

- TILLEY, C. E. (1951) The zoned contact-skarns of the Broadford area, Skye: a study of boron-fluorine metasomatism in dolomites. *Mineral. Mag.*, 29, 621-666.
- WINCHELL, A. N., AND H. WINCHELL (1964) *Elements of Optical Mineralogy*, 4th ed., vol. II. John Wiley and Sons, New York, pp. 512-515.

THE AMERICAN MINERALOGIST, VOL. 54, JANUARY-FEBRUARY, 1969

A RAPID VISUO-COLORIMETRIC METHOD FOR THE DETERMINATION OF PHOSPHATE IN PHOSPHATIC ROCKS

P. D. MALHOTRA^a AND J. K. SACHER, *Geological Survey of India, Lucknow.*

ABSTRACT

A rapid field method for determining P_2O_5 in phosphatic rocks based on visual colorimetry has been developed. After dissolution of the sample in dilute nitric acid, the color due to organic matter is removed and an aliquot of the solution reacted with a mixed molybdivanadate reagent. The intensity of molybdivanadophosphoric acid is matched with standards similarly prepared. The results by the method are well within normal sampling errors. It has proved very useful in quickly evaluating the phosphate potentialities of an area.

INTRODUCTION

The Geological Survey of India is currently engaged in a rapid assessment of the rock phosphate potential of the Mussoorie area in the Uttar Pradesh. This work has already involved analysis of several thousand samples. For quick determination of the P_2O_5 content, even under field conditions, a rapid, simple and moderately accurate method has been developed. A three-man team can analyse 120 to 150 samples daily under field conditions, compared with only 10 samples by the gravimetric magnesium pyrophosphate method. The results, though they may deviate by 1-2 percent from the actual phosphate content, can help to quickly assess the potentialities of an area.

In the present method, the sample is digested with nitric acid, color due to organic matter removed and a mixed molybdivanadate reagent added to an aliquot of the solution. The yellow color of molybdivanadophosphoric acid (Mission, 1908) is matched with standards.

EXISTING METHODS

In our early prospecting for rock phosphate the method of Shapiro (1952) was used. In this method, a small quantity of finely powdered rock, measured by a scoop, is shaken with a prepared molybdivanadate reagent in nitric acid. The weight of the sample so measured is about 6

Published by kind permission of the Director General, Geological Survey of India.

^a Present address: United Nations Development Program, P.O. Box 92, Asswan, U.A.R.

mg. The color developed is matched with standards similarly prepared. As rocks in the area are carbonaceous, the results often tended to be high by 5–15 percent on account of highly-colored soluble organic matter. Another field method tried was based on fusion of the rock powder with potassium pyrosulphate for one minute (Ward, *et al.*, 1963). Although the interference from organic matter was not observed in this method, the results tended to be low, possibly either the phosphate was not completely brought into solution or because of its conversion into meta- or pyro-phosphate (Hillebrand and Lundell, 1920). The results were low by as much as 3.5 percent for rocks containing 15 percent P_2O_5 , or 7.5 percent for rocks with 25 percent P_2O_5 .

REAGENTS AND APPARATUS

Nitric acid, concentrated, reagent grade.

Nitric acid, 1:1.

Molybdivanadate reagent:

(i) Dissolve 1.25 g ammonium metavanadate in 400 ml. 1:1 nitric acid.

(ii) Dissolve 50 g. ammonium molybdate in 400 ml of distilled water.

Mix (i) and (ii) and dilute to one litre.

Standard phosphorous solution: Dissolve 0.9590 g of KH_2PO_4 , reagent grade, dried at $105^\circ C$ in 500 ml of distilled water.

Working phosphorous solution: Dilute 25 ml of the above to 250 ml. 1 ml of this contains 0.1 mg P_2O_5 .

Activated charcoal, phosphate free.

Potassium permanganate solution: 2 percent.

Sodium sulphite solution: 1 percent.

Test tubes 16×150 mm., Pyrex glass, rimless, marked at 10 ml and 20 ml. Select tubes having as nearly the same diameter as possible.

Pipettes, automatic, 2 ml and 5 ml.

