# Contributions to Geochemistry 1949

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GEOLOGICAL SURVEY BULLETIN 992

DEPARTMENT OF THE INTERIOR
March 3, 1849

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By W. W. BRANNOCK *and others*

CONTRIBUTIONS TO GEOCHEMISTRY, 1949

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# FOREWORD

By Earl Ingerson

This bulletin is the third of the series "Contributions to Geochemistry" which was begun in 1946 with Bulletin 950, "Contributions to Geochemistry, 1942–45." A second member of the series, "Contributions to Geochemistry, 1950" appeared in 1951 as Bulletin 980. References to earlier reports of work done in the laboratories of the predecessors of the Geochemistry and Petrology Branch can be found in the forewords of the bulletins mentioned above.

A considerable part of the work of the Geochemistry and Petrology Branch is the study and analysis of geologic materials for other Government organizations, especially other branches of the Geologic Division of the U. S. Geological Survey. It is natural, therefore, that an important part of the research work of the Geochemistry and Petrology Branch is concerned with developing new techniques and analytical methods or improving known ones and adapting them to special problems.

The object may be to increase the sensitivity or accuracy of a determination, to increase speed, or to obtain better and more consistent results in the presence of interfering elements. For example, the method for the fluorimetric determination of aluminum in phosphate rock, described by Grimaldi and Levine, was developed in response to a request for such a large number of these analyses that they could not have been done by the personnel available using methods then current. The papers on "The determination of sodium and potassium in silicate rocks by the flame photometer" and "A photometric method for the estimation of the oil yield of oil shale" are also aimed at greater speed without loss of essential accuracy. "Determination of phosphorus in rocks containing vanadium" is an example of a method for better determination of an element in the presence of an interfering one.

Much of the research work of the Geochemistry and Petrology Branch is published in specialized journals. Most of the papers that are largely mineralogical, for example, are published in the *American Mineralogist*. Papers that deal with geochemical interpretation are likely to appear in *Geochimica et Cosmochimica Acta* and some of the work on analytical methods has appeared in *Analytical Chemistry*.

It is considered worth while, however, to have groups of papers dealing with laboratory techniques for work with geologic materials collected and published from time to time as bulletins of the U. S. Geological Survey. It is hoped that the series will come to the attention not only of geochemists and rock analysts, but also of chemists studying artificial inorganic materials to which these methods and techniques are applicable.

# CONTENTS

# ILLUSTRATIONS

# Part 1. THE DETERMINATION OF SODIUM AND POTASSIUM IN SILICATE ROCKS BY FLAME PHOTOMETER

By W. W. Brannock and Sarah M. Berthold

## CONTENTS

## ILLUSTRATIONS

### ABSTRACT

A method is given for the determination of sodium and potassium in silicate rocks using the Perkin-Elmer model 52A flame photometer with a special glass atomizer, which is described. Samples are decomposed by digesting with HF and $H_2SO_4$. The $R_2O_3$ group and calcium are removed by precipitating with an excess of $NH_4OH$ and $(NH_4)_2CO_3$ at a definite volume. $LiNO_3$ is added to a portion of filtrate, and sodium and potassium are determined on this solution. Results are as accurate as are normally obtained by the J. Lawrence Smith method, and analyses require only about one-fifth the usual time.

## INTRODUCTION

In flame photometry, solutions are atomized into the flame of a gas burner, and the concentrations of the relatively easily excited metals are determined by measuring the intensity of a part of their characteristic spectral emissions and comparing the emissions with those of solutions of known concentrations.

Lundegårdh (1929; 1934) described a procedure in which the intensities of spectral emissions obtained when solutions were atomized into a flame were determined by measuring the densities of lines on photographic plates as in spectrographic techniques. Flame photometry differs from Lundegardh's procedure in that spectral emissions are measured directly with a photometer.

Several instruments using filters and photocells or phototubes were in use in Germany during the 1930's (Schmitt and Breitweiser, pp. 750–57). In 1945, a flame photometer was described in this country by Barnes and others (1945, pp. 605–611). This instrument used propane gas for the flame, filters to isolate the desired portions of the spectrum, and a phototube and a galvanometer to measure the intensities of the emissions. This was a direct intensity type of instrument, employing no internal standard.

In 1946, Berry, Chappell, and Barnes (1946, pp. 19–24) described a flame photometer with a dual optical system designed for use with lithium as an internal standard, as well as for direct intensity determination. In procedures using an internal standard the intensity of the emission of the unknown element is compared simultaneously with the emission of the internal standard, which has been added to the sample and standard solution in like amounts. This internal standard technique reduces the disturbing effects of variation in flame character caused by changes in the gas and air pressures, the presence of foreign salts, and differences in viscosity of the solutions.

In 1947 the Perkin-Elmer Corp. brought out their model 52A flame photometer, which was similar to the instrument described by Berry, Chappell, and Barnes. This is the instrument which has been used in the procedure described in this paper.

Sodium and potassium in solution can be rapidly and conveniently determined with the model 52A flame photometer by internal-standard procedures. A comparatively simple and rapid procedure can be employed for preparation of the sample solution for analysis of silicate rocks, as most silicate rocks can be decomposed by digestion with HF and $H_2SO_4$. Complete solution of the sample is definitely more desirable than an extraction such as is necessary in the commonly used J. Lawrence Smith method.

By using the method described in this paper, a person with comparatively little training in chemistry can determine sodium and potassium in a group of silicate rock samples in approximately one-fifth the time that would be required by a trained analyst using the J. Lawrence Smith procedure.

## ACKNOWLEDGMENTS

The authors are indebted to Michael Fleischer, Rollin E. Stevens, William G. Schlecht, and Leonard Shapiro, colleagues at the U. S. Geological Survey, for their helpful suggestions and criticisms.

## PROCEDURE

### OUTLINE AND DISCUSSION

1. The sample is decomposed by overnight digestion with $HF+H_2SO_4$ in a 100 ml platinum crucible.
2. $R_2O_3$ plus $CaCO_3$ is precipitated once with $NH_4OH$ and $(NH_4)_2CO_3$ at a fixed volume. Only a part of the solution is filtered.
3. The sample solution is prepared for analysis by mixing 50 ml of the filtrate from the precipitation of $R_2O_3$ plus $CaCO_3$ with 50 ml of solution containing 200 ppm lithium as $LiNO_3$ for internal standard.
4. Potassium is determined with the flame photometer by comparison with standard solutions of potassium containing 100 ppm lithium.
5. Sodium is determined with the flame photometer by comparison with standard solutions of sodium containing 100 ppm lithium.

Most silicate rocks and minerals are completely decomposed by digesting a sample overnight with HF and $H_2SO_4$ in a covered platinum crucible. The sample must have been ground to pass a 100-mesh screen. Boiling the sample with HF and $H_2SO_4$ for one-half hour to an hour in a covered crucible will decompose most silicate rocks and minerals also. Samples which are not completely decomposed after overnight digestion should, in addition, be boiled for approximately one-half hour. Zircon and tourmaline are not completely decomposed by either treatment. Zircon does not contain sodium or potassium and so decomposition of zircon is not essential. Tourmaline, on the other hand, may contain as much as 2 percent $Na_2O$, 2 percent $Li_2O$, and 0.2 percent $K_2O$. Most rocks, however, contain little if any tourmaline. When tourmaline, or rocks containing appreciable tourmaline, are analyzed for $Na_2O$ or $K_2O$ it is advisable to use the J. Lawrence Smith decomposition.

After the sample is decomposed, most of the HF is removed by evaporation on the steam bath. A few drops of $HNO_3$ are added to aid in removal of HF and organic matter, if present; and most of the remaining HF is removed by heating until strong fumes of $SO_3$ evolve. It is advisable not to prolong the fuming of $SO_3$ in order not to lose appreciable $H_2SO_4$ and as a consequence reduce the amount of $(NH_4)_2SO_4$ which will be formed when $R_2O_3$ is removed by addition of $NH_4OH$. It is desirable to maintain the $(NH_4)_2SO_4$ at approximately the same concentration in both the sample solutions and the standard solutions. The concentration of $(NH_4)_2SO_4$ is calculated on the basis of the amount of $H_2SO_4$ used. Allowing the material to remain at the fuming temperature of $H_2SO_4$ for an extended time would also tend to form basic salts of iron and aluminum which are difficult to dissolve.

The crucible and contents are allowed to cool and approximately 75 ml of distilled water is added. Fifteen to thirty min. digestion on the steam bath brings about essentially complete solution of the residue.

In order to avoid contamination by solution of alkalies from the volumetric flask, the acid solution, which may contain a small amount of HF, should be at room temperature before transfer to the volumetric flask.

Since iron, aluminum, and calcium have an appreciable disadvantageous effect on the determination of sodium, it is advisable to remove them from the solution to be analyzed. (See table 1.) Precipitating the $R_2O_3$ group and $CaCO_3$ at room temperature with $NH_4OH$ and $(NH_4)_2CO_3$, making to volume in a volumetric flask, and filtering only a part of the solution gives a satisfactory separation which is rapid and simple.

The solution for analysis is prepared to contain 100 ppm lithium for internal standard, by mixing 50 ml of the filtrate above with 50 ml of a solution of $LiNO_3$ in which the concentration of lithium is 200 ppm.

The use of an internal standard in flame-photometer determinations reduces to negligible factors many interferences and variations resulting from changes in flame characteristics brought about by small changes in gas or air pressures, the presence of foreign ions, and differences in viscosities of the solutions being analyzed. The variations mentioned, coupled with a certain "drift," which is considered normal to an electronic instrument such as the flame photometer, at times reach such levels that calibration curves cannot be relied upon to give results as accurate as desired in the analysis of rocks and minerals.

These difficulties are satisfactorily overcome by obtaining readings for a standard of higher concentration than the unknown, then taking the reading for the unknown, and immediately taking a reading for a standard of lower concentration than the unknown. Two or three such series of readings are taken for each determination. This takes only a few minutes and changes or variations in flame or instrument that occur affect readings for both standards and sample in a similar manner.

Readings are not exactly proportional to concentrations of sodium and potassium, but the interval used between the standards is small enough so that deviations are not appreciable.

## APPARATUS AND REAGENTS

Apparatus: Perkin Elmer Model 52A flame photometer with glass atomizer shown in figure 1 and described below, which has been substituted for the atomizer furnished by the manufacturer.
Beaker stand.
Constant-voltage transformer.
Propane gas.
Regulators, pressure: 2 for gas, 1 for air.
Air compressor or constant supply of compressed air, 30 to 150 psi.
Air filter for compressed air.
Glass-stoppered bottles (pyrex):
  250 ml.
  1 l.
  2 l.
  9 l.
Volumetric flasks: 100, 200, 1000, 2000 ml.
Pipettes, transfer: 25, 50, 100 ml.
Tissues: facial type, fairly hard and lint-free.
Burette: 50 ml.
Beakers: 30 ml or 50 ml.

Reagents: KCl, NaCl, $LiNO_3$, $(NH_4)_2SO_4$, $H_2SO_4$, $HNO_3$, HF, all of ACS grade.
  Stock solutions:
    KCl containing 1,000 ppm potassium: 2 l.
    NaCl containing 1,000 ppm sodium: 2 l.
    $LiNO_3$ containing 2,000 ppm lithium: 8 l or more.
  200 ppm lithium solution for internal standard: 2 l.
  Sample diluting solution containing 100 ppm lithium plus 1 percent $(NH_4)_2SO_4$: 2 l.
  Standard potassium solutions containing 2.5, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0 ppm potassium, respectively, plus 100 ppm lithium and 1 percent $(NH_4)_2SO_4$: 1 l each.
  Standard sodium solutions, 2.5, 5.0, 10.0, 20.0, 30 0, 40.0, 50.0 ppm sodium, respectively, plus 100 ppm lithium and 1 percent $(NH_4)_2SO_4$: 1 l each.

## DESCRIPTION OF SPECIAL GLASS ATOMIZER

A special atomizer, shown in figure 1, was designed for use in determining alkalies in solutions prepared from silicate rocks. It has certain advantages, when used for this purpose, over the stainless-steel adjustable funnel-type atomizer which was supplied with the instrument, and also over the all-glass funnel-type now available from the Perkin-Elmer Corp. It atomizes a solution into the flame at the relatively slow fixed rate of approximately 4 ml per minute so that a

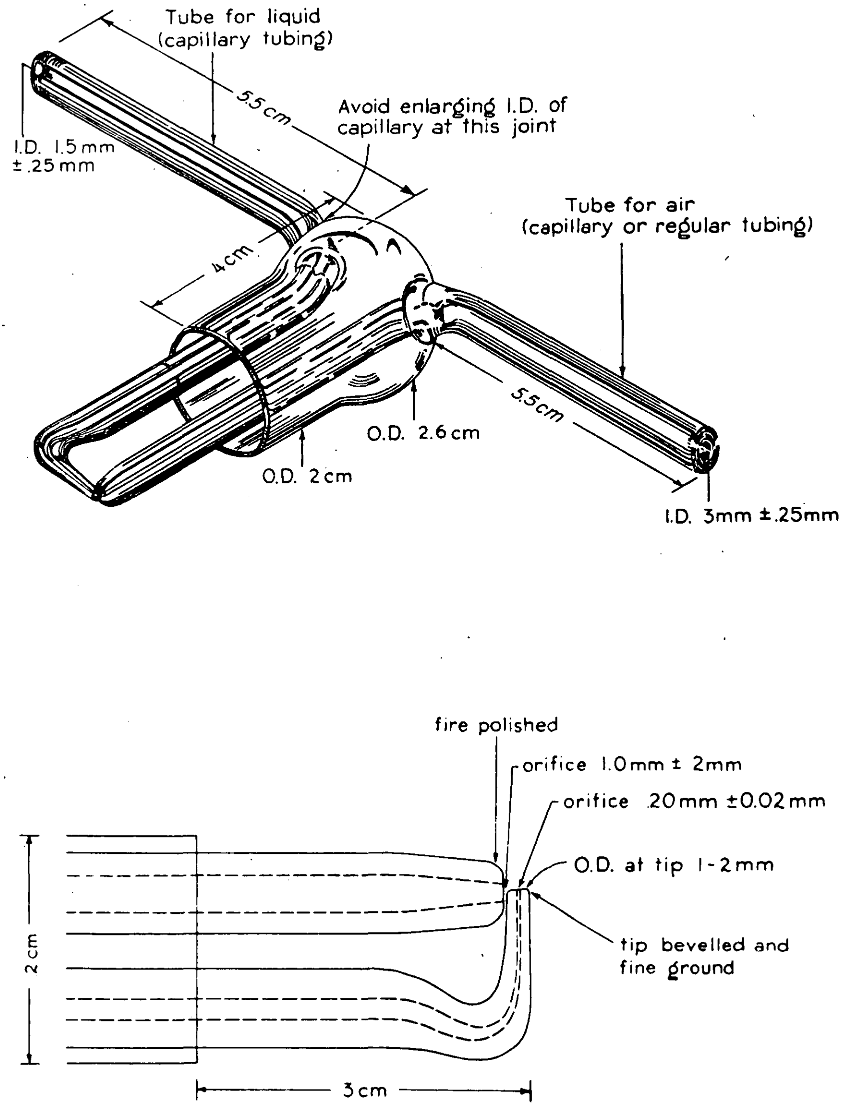

FIGURE 1. Special glass atomizer.

maximum of approximately 10 ml of each sample and standard solution would be consumed for each complete determination. When the air pressure is set at 10 psi and propane gas is used as described under the section "Starting the flame photometer" it gives a steady flame of approximately 15 cm height. This atomizer draws solution up through the capillary intake tube from a beaker. When the beaker is withdrawn the capillary tube empties at once. The outside of the tube can be wiped clean with a hard, lintless tissue; another solution can be passed in, and the capillary is flushed clean almost immediately. Waiting for solutions to clear is eliminated, and deliberate rinsing and flushing is unnecessary with this type of atomizer.

## PRELIMINARY STEPS

### PREPARATION OF THE SAMPLE SOLUTION

1. Transfer 0.5000 g of sample powder (100-mesh or finer) to a 100 ml platinum crucible—a type commonly used in the determination of FeO. If the sample is believed to contain more than 5 percent $Na_2O$ or 5 percent $K_2O$, a 0.2000 g sample should be taken.

2. Add 6 ml of 1+1 $H_2SO_4$ and approximately 25 ml of HF. Cover the crucible and digest overnight on a steam bath or gently boil until the sample is decomposed.

3. Remove and rinse the cover. Allow the solution to evaporate on the steam bath approximately to concentrated $H_2SO_4$.

4. Add 5 or 10 drops of $HNO_3$ and evaporate on a steam bath until acid fumes are no longer given off.

5. Carefully heat the crucible and contents over an electric heater or low flame of a gas burner until strong $SO_3$ fumes evolve.

6. Allow the crucible and contents to cool. Then nearly fill the crucible with distilled water and digest on a steam bath until essentially complete solution of the residue is obtained.

7. Allow the solution to cool to room temperature in the crucible. Then transfer the solution to a 200 ml volumetric flask—preferably one of borosilicate glass—or, if the sample is believed to contain not more than 1 percent $Na_2O$ or 1 percent $K_2O$, use a 100 ml volumetric flask. Wash the residual solution from the crucible into the flask with distilled water and fill the flask to approximately 20 ml from the line.

8. Add $NH_4OH$ to the flask until a slight excess is present as indicated by the change to blue of a small piece of red litmus paper.

9. Then add approximately 0.5 ml of freshly prepared concentrated ammonium carbonate solution.

10. Make up to 200 ml with distilled water and mix well.

11. Filter 75 to 100 ml of the solution into a pyrex bottle or beaker through a dry 12.5 cm Whatman No. 40 paper in a dry funnel.

12. Withdraw 50 ml of the filtrate with a transfer pipette and mix with exactly 50 ml of the $LiNO_3$ solution containing approximately 200 ppm lithium. Mix well and set aside for the determination of potassium and sodium.

### STARTING THE FLAME PHOTOMETER

13. The instrument is set up as described in the instruction manual (Perkin-Elmer Corp., 1948), except for the following changes: A

special glass atomizer as shown in figure 1 and described above is substituted, a second pressure gauge is installed in the gas line to give a steadier flame, the spring suspension for the burner chimney is discarded, and the chimney is allowed to stand upright on the shelf through which the burner protrudes. The red-sensitive phototube is used for the determination of both potassium and sodium.

14. Adjust the air pressure to 10 psi, open the main valve on the propane tank, set the gas regulator which is nearest the main valve to 10 psi, 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 valve, so that the flame is steady and blue with small sharply 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 the center.

15. Turn the electric switch on the panel of the instrument to the "on" position and allow the instrument to warm up for approximately 30 min. before using.

## DETERMINATION OF THE METAL

### POTASSIUM

[Steps 16–29, inclusive]

16. If the approximate concentration of potassium in the solution can be estimated, omit steps 16 to 22 and proceed with step 23. If not, pour 15 to 20 ml of standard potassium solution, in which the potassium concentration is 50 ppm, 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.

17. While this solution (step 16) is 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, using 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. Remove the beaker and wipe the outside of the liquid inlet tube of the atomizer with a clean lintless facial tissue. Record the setting of the internal-standard dial.

18. Put 15 to 20 ml of the sample solution (step 12) 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.

19. Should the meter read more than 50 (step 18) with the internal-standard dial set at 100, while the sample solution is atomizing, a concentration of potassium in the sample solution greater than 50 ppm is indicated. In this case, in order to get an approximate value for the concentration of potassium in the sample solution, set the internal-standard dial to read 100 and adjust the meter to read 50 with the coarse- and fine-gain controls while the sample solution is atomizing into the flame. Remove the sample solution and with no solution passing into the flame set the meter to read 50, using the zero-adjusting knob. Again atomize the sample solution into the flame, set the internal-standard dial to 100, and adjust the meter to read 50, using the coarse- and fine-gain controls. Remove the beaker containing the sample solution and wipe the atomizer tube with a tissue.

20. Place the beaker with the standard solution containing 50 ppm potassium in position to atomize and adjust the internal-standard dial so that the meter again reads 50. Remove the solution, wipe the atomizer tube, and record the setting of the internal-standard dial.

21. Assume the readings recorded to be proportional to the concentrations of potassium in the standard and sample solutions and calculate the approximate concentration of potassium in the sample solution, using either the values obtained in steps 17 and 18 or steps 19 and 20.

22. Should the concentration of potassium in the sample solution be greater than 50 ppm a 50 ml aliquot is mixed with 50 or 100 ml of diluting solution, containing 100 ppm lithium and 1 percent $(NH_4)_2SO_4$ to furnish a solution in which the concentration of potassium does not exceed 50 ppm.

23. Repeat step 17 using the standard solution with the nearest higher concentration to the estimated concentration of potassium in the sample solution.

24. Repeat step 18.

25. Repeat step 18 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.

26. With the same solution (step 25) 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.

27. Repeat step 18.

28. Repeat step 18 using the higher standard instead of the sample solution.

29. The equation below is used to calculate the concentration of potassium in the sample solution after averaging the readings obtained for each standard solution and the sample solution.

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

where $x$=concentration of potassium in the sample solution,
$y$=dial reading for the sample solution,
$x_1$=concentration of potassium in the lower standard solution,
$y_1$=dial reading for the lower standard solution.
$x_2$=concentration of potassium in the higher standard solution, and
$y_2$=dial reading for the higher standard solution.

## SODIUM

[Repeat steps 16–29, substituting sodium for potassium throughout]

Sodium is determined on a portion of the same solution containing the internal standard which was used for the determination of potas-

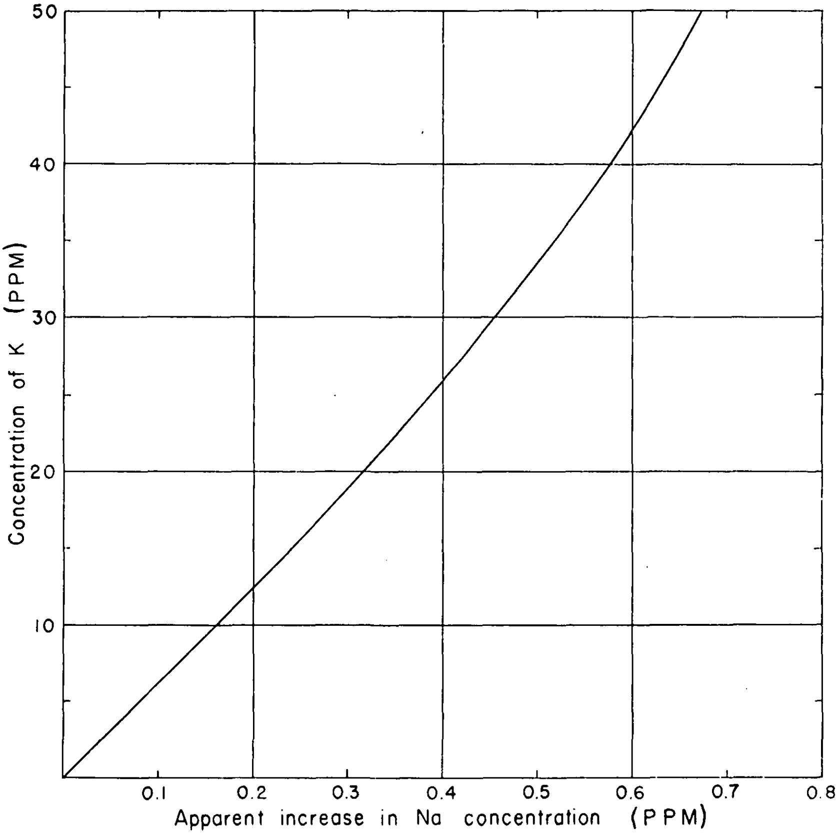

FIGURE 2.—Correction curve for the effect of potassium on sodium.

sium. The element selector is set to the position of maximum response for sodium and the concentration is determined in the same way as that of potassium. Since potassium, when present, causes a small increase in the values for sodium, more accurate results are obtained when a correction is made for this effect. A correction curve obtained for the instrument used in this work from a series of standard sodium solutions to which known amounts of potassium were added is shown in figure 2. The value for concentration of sodium is calculated the same way as for potassium and the correction for potassium is subtracted. Then the percent $Na_2O$ in the original sample can be computed.

## RESULTS OF EXPERIMENTS

### EFFECT OF SALTS OF ALUMINUM, IRON, CALCIUM, MAGNESIUM, AND OF $(NH_4)_2SO_4$ ON VALUES FOR SODIUM

Aluminum, iron, calcium, magnesium, and ammonium sulfates will be present in appreciable amounts after the breakup of the sample and re-solution of the residue. Table 1 shows the results of experiments to determine their effect on the determination of sodium. The concentrations include approximately the maximums that would be encountered in the analysis of silicate rocks. These data indicate the advisability of eliminating the effects due to the presence of aluminum, iron, calcium, and $(NH_4)_2SO_4$. The effects of magnesium on the sodium determination are not serious enough to need consideration.

TABLE 1.—*Effects of salts of aluminum, iron, calcium, magnesium, and of* $(NH_4)_2SO_4$ *on the determinations of sodium*

| Na(ppm) | Added | Apparent Na(ppm) | Change (percent) |
|---|---|---|---|
| 50.0 | 2,500 ppm Al | 51.7 | +3.4 |
| 50.0 | 1,000 ppm Fe | 53.1 | +6.2 |
| 50.0 | 500 ppm Ca | 50.1 | +.2 |
| 5.00 | 500 ppm Ca | 5.84 | +16. |
| 50.0 | 500 ppm Mg | 50.3 | +.6 |
| 5.00 | 500 ppm Mg | 5.11 | +2.2 |
| 50.0 | [1] $(NH_4)_2SO_4$ | 50.8 | +1.6 |
| 5.00 | [1] $(NH_4)_2SO_4$ | 5.01 | +.2 |

[1] Resulting concentration includes 2 percent $(NH_4)_2SO_4$.

### EFFECT OF MAGNESIUM ON VALUES FOR POTASSIUM

After the removal of aluminum, iron, and calcium and the elimination of the effects of $(NH_4)_2SO_4$ by maintaining it at the same concentration in samples and standards, there remain to be considered the effects of magnesium and sodium on the determination of potassium and the effects of potassium on the determination of sodium. Table 2 shows the effects of magnesium on the potassium determination to be negligible.

TABLE 2.—*Effects of magnesium on the determination of potassium*

| K (ppm) | Mg added (ppm) | Apparent K (ppm) | Change (percent) |
|---|---|---|---|
| 50.0 | 500 | 50.3 | +0.6 |
| 5.00 | 500 | 4.97 | −.6 |

## EFFECT OF POTASSIUM ON VALUES FOR SODIUM

Figure 2 shows the curve used to correct the values of sodium for the effects of potassium. It was prepared from results obtained when known amounts of KCl were added to solutions with known sodium concentrations. The effects are independent of the sodium concentration.

## DETERMINATION OF POTASSIUM AND SODIUM IN SOLUTIONS CONTAINING KCl AND NaCl ONLY

A series of solutions containing known amounts of KCl and NaCl were prepared and then analyzed by the flame photometer. The results are shown in table 3. No corrections were applied to the values obtained for KCl.

TABLE 3.—*Determination of potassium and sodium in solutions containing KCl and NaCl only*

| Solution No. | Operator | KCl | | | NaCl | | |
|---|---|---|---|---|---|---|---|
| | | Taken (mg) | Found (mg) | Deviation (percent) | Taken (mg) | Found (mg) | Deviation (percent) |
| 1 | SMB | 36.1 | 36.4 | +0.8 | 7.77 | 7.86 | +1.2 |
| 1 | WWB | 36.1 | 36.0 | −.3 | 7.77 | 7.85 | +1.0 |
| 2 | SMB | 36.1 | 36.0 | −.3 | 26.3 | 26.3 | .0 |
| 2 | WWB | 36.1 | 35.9 | −.6 | 26.3 | 26.4 | +.4 |
| 3 | SMB | 36.1 | 35.7 | −1.1 | 47.0 | 46.7 | −.6 |
| 3 | WWB | 36.1 | 36.1 | .0 | 47.0 | 46.4 | −1.3 |
| 4 | SMB | 20.1 | 20.1 | .0 | 7.77 | 7.92 | +1.9 |
| 4 | WWB | 20.1 | 20.1 | .0 | 7.77 | 7.90 | +1.7 |
| 5 | SMB | 20.1 | 20.2 | +.5 | 26.3 | 26.6 | +1.1 |
| 5 | WWB | 20.1 | 20.1 | .0 | 26.3 | 26.5 | +.8 |
| 6 | SMB | 20.1 | 20.2 | +.5 | 47.0 | 47.1 | +.2 |
| 6 | WWB | 20.1 | 20.0 | −.5 | 47.0 | 47.1 | +.2 |
| 7 | SMB | 6.11 | 6.09 | −.3 | 7.77 | 7.92 | +1.9 |
| 7 | WWB | 6.11 | 6.04 | −1.1 | 7.77 | 7.91 | +1.8 |
| 8 | SMB | 6.11 | 6.10 | −.2 | 26.3 | 26.7 | +1.5 |
| 8 | WWB | 6.11 | 6.11 | .0 | 26.3 | 26.7 | +1.5 |
| 9 | SMB | 6.11 | 6.16 | +.8 | 47.0 | 47.1 | +.2 |
| 9 | WWB | 6.11 | 6.18 | +1.1 | 47.0 | 47.3 | +.6 |

As indicated by the data the effects of sodium on the values obtained for potassium is insignificant. The values for NaCl were computed after the appropriate corrections, indicated in figure 2, were applied. Each solution was analyzed by two operators using the same flame photometer. The maximum percent deviation between the KCl taken and the KCl found is 1.1 percent. The average of the deviations for KCl is 0.4 percent. The maximum percent deviation between the NaCl taken and NaCl found is 1.9 percent. The average of the deviations for NaCl is 1.0 percent.

### RETENTION OF SODIUM OR POTASSIUM BY $Al(OH)_3$, $Fe(OH)_3$, AND $CaCO_3$

One may expect that some alkali would be retained by the precipitate of $R_2O_3$ plus $CaCO_3$. Experiments were performed to determine if retention of alkalies by the precipitate would be significant when the suggested procedure is followed. Table 4 shows the results obtained when solutions containing various known amounts of $Na_2SO_4$ or $K_2SO_4$; plus $Al_2(SO_4)_3$, equivalent to 0.15g $Al_2O_3$; $Fe_2(SO_4)_3$, equivalent to 0.05g $Fe_2O_3$; and $CaSO_4$, equivalent to 0.05g CaO, were carried through the procedure outlined for removal of the $R_2O_3$ group and calcium. The amounts of aluminum, iron, and calcium present were approximately the amounts which would be expected in a typical silicate-rock sample. The experiments indicate that sodium and potassium are not retained by the precipitate of $R_2O_3$ plus $CaCO_3$ and also that the volumetric error due to the precipitate is insignificant.

TABLE 4.—*Retention of sodium or potassium by* $Al(OH)_3+Fe(OH)_3+CaCO_3$

| $Na_2O$ | | $K_2O$ | |
|---|---|---|---|
| Taken (mg) | Found (mg) | Taken (mg) | Found (mg) |
| 1.3 | 1.3 | 1.3 | 1.3 |
| 6.2 | 6.3 | 6.2 | 6.2 |
| 12.5 | 12.6 | 12.5 | 12.5 |
| 25.0 | 25.2 | 25.0 | 25.0 |

### DETERMINATION OF SODIUM AND POTASSIUM IN NATIONAL BUREAU OF STANDARDS STANDARD SAMPLES

Six National Bureau of Standards standard samples were analyzed by the suggested procedure. In table 5 the results with the flame-photometer method are compared with values reported by the National Bureau of Standards. The results obtained with the flame photometer seem to be as good or better than would be expected by gravimetric procedures where the $Na_2O$ or $K_2O$ content is above 1 percent; below this percentage the flame-photometer method is much to be preferred. With the flame photometer measurements can be made in these lower ranges of alkali content with essentially the same precision as with larger percentages. With gravimetric procedures, on the other hand, small percentages are determined with less certainty owing to limitations in accuracy of weighings and possible contamination of the separated compounds.

