amount of oxygen actually removed from the sample of water was equal to one-half of the hydrogen volume used up in the reduction as the combining volume; ratios of oxygen to hydrogen is as 1 : 2. From the amount of oxygen thus determined a knowledge of the actual amount of dissolved oxygen in the sample of water was obtained by use of the formula given in the first part of this paper.

It was evident when making a run that all of the oxygen was being picked up, as a considerable portion of the glowing copper opposite the end at which the gas mixture entered remained bright, showing no trace of oxidation.

In the following table are given the results obtained by the use of this method in determining the amount of dissolved oxygen in distilled water. Both the Winkler[1] and our first method for determining oxygen were run as checks on the above method.

TABLE VIII.

Amt. of oxygen removed.	Equil. temp.	Room temp.	Bar. pressure.	New meth. Cc. per liter.	Winkler meth.
3.22 cc.	21.0	20.8	755.00	6.42	6.40
3.25	20.5	21.0	755.00	6.48	6.40
3.26	21.8	20.5	755.00	6.49	6.46
3.22 21.8	21.8	20.5	755.00	6.43	6.45
3.25	21.8	20.5	755.00	6.47	6.44
3.20	21.5	20.0	755.02	6.39	6.40
3.22	21.7	20.1	755.02	6.42	6.40
3.20	21.6	20.0	755.02	6.40	6.40
3.22	21.5	20.2	755.02	6.42	6.40
3.24	21.7	20.0	754.00	6.47	6.40
3.20	21.4	20.1	754.00	6.39	6.40

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OBSERVATIONS UPON THE QUANTITATIVE DETERMINATION OF FLUORINE.

BY WILLIAM H. ADOLPH.

Berzelius[2] originally precipitated and weighed fluorine as calcium fluoride. Rose[3] suggested the precipitation of the fluoride in the presence of carbonate to facilitate filtering. The ignition of this combined precipitate and its subsequent extraction with acetic acid left calcium fluoride in a granular form which was easily filtered. The extraction has usually been made with 1.5 N acetic acid. To test the solubility of calcium

[1] Ber., 21, 2843 (1888).
[2] Schweigg. Jour., 16, 426 (1816).
[3] Leib. Ann., 72, 343 (1849).

fluoride in acetic acid of this strength, weighed amounts of perfectly pure material were digested in 10 cc. of the acid on the water bath for an hour, filtered, washed and weighed. The mean loss for 10 cc. of the acid equaled 0.0015 g. calcium fluoride.

A portion of the same calcium fluoride, after treatment with acetic acid, was exposed for one hour to a red heat over an ordinary Bunsen flame, when 0.0886 g. of material lost 0.0016 g. The change upon ignition was probably due to the formation of calcium oxide with the evolution of hydrogen fluoride.

It was found by repeated experiments that, if the substance which had been ignited with consequent loss of weight was covered with hydrofluoric acid, evaporated to dryness and weighed, the original weight was restored. Thorium and cerium fluorides, upon ignition, pass into the corresponding dioxides.

To a solution of sodium fluoride, there was added a small amount of sodium carbonate, the precipitate produced in this solution, by calcium chloride, was filtered, ignited and treated with 10 cc. of 1.5 N acetic acid. The acid was evaporated to dryness, the residue taken up in hot water, filtered and weighed. This was done with several samples.

F. present........	0.0344 g.	0.0344 g.	0.0344 g.	0.0688 g.	0.1423 g.
F. found.........	0.0329 g.	0.0330 g.	0.0328 g.	0.0664 g.	0.1401 g.
Loss.............	0.0015 g.	0.0014 g.	0.0016 g.	0.0024 g.	0.0022 g.

The error here is not proportional to the amount of fluorine present, but is an additive one depending upon the solubility of calcium fluoride in a given quantity of acetic acid. Consequently the method which has been suggested may be successfully employed by applying a constant correction factor.

To test the delicacy of the calcium fluoride precipitation, quantities of sodium fluoride were dissolved in 50 cc. of water, warmed and treated with a solution of calcium chloride.

NaF present.	F present.	CaF$_2$ found.	F found.
0.0003 g.	0.0001 g.	No precipitate	....
0.0009	0.0004	No precipitate	....
0.0015	0.0006	No precipitate	....
0.0022	0.0009	Slight turbidity	....
0.0037	0.0016	Distinct turbidity	....
0.0066	0.0028	0.0047	0.0023 g.

It has been long known that simple fusion of fluorspar or calcium fluoride with sodium carbonate will not convert all of the fluorine into a soluble form. The addition of silica to the fusion mixture does, however, bring this about. So, in applying the method of Berzelius to insoluble fluorides and minerals, it has been customary to mix the fluorspar, let us say, with four times its weight of silica and six times its weight of a

mixture of sodium and potassium carbonates. After fusing, extracting and filtering, the greater portion of the silica is precipitated by evaporation with ammonium carbonate; the last traces by ammoniacal zinc oxide and the fluorine then precipitated with calcium chloride in the presence of carbonate. The details of the procedure have been carefully investigated by Seemann.[1] In the present study, the evaporations and the precipitations were made in vessels of gutta percha and platinum. Obviously, in the case of minerals containing silica, less silica need be added to the flux. Seemann employs mercuric oxide instead of zinc oxide in precipitating the silica, an essentially valuable method when the silica is to be weighed. The following determinations were made by the Berzelius-Rose method.

CaF$_2$ present	0.1098 g.	0.1148 g.	0.1648 g.
CaF$_2$ found	0.0882 g.	0.1018 g.	0.1403 g.
CaF$_2$ found	80.3%	88.7%	85.0%

The results are low, but in harmony with those obtained by Seemann. Qualitative tests were applied to the residue from the original fusion and to the precipitates obtained by ammonium carbonate and zinc oxide, but the loss of fluoride could not be located. Stadeler[2] thought that an appreciable amount of the fluorine was volatilized in the fusion. Seemann could not satisfy himself upon this point, but called attention to the existence of an insoluble compound, SiOF$_2$, and concluded that the fluorine retained in the residue from the extracted melt and in the silica precipitates existed in this form.

As an idea prevailed that some of the fluorine might be lost during evaporation as volatilized ammonium fluoride, the following blank tests were made with sodium fluoride, the fluorine being determined directly as lead chlorofluoride: (1) Sodium fluoride was dissolved in 25 cc. of water and evaporated to dryness on the water bath. (2) Sodium fluoride was dissolved in 25 cc. of water and boiled vigorously to dryness. (3) A solution of sodium fluoride was treated with a large excess of ammonia and evaporated to dryness. The results were as follows:

	F present.	PbFCl found.	F found.
(1)	0.0491 g.	0.6745 g.	0.0490 g.
(2)	0.0430 g.	0.5950 g.	0.0432 g.
(3)	0.0361 g.	0.5047 g.	0.0366 g.

These tests show that the losses, if any, were of very small magnitude.

Determinations were next made to ascertain how much fluorine might be recovered from the silica precipitates and residue from the fusion, if the lost fluorine was really to be found there. The residue, therefore, from the extracted melt was united with the silica precipitated by am-

[1] Z. anal. Chem., 44, 343 (1905).
[2] J. prakt. Chem., 99, 66 (1866).

monium carbonate and ammoniacal zinc oxide and all refused with a
fresh charge of flux. The following results were obtained (Table I):

TABLE I.

		Grams CaF_2 found.			
Flux.	CaF_2 present.	1st fusion.	Refusion.	Total.	Error.
1. Na_2CO_3.........	0.1158	0.0988	0.0148	0.1136	—0.0022
2. NaOH..........	0.1237	0.0885	0	....	....
3. K_2CO_3..........	0.1108	0.0928	0.0159	0.1087	—0.0021
4. KOH...........	0.1197	0.1067	0	....	....
5. KOH...........	0.1193	0.1096	0.0104	0.1200	+0.0007
6. $NaKCO_3$.........	0.1549	0.1400	0.0146	0.1546	—0.0003

Caustic soda and caustic potash, as fluxing agents, did not recover any
of the fluorine. The error noticeable in the other experiments is not so
large as it should be if allowance is made for the known solubility of
calcium fluoride. Compensation is probably secured by very small amounts
of silica or zinc oxide in the precipitates.

Controls were made by converting the calcium fluoride into calcium
sulfate with excellent agreement. Verification of results by conversion
into sulfate is always reliable in the absence of phosphates. This treat-
ment with sulfuric acid, of course, may be used at the same time as a
qualitative test for the fluorine.

While Hillebrand had indicated the possibility of recovery of the lost
fluorine in this way, by a refusion these results show that the procedure
may be made to yield acceptable quantitative figures. They also serve
to establish the fact that the qualitative test for fluorine in complex
combinations with silica may overlook quantities of several milligrams.
The fluorine does, evidently, form a compound with the silica which is
not decomposed by sulfuric acid in making the qualitative tests. The
process of recovering fluorine from a mineral more complex than fluor-
spar deserves further study.