Pipettes, volumetric, 25 ml, 2.0 ml and 1.0 ml.

Pipettes, graduated, 1 ml marked at 0.01 ml.

Balance, torsion sensitivity 1 mg.

Digestion racks made of aluminium sheet $1/16''$ thick with 20 holes $3/4''$ diameter, arranged in four rows or concentrically.

Reagent bottles: polythene, 1 litre and 500 ml.

Polythene wash bottle.

Pestle and mortar, cast iron.

Kerosene oil stove.

PROCEDURE

1. Weight 0.1 g finely powdered sample into a dry test tube.
2. Add 3 ml 1:1 nitric acid.
3. Heat to boiling and gently simmer for 30 minutes in the digestion rack.
4. Observe the color of the solution. If colorless, dilute to 20 ml. Shake by holding the thumb over the top and allow to settle.
5. Transfer a suitable aliquot (0.1 ml to 2.00 ml) to a clean 16×150 mm. test tube.
6. Add 2 ml of the molybdivanadate reagent using an automatic pipette, shake and dilute to 10 ml. Let stand for 10 minutes.

7. Compare the color with the color of standards similarly prepared. It is easier to judge the color intensity by looking along the length of the test tube and holding it over a white background.

8. Calculate the phosphorous concentration in the sample.

REMOVAL OF COLOR DUE TO ORGANIC MATTER

If the solution is observed to be colored due to organic matter in step 3 above, the color has to be removed by either of the methods given below:

1. The hot solution after digestion is treated with a few drips of potassium permanganate solution till the permanganate color persists. Its excess is then destroyed by a few drops of sodium sulphite solution, followed by boiling for 2 or 3 minutes. Dilute to 20 ml and carry out the analysis from steps 5 to 8 as above, after settling.
2. The solution is treated with a pinch (5–10 mg.) of activated charcoal, diluted to 20 ml. and vigorously shaken. The analysis is continued from steps 5 to 8 as above, after settling.

PREPARATION OF STANDARDS

Transfer 0, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 ml of the working phosphate solution to clean test tubes. Add 0.2 ml of 1:1 nitric acid, followed by 2 ml of molybdivanadate reagent. Mix and dilute to 10 ml. The standards corresponds to 0, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, and 0.5 mg. of P_2O_5 in the solution.

The standards are stable for at least one week.

EFFECTIVENESS OF SAMPLE DECOMPOSITION

To study the effectiveness of sample decomposition by digestion with 1:1 nitric acid, the phosphate content of a number of samples was determined after decomposition by this method. The results were very similar to those obtained by the more drastic decomposition of Hillebrand and Lundell (1959).

RESULTS

A large number of samples of rock phosphate have been analysed by both the rapid visuo-colorimetric and gravimetric methods. The results of replicate analysis of some samples are given in Table 1. It has been found that for samples yielding up to about 10 percent P_2O_5 content, the

TABLE 1. REPLICATE DETERMINATIONS OF PHOSPHATE CONTENT

| Sample no. | Visual colorimetric method % P_2O_5 | Gravimetric method % P_2O_5 |
|------------|---------------------------------------|-------------------------------|
| 1. | 20.0, 20.0, 20.0, 20.0, 20.0 | 20.84 |
| 2. | 35.0, 32.5, 35.0, 35.0, 35.0 | 35.20 |
| 3. | 27.5, 27.5, 27.5, 26.0, 26.0 | 28.20 |
| 4. | 8.8, 8.8, 8.8, 9.0, 8.8 | 8.69 |
| 5. | 15.0, 15.0, 16.0, 16.3, 16.3 | 15.86 |

results of the rapid method are quite comparable with gravimetric values. When the P_2O_5 content is about 15–20 percent the results may deviate by 1 to 2 percent, whereas at higher phosphate content (above about 25 percent), the results may vary more. This is as expected on account of dilution factors and a slight difference in matching of colours getting magnified several times.

INTERFERENCE

The method is quite free of interference. Possible interference from soluble silicate was studied: at the concentration of nitric acid present during color development, silica interference is negligible. The optical density at 430 nm of a solution containing 2 mg of soluble silica per 100 ml was studied with varying amounts of nitric acid added to it. 25 ml of the molybdivanadate reagent was added in each case.

