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FIELD METHOD FOR THE DETERMINATION OF TITANIUM IN ROCKS

by

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Field method for the determination of titanium in rocks

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Leonard Shapiro and W. W. Brannock

This paper is adapted from an article in "Economic Geology" for June-July 1953, volume 48, pages 282 through 287.

With the method discussed here, persons with meager experience in chemical analysis can differentiate rocks containing 0, 0.5, 1, and 2 percent titanium dioxide by means of simple and inexpensive apparatus. Although intended primarily for low concentration of titanium, the test can be used for higher concentrations by appropriate dilution of the colored solutions produced in the determination.

The procedure outlined is based on the yellow color produced by the reaction of titanium with tiron (disodium-1, 2-dihydroxybenzene-3, 5-disulfonate). The effect of iron, which forms a purple solution with tiron, is eliminated by reduction with sodium dithionite.

Reagents

Potassium bisulfate ($KHSO_4$), fused powder.

Tiron (disodium-1, 2-dihydroxybenzene-3, 5-disulfonate), the dry reagent powder.

Buffer solution, 40 g of ammonium acetate and 15 ml of glacial acetic acid made to 1 liter volume with distilled water.

Sodium dithionite ($Na_2S_2O_4$) (sold as sodium hydrosulfite), the dry reagent powder.

Potassium dichromate ($K_2Cr_2O_7$).

Apparatus

Test tubes, 18 x 150 mm pyrex, marked with a stylus at the 15-ml volume level, for fusions and color comparisons. At least 12 tubes are desirable; 4 are necessary.

Graduated cylinder, 25 ml.

Sample scoop. A strip of metal 1/8 x 3/16 x 7 in. with a hole 1/16 in. in diameter and approximately 1/16 in. in depth drilled near one end.

Reagent scoop. A strip of metal 3/8 x 3/8 x 4 in. with a hole 7/32 in. in diameter and approximately 1/4 in. in depth drilled near one end.

Small spatula.

Plattner mortar for crushing rock samples. Mortar and pestle of special type; diameter 20 to 25 mm.

Blowtorch, Bunsen burner, or other source of heat with sufficient capacity to heat a test tube to red heat.

Mortar and pestle for powdering samples. Conventional mortar and pestle of hard material such as agate, mullite, or porcelain. Mortar diameter should be about 65 mm.

Hammer, for breaking large pieces of rock to size suitable for crushing in Plattner mortar

Preparation of standards

It is advisable to prepare and use a series of permanent color-comparison standards. Satisfactory permanent standards can be prepared from potassium dichromate solutions by adjusting the concentration of a dichromate solution to match the color intensity of a solution prepared by using a sample powder of known TiO_2 concentration. This procedure is outlined below.

In order to eliminate error in the preparation of the standards, three separate portions of the sample of known TiO_2 concentration should be prepared as outlined below. The initial permanent dichromate standard solution is then made to match the color of that sample solution which has the median color intensity.

National Bureau of Standards standard clay sample No. 97, in which the TiO_2 concentration is 2.38 percent, can be used conveniently for the preparation of a standard solution equivalent to 2 percent TiO_2 in a sample; this is described below. The standard clay sample No. 97 can be obtained from the National Bureau of Standards, Washington 25, D. C., at a price of three dollars ($3.00) per 60-gram unit. For this test 60 grams is sufficient.

1. Place about 100 mg of National Bureau of Standards standard sample No. 97 on a small piece of clean paper resting on a smooth flat surface, and press the sample scoop several times into the powder until the hole is filled. Wipe off the excess powder so that the powder in the hole is level.
2. Tap the powder into one of the test tubes.
3. Measure two additional sample portions by repeating steps 1 and 2 two times.
4. Add a scoopful (reagent scoop) of potassium bisulfate to each test tube.
5. Heat each test tube in a hot flame until the flux has been molten and fluid for 1 to 2 minutes.
6. After the test tubes cool add about a scoopful (reagent scoop) of tiron to each test tube.
7. Add 18 ml of buffer solution to each tube and gently heat until the fused cakes dissolve.
8. Allow the solutions to cool on standing, or cool to air temperature in cool water.
9. Add several mg of sodium dithionite to each tube, with a spatula. Cap with the thumb and invert each tube once.
10. Dilute a solution of potassium dichromate (at least 50 ml) with water until, in a test tube, its color matches the color of the solution of median intensity obtained in step 9.
11. Transfer 15 ml of the dichromate solution from step 10 to a test tube. Stopper or seal, and retain as a permanent standard equivalent to 2% TiO_2 in a sample.

12. Mix 25 ml of the dichromate solution from step 10, equivalent to 2% TiO_2, with 25 ml of distilled water.

13. Transfer 15 ml of the dichromate solution from step 12 to a test tube. Stopper or seal, and retain as a permanent standard equivalent to 1% TiO_2 in a sample.

14. Mix 25 ml of the dichromate solution equivalent to 1% TiO_2 with 25 ml of distilled water.

15. Transfer 15 ml of the dichromate solution from step 14 to a test tube. Stopper or seal, and retain as a permanent standard equivalent to 0.5% TiO_2.

Procedure for Testing

After the standard solutions have been prepared as outlined above, unknown titanium-bearing samples are prepared as follows:

1. With a hammer, break the original sample to size small enough for the Plattner mortar, crush it in the Plattner mortar, and grind it to fine powder by means of the conventional mortar and pestle. By the quartering method, split the sample to about 50 mg.

2. Place the sample powder on a small piece of clean paper resting on a smooth flat surface and press the sample scoop several times into the powder until the hole in the scoop is filled. Wipe off the excess sample powder with the finger so that the powder in the hole is level.

3. Tap the powder into the bottom of one of the test tubes.

4. Add a scoopful (reagent scoop) of potassium bisulfate.

5. Heat the test tube in a hot flame until the flux has been molten and fluid for 1 or 2 minutes.

6. After the test tube cools add a scoopful (reagent scoop) of tiron.

7. Add 15 ml of buffer solution and gently heat until the fused cake dissolves.
8. Allow the solution to cool to air temperature or cool by dipping the test tube in cool water.
9. Add several mg of sodium dithionite with a spatula, cap the test tube with the finger and invert once.
10. After 1 minute compare the color with that of the standards to estimate the concentration of TiO_2 in the sample.

Precautions

The test cannot be used for analysis of glassy volcanic rocks. For material of low titanium content the test is adequate, but corrections may be necessary for rocks of higher titanium content, or of high density. One method of correction is to prepare another set of standard solutions by using a test sample with a known, higher titanium content, and preferably near that of the rocks to be tested. The sample used for this standardization should also have approximately the same density as the sample to be tested, and must be accurately analyzed to determine its titanium content. The dichromate standard solution obtained by matching can be diluted to various proportions to cover a wide range of titanium values.

Availability of Chemicals and Apparatus

Apparatus and all the chemicals except tiron can be obtained from one of the larger chemical supply houses, such as:

Central Scientific Co., 1700 Irving Park Road,
Chicago 13, Illinois

Fischer Scientific Co., 717 Forbes St. Pittsburgh 19, Pa.

E. H. Sargent & Co., 4647 W. Foster Avenue,
Chicago 30, Illinois

Arthur H. Thomas Co., West Washington Square,
Philadelphia 5, Pa.

Tiron can be purchased only from the Eastern Chemical Corporation, 34 Spring Street, Newark 2, N. J. The present price (1953) is $3.50 for ten grams.

Glacial acetic acid, ammonium acetate, potassium dichromate, and potassium bisulfate probably can be obtained through a local druggist.