TABLE 5.—*Determinations of sodium and potassium in National Bureau of Standards standard samples*

| N. B. S. sample No. and type | Determination | N. B. S. values | Flame-photometer method | | |
|---|---|---|---|---|---|
| 70 (feldspar) | $Na_2O$ | 2.38 | 2.33 | 2.35 | 2.32 |
| | $K_2O$ | 12.58 | 12.73 | 12.79 | 12.63 |
| 91 (opal glass) | $Na_2O$ | 8.48 | 8.50 | 8.51 | ---------- |
| | $K_2O$ | 3.25 | 3.22 | 3.25 | ---------- |
| 97 (clay) | $Na_2O$ | .12 | .07 | .07 | .07 |
| | $K_2O$ | .54 | .54 | .54 | .55 |
| 98 (clay) | $Na_2O$ | .28 | .25 | .25 | .28 |
| | $K_2O$ | 3.17 | 3.24 | 3.23 | 3.23 |
| 99 (feldspar) | $Na_2O$ | 10.73 | 10.70 | 10.69 | 10.72 |
| | $K_2O$ | .41 | .41 | .43 | .43 |
| 93 (high-boron glass) | $Na_2O$ | 4.16 | 4.30 | 4.28 | 4.28 |
| | $K_2O$ | .16 | .15 | .14 | .15 |

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# Part 2. A PHOTOMETRIC METHOD FOR THE ESTIMATION OF THE OIL YIELD OF OIL SHALE

By Frank Cuttitta

## CONTENTS

## ILLUSTRATIONS

## TABLES

## ABSTRACT

A method is presented for the distillation and photometric estimation of the oil yield of oil-bearing shales. The oil shale is distilled in a closed test tube and the oil extracted with toluene. The optical density of the toluene extract is used in the estimation of oil content and is converted to percentage of oil by reference to a standard curve. This curve is obtained by relating the oil yields determined by the Fischer assay method to the optical density of the toluene extract of the oil evolved by the new procedure. The new method gives in a much shorter time results similar to those obtained by the Fischer assay method. The applicability of the new method to oil-bearing shale and phosphatic shale has been tested.

## INTRODUCTION

As thousands of oil-shale samples have been assayed in the Trace Elements laboratory, Geochemistry and Petrology Branch, the purpose of the investigation was to study the applicability of photometric procedures to the estimation of oil yield of oil-bearing shales in an effort to develop a simple and rapid method for the determination of oil content of shales and phosphatic shales.

The results of the determination should have a direct correlation with the results obtained by the Fischer assay method so that Fischer determinations could still be used.

The analysis of oil shales is usually made by the modified Fischer retort method—hereinafter referred to as the Fischer method or Fischer assay (Stanfield and Frost, 1946, 1949; Karrick, 1926; Guthrie, 1938). In this method the shale is heated in a special cast-aluminum retort, and the oil yield is determined by condensing and measuring the volatilized oil. Using one still, an assay by the Fischer method requires approximately 2 hours for completion. The Fischer method also requires rather elaborate apparatus and is not a convenient method for fast routine work where the primary object is to screen large numbers of samples.

Closed-tube distillation of oil has been used for qualitative determinations by Trask (1932) and Takahashi (1923). When a rock rich in bitumens is subjected to destructive distillation, the oil formed by the

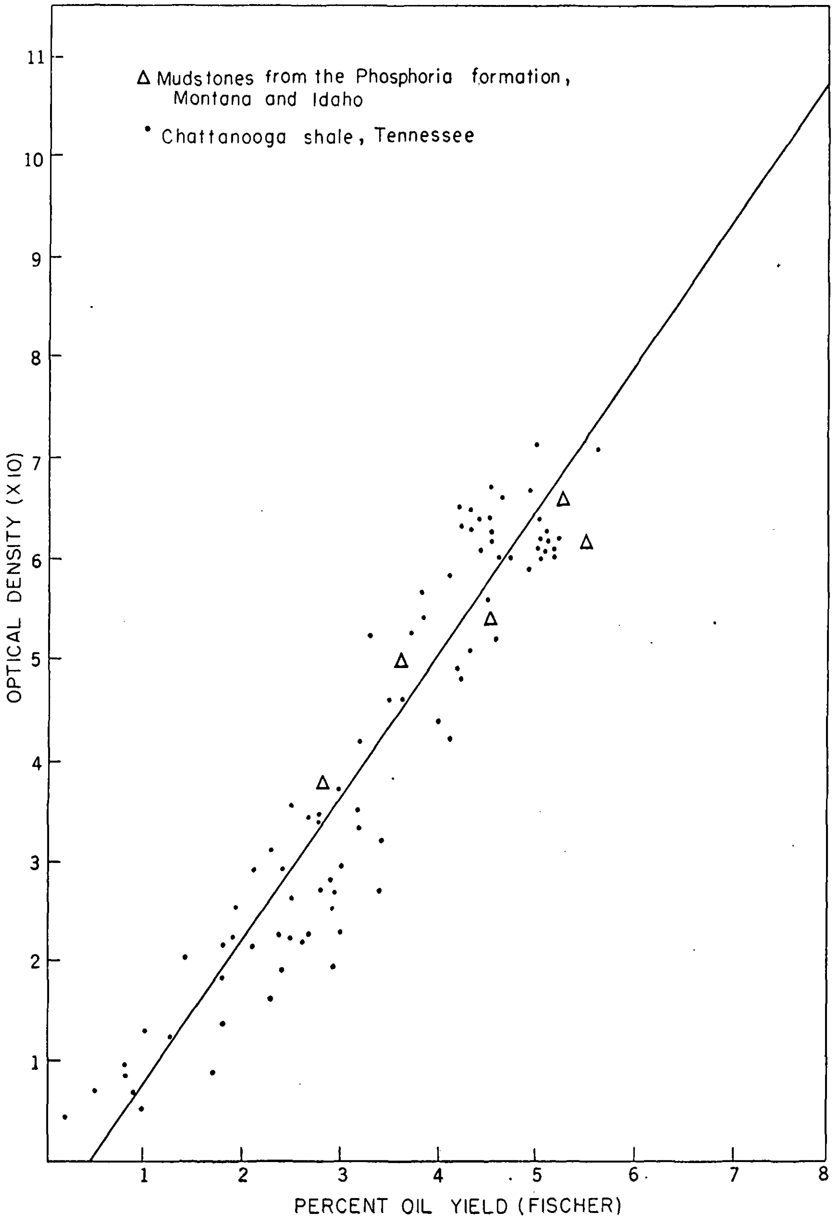

FIGURE 3.—Relation of optical density (X10) to percentage oil yield by Fischer assay method.

distillation accumulates in the horizontal test tube just behind the water. Generally, the lightest constituents of the oil are partly mixed with the water, and the heavier and darker fractions are found toward the hot end of the tube. Looking down the tube during the heating, one sees droplets of oil issuing as a fine mist from the sample

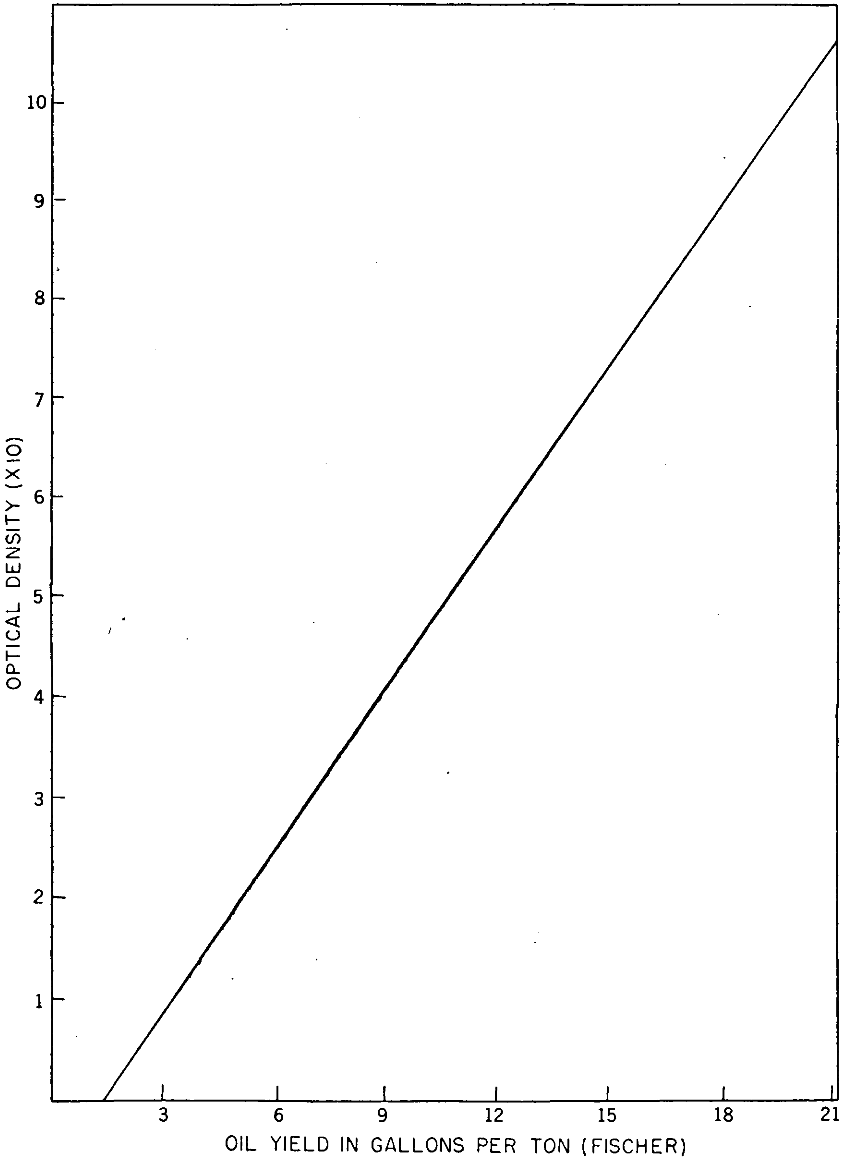

FIGURE 4.—Relation of optical density (×10) to Fischer oil yield, in gallons per ton.

and condensing on the sides. The volume of oil produced by distillation varies greatly and may be so slight that no distillate is visible and only the odor of oil can be detected.

In attempting to estimate the oil content of oil-bearing shale, no correlation could be established between the Fischer assay and a gravimetric determination of the oil evolved in the closed-tube distillation. However, volumetric determination of the oil evolved in the closed-tube distillation was about twice as rapid as the Fischer assay method and gave results comparable to those obtained by the Fischer method. Details of the volumetric determination are given in figure 3.

The present report shows the feasibility of using the optical density of a toluene solution of the oil evolved in a closed-tube distillation as a rapid and quantitative method for the estimation of the oil yield. The method consists of destructively distilling a 0.5g sample of oil shale in a closed test tube, extracting the oil evolved with toluene, and measuring the optical density of the solution with a filter photometer. The amount of oil is read from a curve (fig. 3) relating the oil yields by Fischer assay to the optical density of the toluene extract of the oil distilled by the new procedure. To obtain this curve the optical densities (×10) of the oil obtained by the new procedure were plotted against the percentage of oil as given by the Fischer method. A scatter diagram was obtained and a mean straight curve was fitted visually through the points. The estimated oil yields as obtained by using the standard curve (fig. 1) differed from the Fischer oil yields by an average of 0.37 percent absolute or approximately 1 gal per ton. The maximum difference between the determined (Fischer assay) and the estimated oil yields was 0.94 percent or about 2.5 gal per ton. Figure 4 is the same curve expressed in terms of the relation of optical density (×10) to Fischer oil yield in gallons per ton of shale.

This linear relationship (fig. 3) was established from a study of 75 samples of Chattanooga shale from Tennessee chosen to represent the different grades of shale likely to be encountered in that area. The recommended procedure is to establish similar relationships of optical density to oil yield for other specific areas, such as Idaho and Montana, from representative samples. However, a study of 10 samples from the Phosphoria formation in Montana and Idaho showed that figure 3—established for samples of Chattanooga shale—was applicable also for assay of these samples. This similarity in relationship of optical density to oil yield for the two areas gives some hope that the same curve can be applied to the use of this method for oil shales from other areas.

The method is simple, rapid, and accurate, and 8 to 10 determinations can be made in the same length of time required for the completion of one Fischer assay.

## ACKNOWLEDGMENTS

This work was completed as part of a program undertaken by the Geological Survey on behalf of the U. S. Atomic Energy Commission.

## PROCEDURE FOR ESTIMATING THE OIL YIELD

### PREPARATION OF THE SAMPLE

A representative portion of the sample, ground to −80 mesh, is dried in an oven at 110 C for 1 hour. Oven drying may be omitted for samples to be assayed on the "as received" basis. A −80 mesh sample size was selected because this is the size generally used in the U. S. Geological Survey for chemical analysis. No attempt was made to determine the effect of particle size upon oil yield.

### APPARATUS

The test tube used in the closed-tube distillation of the shale is a pyrex glass-stoppered tube, 15×50 mm with a no. 16 standard taper glass stopper.

The centrifuge tube used to measure the oil yield of the oil shale is the Goetz Phosphorus tube, and the centrifuge must be large enough to handle the centrifuge tube.

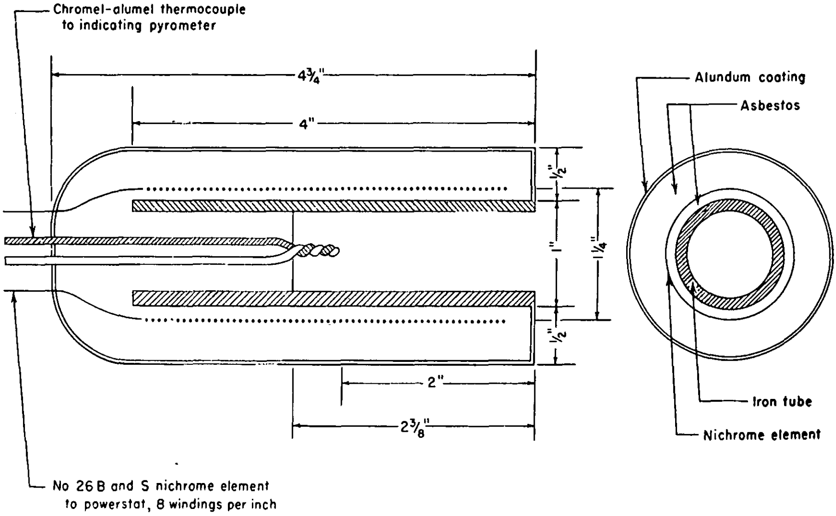

FIGURE 5.—Details of tubular electric furnace.

The tube furnace used was made by winding a coil of nichrome (no. 26 B and S,) the coils spaced about ⅛ inch apart, on an iron tube that has been covered with a piece of asbestos (or mica) to avoid short circuiting the winding. The inner tube and its resistance wire are covered with several layers of asbestos and finally coated with alundum (alumina with clay binder). The details of this furnace are shown in figure 5. The embedding of the nichrome element in asbestos and alundum offers protection from physical damage, minimizes oxidation, and assures a uniform distribution of heat.

A chromel-alumel thermocouple is used for the temperature measurement. Such couples, matched to give the temperature to ±5 C, are obtainable from various manufacturers. The indicating pyrometer is calibrated in both Fahrenheit and centigrade scales in 50-degree increments up to 2,000 F and 1,100 C.

Temperatures are regulated by an input control. The variable transformer used was for 115-volt line, frequency 50/60, output voltage of 0–135, and a maximum output amperage of 7.5. A fixed setting of the variable transformer permitted a reasonably constant temperature in spite of the usual line-voltage fluctuations.

The furnace is designed to provide a fast rate of heating with good temperature control. It will stand nearly continuous use at temperatures up to 600 C and may be used for short intermittent periods up to a maximum of 900 C.

## RECOMMENDED PROCEDURE

A 0.500g sample of the dry shale crushed to pass an 80-mesh sieve is weighed into a 25ml pyrex, glass-stoppered test tube. The lower one-third of the test tube is heated in a horizontal position in the specially constructed small tubular electric furnace at 480 to 500 C for 11 to 14 min. It is essential that strict adherence to the predetermined time and temperature conditions be observed. The exposed upper two-thirds of the stoppered test tube acts as an air condenser. When the distillation period is complete, the closed test tube is removed from the tube furnace and is then allowed to air cool to room temperature.

Then 10ml of toluene are added, the tube is stoppered, and vigorously shaken for 20 sec. The oil evolved by the destructive distillation and extracted by the toluene is filtered through a 9cm, white, no. 589 S and S paper, and the filter paper and residue are washed with two 5ml portions of toluene. The combined extract and washings are diluted to a final volume of 25ml with toluene. The optical density (×10) of the solution of toluene and oil is measured at 420 m$\mu$ (blue filter) on a filter photometer with pure toluene set at 100-percent transmission. The instrument used in this investigation was the Lumetron Colorimeter.

The oil yield of the shale is then determined by reference to the standard curve established for that particular oil-shale deposit. The standard curve was obtained from a study of 80 shale samples assayed in the manner described above. The optical densities (×10) of oil obtained by the new procedure were plotted against the percentage of oil as given by the modified Fischer retort method (fig. 3.) A scatter diagram was obtained and a mean straight line was drawn through the points. (See section on relation of optical density (×10) to

Fischer oil yield under "Experimental data and discussion" for further details.)

To avoid the effect of regional differences in oil yield the recommended procedure is to establish standard curves, as in figure 3, for specific areas. A study of these particular samples from Tennessee, Montana, and Idaho showed the applicability of the relation between optical density and oil yield (fig. 3) to the two deposits. It is possible that the same standard curve may be applicable to oil shales from other areas.

In order to obtain reproducible results, the following precautions must be observed:

1. The sample must be mixed thoroughly and be representative of the material submitted for assay.
2. The closed-tube system must be gas tight. As a precaution against loosening of the stopper, it is advisable to stopper the test tube after heating has begun and prior to the evolution of vapors from the sample.
3. The proper heating must be maintained within the prescribed limits of time and temperature. To insure correct temperature measurements, the pyrometer must be checked or standardized periodically.

### CALCULATIONS

The graph relating the optical density (×10) to the percentage of oil yield by the Fischer method is shown in figure 3. The relation of optical density (×10) to oil yield in gallons per ton (Fischer) is illustrated in figure 4. Figure 4 was derived from figure 3 by taking an average specific gravity of oil as 0.903. For oil-shale samples from Tennessee, the standard deviation of the specific gravity of the oil (table 1) is 0.013. The following formula is used to convert percentage of oil to gallons per ton:

Gallons of oil per ton of shale $=2.65\times$ percentage of oil yield.

## EXPERIMENTAL DATA AND DISCUSSION

The initial work in the development of a new method to determine the oil content of oil shales was to ascertain the effects of different experimental conditions upon the oil yield.

### EFFECT OF SAMPLE WEIGHT ON OIL YIELD

Samples of Chattanooga shale having a Fischer assay oil yield of 3 percent ranging from 0.250g to 2.000g, in 0.250g intervals, were heated at 480 C to 500 C for 11 to 14 min. The oil evolved was extracted with toluene, filtered, and diluted to a final volume of 25 ml.

The results of these tests are shown in table 2. Within limits of experimental error, there was no significant difference in the oil yields for the different weights of sample. The oil yield of the shale was determined by using the standard curve (fig. 3) and interpolated to a percent-by-weight yield.

The 0.500g sample was adopted primarily because this size sample gives favorable density readings for the range of 0.1 percent to 9.9 percent oil.

TABLE 1.—*Specific gravities of oil distillates.* (*60 F/60 F*)

Number of samples, 33
Specific-gravity, mean, 0.903
Σd, 0.367
Average deviation, 0.011 absolute
Standard deviation, 0.013

| Sample No. | Specific gravity | Deviation (d) from mean | Deviation squared $(d^2)\times10^6$ |
|---|---|---|---|
| LC-15-12 | 0.924 | +0.021 | 441 |
| 15 | .920 | +.017 | 289 |
| 31 | .902 | −.001 | 1 |
| 33 | .910 | +.007 | 49 |
| 52 | .895 | −.008 | 64 |
| LC-10-32 | .915 | +.012 | 144 |
| 33 | .926 | +.023 | 529 |
| 34 | .915 | +.012 | 144 |
| 35 | .926 | +.023 | 529 |
| LC-11-13 | .903 | .000 | 0 |
| 15 | .918 | +.015 | 225 |
| 21 | 920 | + 017 | 289 |
| 22 | 921 | +.018 | 324 |
| 31 | .923 | +.020 | 400 |
| 52 | .888 | −.015 | 225 |
| 17R-6-1 | .899 | −.004 | 16 |
| 2 | .906 | +.003 | 9 |
| 3 | .905 | +.002 | 4 |
| 4 | .904 | +.001 | 1 |
| 5 | .903 | .000 | 0 |
| 6 | .889 | −.014 | 196 |
| 7 | .896 | −.007 | 49 |
| 8 | .891 | −.012 | 144 |
| 9 | .891 | −.012 | 144 |
| 10 | .886 | −.017 | 289 |
| 11 | .883 | −.020 | 400 |
| 13 | .897 | −.006 | 36 |
| 14 | .899 | −.004 | 16 |
| 15 | .903 | .000 | 0 |
| 16 | .914 | +.011 | 121 |
| 17 | .922 | +.019 | 361 |
| 18 | .916 | +.013 | 169 |
| 19 | .916 | + 013 | 169 |

TABLE 2.—*Effect of sample weight on oil yield*

| Sample weight (grams) | Optical density (× 10) | Oil yield (percent by weight) | Sample weight (grams) | Optical density (× 10) | Oil yield (percent by weight) |
|---|---|---|---|---|---|
| 0.250 | 1.55 | 3.10 | 1.250 | 10.40 | 3.10 |
| .500 | 3.50 | 2.95 | 1.500 | 12.00 | 2.92 |
| .750 | 5.55 | 2.86 | 1.750 | 14.50 | 3.00 |
| 1.000 | 7.70 | 2.90 | 2.000 | 17.10 | 3.09 |

## EFFECT OF HEATING TEMPERATURE ON OIL YIELD

A study was made of the effect of temperature on the oil yield. A heating time of 13 min was chosen arbitrarily. A 0.500g aliquot of a Chattanooga shale sample containing 4.5 percent oil—determined by the modified Fischer assay—was heated in the manner prescribed under Recommended procedure (p. 21) at the temperatures indicated in table 3. The oil evolved by the distillation was extracted with toluene, filtered, and diluted to a final volume of 25 ml. Measurements of the optical densities (× 10) were made with a Lumetron Colorimeter at 420 mμ (blue filter).

The results showed that the oil yield is dependent upon the temperature of heating. Table 3 shows that the best temperature range for obtaining reproducible oil yields is from 480 C to 500 C. The average optical density (× 10) of the toluene solution of the oil distilled at this temperature range (480 C to 500 C) was 5.95. By consulting the standard curve (fig. 3), it was determined that an optical density of 5.95 coincides with a 4.65-percent oil yield, which is very near the oil content of the shale by Fischer assay.

TABLE 3.—*Effect of heating temperature on oil yield*

| Temperature (C) | Optical density (× 10) | Temperature (C) | Optical density (× 10) | Temperature (C) | Optical density (× 10) |
|---|---|---|---|---|---|
| 260 | 0.10 | [1] 480 | 5.90 | 575 | 7.30 |
| 335 | .40 | [1] 480 | 6.00 | 600 | 7.60 |
| 400 | 2.95 | [1] 480 | 5.90 | 650 | 8.10 |
| 420 | 3.80 | [1] 500 | 6.00 | 675 | 8.50 |
| 440 | 4.90 | 520 | 6.20 | 705 | 9.25 |
| 460 | 5.60 | 540 | 6.90 | | |

[1] Average optical density (×10) in the temperature range 480–500 C is 5.95.

## EFFECT OF HEATING TIME ON YIELD

The effect of heating time on the oil yield was studied. A 0.500-g sample of Chattanooga shale containing 4.5 percent oil was heated at 480 C to 500 C for the times indicated in table 4. The oil evolved by destructive distillation was extracted with toluene, filtered, and diluted to a final volume of 25 ml. Measurements of the optical densities (× 10) were made with a Lumetron Colorimeter at 420 mμ (blue filter).

The results of these tests are shown in table 4. It should be noted that two apparently optimum heating times exist, one from 8 to 10 min and the other from 11 to 14 min. A series of tests with low-grade oil shales showed that a greater degree of reproducibility was attained when the samples were heated from 11 to 14 min than if heated from 8 to 10 min. Thus, it was concluded that heating at 480 C to 500 C for 11 to 14 min gives the most satisfactory and reproducible oil yields. The average optical density (× 10) of the toluene solution of the oil distilled at 480 C to 500 C for 11 to 14 min was 6.11. Using the standard curve (fig. 3), the oil yield related to an optical density of 6.11 is 4.72 percent. It should be noted that these conditions—

heating a 0.500-g sample at 480 C to 500 C for 11 to 14 min—give results that are in agreement with the Fischer method.

TABLE 4.—*Effect of heating time on oil yield*

| Time of heating (minutes) | Optical density (× 10) | Time of heating (minutes) | Optical density (× 10) | Time of heating (minutes) | Optical density (× 10) |
|---|---|---|---|---|---|
| 2 | 1.35 | 11 | 5.90 | 20 | 6.90 |
| 4 | 4.80 | 12 | 6.15 | 22 | 6.70 |
| 6 | 5.00 | 13 | 6.20 | 24 | 6.80 |
| 7 | 5.70 | 14 | 6.28 | 30 | 6.90 |
| 8 | 5.85 | 15 | 6.35 | 35 | 7,00 |
| 9 | 5.80 | 16 | 6.60 | 40 | 5.38 |
| 10 | 5.82 | 18 | 6.70 | | |

## SELECTION OF SUITABLE FILTER

The following tests were made to determine the best filter for density measurements. A composite oil was made by combining 1 ml of each of the oil distillates obtained by the Fischer method from 19 samples of Chattanooga shale. Series of 0.50-ml aliquots of the composite oil were diluted to 50 ml with the solvents indicated in table 5 to form stock solutions. A 2-ml aliquot of each of the stock solutions was further diluted to 25 ml with the respective solvents. The optical densities (× 10) were measured with a Lumetron Colorimeter. A number of filters were available with the filter photometer used. The one which gave the greatest optical density with the oil solution—referred to pure toluene as a blank—was the blue filter (420 mμ). Table 5 shows the variation of the optical density measured with the various filters. The blue filter (420 mμ) was found to be best for all solvents tried; it was therefor selected for the final procedure.

TABLE 5.—*Selection of suitable filter*

| Filter | | Optical density (× 10) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Color | Wave-length (mμ) | Chloroform | Carbon tetrachloride | Ethyl acetate | Carbon disulfide | Benzene | Diethyl ether | Toluene |
| Red | 650 | 0.40 | 0.70 | 0.15 | 0.40 | 0.25 | 0.15 | 0.25 |
| Orange | 580 | .53 | .95 | .20 | .56 | .34 | .16 | .34 |
| Yellow green | 530 | 1.05 | 1.54 | .50 | 1.04 | .68 | .54 | .70 |
| Blue green | 490 | 1.25 | 1.75 | .60 | 1.28 | .87 | .68 | .85 |
| Blue | 420 | 3.29 | 3.57 | 2.59 | 3.62 | 3.02 | 2.58 | 3.00 |
| Violet | 370 | 1.14 | 1.50 | .72 | 1.08 | .90 | .70 | .88 |

## EFFECT OF SOLVENT ON COLOR

The effect of solvent on color and the stability with time was studied. A composite oil was made by combining 1 ml of each of the oil distillates obtained by the Fischer method from 19 samples of Chattanooga shale. A 0.50-ml aliquot of the composite oil was diluted to 50 ml with the solvents indicated in table 6 to form stock solutions. Two milliliters of this stock solution were further diluted at once to a final volume of 25 ml with each of the different solvents. Optical densities (× 10) were measured at 420 mμ (blue filter) with a Lumetron Colorimeter after various intervals of time. The results are given in table 6.

TABLE 6.—*Effect of solvent on color through change in optical density*

| Solvent | Measure of optical density (× 10)— | | | | |
|---|---|---|---|---|---|
| | Immediately | After 1 day | After 2 days | After 5 days | After 7 days |
| Chloroform | 3.29 | 3.70 | 4.25 | 4.75 | 5.80 |
| Carbon tetrachloride | 3.57 | 4.25 | 4.80 | 5.00 | 5.90 |
| Ethyl acetate | 2.59 | 2.63 | 2.58 | 2.58 | 2.61 |
| Carbon disulfide | 3.62 | 2.65 | 3.72 | 3.75 | 3.72 |
| Benzene | 3.02 | 3.08 | 3.02 | 3.04 | 3.03 |
| Diethyl ether | 2.58 | 2.59 | 2.64 | 2.69 | 2.68 |
| Toluene | 3.00 | 3.00 | 2.99 | 2.99 | 2.99 |

The color of the oil solution was found to be dependent on the solvent used. For the same oil concentration, the colors in chloroform, carbon tetrachloride, ethyl acetate, carbon disulfide, benzene, diethyl ether, and toluene ranged from pale yellow to reddish amber. Some of the solvents yielded unstable color systems; the color intensities increased with time. Benzene, toluene, and ethyl acetate gave stable reproducible color systems. The use of ethyl acetate as the solvent was precluded by its low boiling point and the ease of its hydrolysis. Toluene was chosen as the solvent because it is somewhat less a fire hazard and less toxic than benzene.

TABLE 7.—*Color stability of the toluene system*

| Aliquot (ml) | Measure of optical density (× 10)— | | |
|---|---|---|---|
| | Immediately | After 3 days | After 3 months |
| 1 | 1.07 | 1.08 | 1.10 |
| 2 | 1.95 | 1.92 | 1.97 |
| 3 | 2.71 | 2.73 | 2.75 |
| 4 | 3.50 | 3.49 | 3.52 |
| 5 | 4.22 | 4.21 | 4.18 |
| 6 | 4.87 | 4.90 | 4.75 |
| 7 | 5.55 | 5.58 | 5.50 |
| 8 | 6.18 | 6.25 | 6.15 |
| 1 | 1.11 | 1.10 | 1.10 |
| 2 | 1.96 | 1.90 | 1.98 |
| 3 | 2.74 | 2.77 | 2.78 |
| 4 | 3.51 | 3.53 | 3.52 |
| 5 | 4.20 | 4.20 | 4.12 |
| 6 | 4.90 | 4.89 | 4.74 |
| 7 | 5.55 | 5.60 | 5.55 |
| 8 | 6.18 | 6.20 | 6.13 |

## COLOR STABILITY OF THE TOLUENE SYSTEM

Table 7 shows that the toluene color system is exceptionally stable. Approximately the same optical-density readings were obtained whether the densities were measured within 5 minutes or after 3 months. The data in table 7 were obtained on various concentrations of the composite oil in toluene.

## COLOR SIMILARITY OF VARIOUS OILS

Tests were made to determine if samples from one formation but taken at different locations would yield oil having about the same color characteristics. A limited number of tests were also made to determine if the relationship of figure 3 would hold for oils from different formations and locations.

Fifteen samples of Chattanooga shale from Tennessee picked at random were checked for possible deviations in the color of the oil. Table 8 gives the optical densities (×10) of solutions of the same concentrations of the various oils in toluene. The results indicate that oils from the same formation but from different locations would yield essentially the same densities. The range of the optical densities (×10) is from 9.90 to 10.90.

TABLE 8.—*Color similarity of various oils*

Number of samples, 15.
Specific gravity, mean, 10.17.
Average deviation, 0.34 absolute.

| Lab. No. | Optical density (× 10) | Deviation from mean (d) | Lab. No. | Optical density (× 10) | Deviation from mean (d) |
|---|---|---|---|---|---|
| 3215 | 9.90 | −0.27 | 2053 | 10.40 | +0.23 |
| 3213 | 10.00 | −.17 | 3209 | 10.60 | +.43 |
| 2027 | 10.00 | −.17 | 2052 | 10.70 | +.53 |
| 2029 | 10.00 | −.17 | 2050 | 10.80 | +.63 |
| 3207 | 10.10 | −.07 | 2051 | 10.80 | +.63 |
| 3208 | 10.30 | +.13 | 2054 | 10.80 | +.63 |
| 3216 | 10.30 | +.13 | 2046 | 10.90 | +.73 |
| 3212 | 10.40 | +.23 | | | |

In addition, it should be noted that the 80 samples studied in the determination of the optical density—oil yield relationship (fig. 3) showed from the linear nature of the scatter diagram that oils from different formations and localities were similar.

This relationship was used as the basis for correlating the proposed photometric procedure to the modified Fischer retort method.

## RELATION OF OPTICAL DENSITY TO FISCHER OIL YIELD

Seventy-five samples of oil shale of the Chattanooga were distilled in the manner described under Procedure. The oil evolved was extracted with toluene, filtered, and diluted to a final volume of 25 ml. Measurements of the optical densities (×10) were made with a Lumetron Colorimeter at 420 $\mu$ (blue filter). The optical densities (×10) were plotted against the percentage of oil yield as given by a Fischer assay. A scatter diagram was obtained, and a straight line was drawn which was the mean of the points. The average difference of the Fischer assays from the curve is 0.37 percent absolute (or approximately 1 gal. per ton). The maximum difference between the determined (Fischer assay) and the curve is 0.94 percent (or about 2.5 gal. per ton). The percentages of oil yield and the optical densities (×10) of the toluene-oil solutions are given in table 9.

TABLE 9.—*Relation of optical density to Fischer oil yield—Chattanooga shale (Tennessee)*

| Sample | Percentage oil (Fischer) | Optical density (× 10) | Difference of Fischer assay from standard curve |
|---|---|---|---|
| Lot 1001 | | | |
| LC-15-11 | 0.2 | 0.40 | −0.35 |
| 51 | .8 | .85 | −.30 |
| 21 | 1.7 | .85 | +.62 |
| 53 | 1.8 | 1.35 | +.38 |
| 31 | 1.9 | 2.18 | −.10 |
| 12 | 2.4 | 1.90 | +.60 |
| 52 | 2.4 | 2.25 | +.36 |
| 13 | 2.7 | 2.25 | +.44 |
| 15 | 2.8 | 2.70 | +.44 |
| 14 | 3.4 | 3.20 | +.70 |
| LC-15-33 | 4.1 | 4.80 | +.30 |
| Lot 1002 | | | |
| LC-10-14 | 0.8 | 0.95 | −0.36 |
| 15 | 1.0 | 1.28 | −.38 |
| 31 | 1.4 | 2.00 | −.48 |
| LC-11-14 | 1.8 | 1.80 | +.06 |
| LC-10-13 | 1.8 | 2.15 | −.16 |
| LC-11-13 | 2.1 | 2.15 | +.12 |
| LC-10-32 | 2.7 | 3.45 | −.18 |
| LC-11-15 | 2.9 | 2.70 | +.52 |
| 51 | 3.0 | 2.25 | +.94 |
| LC-10-34 | 3.0 | 3.70 | −.06 |
| 33 | 3.5 | 4.60 | −.16 |
| LC-11-52 | 4.2 | 4.90 | +.32 |
| 31 | 4.3 | 6.60 | −.74 |
| LC-10-35 | 4.5 | 6.25 | −.32 |
| LC-11-32 | 4.9 | 6.70 | −.22 |
| LC-11-22 | 5.0 | 6.40 | +.08 |
| Lot 1005 (sample LC-105A-X) | | | |
| LC-105A-43 | 0.9 | 0.65 | −0.04 |
| 42 | 1.0 | .00 | +.50 |
| 45 | 1.0 | .50 | +.18 |
| 41 | 1.3 | .10 | +.74 |
| 15 | 2.1 | 2.90 | −.40 |
| 21 | 2.4 | 2.90 | −.10 |
| 12 | 3.8 | 5.40 | −.40 |
| 31 | 4.0 | 4.40 | +.46 |
| 14 | 4.1 | 5.80 | −.40 |
| 13 | 4.2 | 4.80 | +.40 |
| 33-#2 | 4.2 | 6.30 | −.64 |
| 33-#1 | 4.2 | 6.50 | −.78 |
| 34 | 4.4 | 6.10 | −.30 |
| 35-#1 | 4.5 | 5.60 | +.12 |
| 35-#2 | 4.5 | 6.20 | −.28 |
| 32 | 4.6 | 6.60 | −.44 |

TABLE 9.—*Relation of optical density to Fischer oil yield—Chattanooga shale (Tennessee)*—Continued

| Sample | Percentage oil (Fischer) | Optical density (× 10) | Difference of Fischer assay from standard curve |
|---|---|---|---|
| Lot 1012 (sample 13M-7-X) | | | |
| 13M-7-22 | 1.3 | 1.20 | −0.02 |
| 11 | 2.3 | 3.10 | −.34 |
| 31 | 2.5 | 3.55 | −.44 |
| 52 | 2.8 | 3.45 | −.10 |
| 21 | 3.2 | 3.30 | +.42 |
| 33 | 3.3 | 5.25 | −.80 |
| 16 | 3.6 | 4.60 | −.06 |
| 15 | 3.7 | 5.25 | −.42 |
| 14 | 4.4 | 6.40 | −.50 |
| 32 | 4.5 | 6.70 | −.62 |
| 51 | 4.6 | 5.20 | +.52 |
| 12 | 4.9 | 5.90 | +.32 |
| 13 | 5.6 | 7.10 | +.20 |
| Lot 1052 (Sample 17R-6-X) | | | |
| 17R-6-10 | 2.3 | 1.60 | +0.70 |
| 9 | 2.5 | 2.60 | +.20 |
| 8 | 2.5 | 2.20 | +.50 |
| 11 | 2.7 | 2.15 | +.70 |
| 7 | 2.8 | 3.40 | −.04 |
| 15 | 2.9 | 2.50 | +.68 |
| 12 | 2.9 | 2.80 | +.48 |
| 18 | 2.9 | 3.70 | −.14 |
| 6 | 2.9 | 3.80 | −.22 |
| 13 | 3.0 | 2.95 | +.42 |
| 14 | 3.2 | 3.50 | +.28 |
| 16 | 3.2 | 4.20 | −.18 |
| 17 | 4.3 | 5.10 | +.30 |
| 4 | 4.3 | 6.50 | −.70 |
| 5 | 4.5 | 6.40 | −.40 |
| 19 | 4.6 | 6.00 | −.02 |
| 3 | 5.2 | 6.20 | +.40 |
| 2 | 6.0 | 6.60 | +.92 |
| 1 | 6.7 | 9.00 | −.10 |

The choice (visual fitting) of the standard curve is based upon the assumption that positive and negative deviations of the same magnitude are equally probable. This assumption is verified by the fact that a visual inspection shows the pattern of the scatter diagram to be essentially symmetrical with respect to the standard curve. Thus, the standard curve can be compared to a distribution function of a random sequence.

$n=80$
$\Sigma d=29.81$

Average difference of the Fischer assays from the curve

$$\frac{|d_1|+|d_2|+\ldots+|d_n|}{n}=\frac{29.81}{80}=0.37 \text{ percent absolute.}$$

From appearances of the scatter diagram (fig. 3), it is believed that the oil content of shales may be determined by the photometric procedure with essentially the same accuracy as by other methods now in use.

To show whether there are variations in the optical properties of the oil from widely separated areas (Phosphoria formation and Chattanooga shale) a closed-tube distillation was made of 10 samples of mudstone from the Phosphoria formation in Montana and Idaho (indicated on fig. 3 by the symbol △). The percentage of oil yield and the optical densities of the toluene-oil solutions are given in table 9 (f). Figure 3 shows that the data for the Phosphoria formation fit the curve that was drawn for the Chattanooga shale.

TABLE 10.—*Relation of optical density to Fischer oil yield Mudstone from the Phosphoria formation of Montana and Idaho, Lot 1243*

[$n$, 5 (samples containing no oil were not considered) $\Sigma d$, 1.80]

| Sample | Percentage oil (Fischer) | Optical density (× 10) | Difference of Fischer assay from standard curve |
|---|---|---|---|
| FCA-150-47 | 0.0 | 0.00 | |
| FCA-181-47 | .0 | .05 | |
| RAG-57-47 | .0 | .00 | |
| RAH-250-47 | .0 | .00 | |
| RAH-253-47 | .0 | .05 | |
| DAB-39 | 2.8 | 3.75 | −0.30 |
| ERC-36 | 3.6 | 5.00 | −.35 |
| LAT-22 [1] | 4.5 | 5.40 | +.30 |
| ERC-26 [1] | 5.2 | 6.60 | +.15 |
| LAT-24 | 5.5 | 6.20 | +.70 |

[1] 0.250-g samples of ERC-26 and LAT-22 were used.

The recommended procedure in making a standard curve is to base it on those samples under study. For other samples, a new curve should be made.

## SUMMARY

A photometric method for the determination of the oil content of oil shale is presented. The proposed method, which utilizes distillation in a closed test tube followed by measurement of the density of a toluene solution of the oil, provides a means of determining arbitrarily the oil content of oil shale by the destructive distillation of its organic matter. This method, like the Fischer method, does not determine the total organic matter in shale that may be converted more completely to oil under more favorable conditions. The proposed method has several immediate advantages over the modified Fischer retort method and is recommended for oil-shale assays. The advantages are:

1. Less time is required for the assay. Oil-shale assays by the Fischer method require approximately 2 hours for completion, whereas by the proposed method 8 to 10 determinations can be completed in the same length of time.

2. Less sample is required. A 100-g sample is used in the Fischer assay whereas a 0.500-g sample is used in the proposed method. In

addition, the same representative sample (−80 mesh) can be used for other analyses.

3. The operation is less difficult and can be controlled more precisely.

The effects are shown of different experimental conditions upon the oil yield by the proposed method: effect of heating time on yield, effect of heating temperature on yield, effect of solvent on color, stability of color in toluene, color similarity of oils, and the relation of optical density to the Fischer yield.

The proposed method, like the modified Fischer retort method, is an empirical measure, and it has been directly correlated with the Fischer method. The estimated oil yields are considered as reliable as the values obtained directly by the Fischer assay of the samples. The method is fast enough for certain control purposes in mining and processing oil shale for which rapid and accurate results are desired, such as in the assay of thousands of samples.

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# Part 3. A VOLUMETRIC METHOD FOR THE ESTIMATION OF THE OIL YIELD OF OIL SHALE

By Frank Cuttitta

## CONTENTS

## TABLE

### ABSTRACT

A method is presented for the volumetric estimation of the oil yield of oil-bearing shale. The shale is distilled in a closed test tube and the oil extracted with ethyl acetate. The ethyl acetate is volatilized on a steam bath, and the oil residue, while still hot, is centrifuged in a graduated tube at 1,500 revolutions per minute (rpm). The volume of the oil yield is read directly off the calibrated stem of the centrifuge tube. The method yields much the same results as the Fischer assay method in a much shorter time. It is applicable to shale and phosphatic shale.

### INTRODUCTION

Oil shales have been assayed by the Bureau of Mines retort method proposed by Karrick (1926), described by Guthrie (1938) and later modified by Stanfield and Frost (1946, 1949). Recently a method relating the specific gravity of the oil shale to its oil yield was developed by the Bureau of Mines (Frost and Stanfield, 1950). In this procedure the oil yield is determined using a standard curve established for the particular oil-shale deposit. The standard curve is obtained by plotting the specific gravities of more than 50 oil-shale samples, picked at random, against the percentage of oil given by the modified Fischer retort method, hereinafter referred to as the Fischer method or Fischer assay.

A rapid method for the photometric estimation of the oil yield of oil-bearing shale is described on page 15 of this report. In this method the oil shale is destructively distilled in a closed test tube, and the oil evolved is extracted with toluene. The optical density of the toluene extract is converted to percentage of oil by reference to a standard curve. This curve is obtained by relating the oil yields by the Fischer assay method (Stanfield and Frost, 1946, 1949) to the optical density of the toluene extract.

All these methods are empirical, and the following study is another empirical measure that can be directly correlated with the Fischer method. Although the proposed method does not supersede the photometric method, it can be used to advantage in the estimation of the oil yield of comparatively small samples (as small as 1 g) where a standard curve is not available for a particular oil-shale deposit. In addition the method is rapid, so that four or five determinations can be made in the length of time required for the completion of one Fischer-method determination.

In this proposed method the shale is distilled in a closed test tube and the oil extracted with ethyl acetate. The ethyl acetate is volatilized on a steam bath, and the oil residue, while still hot, is centrifuged in a graduated tube at 1,500 rpm. The volume of the oil yield is read directly from the calibrated stem of the centrifuge tube.

This work was completed as part of a program undertaken by the Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

## PROCEDURE FOR ESTIMATING THE OIL YIELD

### PREPARATION OF THE SAMPLE

The sample is prepared as in the photometric method (p. 20).

A representative portion, ground to −80-mesh, is dried in an oven at 110 C for 1 hr, unless the samples are to be assayed on the "as received" basis.

### APPARATUS

The test tube used in the closed-tube distillation of the shale is a pyrex glass-stoppered tube, 15 by 50 mm with a no. 16 standard-taper glass stopper. The centrifuge tube used to measure the oil yield of oil shale is the Goetz phosphorous tube. The tube furnace is the same as that used in the photometric method, described and illustrated on page 20.

### RECOMMENDED PROCEDURE

A 1.000-g sample of the dry shale, ground to pass a −80-mesh sieve, is weighed into the test tube. The lower one-third of the glass-stoppered test tube is heated in a horizontal position in the specially constructed small tube furnace at 480 to 500 C for 11 to 14 min. It has been found (see p. 23) that this method of heating gives yields of oil that compare with those determined in the Fischer assay method; therefore it is essential that strict adherence to the time and temperature conditions be observed. The exposed upper two-thirds of the stoppered test tube serves as an air condenser. After the distillation period is complete, the closed test tube is removed from the tube furnace and allowed to air cool to room temperature.

Ten ml of ethyl acetate is added, the tube is stoppered and shaken vigorously for 20 sec. The oil extracted by the ethyl acetate is filtered through a dry, 9-cm, no. 589 (white ribbon) S and S filter paper directly into the centrifuge tube. The filter paper and residue are washed with two 3-ml portions of ethyl acetate. The combined extract and washings, now in the centrifuge tube, are placed on a steam bath to volatilize the ethyl acetate.

To aid in the complete volatilization of the ethyl acetate during the final stage of the evaporation, the centrifuge tube is removed from the steam bath and tilted to allow the hot oil residue to flow from the stem into the pear-shaped body of the centrifuge tube. The tube is rotated so that the oil residue coats the lower walls of the tube. The centrifuge tube is now returned to the steam bath for further evaporation. This removal-and-tilting process is repeated until constant volume is obtained. Three to four repetitions generally volatilizes the ethyl acetate completely.

The remaining oil residue is then centrifuged at 1,500 rpm for 3 min. while still hot. The tube is allowed to cool to room temperature, and the volume of oil obtained is read directly from the calibrated stem of the centrifuge tube.

### CALCULATIONS

The oil yield of the shale is determined by the use of the following formula which converts the measured volume, in milliliters of oil, to percent oil yield:

$$\text{Percent oil yield} = 90.3 \times \text{ml oil yield}$$

The following formula is used to convert the measured volume, in milliliters of oil, to gallons of oil per ton:

$$\text{Gallons of oil per ton shale} = 239.3 \times \text{ml oil yield}$$

Both of the foregoing formulas were derived by taking an average specific gravity of oil as 0.903, which is essentially the density of shale oils. (See p. 23.)

## DISCUSSION

### REPRODUCIBILITY

In order to obtain reproducible results the following precautions must be observed:

1. The closed-tube system must be gas tight. As a precaution against loosening of the stopper, it is advisable to stopper the test tube *after* heating has begun and *prior* to the evolution of vapors from the sample.
2. The proper heating must be maintained within the prescribed limits of time and temperature. Although no data are shown in this report, conditions have been established in the preliminary experimental work done on the photometric method (see p. 23), which showed that the closed-tube distillation of the sample at 480 to 500 C for 11 to 14 min. gave the most reproducible results.
3. If the ethyl acetate is not completely volatilized, positive errors will result.
4. The centrifuging of the oil residue after volatilization of the ethyl acetate must be done while the oil is still hot. Because the viscosity of the oil increases with decreasing temperature, negative errors may result from oil coating the interior walls of the centrifuge tube.

This report does not attempt to show the effects upon the oil yield of such different experimental conditions as sample size, particle size, heating temperature, heating time, and the stability of the ethyl acetate system. For details and experimental data on the effects of these conditions, the reader is referred to pages 22 to 30.

To test this method 19 samples of Chattanooga shale from Tennessee were picked at random. The oil content of the shale samples, having a Fischer-assay oil yield ranging from 2.3 to 6.7 percent, was determined by the above method. The results of these tests (table 1) show a good correlation with the Fischer-assay results.

### ADVANTAGES OF THE METHOD

The proposed method is recommended for oil-shale assays; it has two immediate advantages over the modified Fischer retort method, as follows:

1. Less time is required for an assay by this method. An oil-shale assay by the Fischer method requires approximately 2 hrs. for completion, whereas by the proposed method four or five determinations can be completed in the same length of time.

2. Less sample is required. A 100-g sample is used in the Fischer method, whereas a 1.000-g sample is used in the proposed method. In addition, the same representative sample (−80 mesh) can be used for other analyses.

TABLE 1.—*Volumetric estimation of oil yield of Chattanooga shale samples*

*n*, 19
$\Sigma d$, 5.7
Average difference, 0.3 percent absolute
Maximum difference, 0.7 percent

| Sample | Fischer assay (percent) | Oil yield | | Difference from Fischer assay |
|---|---|---|---|---|
| | | Milliliters | Percent | |
| 10 | 2.3 | 0.03 | 2.7 | +0.4 |
| 9 | 2.5 | .03 | 2.7 | +.2 |
| 8 | 2.5 | .03 | 2.7 | +.2 |
| 11 | 2.7 | .03 | 2.7 | .0 |
| 7 | 2.8 | .03 | 2.7 | −.1 |
| 6 | 2.9 | .04 | 3.6 | +.7 |
| 12 | 2.9 | .03 | 2.7 | −.2 |
| 18 | 2.9 | .04 | 3.6 | +.7 |
| 13 | 3.0 | .04 | 3.6 | +.6 |
| 14 | 3.2 | .04 | 3.6 | +.4 |
| 16 | 3.2 | .04 | 3.6 | +.4 |
| 15 | 3.9 | .04 | 3.6 | −.3 |
| 4 | 4.3 | .05 | 4.5 | +.2 |
| 17 | 4.3 | .05 | 4.5 | +.2 |
| 5 | 4.5 | .05 | 4.5 | .0 |
| 19 | 4.6 | .05 | 4.5 | −.1 |
| 3 | 5.2 | .06 | 5.4 | +.2 |
| 2 | 6.0 | .07 | 6.3 | +.3 |
| 1 | 6.7 | .08 | 7.2 | +.5 |

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# Part 4. THE FLUORIMETRIC DETERMINATION OF ALUMINUM IN PHOSPHATE ROCK WITH 8-HYDROXY-QUINOLINE

By F. S. Grimaldi and Harry Levine

## CONTENTS

## ILLUSTRATIONS

## TABLES

## ABSTRACT

A method is described whereby aluminum in phosphate rock is determined by the fluorescence of aluminum hydroxyquinolate in chloroform solution. The procedure is designed to determine 0.01 to 3 percent $Al_2O_3$ in a 0.1-mg sample of rock. The results are accurate to ±5 percent of the aluminum content. No element, in the percentages commonly occurring in phosphate rock, interferes in the procedure.

## INTRODUCTION

In connection with certain geochemical investigations, the U. S. Geological Survey had occasion to analyze many phosphate-rock samples for aluminum. For this project a rapid, simple, and reasonably accurate method of analysis was necessary.

The accurate determination of aluminum in phosphate rock by gravimetric procedure is difficult, rather tedious, and lengthy. For example in the method of Hoffman and Lundell (1938), aluminum is separated from most of the calcium, magnesium, and phosphorus by several precipitations of the phosphate from acetate-acetic acid solutions, and from iron by several precipitations with sodium hydroxide and sodium carbonate. The aluminum is finally determined as aluminum phosphate. It is to be expected that some loss of aluminum will occur in the sodium hydroxide precipitation—especially if iron is high—and that some chromium and vanadium and possibly some rare earths will contaminate the final aluminum phosphate precipitate. Chromium and vanadium are present in western phosphates, and the rare earths have been reported in many phosphate rocks.

Colorimetric methods for determining aluminum are based on the formation of strongly colored lakes with either aluminon, alizarin S, eriochromcyanin, or hematoxylin. These methods usually require preliminary separation of aluminum from interfering ions, especially iron. Barton (1948) used alizarin S for the determination of aluminum in phosphate rock and showed that in measurements at wavelength of 370 mu there was practically no interference from iron. He gave no data on the effects of other common constituents of phosphate rocks.

For the gravimetric determination of aluminum 8-hydroxyquinoline (oxine) is commonly used; it is used also for the colorimetric determination of aluminum. Goto (1940) has described the detection of aluminum, zinc, calcium, cadmium, magnesium, beryllium, and zirconium by means of the fluorescence of their hydroxyquinolates. Tullo (1949) used the fluorescence of aluminum quinolate in chloroform solution for the estimation of aluminum in beer. His procedure calls for the extraction of the aluminum from slightly alkaline solutions with a chloroform solution of 8-hydroxyquinoline. Sandell (1941) used the fluorescence of gallium hydroxyquinolate for the detection and determination of gallium, and Merritt (1944) determined zinc fluorimetrically with the same reagent. Other elements mentioned in the literature as giving fluorescent quinolates under certain conditions are lithium, scandium, and indium.

The method presented in this paper is based on a study of the fluorescence of aluminum hydroxyquinolate in chloroform solution. No elements interfere in the concentrations usually occurring in phosphate rock. The procedure is designed to determine 0.01 to 3.0 percent $Al_2O_3$ in 0.1 mg samples of rock. The data given in table 2 indicate that the method should also be applicable to silicate and carbonate rocks.

## APPARATUS AND REAGENTS

Fluorimeter: The fluorimeter (Fletcher and Warner, 1951) uses the Photovolt electronic photometer model 512 with C search unit. The B–H4 high-pressure mercury lamp, operated from a Sola constant-voltage transformer no. 30852 for H4 type lamps, supplies the ultra-violet light source. The lamp is cooled by a dark-room ventilating fan. Primary filter, Corning no. 5874; secondary filter, Corning no. 3385. Diaphragm opening 0.8 in. diamter. Square glass cells of 30 ml capacity.

8-hydroxyquinoline (oxine) solution: Dissolve 1.5 g of 8-hydroxyquinoline in 2M acetic acid. 1 ml equals 0.015 g of oxine.

Standard aluminum solution: Prepare a solution of concentration 1 $\gamma$ (microgram) $Al_2O_3$ per ml from purified potassium alum.

Buffer: Mix equal volumes of 2M acetic acid (12 g $CH_3COOH$ per 100 ml of solution) and 2M ammonium acetate (15.4 g $NH_4C_2H_3O_2$ per 100 ml of solution).

Distilled water: If blank is high, redistill from all-glass apparatus.

Chloroform: Technical chloroform, distilled from all-glass apparatus, was as good as redistilled C. P. chloroform.

Fluorescein solution A: Dissolve 0.05 g of fluorescein in 200 ml (1 : 1) ethyl alcohol and make up to 2 liters.

Fluorescein solution B: Take 3 ml of solution A, add 3 ml of ethyl alcohol, and make up to 1 liter.

## EXPERIMENTS AND DISCUSSION

Experiments were made to study the following factors that affect the fluorescence of the oxine complex of aluminum: (1) Order of addition of reagents, (2) pH, (3) concentration of 8-hydroxyquinoline, (4) time, and (5) concentration of buffer.

Preliminary work consistently showed that when the aluminum-oxine complex is extracted with chloroform from solutions containing no phosphate, the intensity of fluorescence of the chloroform solution is independent of the order of addition of reagents or time of standing of the test solution before extraction. However, when phosphate is present, the order of addition of reagents and the time of standing before extracting with chloroform affect the intensity of fluorescence. The phosphate ion forms a complex with aluminum, but 8-hydroxyquinoline forms a more stable complex with aluminum. The aluminum quinolate is formed immediately if the solution containing aluminum and phosphate is added to the 8-hydroxyquinoline. If the order of addition is reversed—that is, if the 8-hydroxyquinoline is added to the aluminum phosphate solution—the system reaches the same equilibrium in about 20 min. In the first order of addition equilibrium is established immediately, because the ratio of concentration of oxine to aluminum phosphate is at each instant relatively higher than if the order of addition were reversed. The faster procedure of adding test solution to 8-hydroxyquinoline solution and extracting immediately with chloroform was adopted.

By this procedure the intensity of fluorescence of the chloroform solution of aluminum quinolate is independent of the time the test solution stands before extracting the aluminum quinolate. The chloroform solution is stable and the intensity of its fluorescence is constant for at least 4 hours.

Table 1 shows the effect of time and order of addition of reagents. The aluminum phosphate solution was slightly acid and 2 ml (containing 2 γ $Al_2O_3$ and 50 γ $P_2O_5$ was always used. The other reagents were water (17 ml), 8-hydroxyquinoline solution (1 ml), 1M acetic acid–1M ammonium acetate buffer (2 ml), and chloroform for extraction (30 ml). Additional data obtained in the absence of phosphate are not included in table 1 because the fluorescence intensity obtained was independent of time or order of addition of reagents. On the basis of these tests, the standard order of addition selected is as follows: oxine, aluminum solution, buffer, water, immediate extraction with chloroform.

TABLE 1.—*Effect of time and order of addition of reagents on the fluorescence intensity of chloroform solution of aluminum hydroxyquinolate*

[Test solutions contain 2γ$Al_2O_3$ and 50γ$P_2O_5$, and order of addition is from left to right]

| Reagents in order of addition | Meter readings | |
|---|---|---|
| | Immediate extraction | Extraction after 20 min. |
| 1. $AlPO_4$, water, oxine, buffer | 58 | 73 |
| 2. $AlPO_4$, oxine, buffer, water | 62 | 72<br>[1] 72 |
| 3. $AlPO_4$, oxine, water, buffer | 61 | 72 |
| 4. Oxine, $AlPO_4$, buffer, water | 73 | 72<br>[1] 73 |
| 5. Oxine, $AlPO_4$, water, buffer | 71 | 72 |
| 6. $Al^{+++}$ (no phosphate), oxine, water, buffer | 72 | ------------ |

---

[1] Water added after 20 min., before extraction.

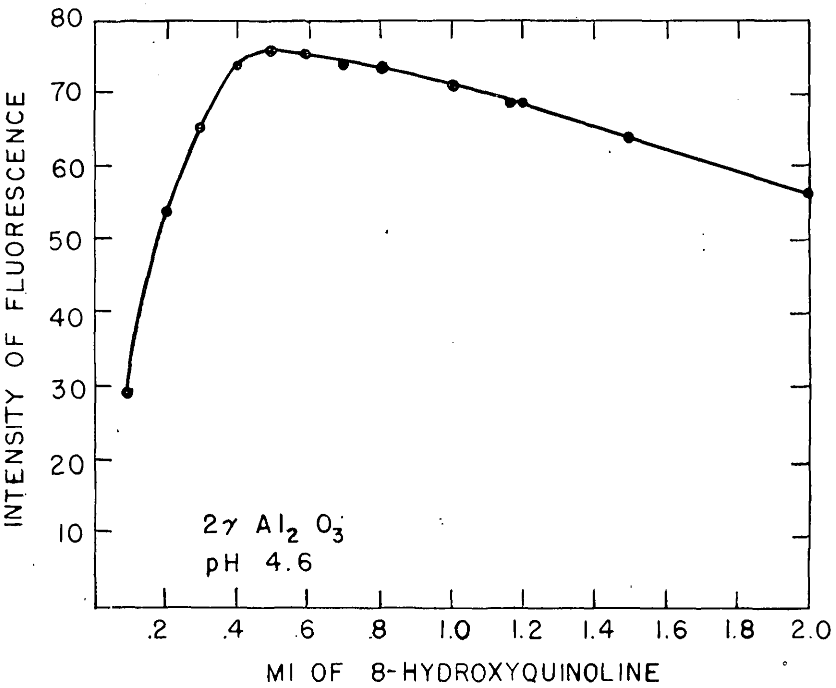

FIGURE 6.—Effect of 8-hydroxyquinoline concentration on fluorescence intensity.

Figure 6 shows the variation in fluorescence of 2 $\gamma$ of $Al_2O_3$ with different concentrations of oxine. It is seen that 0.5 ml of 8-hydroxyquinoline gives the greatest sensitivity. The fluorescence of aluminum quinolate is particularly sensitive to change of oxine concentration when the amount of quinolate is less than 0.5 ml. Because other elements consume oxine, it was preferable to standardize on 1 ml of oxine.

Figure 7 illustrates graphically the relationship between the fluorescence intensity of 2 $\gamma$ $Al_2O_3$ and the pH of the solution before extraction with chloroform. Different pH's were obtained by varying the proportions of 1M ammonium acetate and 1M acetic acid in the 2 ml of buffer solution. The optimum pH is clearly 5.4. Because more elements react either with phosphate or with 8-hydroxyquinoline at higher pH's, standardization was on a pH of 4.6.

The data on the fluorescence of aluminum quinolate obtained with different shaking periods are shown in figure 8. The solutions were shaken with chloroform for the prescribed period (at the rate of four shakes per second), the chloroform layer was then withdrawn, and the fluorescence measured. It is seen that, for periods between 5 and 25 sec. essentially the same fluorescence is obtained. Standardization was on a 10-sec. shaking period.

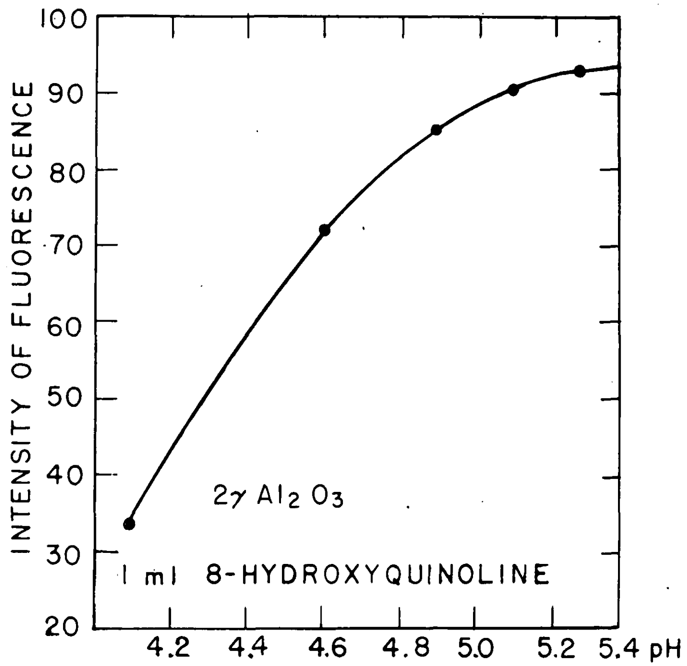

FIGURE 7.—Effect of pH on fluorescence intensity.

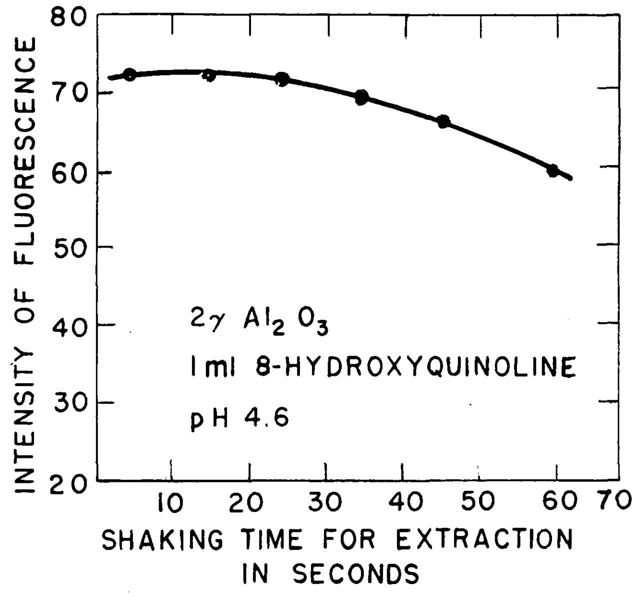

FIGURE 8.—Effect of extraction time on fluorescence intensity of aluminum quinolate.

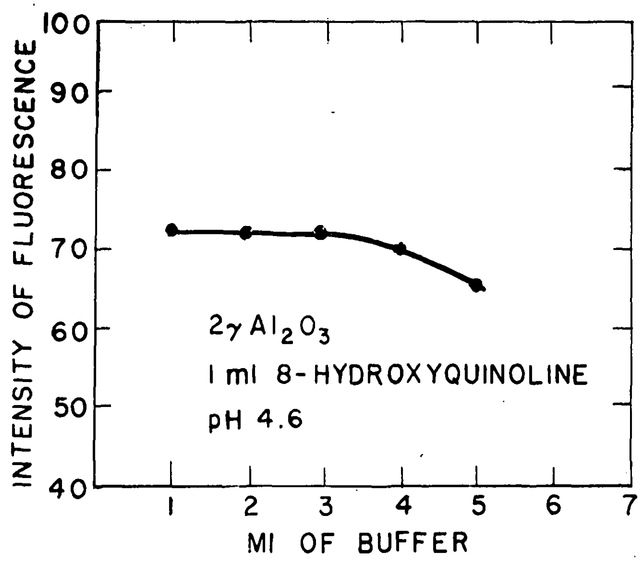

FIGURE 9.—Effect of different amounts of same buffer on fluorescence intensity.

Figure 9 shows the effect of varying amounts of buffer solution on the fluorescence intensity of aluminum quinolate.

The working curve of figure 10 is obtained by plotting the fluorescence intensity of aluminum quinolate against micrograms of $Al_2O_3$. The order of addition of reagents is the standard order: 8-hydroxy. quinoline (1 ml), $Al_2O_3$ (varying amounts in 2 ml), buffer (2 ml), water (17 ml), 10 sec. extraction with 30 ml of chloroform. The photometer was set to read 72 for 2 $\gamma$ $Al_2O_3$. The same curve was obtained in the presence of 50 $\gamma$ $P_2O_5$.

## EFFECT OF OTHER IONS

Tests were made on the elements occurring in phosphate rock to determine possible interference. In general the amounts tested were considerably in excess of what would normally be present in phosphate rock. Fluorine interferes seriously, but it is removed in the preparation of the solution for analysis. Large quantities of zirconium give a positive error. In phosphate rocks no interference should be expected from zirconium, because it is present only in small amounts and because it precipitates out of solution as phosphate.

Table 2 gives the results obtained in testing the effect of various ions. In the analysis of phosphate rock 0.1 mg (100$\gamma$) of sample is always used; therefore the quantity ($\gamma$) of the element represents the percentage.

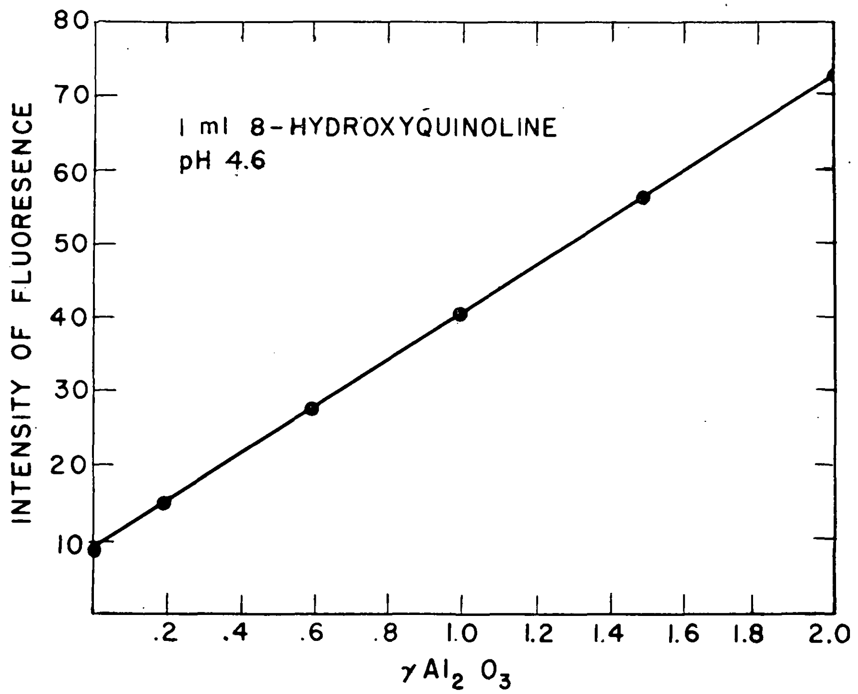

FIGURE 10.—Working curve.

TABLE 2.—*Tests of the effect of various ions especially those elements present in phosphate rocks* [Instrument set to read 72 for $2\gamma Al_2O_3$; blank reading 10]

| Material added to test solution as soluble ion | Meter readings | | Material added to test solution as soluble ion | Meter readings | |
|---|---|---|---|---|---|
| | No $Al_2O_3$ present | $2\gamma Al_2O_3$ present | | No $Al_2O_3$ present | $2\gamma Al_2O_3$ present |
| $2\gamma MnO$ | 9 | 74 | $5\gamma Fe_2O_3$ | 10 | 74 |
| $1\gamma Y_2O_3$ | 9 | 70 | $10\gamma Fe_2O_3$ | 10 | 71 |
| $1\gamma La_2O_3$ | 9 | 70 | $50\gamma P_2O_5$ | 9 | 72 |
| $1\gamma Ce_2O_3$ | 10 | 71 | $4\gamma F$ | ---------- | 54 |
| $1\gamma Nd_2O_3$ | 10 | 71 | $36\gamma K_2O$ | 10 | 74 |
| $2\gamma ThO_2$ | 10 | 73 | $67\gamma Na_2O$ | 10 | 72 |
| $1\gamma TiO_2$ | 10 | 72 | $20\gamma Li_2O$ | 10 | 72 |
| $.4\gamma ZrO_2$ | 10 | 74 | $60\gamma CaO$ | 10 | 73 |
| $50\gamma ZrO_2$ | ---------- | 97 | $50\gamma MgO$ | 10 | 73 |
| $2\gamma Cr_2O_3$ | 9 | 73 | $4\gamma ZnO$ | 13 | ---------- |
| $2\gamma V_2O_5$ | 10 | 72 | | | |

## THE DETERMINATION OF ALUMINUM IN PHOSPHATE ROCK

### PROCEDURE

1. Weigh 0.1000 g of sample, ground to pass 80-mesh, into a 50 ml beaker.
2. Add 5 ml $HNO_3$ (1 : 1) and 3 ml of perchloric acid.
3. Evaporate the solution to fumes of perchloric acid and allow to fume for several minutes. Cool.

4. Add 5 ml of $HNO_3$ (1 : 1) and 20 ml of water. Digest on steam bath for several minutes to dissolve soluble salts.

5. Filter on a small no. 40 Whatman filter paper and wash with water. Reserve filtrate in 100 ml beaker. Ignite residue in a platinum crucible.

6. Fuse the residue with a minimum amount of sodium carbonate. Cool the melt.

7. Pour a slight excess of $HNO_3$ (1 : 1) into the crucible to dissolve the cake. Transfer this solution to the beaker containing the main solution.

8. Add 2 ml of perchloric acid and evaporate to fumes of $HClO_4$. Allow to fume until about 1 ml of $HClO_4$ remains. Cool.

9. Add 30 ml of water and digest the solution on the steam bath to dissolve soluble salts.

10. Filter off the silica and wash with water. Reject residue.

11. Make the solution to 1 liter in a volumetric flask and mix.

12. Take a 1 ml aliquot—if a higher dilution is used, aliquots up to 15 ml containing 0.1 mg of sample may be used—and transfer it to a 60 ml separatory funnel containing 1 ml of 8-hydroxyquinoline and mix.

13. Add 2 ml of buffer solution, mix, and then add 17 ml of $H_2O$.

14. Add 30 ml of $CHCl_3$ and shake the vessel for 10 sec. (a total of about 40 shakes).

15. Remove chloroform layer and measure the fluorescence with the photometer.

16. Determine the amount of aluminum from the working curve (fig. 10). The photometer may be set to read 72 against a chloroform solution of aluminum quinolate ($2\gamma Al_2O_3$) or, alternately, set for a standard deflection against fluorescein solution B, whose fluorescence has been compared against $2\gamma Al_2O_3$. If the fluorescein solution is used, it should be checked daily against the standard chloroform solution of aluminum quinolate.

## RESULTS

Two National Bureau of Standards standard samples of phosphate rocks were analyzed by the fluorimetric procedure. One of these samples was reanalyzed after the addition of known amounts of aluminum. Four western phosphates were also run and again one was reanalyzed after the addition of known amounts of aluminum. The western phosphates were previously analyzed by the following unpublished procedure, as developed by the late Norman Davidson, of the U. S. Geological Survey. The acid solution of the sample was treated with cupferron, and such cupferrates as those of iron and titanium were extracted with ethyl acetate. The water layer was treated with 8-hydroxyquinoline and the aluminum precipitated at a pH of 5.2. The aluminum quinolate was filtered off, dissolved in acid, and reprecipitated with oxine. The precipitate was again filtered and ignited to $Al_2O_3$ under cover of oxalic acid. The results obtained by the fluorimetric procedure (table 3) show good agreement with those obtained by other methods.

TABLE 3.—*Results of analysis of phosphate rock*

| Sample no. and source | $Al_2O_3$ (percent) obtained— | |
|---|---|---|
| | Fluorimetrically | Gravimetrically |
| National Bureau of Standards, standard sample: | | |
| 120 | 0.81<br>.82<br>.80<br>.81 | [1] 0.80 |
| 120. $Al_2O_3$ added to raise percentage in sample to— | | |
| 1.50 | 1.52 | |
| 2.00 | 2.07 | |
| 2.50 | 2.56 | |
| 56 [2] | 2.00<br>2.02<br>2.04<br>2.03 | [1] 2.02 |
| Western phosphates: | | |
| 1 [2] | 6.4 | 6.5 |
| 2 [3] | 2.3 | 2.2 |
| 3 [4] | 2.6 | 2.6 |
| 4 [5] | 1.8 | 1.7 |
| 4. $Al_2O_3$ added to raise percentage in sample to— | | |
| 2.2 | 2.2 | |
| 2.6 | 2.6 | |

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[1] Average obtained from National Bureau of Standards report.
[2] Sample contained 5.8 percent $Fe_2O_3$.
[3] Sample contained 2.9 percent $Fe_2O_3$.
[4] Sample contained 3.2 percent $Fe_2O_3$.
[5] Sample contained 3.8 percent $Fe_2O_3$.

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# Part 5. THE DETERMINATION OF PHOSPHORUS IN ROCKS CONTAINING VANADIUM

By R. B. Randolph and F. S. Grimaldi

## CONTENTS

## TABLES

## ABSTRACT

This paper describes a routine procedure for the determination of phosphorus in the presence of vanadium. The vanadium is reduced with formic acid prior to precipitation of the phosphorus as ammonium phosphomolybdate, and the ammonium phosphomolybdate is weighed as such. Ratios of $V_2O_5$ to $P_2O_5$ as high as 100 to 1—the highest tested—give no interference. $P_2O_5$ in amounts from 0.1 mg to 0.2 g may be determined with no changes in conditions or quantity of reagents. The separation of molybdic acid is prevented and the molybdate precipitate has a constant composition.

## INTRODUCTION

Volumetric and gravimetric methods for the determination of phosphorus usually involve preliminary separation of the phosphate as ammonium phosphomolybdate. For volumetric determination the phosphomolybdate precipitate is titrated with standard alkali using a suitable acid-base indicator. For gravimetric analysis the ammonium phosphomolybdate is sometimes weighed as such but for most accurate work it is dissolved in ammonia and the phosphate precipitated as magnesium ammonium phosphate. After two precipitations the magnesium ammonium phosphate is ignited to magnesium pyrophosphate, which is then weighed.

Procedures depending on either the weighing or titrating of the ammonium phosphomolybdate presuppose that the ammonium phosphomolybdate precipitate is pure and of definite constant composition. It is difficult to get this purity under conditions that usually obtain in the determination of phosphorus. The precipitate may be contaminated with arsenic, vanadium, and silica, which form heteropoly compounds like phosphorus; with titanium and zirconium phosphates, unless some provision is made to prevent their formation; and with molybdenum, which may precipitate out as oxide or which may be present in the phosphomolybdate in higher proportion than in the ideal formula—especially if the precipitate is formed at elevated temperatures. Silica is easily removed in the preparation of the solution for the analysis. Arsenic interference may be reduced by precipitating at room temperature or eliminated entirely by reducing the arsenic to the trivalent state and removing it from the solution by volatilizing the chloride.

The proper conditions for the prevention of the separation of molybdic acid are not fully appreciated in standard procedures. For example, the procedure used by Hillebrand and Lundell (1929) calls for the addition of a nitric acid solution (20 to 25 percent $HNO_3$ by volume) of ammonium molybdate to the phosphate solution containing 5 to 10 percent of nitric acid, by volume. Depending on the phosphate concentration, a varying quantity of ammonium molybdate is added. The concentration of nitric acid in the final solution could thus vary from 8 percent to more than 15 percent, depending on the amount of phosphate being precipitated. The final nitric acid concentration is critical, and unless it is kept above 12 percent by volume molybdic acid is likely to precipitate. Kassner and others (1948) prevent the precipitation of molybdic acid by the addition of citric acid.

Pentavalent vanadium in solution presents a more serious difficulty. If the ratio of the concentration of $P_2O_5$ to $V_2O_5$ is high, vanadium is largely co-precipitated with phosphorus. If the amount of vanadium exceeds that of phosphorus, the precipitation of the phosphomolybdate is seriously retarded and may not be complete even after long standing. We have found that no phosphorus is precipitated at all when the ratio of the concentrations of $V_2O_5$ to $P_2O_5$ is over 5 and the phosphorus content of the solution is small.

The interference of vanadium may be eliminated by reduction of the vanadium to the quadrivalent state, and precipitation of the phosphomolybdate at room temperature or lower. Under these conditions little if any vanadium precipitates, and the retarding effect of vanadium on the precipitation of phosphorus is largely overcome. Hillebrand and Lundell (1929) advise using $FeSO_4$ for the reduction followed by the addition of one gram of iron as ferric nitrate to prevent subsequent reduction of the molybdenum.

This report deals with the use of formic acid for the reduction of vanadium. Proper conditions were developed such that

1. The phosphomolybdate precipitate obtained is constant in composition.
2. The separation of molybdic acid is prevented.
3. From 0.1 mg to 0.2 g of $P_2O_5$ may be determined, with no change in conditions, or amounts or types of reagents.

The analyst simply prepares a solution of the sample, adds a fixed amount of reagents and filters, dries, and weighs the precipitate. No guesswork or prior knowledge of the phosphorus and vanadium content is required. The procedure will determine phosphorus with good accuracy when the $V_2O_5$ to $P_2O_5$ ratio is as high as 100 to 1, the highest tested. Because the composition of the precipitate is constant, titrimetric procedures may also be used.

## DISCUSSION OF PROCEDURE

Preliminary investigations determined optimum conditions for the precipitation of phosphate with ammonium molybdate. These conditions are always set up for any amount of $P_2O_5$ present up to 0.2 g, thus:

1. The precipitation is made at room temperature.
2. The total volume of solution is 100 ml after all reagents and water are added. It contains 5 ml of formic acid, about 8 g of ammonium nitrate, 15 ml of nitric acid (sp gr 1.42), and 45 ml of molybdate solution. (See below.)

These conditions are flexible enough to allow of some variation. The nitric acid content is a critical factor and should be controlled closely. For example, if the concentration of nitric acid in the final solution is as low as 9 percent by volume—that is, 100 ml of solution contains 9 ml of nitric acid, sp gr 1.42—molybdic acid tends to precipitate. A few tests showed that molybdic acid does not separate out from solutions containing 12 percent by volume of nitric acid. The amount of ammonium molybdate is more than is needed for precipitation of small amounts of $P_2O_5$, but it is advantageous to keep the amount added constant; thus, enough is specified to precipitate quantitatively as much as 0.2 g $P_2O_5$. Formic acid is necessary to eliminate vanadium interference, but it is rapidly destroyed by nitric acid if the solution is warmed. For this reason the nitric acid content of the solution is kept at a minimum prior to the addition of formic acid, and the solution is cooled to room temperature before and after the addition of the nitric acid. If the temperature of the room is high enough to cause a slow decomposition of the formic acid, it is preferable to cool the solution to a lower temperature. For uniformity of procedure formic acid is used even when vanadium is absent. Under these conditions, the composition of the phosphomolybdate precipitate when dried at 110 C is $(NH_4)_3PO_4.12MoO_3$, and the factor for $P_2O_5$ is 0.03783.

## PROCEDURE

The special reagents needed are formic acid (reagent grade, sp gr 1.2, 90 percent) and ammonium molybdate solution. The ammonium molybdate solution is prepared by dissolving 16 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 90 ml of hot water. The solution is cooled and then filtered if necessary.

## PREPARATION OF THE SOLUTION

### 1. PHOSPHATE ROCK

Add 20 ml of $HNO_3$ (1:1) to a 0.5-g sample in a glass container, and evaporate the solution to dryness. Repeat with 20 ml more of $HNO_3$ (1:1). Digest the residue with 20 ml $HNO_3$ (1:3) and filter; wash with water. Reserve the filtrate. Fuse the residue with a minimum of $Na_2CO_3$ in platinum. Leach the cool melt with water and filter. Wash the precipitate with 1 percent $Na_2CO_3$ solution. Combine the filtrate with the filtrate reserved above. Reject the residue. Add 5 ml of $HNO_3$ and evaporate the combined filtrates to dryness. Add 20 ml of $HNO_3$ (1:3), warm to dissolve the salts, and transfer the solution to a 100-ml volumetric flask, filtering if necessary. For rapid control work, the carbonate fusion need not be made, and the residue from the initial attack with nitric acid may be rejected. If the sample contains much material that is insoluble in nitric acid, prepare solution as in 2.

### 2. SILICEOUS AND CLAYEY MATERIAL

Treat a 0.5-g sample in a platinum dish with 10 ml of $HNO_3$ (1:1) and 10 ml of HF. Cover with a platinum cover and digest on a steam bath for 10 min. Remove cover and evaporate to dryness. Fluorides are removed by evaporating twice more after additions of 15 ml of $HNO_3$ (1:1). Add 20 ml of $HNO_3$ (1:3), digest, and filter, washing with water. Reserve the filtrate. Ignite the residue in platinum and fuse with a minimum of $Na_2CO_3$. Leach the cooled melt with hot water. Filter and wash with dilute $Na_2CO_3$ solution. Reject the residue. Combine the filtrate with that reserved previously. Add 5 ml of $HNO_3$ and evaporate the combined filtrates to dryness. Add 20 ml of $HNO_3$ (1:3), warm to dissolve the salts, and transfer the solution to a 100-ml volumetric flask, filtering if necessary.

### DETERMINATION AS AMMONIUM PHOSPHOMOLYBDATE

1. Transfer an aliquot of the prepared solution, containing 50 mg of $P_2O_5$ or preferably less, to a 150-ml beaker.
2. Add $NH_4OH$ until methyl red indicates neutral.
3. Add 5 ml of formic acid and heat the solution just to boiling.
4. Remove from the source of heat immediately, and cool the solution to room temperature in a water bath.
5. Add 8 g of $NH_4NO_3$ (solid) and stir until it dissolves.
6. Add 15 ml of $HNO_3$. Cool if necessary.
7. Immediately add 45 ml of ammonium molybdate solution slowly and stir.
8. Add water to make the total volume 100 ml. Let stand until the precipitate settles. The precipate is ready to filter as soon as it has settled out. This usually takes about an hour.
9. Filter thru a weighed sintered-glass medium filter or Gooch crucible.
10. Wash several times with $HNO_3$ (1:99) solution.
11. Dry the precipate at 110 C and weigh.

$$\text{The percent } P_2O_5 = \frac{\text{weight of ammonium phosphomolybdate} \times 3.783}{\text{weight of sample}}$$

## RESULTS OF ANALYSES

### COMPOSITION OF AMMONIUM PHOSPHOMOLYBDATE

A standard phosphate solution was made from Bureau of Standards sample No. 186 II ($Na_2HPO_4$) by direct weight and was added to 12 beakers. The first 6 (series A) contained 0.2, 5, 10, 20, 30, and 50 mg of $P_2O_5$. The second 6 (series B) contained duplicate amounts of $P_2O_5$ and, in addition, 20 mg of $V_2O_5$ added as ammonium metavanadate solution. Phosphorus was determined as described in the procedure. The results in table 1 established the composition of the precipitate dried at 110 C as $(NH_4)_3PO_4.12MoO_3$.

TABLE 1.—*Results in milligrams of analyses of pure solutions*

| *$P_2O_5$ taken* | *$P_2O_5$ found, based on $(NH_4)_3PO_4.12MoO_3$* | *$P_2O_5$ taken* | *$P_2O_5$ found, based on $(NH_4)_3PO_4.12MoO_3$* |
|---|---|---|---|
| SERIES A | | SERIES B | |
| 0.2 | 0. 2 | 0.2 | 0. 2 |
| 5.0 | 5. 0 | 5.0 | 5. 0 |
| 10.0 | 10. 1 | 10.0 | 10. 0 |
| 20.0 | 20. 0 | 20.0 | 20. 2 |
| 30.0 | 29. 8 | 30.0 | 30. 1 |
| 50.0 | 50. 1 | 50.0 | 50. 2 |

## ANALYSES OF PHOSPHATE ROCKS

Nitric acid solutions were prepared from three Bureau of Standards standard samples of phosphate rocks. The certified composition of these standard samples follows:

| *Sample no.* | *Phosphate deposits* | *$P_2O_5$ percent* |
|---|---|---|
| 120 | Florida land pebble | 35. 33 |
| 56 | Tennessee phosphate | 31. 33 |
| 56a | Tennessee brown | 33. 01 |

Duplicate sets of aliquots of each sample were tested, each set representing 5.0, 17.0, and 44.0 mg $P_2O_5$. No vanadium was added to the samples in series A. Twenty milligrams of $V_2O_5$ were added as ammonium vanadate solution to each sample in series B. $P_2O_5$ was then determined according to the procedure described. Table 2 lists the results obtained.

TABLE 2.—*Analyses (in milligrams) of standard samples*

| *Sample no. and series* | *$P_2O_5$ Taken* | *$P_2O_5$ Found* |
|---|---|---|
| 120: | | |
| Series A | 5. 0<br>17. 0<br>44. 0 | 5. 1<br>17. 2<br>43. 8 |
| Series B | 5. 0<br>17. 0<br>44. 0 | 5. 0<br>17. 0<br>44. 0 |
| 56: | | |
| Series A | 5. 0<br>17. 0<br>44. 0 | 4. 9<br>16. 8<br>44. 1 |
| Series B | 5. 0<br>17. 0<br>44. 0 | 4. 9<br>17. 1<br>43. 9 |
| 56a: | | |
| Series A | 5. 0<br>17. 0<br>44. 0 | 4. 9<br>17. 1<br>44. 0 |
| Series B | 5. 0<br>17. 0<br>44. 0 | 5. 0<br>17. 2<br>44. 1 |

## PERFORMANCE OF THE PROCEDURE BY OTHER CHEMISTS

Robert Meyrowitz, of the Geological Survey laboratory tested the procedure against the Bureau of Standards sample no. 120, employing aliquots containing 0.14, 7.1, 17.7, and 35.4 mg of $P_2O_5$ to which 20 mg $V_2O_5$ were added.

Table 3 shows the results obtained.

TABLE 3.—*Test of the procedure by Robert Meyrowitz on Bureau of Standards sample no. 120 with added vanadium*

| *$P_2O_5$ taken (milligrams)* | *$P_2O_5$ found (milligrams)* |
|---|---|
| 0. 14 | 0. 18 |
| 7. 1 | 7. 3 |
| 17. 7 | 17. 8 |
| 35. 4 | 35. 2 |

In table 4 Bureau of Standards sample no. 186 II ($Na_2HPO_5$) was used and aliquots containing 100, 150, and 200 mg of $P_2O_5$ were analyzed by Robert Meyrowitz. No vanadium was added to these samples.

TABLE 4.—*Test of the procedure by Robert Meyrowitz on Bureau of Standards sample no. 186 II*

| *$P_2O_5$ taken (milligrams)* | *$P_2O_5$ found (milligrams)* |
|---|---|
| 100 | 99. 8 |
| 150 | 150. 3 |
| 200 | 200. 8 |

The results show that the maximum error is ±0.2 mg of $P_2O_5$ when the $P_2O_5$ content is 50 mg or less. For greater amounts of $P_2O_5$—for example, 0.2 g of $P_2O_5$—the maximum error may be ±0.8 mg, which may be due to incomplete washing of the precipitate. Although this figure seems large, it is actually a small percentage of the total phosphorus present.

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# Part 6. THE PROBABLE ERROR OF A CHEMICAL ANALYSIS [1]

By WILLIAM G. SCHLECHT

## CONTENTS

## ILLUSTRATIONS

## DISCUSSION

My title may lead the reader to expect me to tell him what the probable error of a chemical analysis is, but my thesis is that there generally is none. Chemists in the Geological Survey have noticed the increasing tendency to express estimates of errors of chemical analyses in terms of statistical formulas for "probable error," "standard deviation," and the like. Anyone using such formulas ought to consider what statistical errors mean, and whether analytical chemical processes are of such a nature that statistical ideas can be useful in studying those processes.

The simple statistical formulas and tables have been widely reprinted in textbooks and handbooks, but without any explanation of their basic assumptions. This is unfortunate, because the use of these devices without a clear understanding of what they mean can be very misleading. Their popularity suggests a spreading uncritical belief that they have a magical power to improve observations; statisticians intend, on the contrary, that they should be used as skeptical tests of hypotheses (1). Statistical calculations are no substitute for practical experience and fundamental understanding of analytical chemical processes. If we use algebraic formulas before inquiring into the meaning of the numbers we put into them, we may delude ourselves

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[1] Revision of an informal communication that was presented before the Geological Society of Washington, February 23, 1949.

with what Professor Dingle calls "knowledge without understanding" (2). This seems to have happened at times in various fields; a blind faith in precision for its own sake has been pushed too far ahead of a thoughtful and critical search for sound conceptual schemes (3, 4, 5). I think the reason for this premature straining for precision is the idea that a thing is not really scientific unless it is quantitative and precise (6).

Statistical formulas are designed for treating random errors, but the important errors in chemical analysis are not generally random. Analytical errors are affected by (a) the nature of the material, (b) the way of taking and preparing the sample, (c) the kind of analytical procedure used, (d) environmental conditions in the laboratory, and (e) the personal traits of the analyst. In practical analytical chemistry we take complex materials, and we subject them to harsh and complicated disturbances; the errors we make in instrumental readings are likely to be small compared with the uncontrolled variations in the chemical processes. The nature of these processes is such that for some procedures losses of material are more likely than contamination, so that results are likely to be too low (7), whereas for other procedures the reverse is true (8). When losses and gains are equal—the condition known as "compensating errors" (9)—the processes are hardest to control.

Many statistical calculations for analytical results have been made on the hidden assumption that the errors are all committed in the determination or final instrumental reading; but in analyzing complex materials the greatest and hardest-to-control errors occur in the chemical separations, not in the measuring instrument. The central role of chemical separation processes in practical analysis is stressed by few writers (10, 11, 12). The chemist generally has satisfactory control of the errors in his balance, burets, and other measuring instruments; he shares this problem with all users of instruments. His special problem is to control what goes on in his beakers; that is why an analyst needs to be a chemist (13). A discussion of errors of analysis is likely to be irrelevant if it ignores the chemical behavior of the substances involved. The question is seldom one of how accurately we know the weight of a precipitate, but rather how pure and how complete the precipitate is. The kinds of chemical errors likely to occur in inorganic analyses are discussed in the better textbooks (13, 14).

It was long ago pointed out that the errors in duplicate determinations run at the same time are not likely to be random (15, 16, 17). Thus so simple a calculation as taking the mean of several analyses may be misleading. When statistical calculations are valid, the mean is the best estimate of a quantity. Dr. Lundell, in his paper, "The chemical analysis of things as they are" (10), discussed some analyses whose averages are very unlikely to be correct, and stressed the importance of understanding the chemical processes by which they were made. The best way to report such results is to give all the values, accompanied by any facts or opinions that bear on their worth (18, 19, 20, 21). I wish that consumers of chemical analyses would study Dr. Lundell's paper.

A particularly misleading practice is to use a formula for "rejection of observations." Even statisticians, working with truly random phenomena, do not blindly "reject" observations; an unusually large discrepancy may call for special attention and should not be ignored in deciding on an action. For one thing, a large discrepancy may be a warning that the process is not in statistical control; in that case the formulas are not valid. Youden (22) points out that the user of these formulas is almost never warned of the penalty involved—namely, that any arbitrary criterion for rejection of bad observations is bound to throw out at the same time a fixed percentage of the good observations. Eisenhart (23) quotes a joking suggestion that the safest criterion is to reject the observations nearest to the mean, because they affect the result least.

In judging the results of a process, statistical tests are no substitute for experience (23, 24, 25), but statistical theory can be very helpful to the practical man. For example, statisticians have found that those who judge results by inspection must be conservative about rejection; the fact that ~~one of a set of measure~~ments differs markedly from the rest is not in itself sufficient evidence that it is wrong (23). A study of sets of three measurements, made by the Statistical Engineering Group at the National Bureau of Standards (26), shows a surprising frequency of cases in which one of the results differs greatly from the other two. Even when the variations are random, the most discrepant result will differ from the middle one by at least 16 times as much as the smaller difference, in about 10 percent of the sets.

In figure 11, a simple diagram shows the meaning of the terms used in studying errors. Suppose that there is a *"true value"* (represented by the heavy horizontal line) for a thing being measured. If successive observations are plotted in sequence, they will cluster around the line marked *"average"*, which in general may be either above or below the *true value*. If the *average* differs significantly from the *true value*, the difference is called the *"bias"* (sometimes called the "constant error"), and is a measure of the *"accuracy."* This bias is not always constant; it may have a trend, or may even shift or oscillate. If limits can be found within which the observations will practically always fall, the width of the limits measures the reproducibility of the

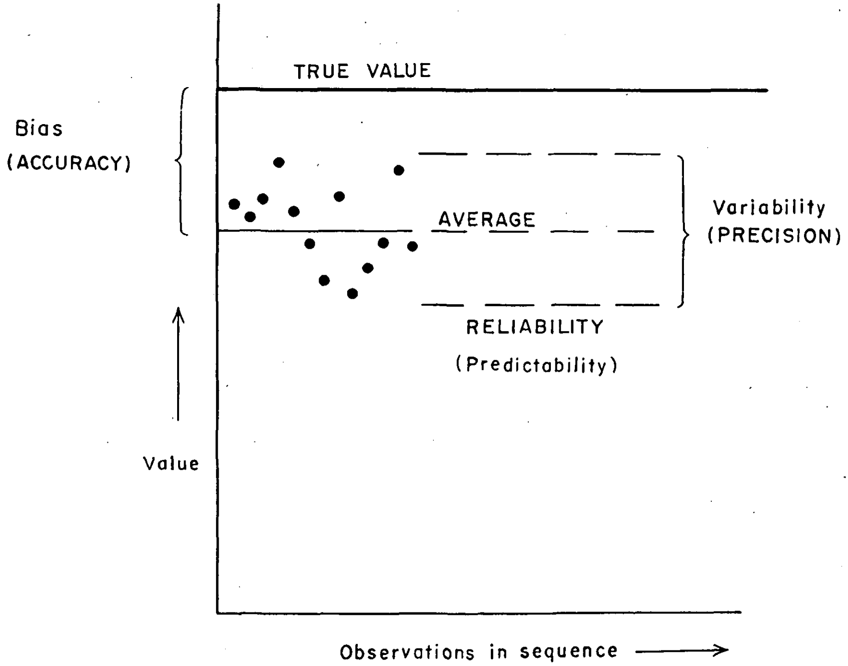

FIGURE 11.—Meaning of the terms "accuracy," "precision," and "reliability" of measurements. After Mitchell (27).

process, and is called the "limits of variation"; it is a measure of the "*precision.*" If a process is fairly stable, the average and the precision should be fairly reproducible any time that observations are repeated. Statistically, a process is said to be "in control" if the *precision* limits do not change much in repeated series of observations. Mitchell (27) has proposed that if the process is in control, the condition be called "*reliability.*" If the precision and accuracy of a method are reproducible over a period of time, then the method is reliable.

There are various ways of expressing precision. The simplest of these "measures of dispersion" is the range (difference of maximum and minimum); some other popular ones are "standard deviation" and "probable error." Professional statisticians have abandoned the use of probable-error formulas, even where they are valid, in favor of the simpler and more noncommittal expressions involving standard deviation (28, 29, 30). "Average deviation" has been a favorite among chemists, because it is easy to calculate; its pitfalls have been described (31, 32).

Now if the precision is to be calculated by statistical formulas, two assumptions are made: first, that the errors are distributed about the mean in a certain way—approximately in the "normal distribution"—and second, that they are random in sequence—that no trends

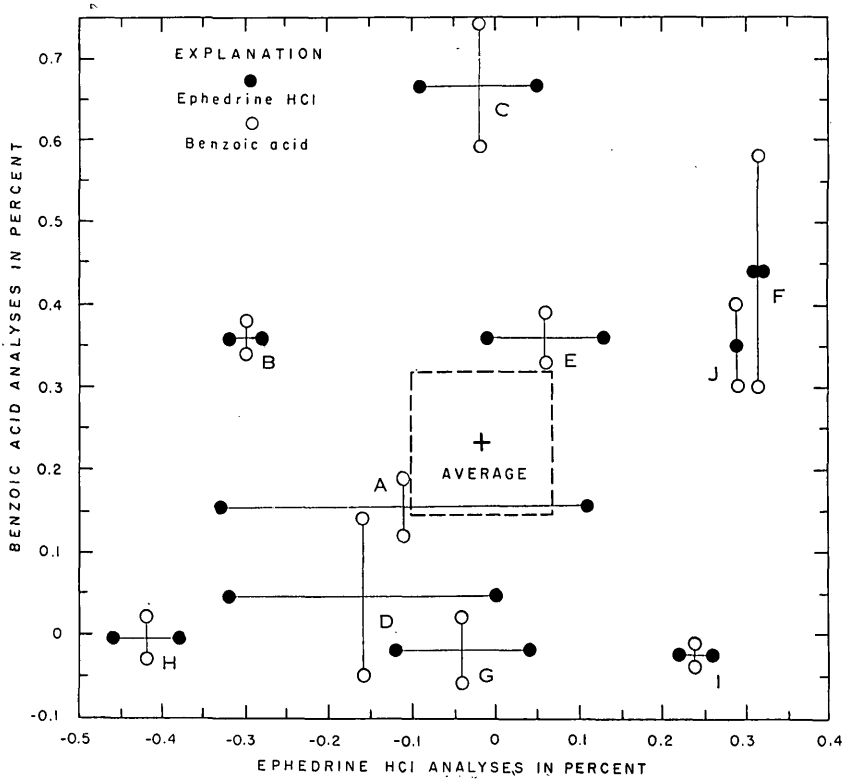

FIGURE 12.—Non-normal distribution of errors in analyses by 10 laboratories. From Youden (38).

or patterns are shown by successive observations. Incidentally, there is nothing inherently "normal" or natural about the so-called normal distribution; it simply happens to be the simplest and easiest artifice for computing a good approximation to most of the random distributions found in practice (33, 34).

To establish the validity of these assumptions, a large sequence of observations (35) must be studied according to the modern statistical methods worked out by Shewhart (18, 36): they are grouped, plotted on control charts, and examined for stability of the mean and control limits, and for absence of "runs" or patterns. The subgrouping procedure is also essential for detecting and studying systematic errors; Deming and Birge (35, p. 160) remind us that "* * * no amount of analysis of a single sample, regardless of how large it is, can of itself lead one to suspect the presence of constant errors." (Note that Deming and Birge use the words "single sample" in the statistician's sense, to mean a single group of observations, rather than in the chemist's sense of a single lot of material).

The few most thorough of the studies that have been made of chemical analyses indicate that analytical errors are not likely to be

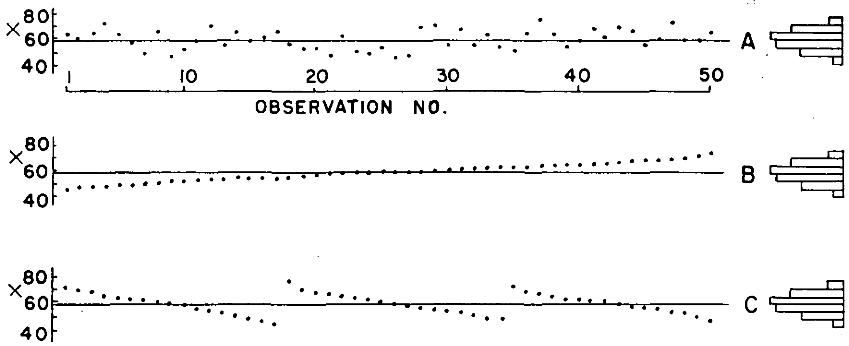

FIGURE 13.—*A*, A random sequence, *B*, *C*, Two non-random sequences. All have the same distribution function. From Schlecht (36).

normally distributed. V. J. Clancey (37) has studied some 250 distributions, involving about 50,000 chemical analyses of industrial products, and found 85 to 90 percent of them to be significantly nonnormal. He concludes that "* * * great caution should be exercised in applying the ordinary simple statistical methods to the data of chemical analyses * * *."

Figure 12 shows a set of especially careful analyses made of 2 pure substances by 10 different laboratories. If the errors computed from duplicate analyses were normally distributed, about half of the results, as plotted (38), would fall inside the dotted box. *None* of them do.

Thus we have some actual examples of chemical analyses that do not have a probable error.

Many observations—generally at least 200—are required to establish adequately that a process is in statistical control. Most workers cannot afford to make so many (39); nevertheless, they often assume that the process is in control (40, 41, 42). Many workers, when they have made enough observations to establish that their distribution was normal, have concluded that therefore it was random. This conclusion is not true; Figure 13 shows that a distribution may be normal without being random (36). In this figure sequences *A*, *B*, and *C* have the same distribution curve, but only *A* does not show patterns in the sequence.

Correspondence with a distribution curve is a necessary but not a sufficient condition for statistical control. The reader can see this by imagining a sequence of samples scooped from a bucket full of gravel with the larger pebbles on the bottom and the smaller ones on top. The mean particle sizes of the samples will give a sequence something like the plot in figure 13*B*. If the gravel is well stirred, the mixture becomes more random, and the sequence of samples will be more like that shown in figure 13*A;* but of course stirring does not change the sizes of the particles, and so the distribution curve of particle sizes remains the same.

Probable error and similar formulas take into consideration only the distribution curve which, as we have seen, may be the same whether the sequence is random or not. Such formulas thus suppress a critical part of the evidence for statistical control, and before we can trust them we must examine the sequence to see whether or not it is random (23, lecture 3).

I have said that statistical methods are no substitute for understanding. We should by all means use them when we are ready for them. But before we can study a given analytical method statistically, we must have adequate experience to base our study on—a large number of experiments under various carefully controlled conditions, and a sound theoretical understanding of the process. These must be laboriously worked out for each kind of determination and material.

When we do use them, we must do so responsibly, with a reasonable understanding of their meaning, plus the extreme skepticism traditionally expected of scientists. This means checking with professional statisticians (43, 44), and not putting too much trust in books written by such statistical laymen as chemists, physicists, engineers, economists, and psychologists (45,46). For reliable guidance to the amateur, a modern and simply written book by the statistical experts of Imperial Chemical Industries, Ltd., is now available. It is "Statistical methods in research and production, with special reference to the chemical industry," edited by Owen L. Davies (29). I single out this particular book for special notice, because its authors are more conscientious than any others that I have read in stressing the underlying assumptions and limitations of the various statistical tests.

An invaluable service that the statistician can give to the chemist has as yet been little appreciated; it relates to the advance planning of experiments in such a way that no work is wasted. Wernimont (45), for example, has called attention to some published experimental data comparing the precision of 10 spectrophotometers. The measurements were numerous, but were so carried out that the results do not justify the conclusions drawn. With properly designed procedure, the same number of observations would have given significant results.

Most important for the analytical chemist is what Tukey (47) calls the "day-to-day part of experimental design," which consists in so planning the work that one can make a realistic estimate of its reliability. He points out, for example, that reliable values for the parallel analysis of three unknowns, with an honest estimate of the errors of analysis, are not most likely to be obtained by the method that most chemists now employ unthinkingly by force of habit, namely to make three determinations of the first unknown on one day, and three of each of the others on the 2 following days. It is better to make one determination of each unknown on one day, another of each on the second day, and still another of each on the third day.

The procedures referred to as "design of experiments" are very pertinent to the investigation of analytical errors, in that they ensure that the evidence collected is complete and significant. Intelligently used, the statistical viewpoint can contribute indispensably to solving the problems of analytical chemistry, and to the realistic interpretation of chemical analyses by the consumer.

*Acknowledgments.*—I thank Dr. W. Edwards Deming, Executive Offices of the President, Bureau of the Budget; Dr. W. J. Youden and Mr. Joseph M. Cameron, Statistical Engineering Laboratory, and Mr. Shuford Schuhmann, Division of Chemistry, National Bureau of Standards; Mrs. Priscilla Schuhmann; and Mr. James A. Mitchell, Cellulose Esters Division, Tennessee Eastman Corp., for invaluable criticisms and suggestions; and Dr. Youden and Mr. Mitchell for permission to use their illustrations.

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3. Heinlein, C. P., 1937, Some consequences of pseudo-mathematics and quasi-measurement in psychometrics, education and the social sciences: Florida Acad. Sci. Proc. 1936, vol. 1, pp. 33–42.

4. Anderson (1).

"* * * statistics tend to mesmerize the beginner into using calculations as a substitute for common sense. Experience shows that it is all too easy to get into a rut in which most investigations are designed mechanically in accordance with standard procedures, and in which the results of statistical analyses are blindly accepted as true. But no mechanical process can substitute for thought."—p. 69.

5. Stevens, N. E., 1941, Botanical research by unfashionable technics: Science, vol. 93, pp. 172–176, reprinted in Stevens, N. E., Factors in botanical publication and other essays: Chronica Botanica, vol. 11, pp. 166–172.

6. The doctrine that a subject is not scientific unless it is quantitative was firmly established through the influence of great men like Lord Kelvin, the physicist, and Sir Francis Galton, the statistician, who were widely

quoted to the effect that they considered knowledge unsatisfactory if it could not be expressed in numbers. John R. van Wazer has pointed out that their criterion would ignore such a logically rigorous science as classical organic chemistry, which was based almost entirely on qualitative observations (Physics Today, 1951, vol. 4, no. 6, pp. 18–20).

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"The results obtained in applying the proposed method to subsilicic rocks as represented by two diabases and to a synthetic solution simulating a basic rock, containing from 2 to 8 p. p. m. of added beryllium, are uniformly slightly low, the worst result corresponding to 80% recovery of beryllium. The average recovery in these samples corresponds to approximately 90%."

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"Experience has shown that most analysts are prone to make a very serious plus error in determining moderate amounts of magnesia, such as are found in limestone and portland cements."

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"* * * there is little chance of discovering any exact method [for separation of sulfate as barium sulfate] which shall at the same time be generally applicable and require no corrections, and yet not owe its accuracy to a compensation of errors; for the reason that some of the requisite conditions appear to be mutually incompatible."

10. Lundell, G. E. F., 1933, The chemical analysis of things as they are: Ind. Eng. Chem., Anal. Ed., vol. 5, pp. 221–225.

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"The early realization of the importance of separations in analytical chemistry is reflected interestingly by the Dutch word for chemistry, *scheikunde*, or the art of separating. It is a centuries-old word which to my knowledge is not used in any other language. * * * The emphasis on separations is entirely justified, even nowadays."

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"The mechanical details of quantitative analysis have been quite satisfactorily worked out, the chemical details have not. In other words, balances, weights, volumetric apparatus, reagents, glass, quartz, porcelain and platinum wear, filtering media, burners, ovens, and even procedures for the determination of elements when occurring by themselves need very little improvement for ordinary purposes. On the other hand, methods for the quantitative separation of the elements from one another are far from perfect."

14. Groves, A. W., 1951, Silicate analysis, 2d ed., London, George Allen & Unwin.

15. "Student", 1909, The distribution of the means of samples which are not drawn at random: Biometrika, vol. 7, p. 210, reprinted in "Student's" collected papers, pp. 43–48 (1942).

"Thus repetitions of analyses in a technical laboratory should never follow one another but an interval of at least a day should occur between them. Otherwise a spurious accuracy will be obtained which greatly reduces the value of the analyses."

16. "Student", 1927, Errors of routine analysis: Biometrika, vol. 19, p. 151, reprinted in "Student's" collected papers, pp. 135–149 (1942).

"We now come to a phenomenon which will be familiar to those who have had astronomical experience, namely that analyses made alongside one another tend to have similar errors; not only so but such errors, which I may call semi-constant, tend to persist throughout the day and some of them throughout the week or the month."

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"Duplicate determinations run at the same time are generally not truly random and the averaging of such results does not improve the precision appreciably."

18. Shewhart, W. A., 1939, Statistical method from the viewpoint of quality control, p. 82, Washington, D. C., Graduate School, U. S. Department of Agriculture.

"* * * the meaning or interpretation of any summary in the form $X \pm \Delta X$ depends upon whether the original data arose under a state of statistical control; such a summary of data does not provide an adequate basis for setting an efficient tolerance range."

19. Hillebrand and Lundell (reference 13, p. 5).

20. American Society for Testing Materials, 1951, ASTM manual on quality control of materials, p. 33, Philadelphia, American Society for Testing Materials.

"Presented data should be accompanied by available relevant information, particularly information on *precisely* the field within which the measurements are supposed to hold and the conditions under which they were made, and evidence that the data are good."

21. Beveridge, W. I. B., no date [1950?], The art of scientific investigation, p. 33, N. Y., W. W. Norton & Co.

"Occasionally scientific reports are marred by the authors giving their results only as averages. Averages often convey little information and may even be misleading. The frequency distribution should be given and some figures relating to individuals are often helpful in giving a complete picture."

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"In the final analysis it would seem that the question of the rejection or retention of a discordant observation reduces to a question of common sense. Certainly the judgment of an experienced observer should be allowed considerable influence in reaching a decision."

25. Barnard, G. A., 1947, 2 x 2 Tables. A note on E. S. Pearson's paper: Biometrika, vol. 34, pp. 168–169.

"* * * while statistics is a most valuable aid to judgement, it cannot wholly replace it."

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"The use of the probable error is declining, and we recommend the student to eschew it."

29. Davies, O. L., Ed., 1949, Statistical methods in research and production with special reference to the chemical industry, 2d. ed., London, Oliver and Boyd.

"Other measures of dispersion, such as *quartile deviation* and *probable error*, are mentioned in the literature, but are to be avoided, especially the latter."

30. ASTM manual (reference 20, p. 42).

"Mention should be made of the practice, currently losing favor in scientific work, of recording such limits as: $X \pm 0.6745\frac{\sigma}{\sqrt{n}}$ * * *. Investigation of this problem has given a more satisfactory alternative (Section 4), a procedure which provides limits that have a definite operational meaning."

31. Anon., 1950, Misuse of the average deviation: Nat. Bur. Standards Tech. News Bull., vol. 34, pp. 9–10.

32. Anon., 1951, Chemists advised to abandon average deviations: Chem. and Eng. News, vol. 29, p. 2380.

33. Power, Francis W., 1939, Accuracy and precision of microanalytical determination of carbon and hydrogen: a statistical study: Ind. Eng. Chem., Anal. Ed., vol. 11, pp. 660–673.

"For practical purposes of error theory the normal curve is only a mathematical convenience, the use of which is based largely on pragmatic grounds."

34. Geary, R. C., 1947, Testing for normality: Biometrika, vol. 34, pp. 209–242.

"*Normality is a myth; there never was, and never will be, a normal distribution.* This is an overstatement from the practical point of view, but it represents a safer initial mental attitude than any in fashion during the past two decades."

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"Until one has a long series of measurements he is not in a position to judge whether his observations are random, and consequently whether he dare apply the theory of errors at all."

36. Schlecht, W. G., 1946, Control chart method applied to errors in radioactive counting: MDDC–695 (declassified Feb. 22, 1947).

37. Clancey, V. J., 1947, Statistical methods in chemical analyses: Nature, vol. 159, pp. 339–340.

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39. Shewhart (reference 18, p. 111).

"* * * *the method of increasing knowledge does not consist in taking more and more repetitive measurements under presumably the same conditions as it does when one is making drawings from a bowl.* In fact, a scientist seldom bothers to take more than five or ten observations under what he considers to be the same essential conditions (drawings from a bowl), although often he experiments with what he thinks may be slightly different conditions."

40. Anderson (reference 1, p. 71).

"It is only when the samples have been selected at random, which does not always happen in laboratory investigations, that it is theoretically sound to generalize beyond the specific samples and conditions represented in the experiment."

41. Shewhart (reference 18, p. 81).

"* * * as emphasized in the previous chapters, measurements of physical properties and quality characteristics, including some of the most refined physical measurements, are not ordinarily in a state of statistical control."

42. Scheffe, Henry, 1951, Some basic concepts of probability and statistics: Ind. Eng. Chem., vol. 43, pp. 1292–1294.

"* * * a state of statistical control practically never exists in manufacturing processes or methods of measurements before the process is stabilized by being analyzed and modified by statistical control techniques."

43. Anderson (reference 1, p. 73).

"Routine statistical analysis of data may present many pitfalls, and the advice of a professional statistician is frequently required."

44. Wiener, Norbert, 1948, Cybernetics, New York, John Wiley and Sons.

"* * * the modern apparatus of the theory of small samples, once it goes beyond the determination of its own specifically defined parameters and becomes a method for positive statistical inference in new cases, does not inspire me with any confidence, unless it is applied by a statistician by whom the main elements of the dynamics of the situation are either explicitly known or implicitly felt."

45. Wernimont, Grant, 1949, Statistics applied to analysis: Anal. Chem., vol. 21, pp. 115–120.

"It is not safe to depend entirely upon any of the books on statistics which have been written by chemists or physicists."

46. Clarke, B. L., 1949, Statistical methods in the chemical industry: Chem. and Eng. News, vol. 27, pp. 1426–1428.

"Dr. Shewhart * * * first asked to see several outstanding modern textbooks on analytical chemistry. After examining these, particularly the treatment given the subject of error, he told me regretfully that even in the best of these books, the discussion of precision and accuracy would have been considered antiquated 40 years ago. Indeed, he pointed out, more in sorrow than in wrath, that the handling of the subject of error in one of these books was based upon a concept that had been abandoned by statisticians in 1888."

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# Part 7. A CONFINED-SPOT METHOD FOR THE DETERMINATION OF TRACES OF SILVER IN SOILS AND ROCKS

By Hy Almond, R. E. Stevens, and H. W. Lakin

## CONTENTS

## ILLUSTRATIONS

## ABSTRACT

A procedure for estimating traces of silver in soils and rocks was developed to provide a method suitable for geochemical prospecting. Silver can be determined in a 0.5 g. sample in concentrations between 0.2 and 20 ppm. A specially designed extractor prevents bumping during the acid digestion of a soil and upon cooling automatically filters the acid digest. The final estimation is made with a chromograph, a device which automatically controls the rate of flow of test solution through a confined spot on filter paper. A preliminary ignition of the sample to eliminate organic matter and mercury is followed by a nitric acid digestion. Silver is separated from the colored ions in the nitric acid solution by collecting the silver salt of *p*-dimethylaminobenzalrhodanine at the interface between amyl alcohol and the aqueous solution and then discarding the aqueous extract. This silver precipitate is dispersed by adding ethyl alcohol and is then collected on a confined spot by means of the chromograph. The intensity of the red color on

the filter paper, compared with spots prepared from standard solutions, is a measure of the silver content of the original sample. About 20 samples can be analyzed per man-day.

## INTRODUCTION

The Geological Survey's project of developing trace methods of analysis applicable under field conditions to geochemical prospecting has resulted in the development of a serviceable method for the determination of traces of silver. The method is an application of the confined-spot technique (Stevens and Lakin, 1949; Yagoda, 1937), using *p*-dimethylaminobenzalrhodanine as the precipitating reagent.

This reagent had the desired sensitivity and was more satisfactory than other reagents for reasons discussed below. Dithizone reacts with silver to form a silver dithizonate which is soluble in carbon tetrachloride, but the yellow color imparted by the silver dithizonate to the carbon tetrachloride is indistinguishable from that imparted by the oxidation product of dithizone, also soluble in the organic solvent. Furthermore, the silver dithizonate-dithizone mixed color is not sufficiently sensitive for visual comparisons in the range desired. Cupric dithizonate as a reagent for silver is unsatisfactory because again silver is determined by the mixed-color method which lacks sensitivity. Turbidimetric and confined-spot methods which involve the precipitation of the chloride, sulfide, or free silver are also not sufficiently sensitive.

To determine the silver content of a soil or rock by the rhodanine method described by Sandell (1950), silver must first be isolated from colored salts or ions as well as from elements that react with *p*-dimethylaminobenzalrhodanine (Ettisch and Tamchyna, 1931; Feigl, 1949). The acidity of the separated silver solution must be carefully adjusted and an exact amount of the reagent added. The color intensity is best determined instrumentally (Sandell, 1950; Schoonover, 1935). The procedures of Schoonover (1935) and of Sandell (1950) do not seem promising for field work because they require precise control of acidity and because colored ions have to be removed.

The method described here is based on the fact that the silver salt of *p*-dimethylaminobenzalrhodanine can be separated quantitatively from a relatively large volume of aqueous solution by collecting the silver precipitate at the interface between aqueous and amyl alcohol phases (Strafford, 1933; Monier William, 1950). Most of the aqueous phase is discarded and the silver precipitate dispersed into the remaining smaller volume by destroying the interface with ethyl alcohol. The dispersion is filtered through filter paper in the chromograph, and silver estimations are made by comparing the intensity of red color on the paper with spots prepared from standard solutions.

The nitric acid digestion used in this procedure dissolves essentially all the silver in the sample without introducing the difficulties and the time-consuming operations of complete sample solution.

Very exact methods require the solution of the entire sample, but the drastic procedures for obtaining complete solution of the sample are usually too complex for ease in rapid field methods. The effectiveness of extraction procedures depends in part upon the state of subdivision. However, an extraction procedure cannot bring into solution material enclosed in a matrix insoluble in the extracting agent.

## REAGENTS AND APPARATUS

Ammonium citrate, 25 percent: Dissolve 25 g of ammonium citrate, $(NH_4)_2HC_6H_5O_7$, in water and dilute to 100 ml. Shake with amyl alcohol and allow to stand 4 hours. Discard both the amyl alcohol and the solids collecting at the interface.

Ammonium hydroxide, conc, sp gr 0.90.

Ammonium hydroxide, 1 N: Add 10 ml of conc ammonium hydroxide to 140 ml of water.

Acetic acid, glacial.

Nitric acid, conc, sp gr 1.41.

Water: Pass tap water through a resin demineralizer to free it of heavy metals. Demineralizers are commercially available that do not require conductivity meters to indicate the quality of water passing through.

*p*-dimethylaminobenzalrhodanine, 0.05 percent: Dissolve 0.05 g in 100 ml of glacial acetic acid.

Amyl alcohol, boiling point 136–138 C.

Ethyl alcohol, 95 percent.

Standard silver solution, 0.01 percent: Dissolve 0.158 g of silver nitrate, dried at 110 C, in 1 l of 1 N ammonium hydroxide.

Standard silver solution, 0.001 percent. Transfer 10 ml of 0.01 percent to a 100 ml volumetric flask containing about 50 ml 1 N ammonium hydroxide and dilute to volume with 1 N ammonium hydroxide.

Standard silver solution, 0.0001 percent: Transfer 10 ml of 0.001 percent standard solution to a 100 ml volumetric flask containing about 50 ml 1 N ammonium hydroxide and dilute to volume with 1 N ammonium hydroxide.

Glass chromographs: These instruments confine areas of definite size on a strip of reagent paper and automatically regulate the rate of flow of the test solution through the confined spot. The plastic parts of the original model (Stevens and Lakin, 1949) are replaced

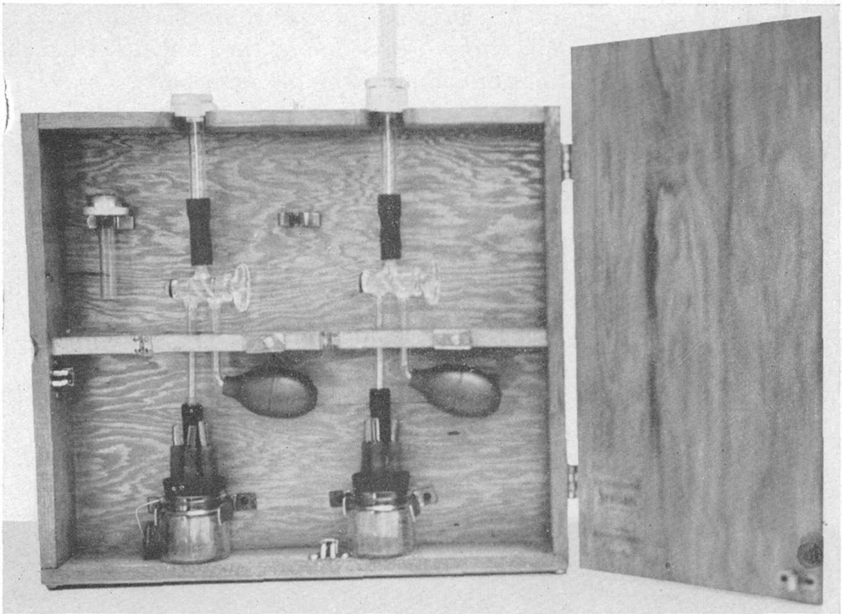

FIGURE 14.—Two complete chromographs in carrying case.

by glass for the silver test because of the destructive action of the amyl alcohol on the plastic. Glass chromographs are illustrated in figure 14.

Extractor: A cheap and simple extractor is made as follows: Crimp a piece of tubing 170 mm in length about ½ inch from one end with a spot flame. To the other end fuse a ground-glass joint. Pack the crimped end with glass wool and fit the other end with a glass stopper. (See fig. 15.)

Glass wool: AAA fineness borosilicate glass fiber, free of heavy metals.

Separatory funnels, 60 ml Squibb.

*Culture tubes*, borosilicate (16 x 150 mm): Calibrate at 2½ ml.

*Portable gasoline stove:* A pocket stove is satisfactory.

Filter paper: Hard, double-washed, retentive, close texture.

Balance, torsion, senstivity, 2 mg.

Crucibles, porcelain, no. 0.

1 serological pipet, 1 ml, graduated in 0.01 ml.

1 serological pipet, 10 ml, graduated in 1.0 ml.

Litmus paper, blue.

Borosilicate glass rod, 150 mm long.

3 graduated cylinders, 5 ml.

1 graduated cylinder, 20 ml.

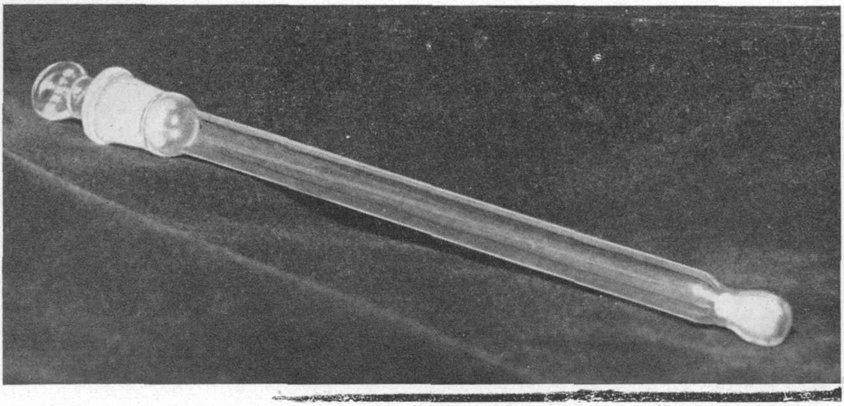

FIGURE 15.—Extractor for removing acid-soluble constituents from rock and soil samples.

Fusion and Digestion Rack: A device to support eight test tubes over the stove during an acid digestion. It consists of two disks of sheet steel welded to a central supporting rod. Each plate has eight holes for test tubes; the holes in the bottom plate are small so that tubes will not slip through, but large enough to permit the ready flow of heat.

Iron mortar and pestle: Any convenient size to crush rocks.

Mullite mortar and pestle; outside diameter of mortar 75 mm.

Sieve, iron, 2 mm mesh.

Sieve: 80-mesh, cloth or stainless steel. Held together by an aluminum holder which fits into an aluminum receiver.

## PROCEDURE

*Preparation of standard spots.*—Prepare a series of spots representing values of silver ranging from 0 to 24 ppm as follows:

Label eight porcelain crucibles "a" through "h", and to each add 0.5 g of finely ground silver-free soil. Ignite each soil sample 10 min., then cool. To crucible "a" add no silver, but to the other seven add 0.1, 0.3, 0.6, 1.0, 3.0, 6.0, and 12.0 micrograms of silver, respectively; the eight samples are considered as standard solutions. Then add 2 ml concentrated nitric acid and continue as the procedure directs to extract the silver and to prepare confined spots containing the red silver dimethylaminobenzalrhodanine compound. Mount the series of spots on the edge of a cardboard chart, cover with cellophane tape, and label each spot with the figure of parts per million to which it corresponds.

*Preparation of sample solution.*—Place a 0.5 g soil or rock sample, ground to pass through an 80-mesh sieve, in a porcelain crucible. Ignite for approximately 10 min., cool, add 2 ml concentrated nitric acid and allow the sample to stand in the acid overnight. In the morning transfer sample and nitric acid to a culture tube and wash the remaining soil into the test tube with ½ ml water. Insert a firmly stoppered extractor into the culture tube and place in a fusion and digestion rack on a gasoline stove. Boil for 10 min. Remove the culture tube from the rack and allow to cool. By the time the culture tube has cooled, the solution has filtered into the extractor.

*Separation and estimation of silver.*—Transfer the filtrate to a separatory funnel containing 10 ml of water. Rinse the extraction stick with 10 ml of water and combine with the original portion in the separatory funnel. Add 3 ml of ammonium citrate, shake, then add ammonium hydroxide in small increments until the solution is strongly alkaline to litmus paper. Acidify with 5 ml of glacial acetic acid. Add 0.1 ml of *p*-dimethylaminobenzalrhodanine solution and shake to mix. Allow the solution to cool for about 15 min. Add 3 ml of amyl alcohol, shake for 30 sec. and allow to stand for 20 min. Drain the aqueous (lower) solution until about ½ ml of aqueous solution remains, add 1 ml of water, and again drain until about ½ ml of the aqueous phase remains. Add 1 ml of ethyl alcohol and shake to disperse the silver precipitate and to dissolve any unreacted reagent that has precipitated.

Adjust the liquid level in the chromograph to the upper timing mark by pressure on the adjustor bulb and turn the stopcock to the closed position. Place a strip of filter paper in the head of the chromograph and tighten the coupling to seal the filter paper between the two sections of glass pipe. Transfer the contents of the separatory funnel to the head of the chromograph, open the fast capillary of the chromograph, then turn the stopcock so that the water in the column drains through the capillary. After the solution has filtered, drain the residual solution from the paper into the deflated adjustor bulb by turning the stopcock. Remove the filter paper containing the silver spot, dry, and then compare the silver precipitate on the filter paper with a standard series of spots. Before using the separatory funnel again wash it with nitric acid; rinse four times with tap water and then with distilled water to remove traces of ethyl alcohol.

## DISCUSSION

Any element or material that may occur in a soil or rock sample, as well as introduced reagents, must be considered possible interferences in quantitative methods of analysis, particularly when trace constituents are determined. In the colorimetric method described herein, copper (I), mercury, palladium, and gold must be eliminated because they react with the reagent, *p*-dimethylaminobenzalrhodanine, just as silver does. Some means must be taken to destroy organic matter, too, because it also may color the confined spot.

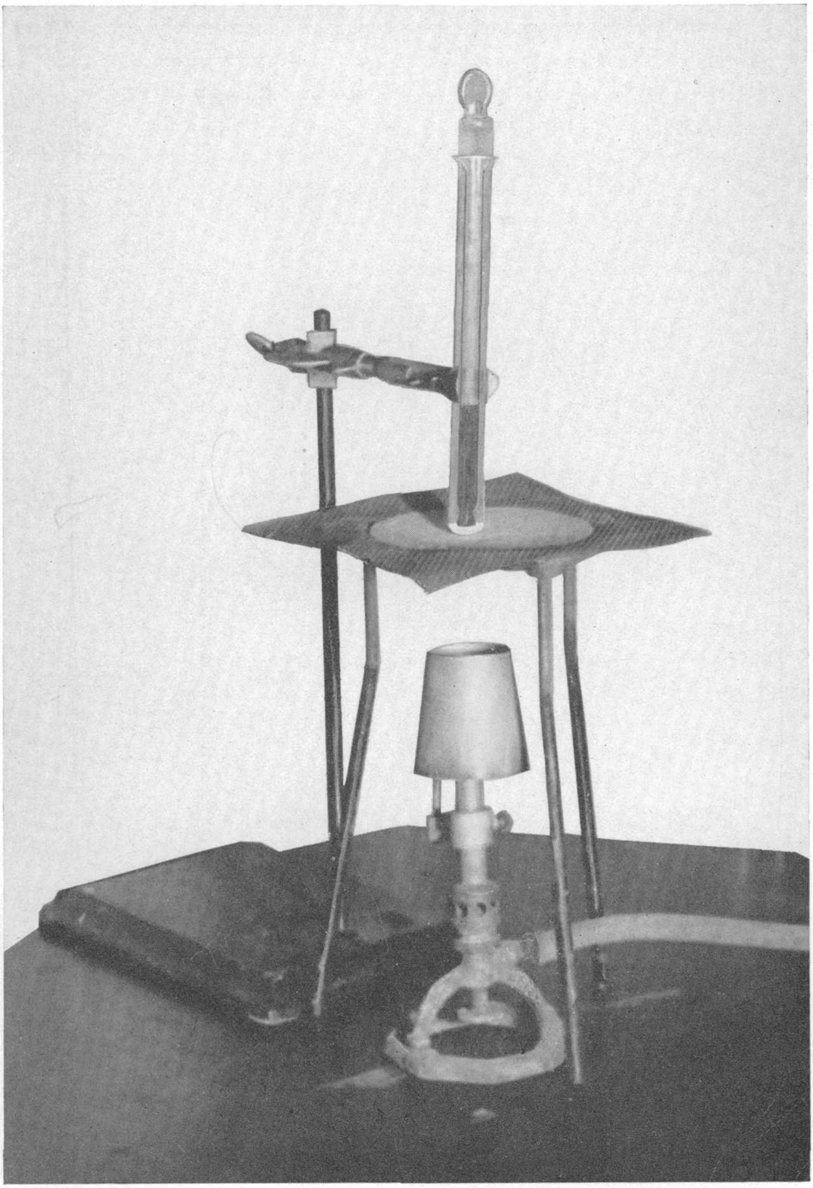

FIGURE 16.—Rock sample being treated with boiling nitric acid in outer chamber.

The various steps in the procedure are designed to minimize these hazards as much as possible and still retain speed. The sample is roasted to expel mercury and to destroy organic matter. Nitric acid dissolves essentially all the silver, but it does not appreciably extract gold, platinum, and palladium. It furthermore oxidizes copper to

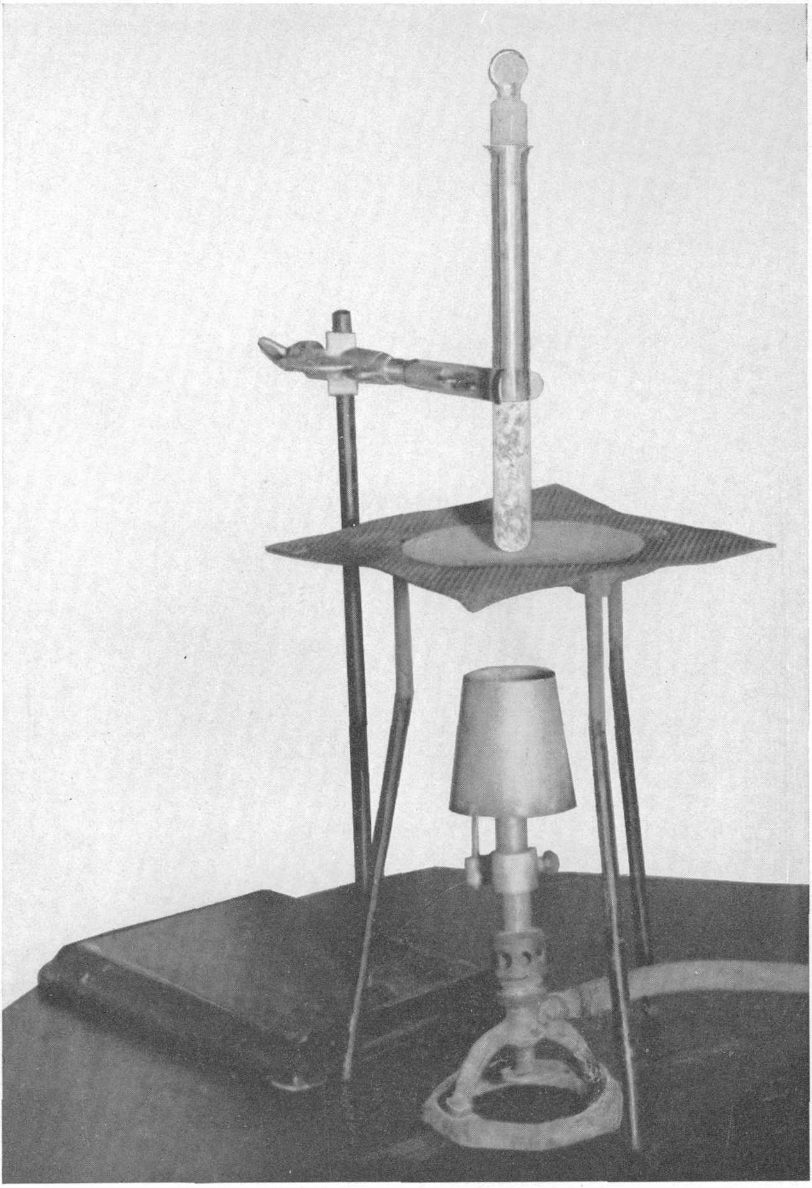

FIGURE 17.—Extract being automatically drawn through filter into inner chamber on cooling.

copper (II), which does not react with the reagent. The nitric acid extract is diluted to prevent precipitation of slightly soluble salts.

The nitric acid digestion of the sample was adopted because other methods of attack were less satisfactory. A fusion of the soil with potassium bisulfate followed by a nitric acid digestion resulted in a large amount of insoluble residue in the aqueous solution. The residue caused the mixture to filter very slowly. To decrease the amount of insoluble residue remaining after fusion, the quantity of bisulfate flux was lowered. Although the speed of filtration was improved, insoluble material now collected at the interface of the amyl alcohol-aqueous phases along with the silver and tended to carry along reagent. This resulted in high values, especially for samples containing little silver.

Treatment of the sample with nitric-hydrofluoric acid proved to be unsatisfactory because some of the dissolved platinum finally appeared on the paper as a dark-red precipitate.

Nitric acid dissolved most of the silver as indicated by the following experiment: Three soil samples were digested with nitric acid. The acid-insoluble residue was fused with a sodium carbonate-sodium nitrate flux. Both the nitric acid extracts and a nitric acid solution of the fused residues were carried through the remainder of the procedure. Considerable silver was found in the nitric acid extracts, none in the residues, showing that extraction of the silver from the samples by nitric acid was essentially complete.

Extraction with nitric acid and filtration are accomplished automatically by means of an extractor, a description of which has not previously been given. A glass-stoppered extractor (fig. 15) is placed in a culture tube containing a soil or rock sample and the acid. While the culture tube is being heated, air within the extraction stick expands, and a continuous stream of air bubbles is forced through the glass-wool filter, producing a stirring action which circulates the soil through the hot acid (fig. 16) and at the same time prevents bumping. When the extraction is complete, the culture tube is allowed to cool. A decrease of pressure within the filter stick upon cooling causes the acid extract to filter into the extraction stick. (See fig. 17.)

The dispersed silver precipitate is collected in a confined area on filter paper by means of a chromograph. (See fig. 14.) Glass pipe was substituted for the plastic head in the original chromograph described by Stevens and Lakin (1949) because of the solvent action of the alcohols on the plastic. Minute amounts of silver in a large volume of solution can be precipitated and subsequently filtered in the confined area with surprisingly good reproducibility.

## RESULTS

The results of the analysis of standard solutions, given in table 1, illustrate the precision of the colorimetric confined-spot method. Each standard solution was analyzed six times. Of the six spots obtained from each solution, one was judged visually as having the average depth of color, and this one was used as a standard spot.

Each value listed in column 1 was similarly analyzed, and a standard series of spots was thus selected. Each of the remaining five spots in each group was compared with the standard series, and the results, as reported, are arranged in order of increasing values under the column "values obtained." Thus for the one microgram of silver the five results are 0.7, 0.8, 1.0, 1.0, and 1.0, respectively. These average 0.9, reported in the last column.

TABLE 1.—*Precision and accuracy of the estimation as determined by analyses of standard solutions*

| Silver added (micrograms) | Values obtained [1] | | | | | Average |
|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1 | 0 | 0.05 | 0.1 | 0.1 | 0.2 | 0.1 |
| .3 | .2 | .2 | .3 | .3 | .4 | .3 |
| .6 | .5 | .6 | .6 | .6 | .8 | .6 |
| 1.0 | .7 | .8 | 1.0 | 1.0 | 1.0 | .9 |
| 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 4.0 | 3 |
| 6.0 | 5.0 | 5.0 | 6.0 | 6.0 | 6.0 | 6 |
| 10.0 | 6.0 | 10.0 | 10.0 | 12.0 | 12.0 | 10 |

[1] Compared to average of six spots.

The results of the analysis of seven soils are given in table 2 to illustrate the precision of the colorimetric spot method on soils. These soils had been assayed and the assay results are given in the first column. Results of repeat determinations are given under the heading "colorimetric confined-spot values." The colorimetric and assay results agree reasonably well for methods of trace analyses that are entirely different. Of the 30 colorimetric values by confined spots 27 fall within 50 percent of the assay values.

The results of the confined-spot tests listed in table 2 may be considered as representative of the over-all precision of the test, as each of the values were obtained on separate soil samples. The precision is considerably less than that obtained in the final spot-test estimation given in table 1. This is attributable to variations in completeness of extraction and to other interferences. The results in table 2 agree fairly well with those obtained by fire assay, but this is no real criterion of accuracy as both methods are subject to error.

TABLE 2.—*Comparative results on soils, in parts per million*

[Assays by Charles O. Parker, Denver, Colo. Analyses by H. Almond]

| Assay value | Colorimetric confined-spot values | | | | | |
|---|---|---|---|---|---|---|
| | | | | | | *Average* |
| 2 | 1 | 1.5 | 2 | 3 | 3 | 2 |
| 2 | 2 | 3 | 4 | 4 | 5 | 4 |
| 2.7 | 1.8 | 2 | 2 | 4 | 4 | 3 |
| 5.4 | 3 | 3 | 3 | 4 | 4 | 4 |
| 6.8 | 5 | 5 | 5 | 5 | 6 | 5 |
| 19 | 10 | 10 | 10 | 15 | 20 | 13 |
| 40 | 20 | 25 | 25 | 30 | 50 | 29 |

## USEFULNESS OF THE METHOD

The method makes possible the determination of traces of silver quickly in a large number of samples and with simple, easily transported equipment. It has been devised particularly for application to geochemical prospecting, for outlining the halos of increasing silver content in soils surrounding hidden silver ores. Under field conditions about 20 determinations can be made per man-day, with accuracy and sensitivity sufficient to discover and evaluate abnormal content of silver. The normal silver content of soils is given by Rankama and Sahama (1950) as 0.1 ppm. The chromographic test for silver, which has been described, will give a positive test for silver when present in this background range, and, where present in larger percentages, it quickly measures the silver to within 50 percent of the actual content, an accuracy sufficient to show significant trends from normal values to those approaching ore.

The test may have application to other investigations as well, where a quick estimate of traces of silver is wanted.

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# Part 8. A PHOTOGRAPHIC TECHNIQUE FOR SHOWING SOME MINERAL RELATIONS

By Waldemar T. Schaller

## CONTENTS

## ILLUSTRATIONS

[Pls. 1-14, at end of Part 8]

### ABSTRACT

A photographic technique is described whereby the parallelism of a group of crystals, or the presence of a certain mineral in an association of other minerals, or a certain structure, can be emphasized and be shown to better advantage than by a straight-on photograph. The requirement is that the particular mineral, whose presence in a specimen is to be shown photographically, must have a brightly reflecting surface, either natural or artificially produced. The simple technique is so to orient the specimen before the camera that this surface reflects a maximum brightness into the camera. In the resulting photograph the bright surface will be in strong contrast to the rest of the picture.

Examples are shown of parallel groups of quartz crystals, their parallelism accentuated by so turning the specimen before the camera that the same faces of the different crystals brightly reflect light into the camera. The presence of microcline, interpreted as being residual in albitized pegmatite, can be emphasized, photographically, if a brightly reflecting surface is present. Two generations of albite, in albitite, can be demonstrated. The presence of graphic granite quartz or of halite in a mixture of halite and sylvite ("potash ore") can be well shown in this way.

The brightly reflecting surface may result from cleavage or parting, or it may be the polished surface remaining after differential etching.

The technique can be used also for making an accurate crystal drawing, as the exact relative lengths of all intersection edges of the various faces present can be measured from the photographs when the crystal is so turned before the camera that a particular face reflects light brightly.

## INTRODUCTION

The object of this paper is to call attention to a photographic technique that illustrates certain relations of minerals much more strikingly than a straight-on photograph of a mineral specimen. The technique, in brief, is so to orient a specimen before the camera that one mineral or one face of a crystal will reflect light into the camera much more brightly than the other minerals or crystal faces present. As a result, the particular mineral or crystal face selected stands out strongly from the rest of the specimen. If the mineral to be emphasized is to reflect a more intense light into the camera, it must possess a brightly reflecting surface or plane or such a highly reflecting surface must be artificially produced. The technique therefore is not of universal application to all specimens. The fundamental requirement is the presence of a highly reflecting surface or plane. The faces of crystals, natural or developed cleavage surfaces, internal reflecting planes, such as a parting that produces schiller, and polished surfaces differentially etched and thereby partly dulled, all fulfill this requirement.

The resultant photographs are similar, in the contrast produced, to those of many associations of metallic minerals where there is a marked difference in the reflectivity of several of these minerals, or where a metallic mineral, appearing white on a polished surface, will reflect light much more brightly than the associated nonmetallic gangue minerals. Those metallic minerals with a maximum (almost total) reflectivity, such as chalcopyrite, will reflect so much more light in comparison with those of greater light absorption and hence lesser reflectivity, as sphalerite, that they will photograph almost white.

The parallelism of a group of crystals can be well shown if the brightly reflecting faces of one form reflect light into the camera by properly orienting the specimen. In a study of the genesis of the gem-tourmaline pegmatites of southern California, it becomes important to show clearly the presence of microcline or of graphic-granite quartz, in parts of the pegmatite. Such microcline or quartz are interpreted as residual remnants indicating their former much more widespread abundance. These remnants are abundantly present in many parts of what are considered to be albitized parts of the original pegmatite. The presence of graphic granite in the albitites of the Pennsylvania-Maryland State line pegmatites is well shown by this method. The relations and distinction between halite and sylvite in the "potash ore" of the Texas-New Mexico potash field, is strikingly shown by this method.

The one necessary condition is that one mineral in an aggregate of minerals will reflect much more light than the rest of the specimen. This may be a natural condition or it may be induced by proper treatment, such as etching.

The brightly reflecting technique can also be used if it is desirable to prepare an accurate crystal drawing showing the correct relative lengths of all intersection edges of a crystal.

The procedure is herein described and illustrated by examples in the hope that others may find it useful and be able to extend it to show mineral relations and associations other than those here described.

It is a great pleasure to acknowledge the patient and skillful cooperation of Nelson W. Shupe, photographer of the Geologic Division of the U. S. Geological Survey, who took the pictures. Several of the specimens here illustrated presented considerable difficulty before the desired results could be obtained.

## TECHNIQUE USED

If a specimen shows a brightly reflecting plane or surface of one mineral, or if such a surface can be produced, the specimen should be so oriented that this plane or surface reflects a maximum brightness into the camera. In order to keep all parts of the picture in focus, the surface to be photographed should be fairly flat and should be placed nearly normal to the optical axis of the camera. By slightly turning the specimen and then changing the position of the lights, the reflecting surface can be made to show a maximum illumination. This produces a striking effect in the resultant photograph, as shown, for example in plate 1.

Much of the microcline in the gem-bearing pegmatites of southern California is so oriented in the dikes that some brightly reflecting plane is nearly normal to the dip of the dike. As many of these dikes are more horizontal than vertical, many specimens with a broken or sawed surface that is nearly vertical will show some brightly reflecting plane, of any microcline present, that also is nearly vertical. These planes may be either induced cleavage surfaces—developed when the pegmatite rock is broken—or parting planes. (See pls. 2 to 7.)

Where a cleavage plane of the microcline is developed by breaking the rock, the rough surface of the specimen is photographed without polishing. (See pls. 2, 3, and 4.) For all sawed specimens the reflecting plane photographs better on the sawed but not polished surface than it does on the polished surface. This applies to a cleavage plane (pl. 7) as well as to an apparent parting plane (pls. 5 and 6). If the sawed surface contains too many saw marks it may be lightly ground smooth.

Similar photographic results may be obtained by differentially etching a polished surface with the proper solution. For quartz and the feldspars, albite and microcline, dilute HF (about 1:3) is very satisfactory. The etching solution is spread uniformly over the polished surface of a hand specimen with an inch-wide strip of white blotting paper, is allowed to stand for a few seconds, and the specimen—handled with tongs—is then well washed, dried, and examined. It is better to repeat the operation several times with dilute acid until the desired effect is obtained. For graphic granite, for example, the polish on the albite and microcline can thus be removed, without dulling the polish of the quartz. When properly oriented the polished quartz will then brightly reflect light into the camera, whereas the etched feldspars will reflect comparatively little light. For the results obtained, see plates 10 and 11.

A very unexpected result was obtained by so etching a polished surface of the albitite from the Maryland-Pennsylvania State line pegmatites. (See pl. 8.) The compact matrix albite, uniformly oriented, which constitutes the bulk of the specimen, was readily depolished but the many veinlets of albite, variously oriented, retained their polish.

That there is considerable graphic granite in parts of these albitites is shown by plates 9 and 10. A straight-on direct photograph yields a very poor presentation of the quartz of the graphic granite. (See pl. 9*A*.) By etching the entire surface the presence of quartz can be shown distinctly (pl. 9*B*) but a much more striking effect is obtained (pl. 10) when only the feldspar is etched and the highly reflecting surfaces of the polished quartz properly oriented before the camera.

For the mixture of halite and sylvite in the "potash ore" of the Texas-New Mexico potash field, the ground and polished surface is immersed in a saturated solution of sodium chloride which attacks the sylvite and destroys its polish but leaves the polished surface of the halite untouched. (See pl. 12.) An immersion of about 10 seconds suffices; the specimen is then removed from the solution and the surface quickly wiped dry. The remaining polish of the halite can readily be accentuated, if necessary, by hand rubbing.

The technique described can be used also if it becomes desirable to make an accurate drawing of a crystal, showing the correct lengths of all intersection edges. The crystal is mounted in polar position on a two-circle goniometer, or set vertical on a one-circle goniometer. The crystal holder is then mounted properly before the camera in an arrangement which presents what is usually called an orthographic, or c-axis-horizontal, projection—a projection on the basal plane or more generally on the plane normal to the prismatic zone. The camera used should give as large an initial magnification as possible, without sacrificing any sharpness. The illustrations of a crystal of bustamite shown on plate 13 are enlarged 5 times.

A photograph of the top of the crystal of bustamite, corresponding in orientation to an orthographic projection, is shown in plate 13*A*. In order to obtain a much sharper picture of the intersection edges of the several faces, the crystal is then revolved on what would correspond to its c-axis, and the position of the lights changed, so that one face brightly reflects light into the camera.

By properly revolving the crystal and adjusting the lights for each face, all the terminal faces can be photographed successively in the position wherein they brightly reflect into the camera. (See pl. 13*B*, *C*, and *D*.) In all these photographs of the terminal faces, the crystal is kept in true position for an orthographic view, as it is moved only by revolving on its own axis. A separate photograph has to be made for each of the larger faces. If the crystal has many terminal faces, many photographs may be required, though obviously very small and line faces need not be photographed, as the lengths of their intersection edges will be given by pictures of the larger faces. For photographs of the crystal faces with the prism zone vertical, corresponding to the clinographic or axiometric projection, the crystal holder is remounted. By the use of two arcs, the crystal—mounted polar on the goniometer—can be turned and tilted the proper amounts, either the conventional revolution of 18°26′ to the left and forward tilt of 9°28′, or in whatever position is desired. Then, by revolving the crystal on its own axis and adjusting the position of the lights so that the desired face brightly reflects, the faces of the prism zone can be successively photographed. (See pl. 13*E* and *F*.)

The second largest terminal face on the crystal is shown in plate 13 *E*, upper right, but the lengths of its intersection edges on the upper left do not show clearly enough to be measurable; all intersection edges show clearly, however, when the crystal is turned so that the face brightly reflects, as in plate 13*G*. The apparent intersection edge cutting diagonally across the face in plate 13*E* is due to the reflection of an edge of the largest terminal face in the rear of this transparent crystal.

The essence of the technique is to have each face brightly reflect light into the camera, the crystal being kept in polar position throughout its turning, the successive bright illumination of the different faces being accomplished by changing the position of the lights.

If greater magnification than that of the initial photograph is desirable, a bromide enlargement is made, as in plate 14, which is a four times enlargement of plate 13*D*, and is of a size similar to that of a crystal drawing.

This illustration shows eight brightly reflecting faces of the same form and the lengths of all intersection edges can easily be measured. The lengths of the intersection edge of the two largest faces (shown black) can also be measured in this illustration as well as the lengths of the three intersection edges of the small triangular face (shown gray) in upper center. This same triangular face is shown brightly reflecting in plate 13*B* and *H*.

For smaller crystals and smaller original magnification, the bromide enlargements may be increased, possibly to 15 times. Special films, prints, and developers can be used to yield minimum grain size of the film and of the paper.

A crystal drawing can be made from the goniometric measurements in the regular way. If it be made of a size to correspond with the bromide enlargements, these will give the exact relative lengths of all intersection edges. They also show the abundance and position of oscillatory repetitions of the same face (pl. 13*E* and *F*) and any imperfections on the crystal which it may be desirable to show in the crystal drawing.

The bromide enlargements can also be used directly, by inking in the intersection edges and any other features to be shown and then bleaching the bromide.

## CRYSTALS OF QUARTZ

The essential parallelism of a group of crystals of quartz on graphic granite can be well shown by turning the specimen so that the same faces of the prism simultaneously reflect light brightly into the camera, as shown in plate 1*A*. The specimen was collected at the Panama-Pacific Exposition mine in a gem-bearing pegmatite in the east side of Chihuahua Valley, San Diego County, California. This pegmatite yielded a small handful of cassiterite crystals obtained from a single pocket and the pegmatite was briefly described by Schaller.[1]

To show the parallelism of a group of euhedral crystals of quartz, which are extensions of the quartz rods of the underlying graphic granite, the specimen is so turned before the camera that the corresponding rhombohedral faces on the different crystals brightly reflect light into the camera, as shown in plate 1*B*. The specimen was collected at the El Molino gem mine in a pegmatite on Hiriart Hill, Pala, San Diego County, Calif.

## MICROCLINE

The writer has previously postulated [2] that the gem-bearing pegmatites of southern California were originally composed essentially of microcline or of microcline graphic granite, both of which were later subjected to hydrothermal replacement yielding in large part an albitized and banded rock. Part of the evidence consists of demonstrating the presence of residual unreplaced microcline, unreplaced microcline graphic granite, and partially replaced microcline graphic granite in the albitized part. The presence of residual microcline and of residual quartz of graphic granite, partially replaced, can very well be illustrated by use of the photographic technique herein described.

Microcline possesses a number of planes which will reflect light brightly. There are the several cleavages, easily developed on breaking the host rock, and the parting that yields a schiller. Much of the microcline in the pegmatites is so oriented that a broken rock surface nearly normal to the dip of the pegmatite dike will show such a brightly reflecting plane.

Similar brightly reflecting planes of microcline were observed in albitized pegmatite from localities other than those in southern California. One such example from the Maryland-Pennsylvania State line albitite pegmatites is shown in plate 7.

Plates 2 to 7 show how clearly the presence of this microcline, interpreted as residual, can be illustrated by using the photographic technique described.

A tapering crystal of residual microcline in a sparsely-banded albitized pegmatite from near Jacumba, San Diego County, Calif., is shown in plate 2*A*. The broken, not polished, rock surface yielded a cleavage face of the microcline which reflects light brightly. The corroded sides of the microcline crystal also are emphasized by using this technique. In the photograph the wavy bands of garnet show as

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[1] Schaller, W. T., 1916, Cassiterite in San Diego County, California: U. S. Geol. Survey Bull. 620, pp 351–354.

[2] Schaller, W. T., 1925, The genesis of lithium pegmatites: Am. Jour. Sci. ,5th ser., vol. 10, pp. 269–279.

nearly vertical lines. In the dike, however, the orientation of these lines is horizontal.

A similar example is shown in plate 2*B*, where the brightly reflecting cleavage planes of two tapering microclines crystal in the banded albitized pegmatite stand out strongly. The microcline is in part graphic granite. The specimen was collected a short distance north of the Panama Pacific Exposition gem mine in the eastern part of San Diego County, Calif.

In the nonpolished specimen of albitized pegmatite shown in plate 3*A*, the cleavage face of the microcline crystal—interpreted as residual—reflects light brightly. The corroded edges of this crystal are accentuated by its bright reflection. Specimen collected in the Himalaya mine, Mesa Grande, San Diego County, Calif.

Plate 3*B* illustrates the largely disconnected residual fragments of microcline, whose uniformly brightly reflecting cleavage surfaces indicate the former presence of a single larger crystal, now much albitized. The broken surface is not polished. The specimen is from the Himalaya mine, Mesa Grande, San Diego County, Calif.

Two views of the unpolished surface of the same specimen are shown in plate 4. The specimen is from the banded albitized pegmatite from the San Diego mine, San Diego County, Calif., and is similar to the specimens shown in plates 5 and 7*A*. Although the slightly darker colored graphic granite, below the upper band of black tourmaline, can be seen in plate 4*A*, the presence of the microcline of the graphic granite is strikingly shown in plate 4 *B*, as the specimen was turned before the camera so that the microcline cleavage faces reflect light brightly. The illustration (pl. 4*B*) does not show the quartz of the graphic granite. It could be shown, if desired, by polishing the surface and destroying the polish of the feldspars but not that of the quartz with HF and then photographing the brightly reflecting polished surfaces of the quartz, as shown in plates 10 and 11*B*.

In plate 5, the microcline (interpreted as residual) in the banded albitized pegmatite is very well shown. The specimen, 14 inches high, represents essentially a vertical section of the lower half of the pegmatite dike of the San Diego mine, Mesa Grande, San Diego County, Calif. Part of it is shown, one-half natural size, in plate 5*A*. The specimen was sawed in two vertically, one-half polished and the one-half unpolished. In plate 5*A*—a straight-on photograph of part of the polished surface—the darker area in the lower center suggests a large crystal of some mineral, readily identified as microcline. The microcline crystal is so oriented in this specimen that a reflecting plane—probably a schiller parting—is nearly parallel to the sawed surface. The reflecting plane also can be seen on the polished surface by slightly turning the specimen. It can be seen to better advantage on the unpolished surface of the other half of the sawed specimen. The large microcline crystal in this half reflects light brightly and when properly oriented before the camera gave the result shown in plate 5*B*.

This illustration (natural size) also shows very clearly the corroded outlines of the microcline crystal produced by its partial albitization. The horizontal straight black line above the microcline is the shadow of a sawmark. The microcline crystal contains graphic quartz—the many small dark areas in the white microcline crystal.

An additional example of the advantage gained by photographing a brightly reflecting plane is shown in plate 6. In *A* is shown, one-half natural size, part of the polished half of a sawed specimen of pegmatite, largely albitized, with a central layer of unreplaced microcline, just above the banded albitized lower portion. On the upper right side is an area of microcline which is much better shown when the unpolished half of the sawed specimen is so turned that the microcline crystal reflects light brightly (pl. 6*C*, natural size). On the lower left side of plate 6*A*, is a darker area of microcline with graphic quartz, hardly detectable in the picture. However, by properly turning the specimen—again the unpolished half of the sawed specimen—the microcline crystal brightly reflects, and in this position is clearly shown in the photograph (pl. 6*B*, natural size). Plate 6*B* also shows the presence of graphic quartz in the microcline and well shows the corrosion produced by the albitization.