TABLE 2. EFFECT OF NITRIC ACID CONCENTRATION ON THE INTERFERENCE OF SOLUBLE SILICA IN P_2O_5 DETERMINATION.
(2 mg silica added as sodium silicate in 100 ml)

| Conc. nitric acid added | Optical density | Equivalent P_2O_5 content in mg/10 ml |
|-------------------------|-----------------|---|
| 0 ml. | 0.265 | 0.116 |
| 1 ml. | 0.115 | 0.050 |
| 2 ml. | 0.050 | 0.020 |
| 3 ml. | 0.030 | 0.013 |
| 4 ml. | 0.02 | 0.009 |

To further confirm that silica in soluble form would be rendered unreactive, 100 mg of sodium silicate was digested with 2 ml of 1:1 nitric acid for 30 minutes. After dilution to 10 ml and settling, the supernatant liquid gave a color reaction with the reagent which was hardly perceptible. The acid concentration is important and should be about 1 M in the final solution at the time of color development. The color development in a solution with an acid concentration of above 1.6 M is very slow (Kitson and Mellon, 1944), whereas below 0.2 M a masking yellow orange color is developed (Ward *et al.*, 1963).

DISCUSSION

Digestion of rock phosphate with dilute nitric acid results in completely dissolving the phosphate, at the same time rendering silica unreactive. Visual matching of the intensity of molybdivanadophosphoric acid color with that of standards can give results that are well within normal sam-

pling errors. The method is rapid and has proved very useful in quickly evaluating the rock phosphate potentialities of an area economically. Several thousand samples were studied by this method.

ACKNOWLEDGMENTS

The authors are grateful to Mr. G. C. Chatterji, Director General, Geological Survey of India and to Mr. S. C. Chakravarty for their keen interest and encouragement in the work. The authors are also grateful to many chemists of the Survey who carried out a very large number of determinations by the method. They also express their thanks to Dr. H. W. Lakin of the U. S. Geological Survey for his critical review of the paper.

REFERENCES

- HILLEBRAND, W. F., AND G. E. F. LUNDELL (1920) Volatilisation losses of phosphorous during evaporation of phosphates with sulphuric acid or fusion with pyrosulphate. *J. Amer. Chem. Soc.*, **42**, 2069.
- AND ——— (1959) *Applied Inorganic Analysis*. 2nd ed. John Wiley and Son, New York, p. 708-709.
- KITSON, R. E., AND M. G. MELLON (1944) Colorimetric determination of phosphorous as molybdivanado-phosphoric acid. *Ind. Eng. Chem., Anal. Ed.* **16**, 379-383.
- MISSION, G. (1908) Colorimetric estimation of phosphorous in steel. *Chem. Zeitung*, **32**, 633.
- SHAPIRO, LEONARD (1952) Simple field method for determining phosphate in phosphate rock. *Amer. Mineral.* **37**, 341-342.
- WARD, F. N., H. W. LAKIN, F. C. CANNEY AND OTHERS (1963) Analytical methods used in geochemical exploration by the U.S. Geological Survey, *U.S. Geol. Surv. Bull.* **1152**.

THE AMERICAN MINERALOGIST, VOL. 54, JANUARY-FEBRUARY, 1969

GEL PREPARATION OF STARTING MATERIALS IN
IRON-CONTAINING SILICATE SYSTEMS

E. F. HEALD, J. R. REEHER¹ AND D. R. HERRINGTON²,
Department of Chemistry, Thiel College
Greenville, Pennsylvania 16125.

ABSTRACT

A solution of ferric benzoate in N,N-dimethylformamide may be used as a source of iron in the gel method of preparing starting materials in the system MgO-SiO₂-Fe-O.

INTRODUCTION

Recently Luth and Ingamells (1965) published an excellent summary of the "gel" method of preparing starting materials for phase equilibrium and thermodynamic studies on silicate systems at high temperatures and

¹ Present address: Department of Chemistry, Iowa State University, Ames, Iowa.

² Present Address: Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania.