QUANTITATIVE DETERMINATION OF FLUORINE IN FLUORIDES EASILY DECOMPOSABLE BY SULPHURIC ACID.[1]

BY W. E. BURK.

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IN determining the purity of commercial fluorite, two methods were found outlined which appealed as practicable, one described by Hillebrand,[2] based upon the method of Rose, and the one of M. Carnot described at length in a paper "Sur le dosage du fluor."[3]

A modification of Carnot's method, as recommended by Cairns, was tried but with little success.

The method described by Hillebrand, while satisfactory for complex silicates, was not found as suitable as that of Carnot, and a modification of the latter with certain precautionary additions was adopted with satisfactory results. Without these additional precautions, however, the method does not give accurate results, but invariably shows too high percentage of fluorine.

The method adopted is as follows:

A perfectly dry mixture of about 3 grams of dry powdered and calcined silicon dioxide and 0.20 gram of dry powdered fluorite with 40 cc. concentrated sulphuric acid is digested at a temperature of 120° to 135°, the silicon tetrafluoride evolved being conducted through a perfectly dry conducting tube to a narrow upright vessel containing about 20 cc. of a freshly prepared 10 per cent. solution of potassium fluoride. The end of the conducting tube dips into a sufficient pool of pure mercury to prevent moisture from entering the tube. A slow current of dry air is passed while the temperature of the sulphuric acid mixture is maintained for one and a half hours.

The reactions involved are as follows:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4;$$
$$4HF + SiO_2 = SiF_4 + 2H_2O.$$

In the receiving vessel:

$$SiF_4 + 2KF = K_2SiF_6.$$

The potassium fluosilicate separates out partially, and after

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[1] This paper is an extract from a portion of a thesis presented to the Rose Polytechnic Institute for the Master's degree.

[2] Bulletin 176 of U. S. Geological Survey.

[3] *Compt. rend.*, **114**, 750 (1892).

transferring to a subsiding vessel and adding an equal volume of 90 per cent. alcohol it subsides perfectly to a heavy pulpy stratum. After a half hour the contents are filtered, using a Gooch crucible with asbestos plate, washed free from potassium fluoride with 90 per cent. alcohol and dried to constant weight at a temperature of 100° C. Two-thirds of the fluorine of the potassium fluosilicate comes from the fluorite, or the weight of the salt, multiplied by the factor 0.34511, gives fluorine; and this multiplied by 2.0527 gives the calcium fluoride.

The detail manipulation must be followed with great care, in which case only will satisfactory results be obtained. The three chief sources of error are:

1. Moisture in air current or conducting tubes, resulting in premature decomposition of the silicon tetrafluoride in the tubes and even clogging of the tubes.

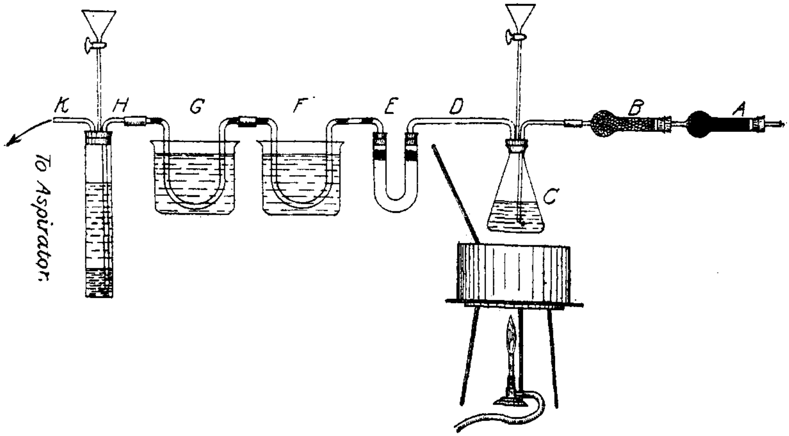
2. Sulphuric acid fumes carried over by a current of air, resulting in the decomposition of the potassium fluoride of the solution in the receiving vessel and the formation of potassium fluosilicate with consequent high percentage determination.

3. Flakes of insoluble addition products of potassium fluoride of the solution with silicon dioxide of the walls of the glass (where used) receiving vessel. A 10 per cent. solution of potassium fluoride attacks glass quite readily and high percentage is usual from this source unless great care is taken.

These sources of error are so serious that early in the experimental work, while using a sample of rather pure fluorite, containing 98.77 per cent. calcium fluoride, values as high as in one case 130 per cent. calcium fluoride, and in another 113 per cent. calcium fluoride were obtained.

Details of the method are as follows, in which statements and references are made to the accompanying sketch of apparatus:

Tube *A* contains glass wool saturated with concentrated sulphuric acid and tube *B* contains fused calcium chloride. From these drying tubes a conducting glass tube extends to the bottom of vessel *C*, which is an Erlenmeyer flask of 150 cc. capacity, closed with a three-holed rubber stopper, the second and third holes of which are closed with a stop-cock funnel and a glass tube *D*, one end of which terminates just below the rubber stopper, the other end of the tube projecting into a U-tube, *E*, plugged at points indicated by cross hatching with pure glass wool. *F* and *G* are



U-loops bent from 5 mm. glass tubing, connected with tight rubber joints and plugged with glass wool at the points indicated, the plugs being designed to interrupt the current of air and effect a stoppage of sulphuric acid fumes which are not otherwise eliminated. *H* is a glass tube extending to the bottom of the vessel *I*, and terminating in a contracted end bent upward. Into the containing vessel *I* is placed sufficient pure dry mercury to seal the opening of the tube *H* by 2 mm. to 3 mm. at least. Vessel *I* is closed with a three-holed rubber stopper, through which a stop-cock funnel, and the tube *K* enter.