The corroded outlines of the microcline crystal shown in plate 6*C* are emphasized when it is photographed in the brightly reflecting position. The large microcline crystal just above the reflecting microcline (C) is albitized and hence does not reflect brightly. The reflecting plane of the microcline is probably a schiller parting. The specimen was collected at the San Diego mine, Mesa Grande, Calif.

The conclusion reached by the writer in 1924 that the albite-rich portions of the gem-bearing pegmatites of the southern California area are hydrothermally replaced microcline pegmatites, led to a study of the albitites in serpentine along the Maryland-Pennsylvania State line. These, and other similar albitites, have been described as "desilicated pegmatites." Abundant microcline, as well as microcline graphic granite, was found in many of them, especially in the area around Pilot, Md. Probably these State-line albitites are simply albitized microcline pegmatites. A few illustrations of selected specimens from this locality are here presented to show how clearly the presence of microcline and of graphic granite in these albitites can be demonstrated by using the technique described herein.

A large shining cleavage surface, 2 in. across, on the outside of a weathered specimen of albitite pegmatite from a feldspar mine on the

Blair farm, near Pilot, Md., gave indication of the presence of microcline. The specimen was sawed in two and one surface polished and photographed straight on (pl. 7*A*). The graphic character of the pegmatite can be seen, though poorly, but the illustration gives no indication of the presence of a large microcline crystal in the lighter-colored area in the center. The unpolished surface of the other half of the sawed specimen shows the residuum of a large microcline crystal, and as the sawed surface is nearly parallel to a shining cleavage of the microcline crystal, by slight turning of the specimen before the camera its brightly reflecting surface can be photographed with marked contrast to the rest of the specimens, as shown in plate 7*B*. A small detached area of the microcline crystal, in parallel position and also reflecting brightly, is shown at the bottom center, just above the black mica. A similar large microcline crystal is at the lower left corner, but because of different orientation, it does not reflect in the same position as the first crystal.

In order to demonstrate that the reflecting plane shown in plate 7*B*, is a cleavage, a little of the microcline crystal was broken off at the top of the specimen, and the induced cleavage surface reflected light even more strongly (pl. 7*C*). The microcline crystal contains graphic quartz.

## ALBITE

A specimen of massive albitite from the Pennsylvania-Maryland State line, appears very uniform when polished. (See pl. 8*A*). The specimen represents the typical albite mined. When slightly etched, however, the apparently homogeneous massive albite is seen to contain many small irregular reflecting veinlets. At first these reflecting veinlets were thought to be quartz, but examination of a thin section showed that they were albite, variously oriented. There is very little quartz in the specimen. No notable difference was seen in the indices of refraction of the two albites. The better retention of the polish by the veinlet albites may be due to their various orientations. As far as a thin section indicates, the massive host albite is uniformly oriented over large areas.

## QUARTZ OF GRAPHIC GRANITE

The technique will show the presence of graphic-granite quartz much better for some specimens than a straight-on photograph. The effect obtained in photographing specimens of graphic granite for reproduction depends on the color and reflecting properties of both the quartz and the feldspars. For the specimens from the Pennsylvania-Maryland State line, the bright-surface technique gives much better results. On the other hand, straight-on photographs of polished specimens of graphic granite (both microcline graphic granite and albitized graphic granite) from the pegmatites of southern California, give results fully as good as those shown in plate 10, with however a reversal of color, the quartz photographing black or very dark and the feldspar white or very light gray. The bright-surface technique would have no advantage over a straight-on photograph for these California specimens. Plate 9 shows two photographs of the same surface of a specimen of albitized graphic granite from the Pennsylvania-Maryland State line albitites. In plate 9*A*, a straight-on photograph of the polished surface presents a very poor picture of the abundant graphic quartz, hardly discernable in places. By etching both the quartz and the feldspar the presence of the abundant quartz, here photographing dark, is much better shown. But it is shown even better, by the bright-surface technique, if the albite only is etched and the polish is left on the quartz, as shown in plate 10*A*, in which the brightly reflecting polished surfaces of the quartz stand out strongly from the dark microcline. A similar effect is produced by partially etching a polished surface of a specimen of microcline graphic granite from the same locality, as shown in plate 10*B*. The graphic quartz in the albitized graphic granite shown in plate 10*A*, is much more corroded than the graphic quartz in the microcline graphic granite shown in plate 10*B*.

The presence of residual quartz rods in the banded albitized lower part of a pegmatite from Pala, Calif., is well shown by the reflection technique here described. Plate 11 gives two views of the same specimen: *A*, polished but not etched; *B*, the same after partial etching, the polish of the quartz rods being retained and the specimen so turned before the camera that the polished surfaces of the quartz reflect brightly.

## HALITE AND SYLVITE

In a photograph of a mixture of halite and sylvite, the "potash ore" of the Texas-New Mexico potash field, the halite can readily be distinguished from sylvite by the procedure already described, as the polished surfaces of the sylvite can be etched and dulled; hence, they do not reflect brightly whereas the surfaces of the halite retain their polish and reflect brightly.

A comparison of the two pictures of the same core specimen before and after etching, as given in plate 12*A*, *B*, illustrates the results obtained. These results are shown in plate 12*C* for another specimen of potash ore. The contrast between the light, almost white, halite and the much darker sylvite, is very striking

## CRYSTAL FACES

The results obtained by photographing a crystal so oriented before the camera that only one crystal face—or the several parallel faces of one form—reflects brightly have already been described. These results are illustrated in plates 13 and 14. The crystal of bustamite (U.S.N.M. R–8309) illustrated on these plates is from the Zinc Corp. mine at Broken Hill, New South Wales, Australia. It is pink and transparent, weighs 0.64 g., and measures 13 mm. by 9 mm. by 3 mm. It is completely terminated at one end with brilliant and singly reflecting faces, giving excellent signals on the goniometer. The crystal has two smaller ones attached on one side, in not quite parallel position. These are shown in plate 13*E* on the left side.

Some trials were made years ago to obtain a photographic record of the exact relative lengths of the intersection edges of the faces of a crystal by covering the faces with an opaque layer of ammonium chloride—produced as a vapor and blown on the crystal. It was hoped that in this way a more even illumination would be obtained and that all the intersection edges would photograph sharply and evenly on account of the dull nonreflecting coating of ammonium chloride. Although the photographs of such coated crystals gave a sharper picture than those of uncoated crystals, the sharpness of the intersection edges is much less than that obtained by the technique here described.

It may be that this technique will find other uses: for etch figures or inclusions of parallel oriented crystals of one mineral in another, as the hematites in aventurine feldspar.

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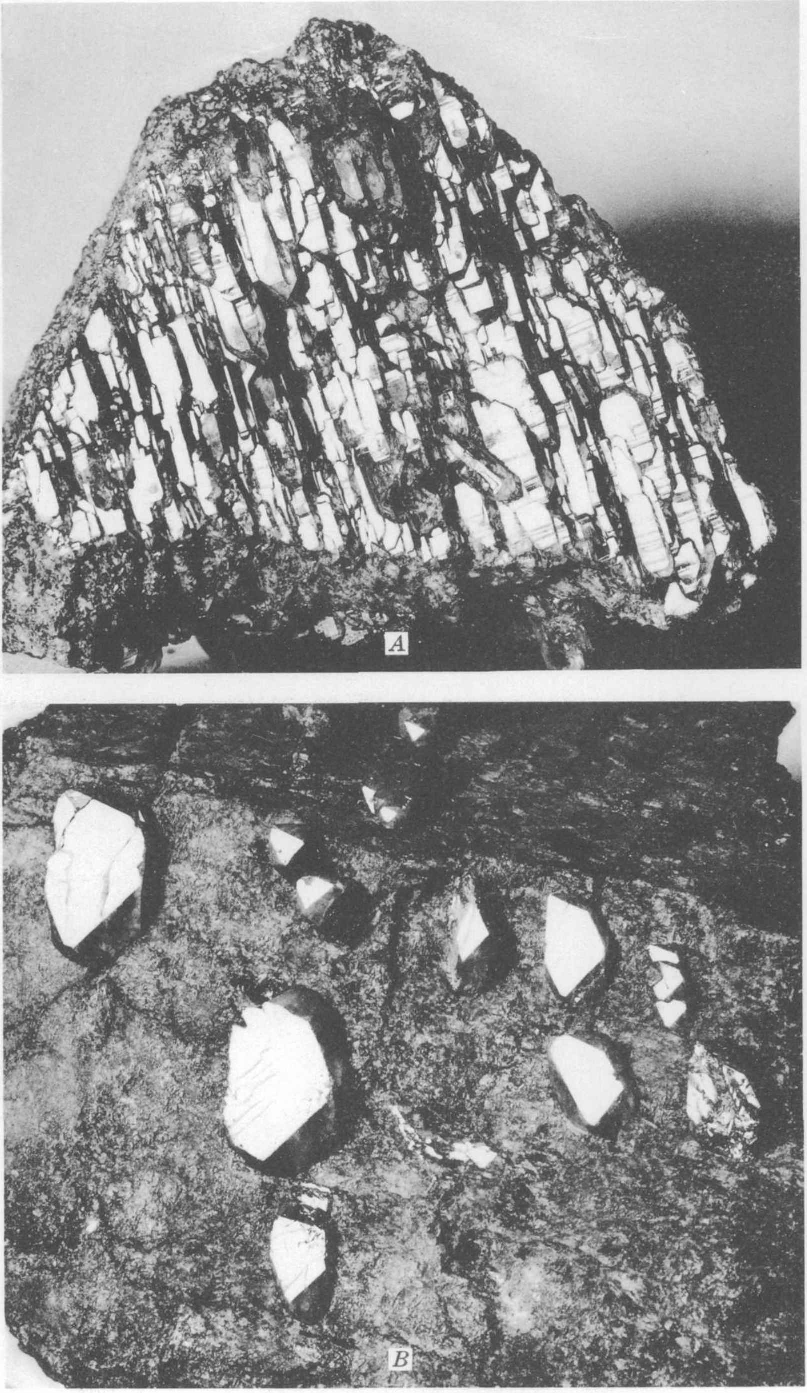
# PLATES 1–14

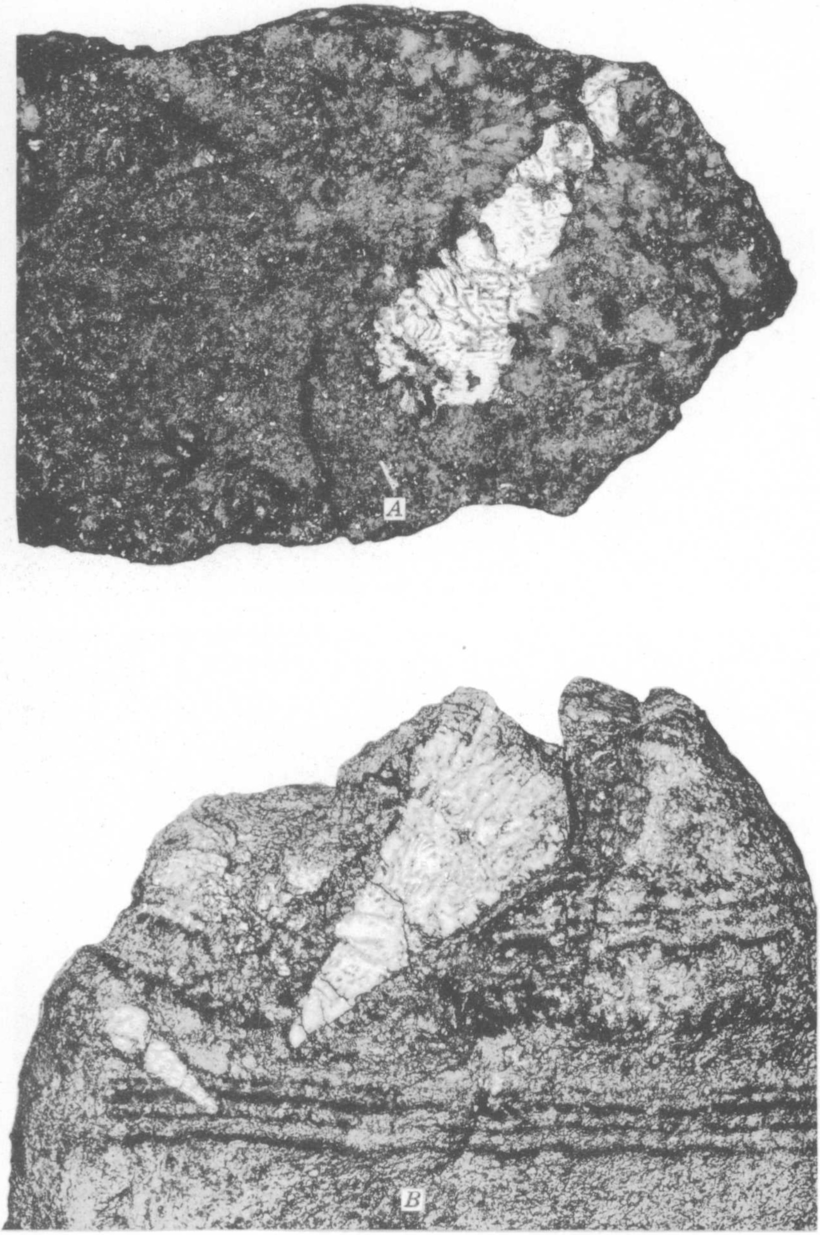
## PLATE 1

*A*. Essentially parallel crystals of quartz on graphic granite. The brightly reflecting faces are the prism. Natural size. From the Panama-Pacific-Exposition mine, Chihuahua Valley, San Diego County, Calif.

*B*. Group of parallel crystals of quartz, which are extensions of the quartz rods of graphic granite. The brightly reflecting faces are the rhombohedron. From the El Molino mine, Hiriart Hill, Pala, San Diego County, Calif.



BRIGHTLY REFLECTING FACES OF PARALLEL QUARTZ CRYSTALS



BRIGHTLY REFLECTING PLANES OF MICROCLINE

# PLATE 2

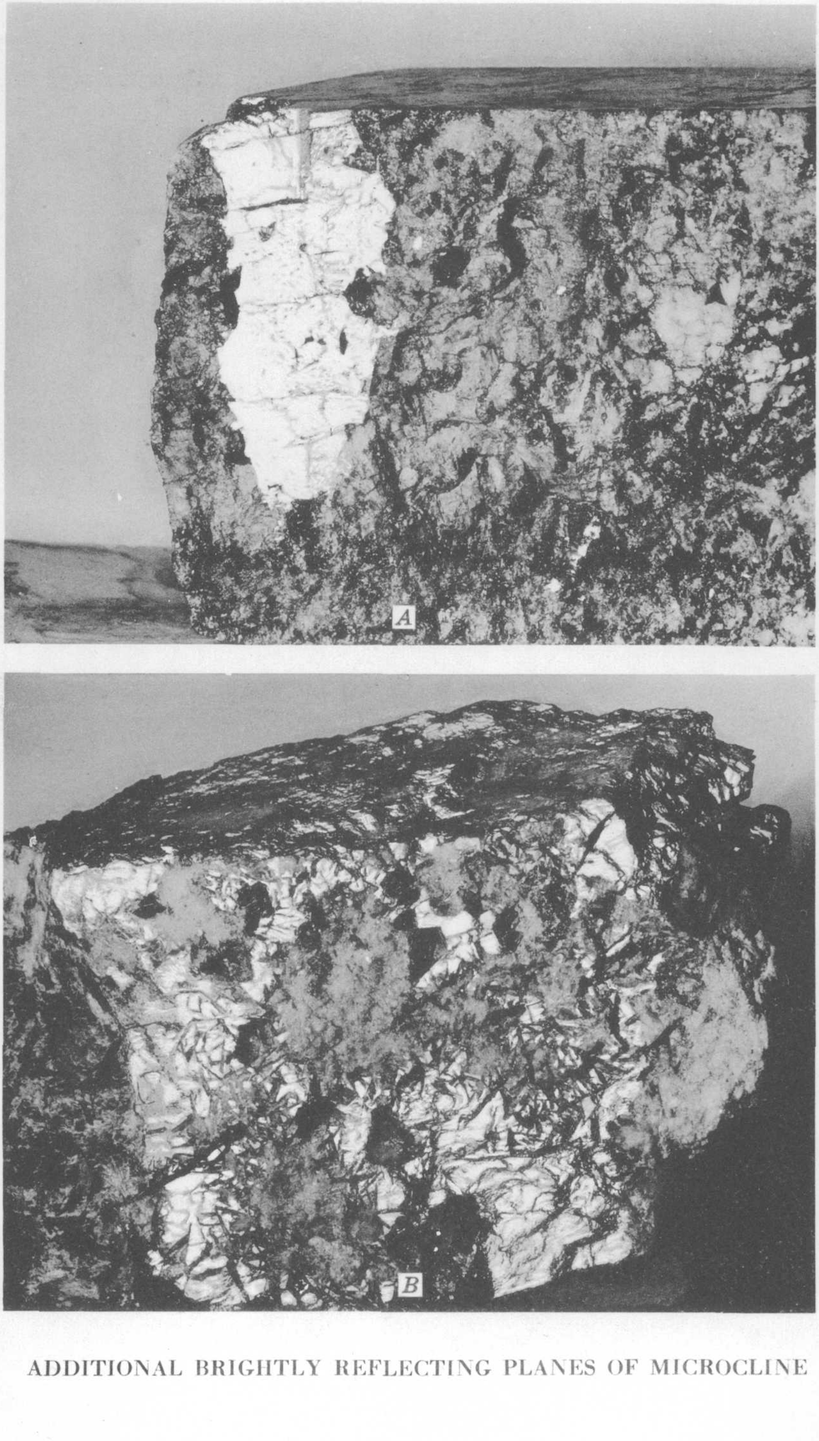
*A.* Reflecting plane of tapering microcline crystal (interpreted as residual) in banded albitized pegmatite. The corroded edges of the microcline are well shown. The wavy bands of garnet from upper left to lower right. Jacumba, San Diego County, Calif.

*B.* Reflecting planes of two tapering microcline crystals (interpreted as residual) in banded albitized pegmatite. Short distance north of Panama-Pacific-Exposition mine, Chihuahua Valley, San Diego County, Calif.

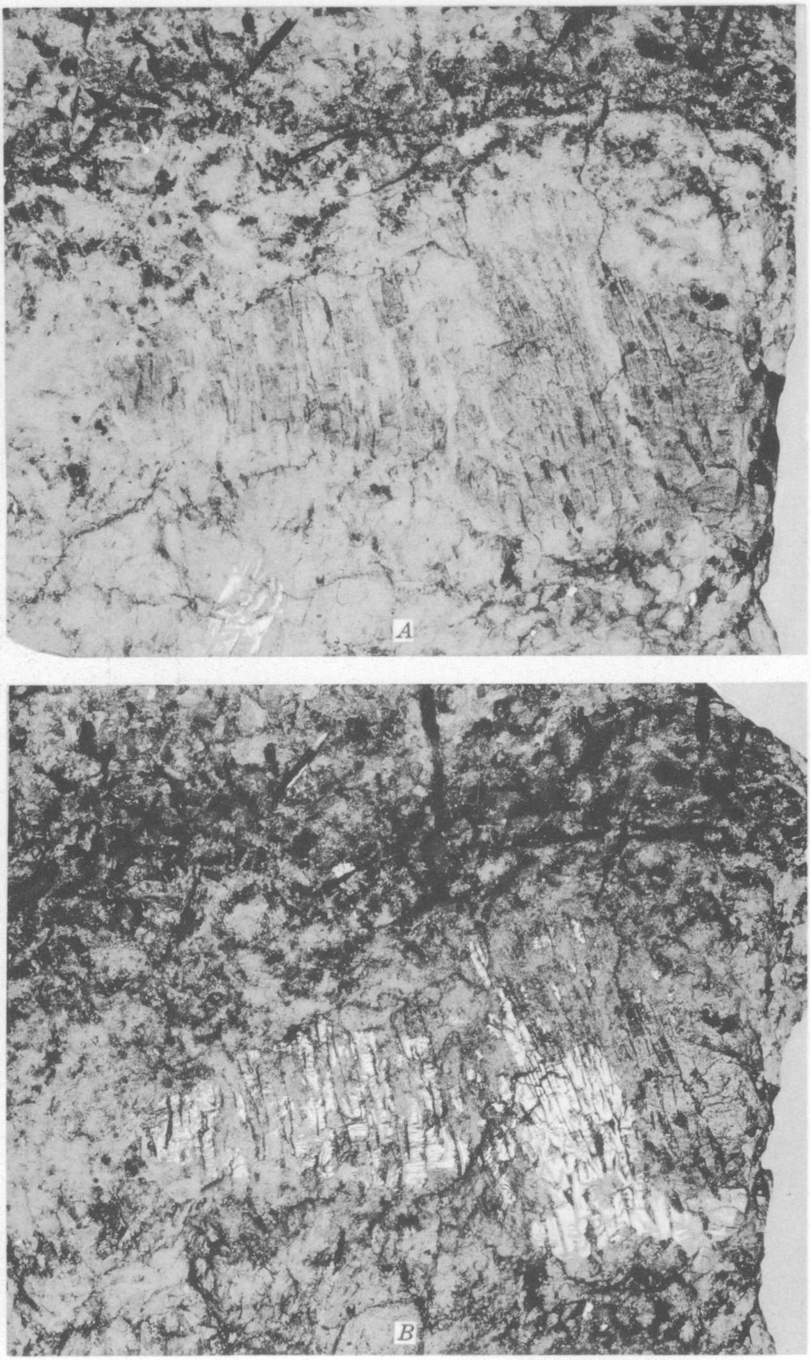
# PLATE 3

*A*. Reflecting plane of microcline (interpreted as residual) in albitized pegmatite. The corroded edges of the microcline are well shown. Himalaya mine, Mesa Grande, San Diego County, Calif.

*B*. Uniformly reflecting cleavage faces of microcline (interpreted as residual). The parallel reflecting surfaces of the disconnected areas of microcline indicate the former presence of a single larger crystal. In albitized pegmatite. Himalaya mine, Mesa Grande, San Diego County, Calif.



ADDITIONAL BRIGHTLY REFLECTING PLANES OF MICROCLINE



BRIGHTLY REFLECTING CLEAVAGE SURFACES OF MICROCLINE

# PLATE 4

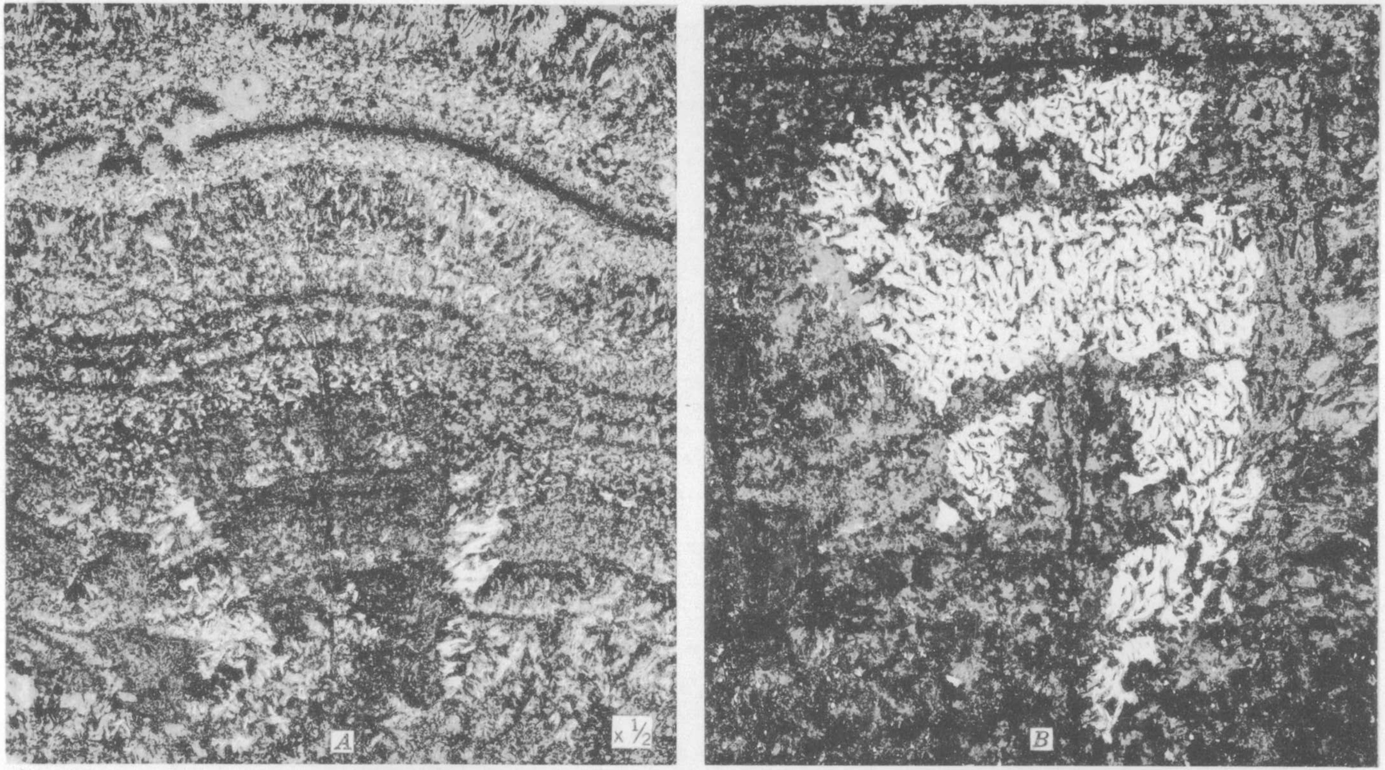
*A*. Graphic granite (interpreted as residual) in banded albitized pegmatite. Natural broken surface, not polished. Although the slightly darker colored graphic granite, below the upper band of black tourmaline, can be seen, its presence is much better shown in *B*. San Diego Mine, Mesa Grande, San Diego County, Calif.

*B*. The same specimen shown in *A*, turned slightly so that the cleavage faces of the microcline in the graphic granite more strongly reflect the light.

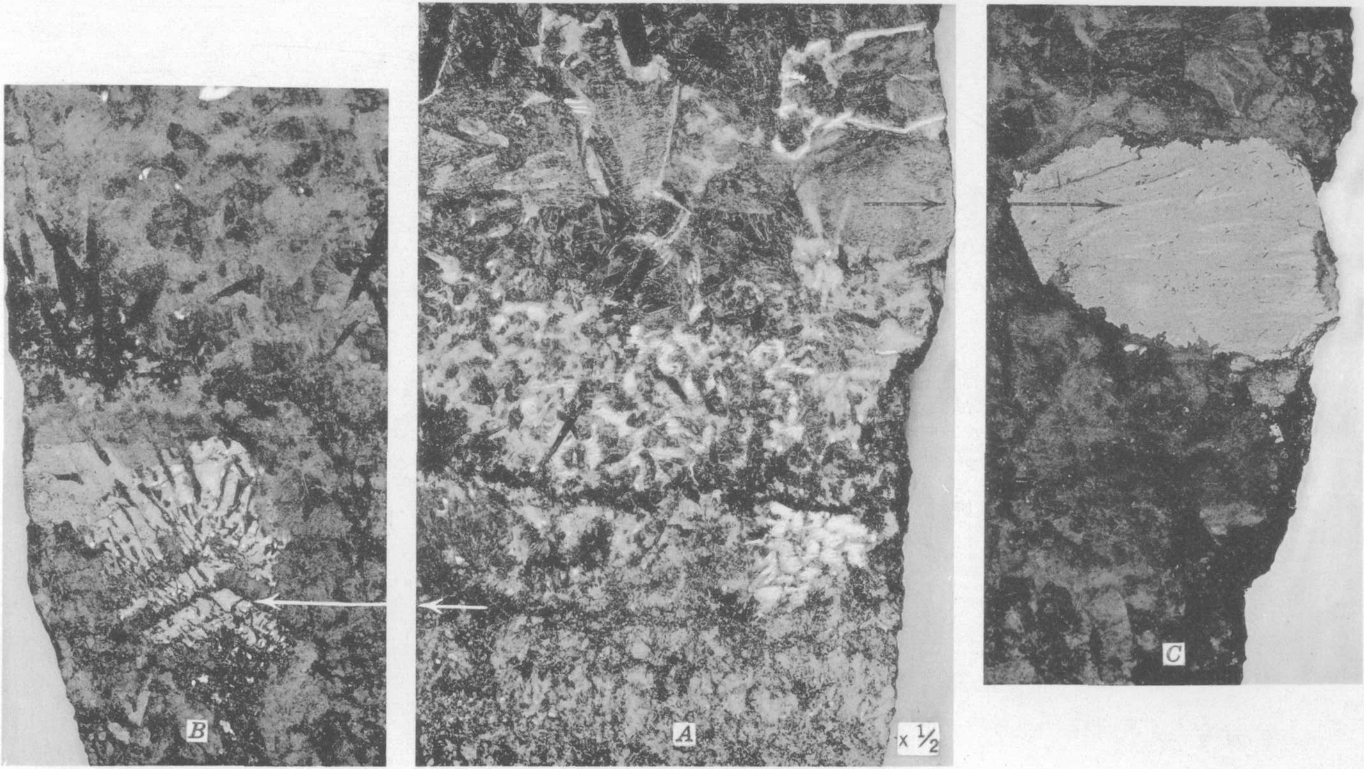
## PLATE 5

*A*. Microcline (interpreted as residual), the darker-colored area in lower center, in banded albitized pegmatite. The microcline is full of graphic quartz. Specimen polished. One-half natural size. San Diego Mine, Mesa Grande, San Diego County, Calif.

*B*. Reflecting plane of the microcline shown in *A*. The other half of the sawed but not polished specimen. Natural size. The horizontal black line above the microcline is the shadow of a saw mark. The corroded character of the microcline is well shown. The entire specimen is 14 inches high.



BRIGHTLY REFLECTING PLANE OF MICROCLINE



BRIGHTLY REFLECTING PLANE OF MICROCLINE

# PLATE 6

*A*. Vertical section of part of complete pegmatite, largely albitized, with a central layer of unreplaced microcline, just above the banded albitized lower portion. One-half natural size. The reflecting plane of the microcline at the right of the central layer is shown, natural size, in *C*. Microcline graphic granite in lower left, just below the band of black tourmaline, is shown, natural size, in *B*. San Diego Mine, Mesa Grande, San Diego County, Calif.

*B*. Reflecting plane of the microcline of graphic granite (interpreted as residual), natural size, in the banded albitized pegmatite. Both *B* and *C* were photographed from the other half of the specimen shown in *A*. Surface of specimen ground but not polished.

