A SIMPLE MICROCHEMICAL TEST FOR SILICON

LLOYD W. STAPLES, *Stanford University.*

A dependable, sensitive, and simple test for silicon is needed in determinative mineralogy. Several tests for silicon or silica have been proposed in the past but none of these is completely satisfactory. The test described here makes use of the precipitate suggested by Bořický[1] for testing for sodium, namely, sodium fluosilicate. Behrens and Kley[2] used this precipitate in testing for silicon, but their test lacks several of the advantages of this new method.

Mineralogists frequently make use of the formation of a gel or the presence of skeletal silica in a sodium metaphosphate bead, when testing for silica or silicates. Although these tests are useful for some work, they are neither sensitive nor entirely dependable. The lack of sensitivity and dependability of the bead test has been discussed by Hirschwald.[3]

The precipitation of silicon as rubidium silicomolybdate and the benzidine test of Feigl and Leitmeier[4] do not give as definite and easily obtainable results as the precipitation of sodium fluosilicate. Both of these tests require previous fusion of the mineral, if it is insoluble, and the presence of phosphates causes further difficulty.

EQUIPMENT AND REAGENTS REQUIRED FOR MAKING TEST

Alcohol Lamp. An alcohol lamp can readily be made from a drawing-ink bottle. A piece of string serves as a wick.

Tripod. Any type of tripod that will permit the test to be performed at about 5 cm. above the flame is suitable. The writer has constructed a removable tripod which rests directly on the shoulder of the alcohol lamp (Fig. 1).

Charcoal Block. An ordinary block of the type used in blowpipe work is hollowed out so that a platinum spoon sets in it. A hole of a slightly smaller diameter than the bowl of the spoon is cut through the charcoal directly under the bowl (Fig. 2).

Platinum Spoon. The platinum spoon shown in Fig. 1 has a bowl ap-

[1] Bořický, E., Elemente einer neuen chemisch-mikroskopischen Mineral- und Gesteinsanalyse: translation by Winchell, N. H., *Geol. and Nat. Hist. Survey of Minn., 19th Ann. Rept. for 1890*, p. 18, **1892.**

[2] Behrens, H., and Kley, P. D. C., *Mikrochemische Analyse*, 4th ed., Leipzig, **1921.**

[3] Hirschwald, J., Ueber das Verhalten der Kieselsäure und ihrer Verbindungen im Phosphorsalzglase: *Jour. prakt. Chemie*, Band **41**, pp. 360–367, 1890.

[4] Feigl, F., and Leitmeier, H., Ein rascher und empfindlicher Nachweis der Kieselsäure: *Min. pet. Mitt.*, Band **40**, pp. 1–5, 1929.

proximately 1 cm. in diameter. The spoon weighs 1.33 g. and can be bought for about $3. A piece of sheet lead may be hammered into a spoon

FIG. 1. Charcoal block with platinum spoon, alcohol lamp, and tripod which rests on shoulder of lamp.

if one of platinum is not available. A disadvantage of the lead spoon is that it is attacked more than the platinum and is consequently more difficult to clean.

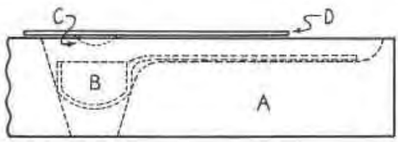

FIG. 2. Front elevation of charcoal block (A), with platinum spoon (B). Drop of dilute nitric acid (C), suspended from celluloid slide (D). Natural size.

Silicon-free Slide. Considerable experimentation has proved that a slide of transparent celluloid[5] serves very well for this work. The slide can be used repeatedly since it is only slightly attacked by HF fumes. Tests with glass slides coated with varnish, canada balsam, collodion, or "New-Skin" showed that it is unwise to have glass present during

[5] Transparent celluloid, sometimes called "xylonite", 0.5 mm. (0.020 in.) thick is used. A slide 25×45 mm. costs only about one-third of a cent.

the test, however carefully it may be protected. Ordinary cellophane is not sufficiently rigid for making tests and is not to be generally recommended. Although celluloid is inflammable, there is no danger in its use because it is not exposed directly to the flame at any time.

The reagents needed for the test are all obtainable in mineralogical laboratories.

Sulfuric Acid. Concentrated, G. = 1.84.

Nitric Acid. A dilution of 1:7 gives good results.

Sodium Chloride. C. P. reagent.

Fluorite. Pure, transparent material is powdered. A blank test should be run in order to make certain that the powder is silicon-free.

Technique and Performance of the Test

The platinum or lead spoon is placed in the charcoal block and the latter is set on the tripod with the bowl of the spoon directly over the flame. A small amount of fluorite (about 2 mg. or enough to cover an area of 9 sq. mm.) is placed in the bowl of the spoon. About 1 mg. or less of the mineral to be tested is also put in the spoon, and the powder is covered with 2 drops of H_2SO_4. A drop of HNO_3, about 3 mm. in diameter, is placed on the celluloid slide and the latter is inverted so that the drop hangs directly over the spoon (Fig. 2). Since the slide rests directly on the charcoal and is not in contact with the spoon, the celluloid does not receive very much heat. After 10 minutes of heating, the slide is removed and placed on the microscope stage. A very small grain of NaCl is added to the drop on the slide. For observing the drop, a medium power (16 mm.) objective provides the most satisfactory magnification. This should be protected from acid fumes by attaching a cover glass to it with a drop of cedar oil.

It is important in making the above test to have the platinum spoon at such a height above the flame that the temperature will not rise above 75°C. For temperatures too far below this point, "opening-up" of some of the difficultly soluble silicates requires too long a time. Higher temperatures are bad because they affect the slide and are likely to cause the volatilization of fluorides other than that of silicon.

Under the conditions described above for making this test, definite results were obtained in 10 minutes or less on all of the silica and silicate minerals tested. Such insoluble minerals as andalusite, staurolite, sillimanite, topaz, kyanite, and schorlite, and the artificial substances, carborundum and ferrosilicon, gave definite tests. A set of unknowns was tested for silicon and in every case there was no doubt as to the absence or presence of silicon after a 10-minute run. If after 10 minutes of heating the finely powdered mineral, a definite precipitate of Na_2SiF_6 cannot be obtained, it is safe to report the absence of silicon in any appreciable amount.

Description of the Precipitate

In testing for silicon according to the procedure described above, the H_2SO_4 decomposes the fluorite and liberates HF. This attacks the mineral and if silicon is present, SiF_4 is volatilized and captured by the drop of HNO_3, with the formation of H_2SiF_6. On the addition of NaCl to the drop, crystals of sodium fluosilicate (Na_2SiF_6) are formed. This precipitate is the microchemical equivalent of the mineral malladrite[6] which is formed at Vesuvius.

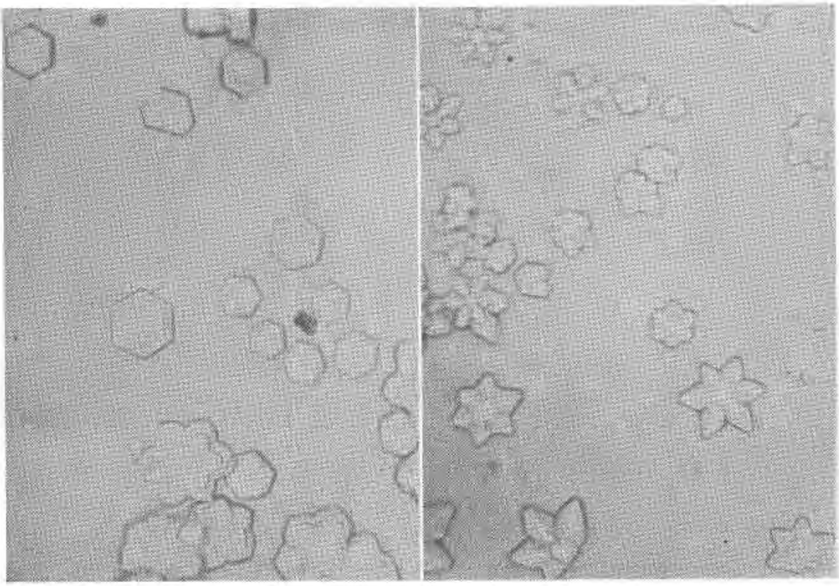

Fig. 3. Crystals of sodium fluosilicate. ×150.

Although sodium fluosilicate may assume several habits, the two most characteristic and common are 6-sided tabular plates and 6-pointed stars (Fig. 3). The crystals are pseudo-hexagonal and belong to the orthorhombic system. As far as observations under the microscope are concerned, the crystals appear to be hexagonal. Winchell[7] describes the crystals as biaxial negative, with small optic angle and with indices of

[6] Zambonini, F., and Carobbi, G., Sulla presenza del fluosilicato sodico e di quello di potassio tra i prodotti dell'attuale attività del Vesuvio: *Atti Accad. Lincei, Rom.*, (6) vol. **4**, pp. 171–175, 1926.

[7] Winchell, A. N., *The Microscopic Characters of Artificial Inorganic Solid Substances or Artificial Minerals*, p. 180, **1931.**

refraction: $n_\alpha = 1.3089$, $n_\gamma = 1.3125$. The index n_β is not given but it is reported as nearly equal to n_γ. Because almost all crystals have indices of refraction higher than that of dilute HNO_3, the low indices of Na_2SiF_6 are helpful in its recognition. The best conditions for observing the crystals are obtained when the iris diaphragm is almost completely closed.

The sodium fluosalts of zirconium, titanium, tin, and boron are similar in appearance to Na_2SiF_6. No difficulty is encountered due to the isomorphism, or similar appearance, of these salts if the method described above is followed. Boron fluoride is not volatilized at the temperature of this test. Tests on colemanite, kernite, ulexite, and C. P. boric acid, produced no precipitate. Similarly the fluotitanates, fluozirconates, and fluostannates of sodium do not form under the conditions of this test. Negative results were obtained on baddeleyite, rutile, cassiterite, and C. P. titanium dioxide and stannic chloride.

Test for Germanium

As might be expected from the position of silicon and germanium in the periodic table, their fluosalts of sodium are isomorphous and form under similar conditions. If there were many germanium minerals, this isomorphism would provide a serious difficulty in testing for silicon, but since there are only three known germanium minerals, germanite, argyrodite, and ultrabasite, and since these are all metallic, there is no real problem raised. Instead, the procedure described above provides a good simple test for germanium. After eight minutes of treating powdered germanite there is formed a heavy and definite precipitate of Na_2GeF_6, isomorphous with Na_2SiF_6, and having low indices of refraction.

Advantages of Newly Described Test for Silicon

To summarize the advantages of this test: (1) the equipment and reagents are inexpensive and available in most laboratories; (2) the test requires no previous treatment of insoluble minerals; (3) it is of about the right sensitivity for careful mineralogical work; (4) the presence of boron, tin, titanium, or zirconium causes no confusion; (5) there is less chance of injuring the microscope with fluoride fumes than in the case where the whole test is made on the microscope stage; (6) by using fluorite as the source of fluorine there is no need to have corrosive HF or NH_4F in wax bottles as part of the reagent set.

Acknowledgments

The writer wishes to express his indebtedness to Professor A. F. Rogers for many helpful suggestions and to Mr. A. Tihonravov for assistance in photography.