Tube *K* leads to an aspirator. The conducting tubing from *C* to *H* measures in length some 2 meters and contains in all 7 plugs of glass wool. Each part of the apparatus is dried by warming and exhausting the air before the apparatus is set up. After the apparatus is adjusted, a current of air is allowed to pass while the parts are again heated with a naked flame. The current of air is now stopped and about 20 cc. of a freshly prepared solution of potassium fluoride (10 per cent.) are poured into the vessel *I* by means of a funnel.

Three grams of pure powdered silicon dioxide are calcined and, while still slightly warm, are intimately mixed in an agate mortar with 0.20 gram of the fluorite, which has been powdered and thoroughly dried. This mixture is transferred to the flask *C* and the same immediately closed. Forty cc. concentrated sulphuric acid are now added through the stop-cock funnel. This acid, before use, should be aerated with a current of dry air while being heated to a temperature of about 165° C.

The flask containing the mixture is now heated in an oil-bath at a temperature of 120° for one and one-half hours, during which time a current of air is allowed to pass at a rate such that bubbles in the vessel *I* can be easily counted. Flask *C* is also shaken vigorously occasionally in order that bubbles of the froth-like scum may be broken. The U-tubes are immersed in beakers filled with cold water. At the end of the operation the stopper, with connections, is removed from the vessel *I*, and the *H* tube rinsed with a little water.

The solution above mercury is removed by means of a bulb pipette and rubber mouth tube, and transferred to a small subsiding beaker. The vessel *I* is then rinsed gently with water and the mercury washed. As little water is used in washing as possible, the solution and rinsings being kept down within 75 cc. A thin, somewhat tenacious coating on the inner wall of the vessel *I* should not be removed, as this is due to addition-products of the potassium fluoride of solution with the glass. Care is also taken that no minute globules of mercury are transferred to the beaker. An equal volume of 90 per cent. alcohol is now added and the beaker allowed to stand to perfect subsidence. Decant and filter through a Gooch filter with reduced pressure. The subsiding vessel should be rinsed well though not rubbed. A tared crucible with asbestos plate is used, and after filtering, the contents are washed with 90 per cent. alcohol till the filtrate gives no turbidity with barium chloride. The crucible and contents are now dried at 100° C. in a hot air oven to constant weight, and fluorine or calcium fluoride estimated.

M. Moissan, in a paper on his investigations of fluorine,[1] mentions the decided tendency of fluorine and its simple compounds to form addition-products. This action, constituting the third chief source of error above mentioned, could be best eliminated by the use of platinum for the vessel *I*, and with this substitution the method would be very satisfactory. Platinum could be used with equal satisfaction and much economy of time for the conducting tubes from vessel *C* to vessel *I*.

The modification of Carnot's method as proposed by Cairns consists in using potassium chloride instead of potassium fluoride,

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[1] Annual report of the Smithsonian Institution for 1897.

and catching any escaping hydrochloric acid gas in a connected wash-bottle. The contents of the two vessels are then titrated with standard alkali solution. The objection to this method is that the end of the titration reaction is very indefinite and indeterminate, due to a secondary reaction. (See "Grundlinien der anorganischen Chemie," Ostwald, pp. 433-436.)

THE REDUCTION, IN AN ALKALINE SOLUTION, OF 2,4,5-TRIMETHYLBENZALAZINE AND THE PREPARATION OF SOME DERIVATIVES OF THE REDUCTION PRODUCTS.

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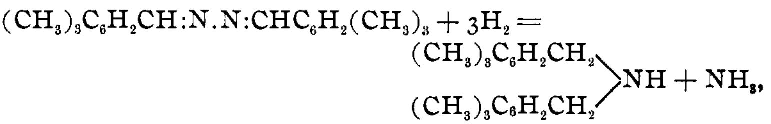
THE experimental part of this paper was carried out in the chemical laboratory at the University of Heidelberg under the supervision of Prof. Curtius, and a short abstract of it has already been published in the July, 1900, number of the *Journal für praktische Chemie*.

The formation of azines by the condensation of aromatic aldehydes with hydrazine and their reduction in an acid or alkaline solution is a comparatively new line of work and the investigation along this line has largely been done by Prof. Curtius and his students at the University of Heidelberg.

2,4,5-Trimethylbenzalazine, $(CH_3)_3C_6H_2CH{:}N.N{:}CHC_6H_2(CH_3)_3$, yields different reduction products, the kind depending upon the quality of the reducing agent used and the degree of the reduction. Curtius and Franzen,[1] by reducing in an acid solution, using zinc dust and acetic acid, obtained 2,4,5-trimethyldibenzylamine, a solid substance melting at 78° and insoluble in water. The reaction may be represented by the equation



$$(CH_3)_3C_6H_2CH{:}N.N{:}CHC_6H_2(CH_3)_3 + 3H_2 = \left.\begin{matrix}(CH_3)_3C_6H_2CH_2\\(CH_3)_3C_6H_2CH_2\end{matrix}\right>NH + NH_3,$$

2,4,5-Trimethyldibenzylamine

part of the nitrogen being reduced to ammonia.

By reducing 2,4,5-trimethylbenzalazine in an alkaline solution, using sodium amalgam as a reducing agent, two reduction prod-

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[1] *Ber. d. chem. Ges.*, 4, 1901.