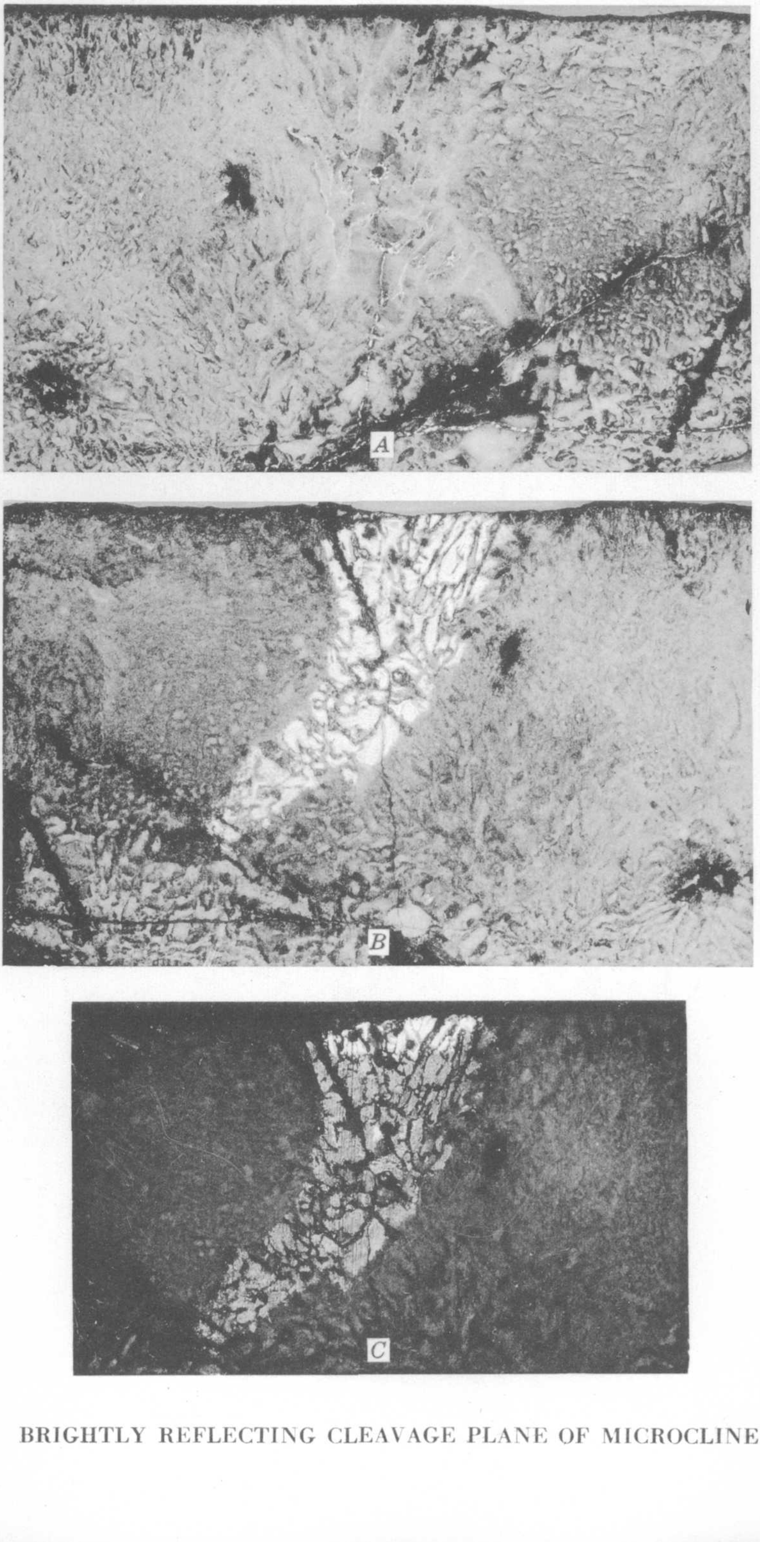
*C*. Reflecting plane of microcline. The corroded edges of the microcline are well shown. The former microcline just above the one shown by the stronger reflecting light, is albitized and does not show any strongly reflecting plane.

## PLATE 7

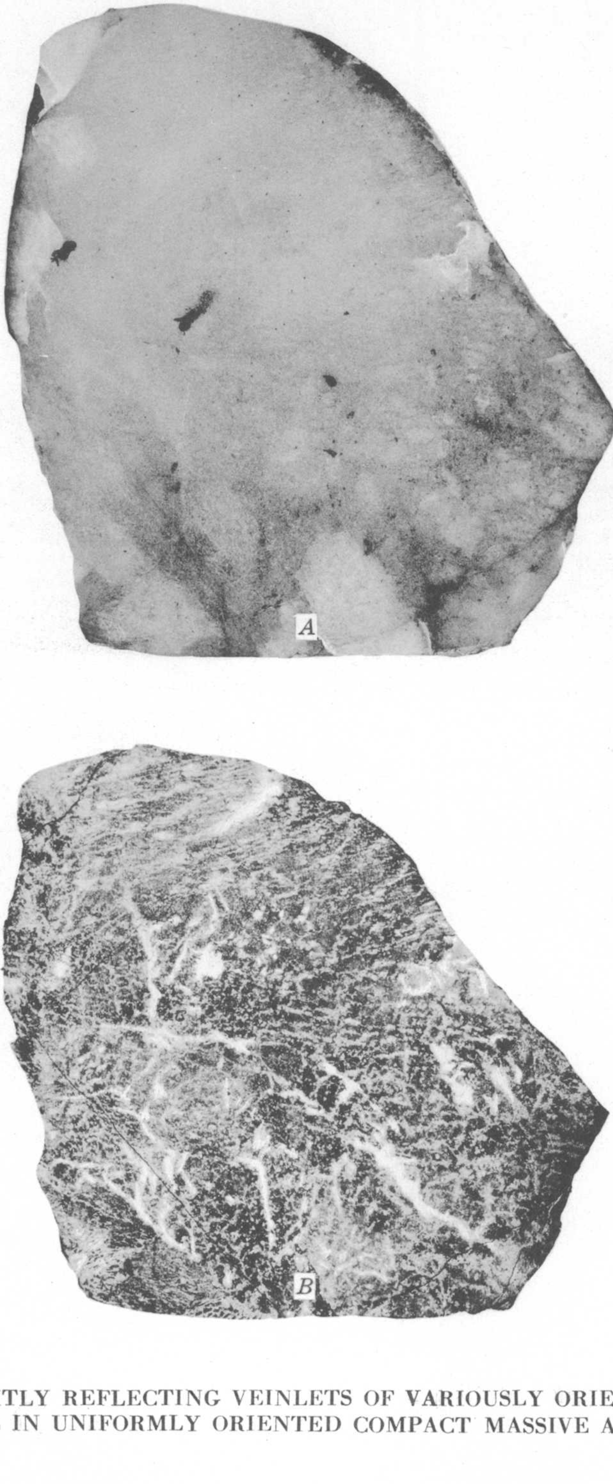
*A*. Polished specimen of albitized pegmatite. The specimen is essentially albite and the outlines of the microcline (interpreted as residual) in the center cannot be definitely traced. From the Blair farm, near Pilot, Md.

*B*. The other half of the specimen shown in *A*. The sawed surface is ground smooth but not polished. The reflecting plane of the microcline readily shows its outline.

*C*. Induced basal cleavage of microcline in upper edge of specimen. The freshly broken cleavage face reflects light even more strongly.



BRIGHTLY REFLECTING CLEAVAGE PLANE OF MICROCLINE



BRIGHTLY REFLECTING VEINLETS OF VARIOUSLY ORIENTED ALBITE IN UNIFORMLY ORIENTED COMPACT MASSIVE ALBITE

## PLATE 8

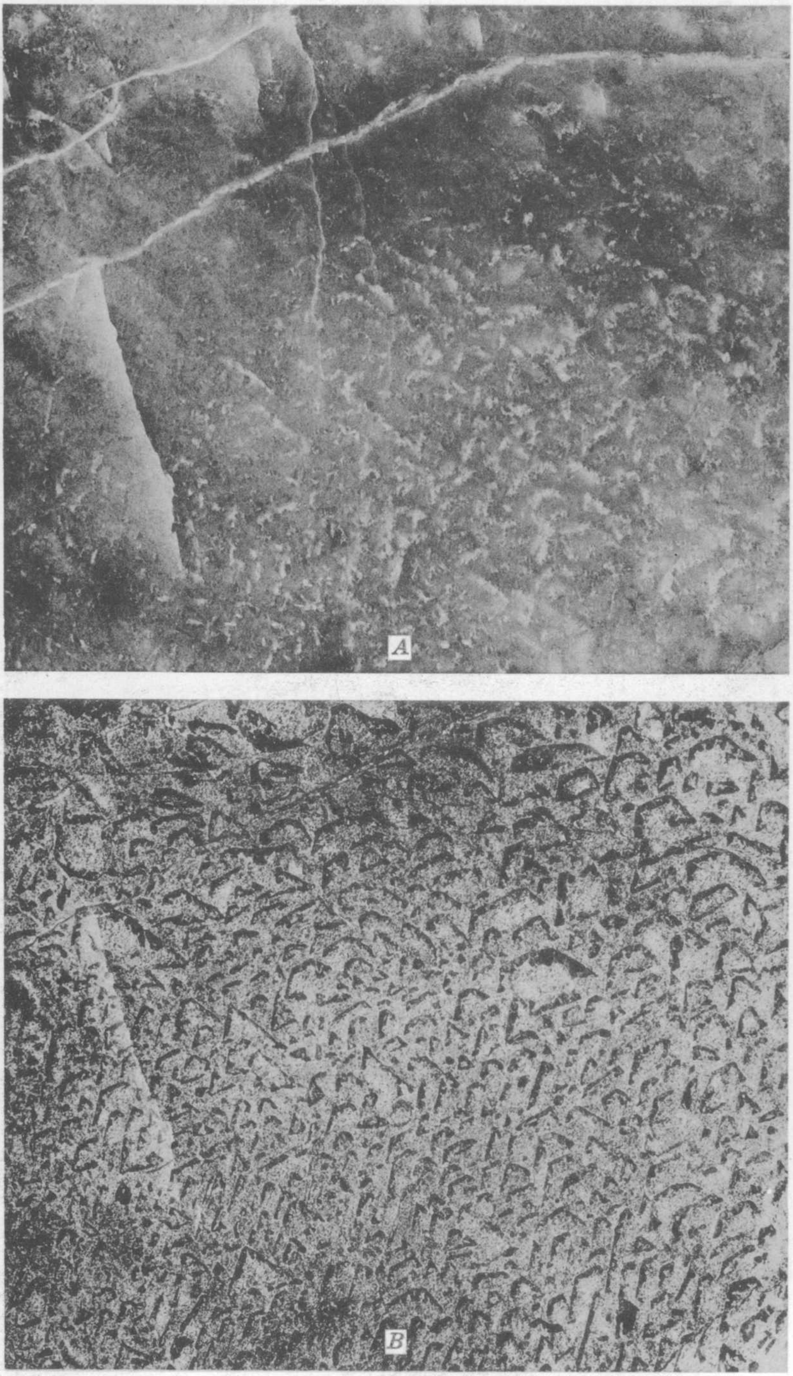
*A.* Albitite pegmatite, nearly all albite, polished and not etched. Photographed straight on. The lighter-colored areas are due to light reflected from incipient cracks. The small black areas represent chloritic material. From Squires Quarry, near Sylmar on Pennsylvania-Maryland State line.

*B.* Same surface etched with dilute HF. The matrix albite is readily etched, loses its polish, and photographs dark. The small irregular veinlets and small masses of variously oriented albite retain their polish and the brightly reflecting surfaces photograph white.

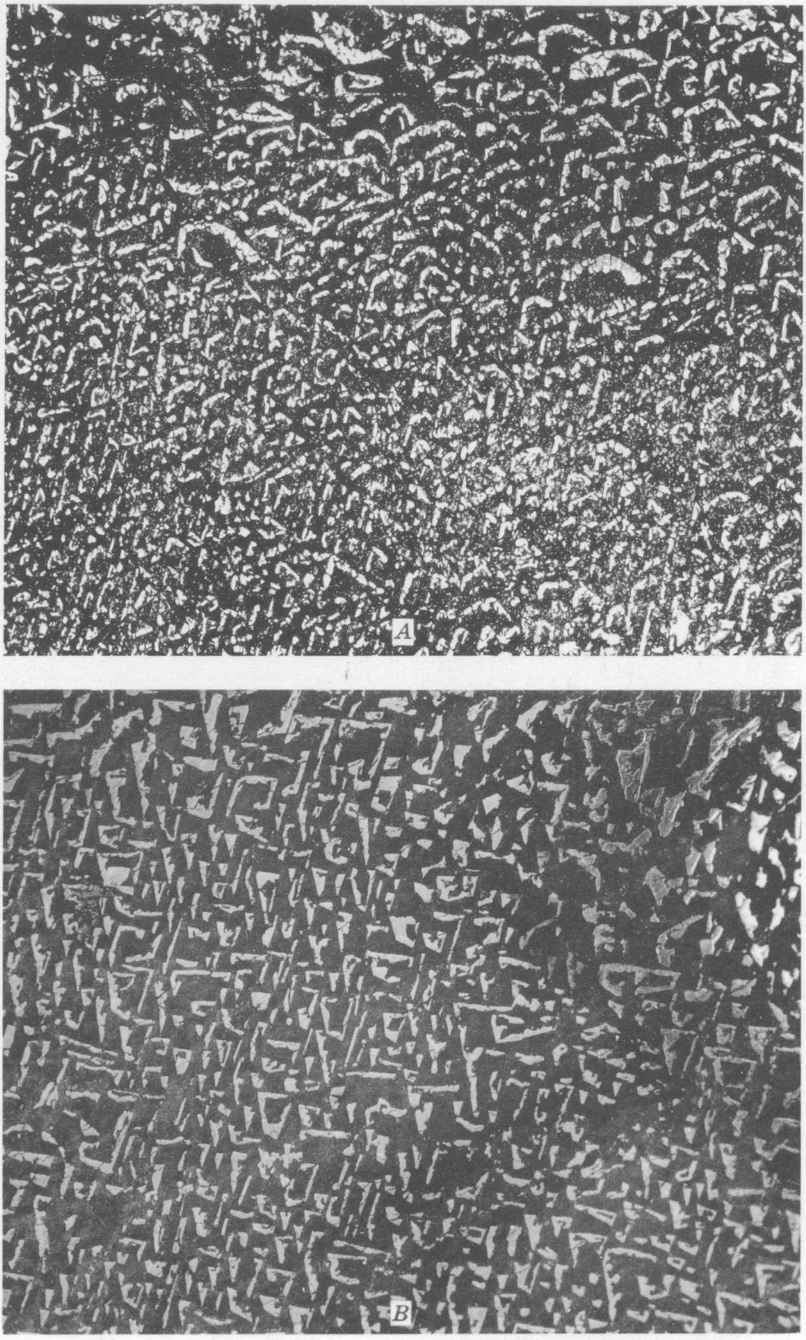
## PLATE 9

*A*. Albitized graphic granite, specimen polished. Photographed straight on with no treatment of polished surface. The quartz is barely visible, practically invisible in places. Compare with *B*, and with plate 10 *A*. Plates 9 *A* and *B*, and plate 10 *A* are from the same specimen. From albitite pegmatite from Bald Friar no. 12 quarry, near Pilot, Md.

*B*. Same specimen surface etched with dilute HF. Both the albite and the quartz are etched and dulled. The quartz stands out much clearer, photographing dark, than it does in *A*. But it stands out even better in plate 10 *A*.



POOR PRESENTATION OF QUARTZ, NOT USING THE BRIGHTLY REFLECTING METHOD



BRIGHTLY REFLECTING POLISHED SURFACES OF QUARTZ

# PLATE 10

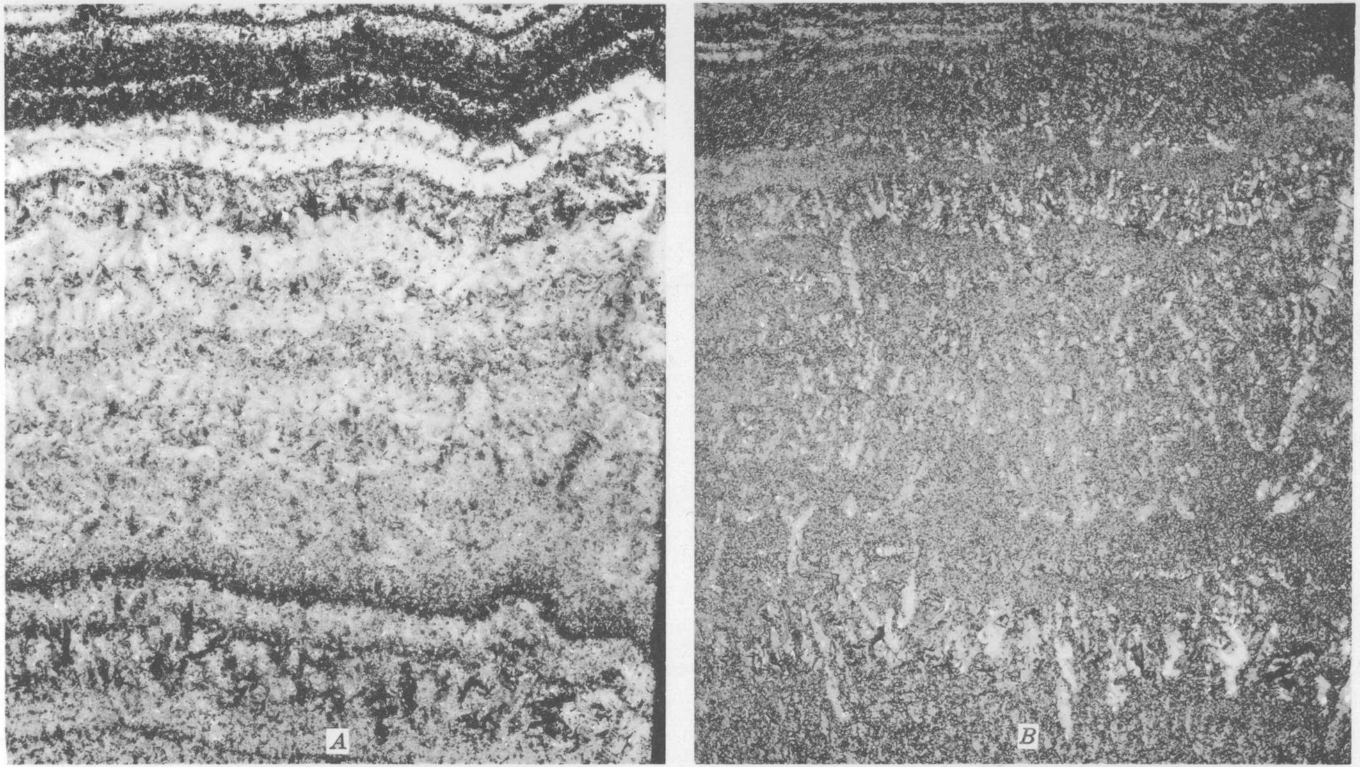
*A*. The same polished surface shown in plate 9, partly etched with dilute HF just enough to dull the polished surface of the albite but leaving the polish on the quartz. Specimen turned before the camera so as to brightly reflect the polished surfaces of the quartz.

*B*. Brightly reflecting polished surfaces of quartz in microcline graphic granite. The polished surface of the specimen was treated the same way as in specimen shown in *A*. From same locality. The albitized graphic granite, plate 9 and plate 10 *A*, is interpreted as having been derived from microcline graphic granite, such as is shown in plate 10 *B*. Note how much more the quartz in *A* is corroded as compared with the quartz in *B*.

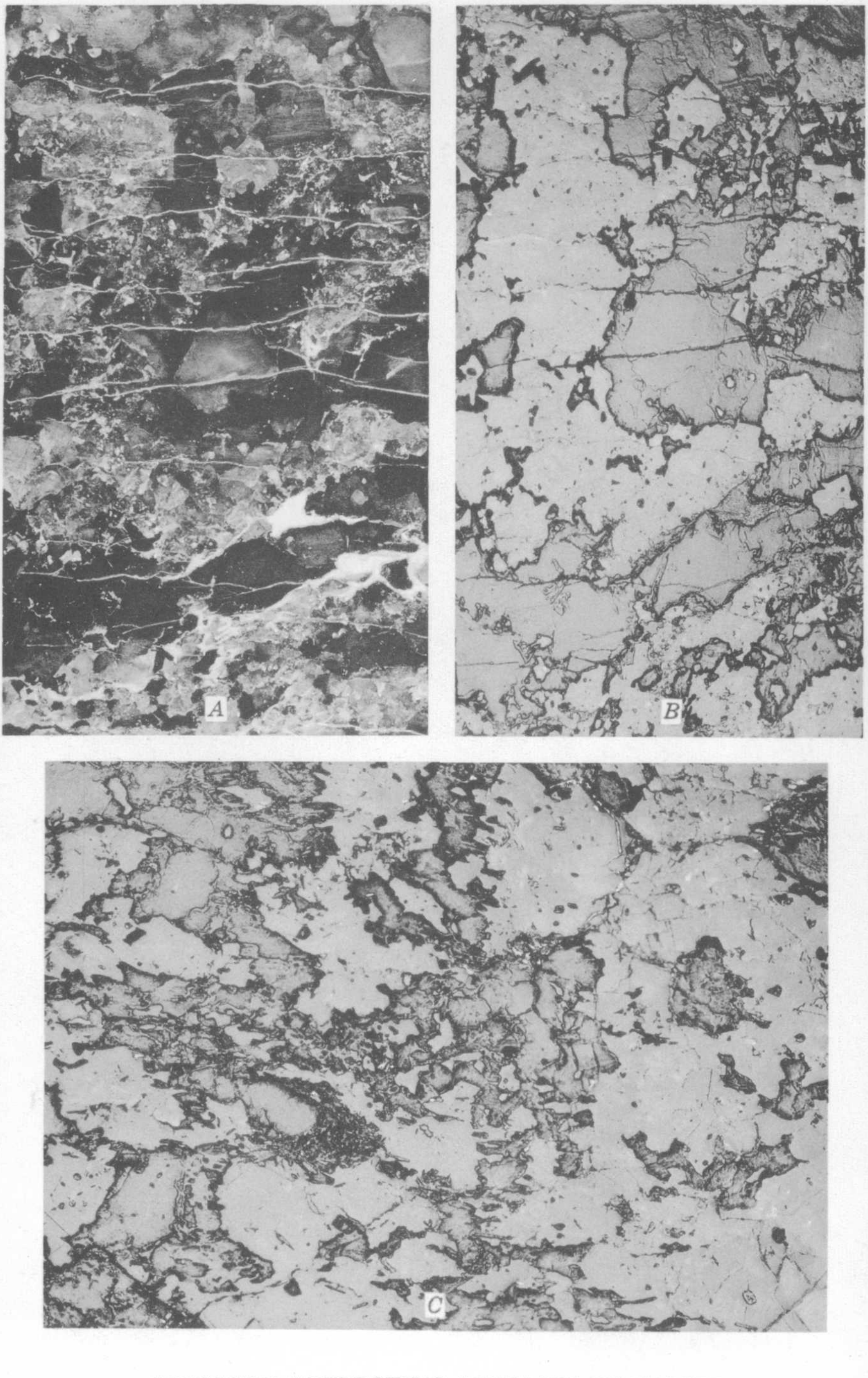
# PLATE 11

*A*. Polished surface of bottom-banded albitized pegmatite from the "Crater", Hiriart Hill, Pala, San Diego County, Calif. Except for a single long nearly vertical quartz rod (right center), there is little evidence shown of the presence of many nearly vertical quartz rods (interpreted as residual quartz rods of former microcline graphic granite).

*B*. Same specimen, etched with HF to depolish the albite but not the quartz, turned before the camera so that the brightly reflecting surfaces of the quartz rods photograph white. (These quartz rods are interpreted as residual quartz rods of former microcline graphic granite). The residual quartz rods, reflecting brightly, are present also in the upper part of the more thickly banded pegmatite, but the specimen would have to be turned more to show them.



BRIGHTLY REFLECTING SURFACES OF QUARTZ



BRIGHTLY REFLECTING SURFACES OF HALITE

# PLATE 12

*A.* Mixture of halite and sylvite, polished, and photographed straight on. Both halite and sylvite are either white or red. Most of the sylvite, being red, photographed dark, but it is not possible to distinguish the two minerals. Part of core from the Blanchard no. 2 well, at a depth of 696 feet to 696½ feet. Near Carlsbad, New Mexico.

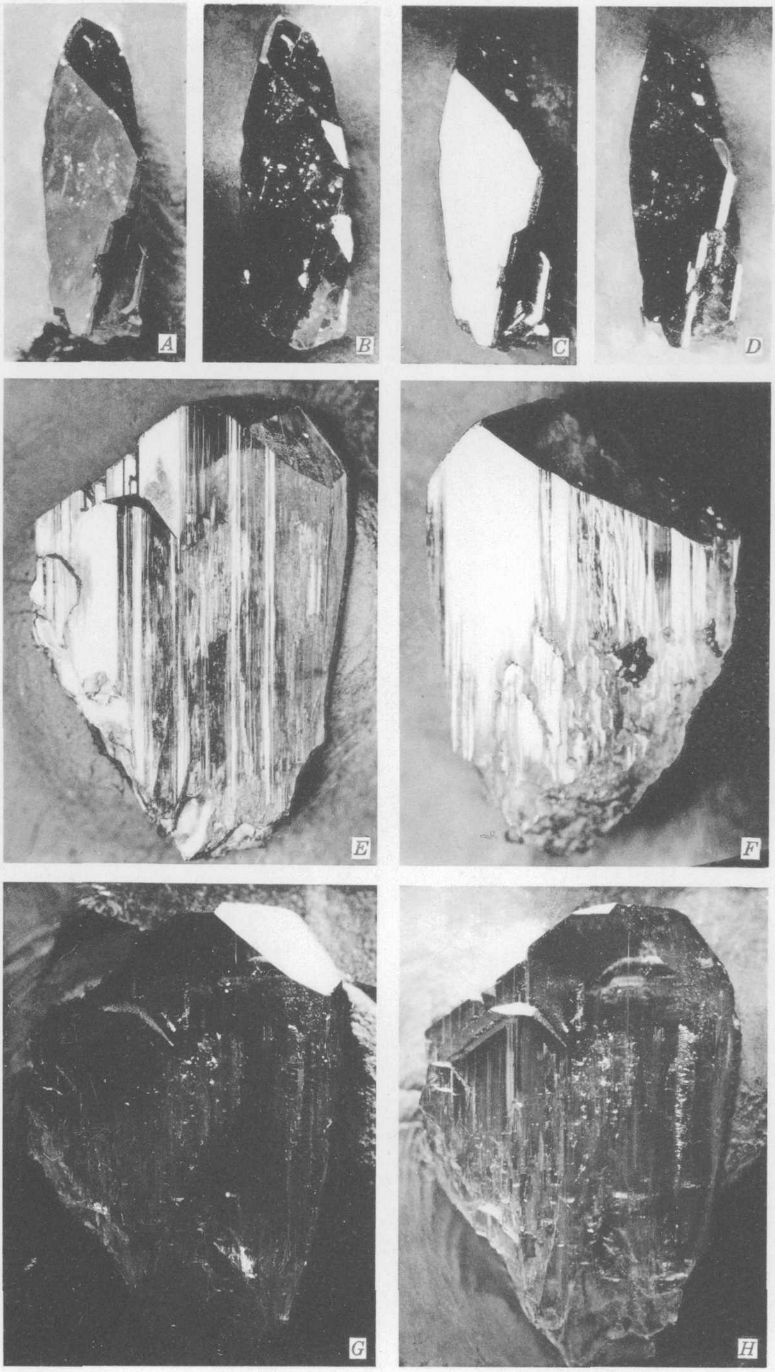
*B.* Same specimen, etched with a saturated solution of sodium chloride, sufficiently to dull the polished surfaces of the sylvite but leaving the surfaces of halite polished. Specimen turned before the camera so that the polished surfaces of the halite reflect light strongly. Note the brightly reflecting surfaces of minute-grains of halite in the darker sylvite and the minute grains of darker sylvite in the reflecting halite.

*C.* Potash ore, mixture of halite and sylvite. From shaft 1 of the U. S. Potash Co., at a depth of 980 feet.

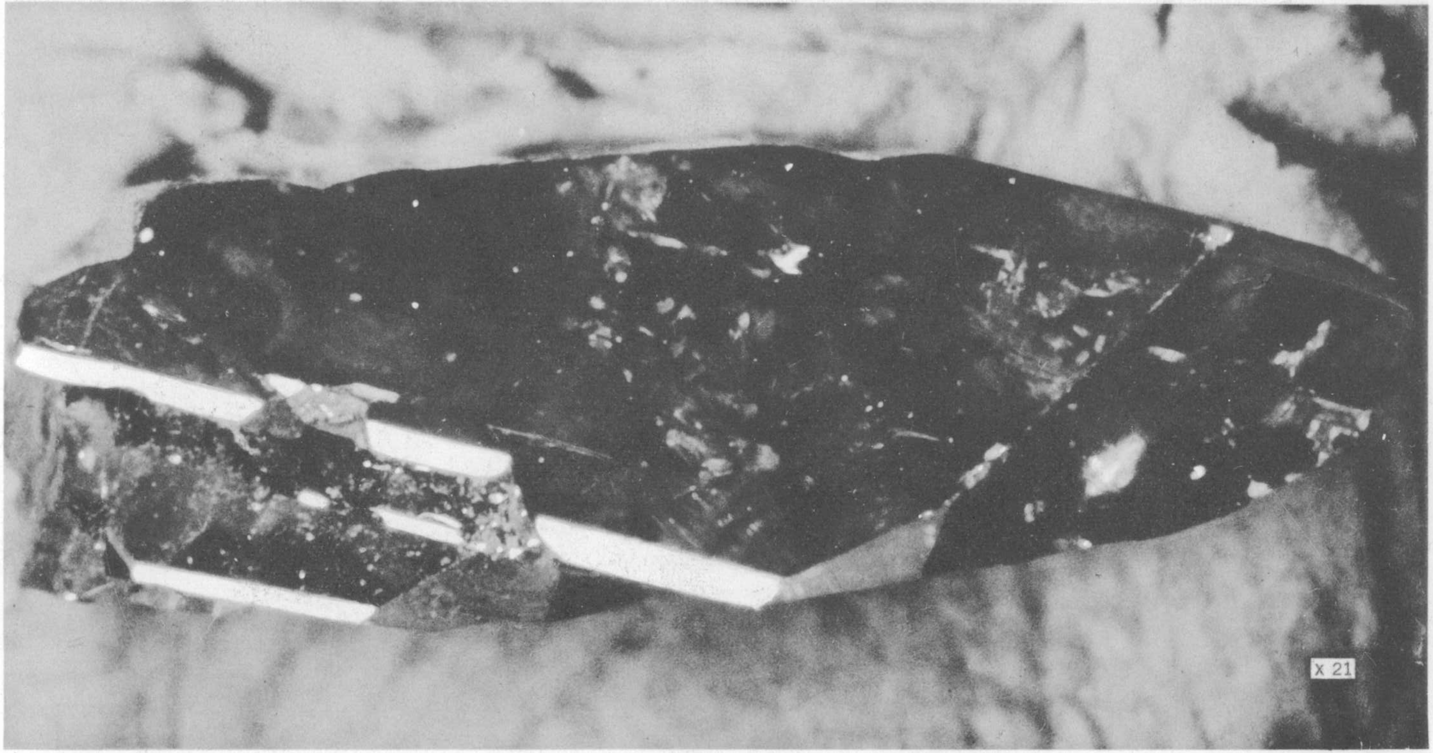
## PLATE 13

Different orientations of a crystal of bustamite (Mn, Ca) $SiO_3$, from Broken Hill, New South Wales, Australia (U. S. N. M. R–8309). All photographs enlarged about 5 times.

*A*, *B*, *C*, and *D*, Orthographic view: *A*, No face brightly reflecting; *B*, small triangular terminal faces brightly reflecting; *C*, large terminal face reflecting; *D*, elongated terminal faces reflecting (shown enlarged in plate 14). *E*, *F*, *G*, and *H*, clinographic view: *E*, large face, with parallel oscillatory line face, reflecting; *F*, large face on other side of crystal, reflecting; *G*, terminal face reflecting; *H*, small triangular terminal faces reflecting (shown in orthographic view in *B*).



BRIGHTLY REFLECTING FACES OF A CRYSTAL OF BUSTAMITE



BROMIDE ENLARGEMENT (4×) OF PLATE 13, D

## PLATE 14

Shows elongated terminal faces reflecting. Crystal enlarged twenty-one times.