 1.6   | .04  | .05   | .06  |
| CaO                              | 12.8 | 13.0  | 13.0  | 14.6 | 14.6  | 14.8  | .10  | .18   | .23  |
| MgO                              | 8.1  | 8.0   | 8.2   | .91  | 1.1   | 1.0   | .36  | .34   | .35  |
| Na <sub>2</sub> O                | 1.4  | 1.3   | 1.4   | 6.5  | 6.4   | 6.5   | .14  | .19   | .20  |
| K <sub>2</sub> O                 | 7.0  | 7.0   | 7.0   | .46  | .51   | .54   | 1.6  | 1.6   | 1.6  |
| Ignition loss                    |      | 18.4  | 18.4  |      | 11.7  | 11.7  |      | 4.2   | 4.2  |
|                                  |      | 100.5 | 100.0 |      | 100.5 | 101.4 |      | 100.0 | 99.7 |

|                                  | J    |       |      | K    |       |       | L    |       |       |
|----------------------------------|------|-------|------|------|-------|-------|------|-------|-------|
|                                  | NBS  | Rapid |      | NBS  | Rapid |       | NBS  | Rapid |       |
| SiO <sub>2</sub>                 | 76.5 | 76.4  | 76.0 | 68.4 | 69.2  | 69.0  | 63.9 | 64.7  | 64.2  |
| Al <sub>2</sub> O <sub>3</sub>   | 13.8 | 13.3  | 13.3 | 20.4 | 20.2  | 20.8  | 22.3 | 22.0  | 22.0  |
| Fe <sub>2</sub> O <sub>3</sub> * | 1.4  | 1.3   | 1.3  | .82  | .78   | .82   | 1.1  | .95   | .98   |
| TiO <sub>2</sub>                 | .80  | .80   | .85  | 1.3  | 1.3   | 1.3   | .72  | .72   | .79   |
| MnO                              | .00  | .01   | --   | .00  | .01   | .01   | .00  | .01   | --    |
| P <sub>2</sub> O <sub>5</sub>    | .05  | .04   | .06  | .05  | .04   | .06   | .11  | .11   | .12   |
| CaO                              | 1.2  | 1.5   | 1.3  | 1.2  | 1.2   | 1.2   | .28  | .32   | .40   |
| MgO                              | .46  | .51   | .50  | .24  | .27   | .26   | .39  | .46   | .44   |
| Na <sub>2</sub> O                | .17  | .19   | .21  | .09  | .10   | .12   | 5.5  | 5.4   | 5.4   |
| K <sub>2</sub> O                 | 1.7  | 1.7   | 1.8  | .42  | .45   | .45   | 1.8  | 1.8   | 1.8   |
| Ignition loss                    |      | 4.2   | 4.2  |      | 7.1   | 7.1   |      | 4.3   | 4.3   |
|                                  |      | 99.7  | 99.4 |      | 100.6 | 100.9 |      | 100.6 | 100.2 |

\* Total iron as Fe<sub>2</sub>O<sub>3</sub>

the National Bureau of Standards standard samples used to make up the mixed samples.

Table 3 shows the results obtained by two rapid analyses (made at different times) of the National Bureau of Standards mixture samples, compared with values computed from the analyses reported on the original samples by the National Bureau of Standards. A single loss on ignition determination was made for each mixture sample and the single value for each

sample was used in computing the sum for both rapid analyses. FeO values were not reported by the National Bureau of Standards and consequently were not determined or shown in the table.

The concentration ranges of the mixture samples and the maximum and average absolute deviations based on the 24 values obtained for each constituent are shown in table 4.

Table 4.--Concentration ranges covered and deviations for National Bureau of Standards (N.B.S.) mixture samples.

| Constituent                                 | Range   | Maximum deviation | Average absolute deviation |
|---|---------|-------------------|----------------------------|
| SiO <sub>2</sub>                            | 24-80   | + 0.8             | 0.38                       |
| Al <sub>2</sub> O <sub>3</sub>              | 9-36    | - .8              | .30                        |
| Total Fe, as Fe <sub>2</sub> O <sub>3</sub> | .8-16   | - .2              | .08                        |
| TiO <sub>2</sub>                            | .01-1.5 | - .2              | .05                        |
| MnO   | .00-.27 | + .02             |                            |
| P <sub>2</sub> O <sub>5</sub>               | .04-2.4 | + .1              | .03                        |
| CaO   | .10-15  | + .2              | .10                        |
| MgO   | .04-8.1 | - .2              | .07                        |
| Na <sub>2</sub> O                           | .09-7.0 | - .1              | .07                        |
| K <sub>2</sub> O                            | .19-8.3 | + .2              | .05                        |

SUGGESTED SCHEDULE FOR RAPID ANALYSIS OF EIGHT SILICATE ROCK SAMPLES

1st day:

- p. m.  
 3:00- 3:20. Weigh 0.1000 g samples for solutions A.  
 3:20- 3:30. Fuse samples for solutions A with NaOH.  
 3:30- 3:50. Weigh 1.000 g samples for solutions B.  
 3:50- 4:00. Add HF and H<sub>2</sub>SO<sub>4</sub> to crucibles containing samples for preparation of solutions B. Place on steambath.  
 4:00- 4:15. Add water to crucibles containing samples for preparation of solutions A.

2d day:

- a. m.  
 7:45- 7:50. Remove covers from crucibles on steambath, solutions B.  
 7:50- 8:50. Prepare solutions A.

2d day--Continued.

- a. m.  
 8:50-10:00. Make solutions and develop the color for SiO<sub>2</sub>, solutions A.  
 10:00-10:15. Transfer crucibles from the steambath to a heater and heat until fumes of SO<sub>3</sub> evolve. Solutions B.  
 10:15-11:00. Take aliquots of Solutions A and develop color for Al<sub>2</sub>O<sub>3</sub>.  
 11:00-11:15. Make readings with spectrophotometer for SiO<sub>2</sub>.  
 11:15-11:30. Add water to platinum crucibles. Place on steambath and allow to digest, solutions B.  
 11:30-12:00. Lunch.  
p. m.  
 12:00-12:05. Remove crucibles from steambath, solutions B.  
 12:05-12:30. Make readings on spectrophotometer for Al<sub>2</sub>O<sub>3</sub>.  
 12:30- 1:00. Prepare solutions B.

## 2d day--Continued

- p. m.
- 1:00- 1:15. Withdraw aliquots of solutions B for alkalies.
- 1:15- 1:30. Withdraw aliquots of solutions B for MnO. Add reagents. Place on hotplate.
- 1:30- 1:55. Withdraw aliquots of solutions B for TiO<sub>2</sub>. Add reagents. Make readings on spectrophotometer.
- 1:55- 2.00. Transfer beakers and solutions for MnO to cooling bath.
- 2:00- 2:30. Withdraw aliquots of solutions B for P<sub>2</sub>O<sub>5</sub>. Add reagents. Make readings on spectrophotometer.
- 2:30- 2:40. Transfer solutions for MnO from beakers to volumetric flasks.
- 2:40- 3:10. Withdraw aliquots of solutions B for total iron. Add to HCl. Make readings on spectrophotometer.
- 3:10- 3:30. Make spectrophotometer readings for MnO.
- 3:30- 4:15. Calculate SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, total iron, MnO.

## 3d day:

- a. m.
- 7:45- 8:15. Weigh samples for ignition loss.
- 8:15- 8:25. Preheat crucibles containing samples for ignition loss.
- 8:25- 8:30. Transfer crucibles containing samples for ignition loss to the muffle furnace.
- 8:30- 9:15. Take aliquots of solutions B for CaO and MgO and separate R<sub>2</sub>O<sub>3</sub>.
- 9:15- 9:55. Titrate CaO.
- 9:55-10:05. Remove crucibles from muffle and transfer to desiccators.
- 10:05-10:45. Titrate MgO.
- 10:45-11:00. Weigh crucibles for determination of ignition loss.

## 3d day--Continued

- a. m.
- 11:00-11:30. Weigh samples for FeO.
- 11:30-12:00. Lunch
- p. m.
- 12:00-12:05. Add reagents to crucibles for FeO.
- 12:05-12:15. Boil solutions for decomposition of samples for FeO.
- 12:15-12:20. Transfer crucibles containing solutions for FeO to beakers.
- 12:20-12:40. Titrate FeO.
- 12:40- 1:40. Transfer solutions for alkalies to 200 ml volumetric flasks and separate R<sub>2</sub>O<sub>3</sub>, solutions B.
- 1:40- 2:00. Mix sample and internal standard solutions.
- 2:00- 2:45. Determine K<sub>2</sub>O with the flame photometer.
- 2:45- 3:30. Determine Na<sub>2</sub>O with the flame photometer.
- 3:30- 4:15. Calculate ignition loss, MgO, CaO, FeO, K<sub>2</sub>O and Na<sub>2</sub>O.

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