Wöhler[1] first estimated fluorine by the formation of silicon tetrafluoride
by the action of concentrated sulfuric acid upon a fluoride in the presence
of some form of silica. This would be a very convenient method for the
determination of fluorine in silicates were it not for the fact that the latter
are not generally decomposed by sulfuric acid. Wöhler determined the
loss in weight of his generating apparatus and called this the weight of
the silicon tetrafluoride. Fresenius[2] absorbed the gas in a tube containing
moistened pumice, weighing the tetrafluoride directly. In later years
these procedures have been regarded with disfavor. Hence those recent
methods have aimed to estimate the evolved silicon tetrafluoride in some
other way.

[1] Pogg. Ann., 48, 87 (1839).
[2] Z. anal. Chem., 5, 190 (1866).

Bein[1] led the gas into water and estimated the separated silica. Lasne[2] adopted the laborious method of precipitation of the fluorine from this solution as calcium fluoride after first separating the silica.

Tammann[3] precipitated the hydrofluosilicic acid formed as potassium silicofluoride in alcoholic solution, filtered and titrated the precipitate with standard caustic potash, while Carnot[4] precipitated K_2SiF_6 by the reaction

$$SiF_4 + 2KF = K_2SiF_6.$$
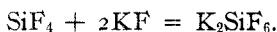
The handling of the gelatinous precipitate of potassium silicofluoride is not a simple matter; it has been shown to be not completely insoluble even in 50% alcohol. The Carnot method has invariably given lower results than the other procedures.

The alkalimetric methods are the most rapid and by far the most convenient. Penfield[5] received the silicon tetrafluoride in an alcoholic solution of potassium chloride, and titrated the hydrochloric acid set free, using cochineal as indicator.

Offermann[6] received the gas in water and, using phenolphthalein, titrated according to this equation

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2.$$
$$2H_2SiF_6 + 12KOH = 12KF + 2SiO_2 + 8H_2O.$$
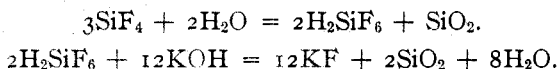
Both of these methods are rapid and in the past have given good results. The method of Offermann[6] is to be preferred.

My experiments were concerned more with the circumstances surrounding the evolution of the silicon tetrafluoride.

The apparatus involved nothing new, but was an attempt to assemble the best recommendations made in previous investigations. A and B contained concentrated sulfuric acid; C soda-lime and D, calcium chloride, these to dry the air current. F was made from a 100 cc. distilling bulb. The entrance tube into F formed a ground joint with the neck. F was heated by means of an air bath. G was a small flask containing concentrated sulfuric acid. H, I and J served to condense any sulfuric acid carried over. H contained glass beads. I and J were empty. H and I were surrounded by cold water. K was an 8-inch test tube containing the water into which the silicon tetrafluoride was received. It was found unnecessary to employ a layer of mercury in the bottom of K. The danger of the tube becoming clogged by deposited silica was obviated by spreading the end of the tube as indicated. Air pressure was furnished at A by a

[1] Z. anal. Chem., 26, 733 (1887).
[2] Bull. soc. chim., [2] 50, 167 (1887).
[3] Z. anal. Chem., 24, 328 (1885).
[4] Compt. rend., 114, 750, 1189 (1892).
[5] Am. Chem. J., 1, 27 (1879).
[6] Z. angew. Chem., 3, 615 (1890).

water pump. This was found more convenient than a gasometer and furnished a more constant stream of air than a suction pump at K. A number of preliminary experiments were made to ascertain the most suit-able conditions of temperature, etc.; 0.1 g. samples of calcium fluoride
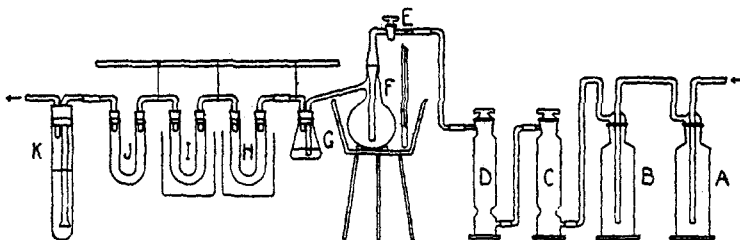

Fig. 1.

were mixed with 0.5 g. powdered quartz and placed in the decomposition flask F. A temperature of 180° was used in the preliminary experiments. These determinations were carried out in the main in accord with the de-tailed description of the method below.

Observations upon the Concentration of Sulfuric Acid Required.— Determinations employing laboratory acid labelled "concentrated" (analysis = 96.9% H_2SO_4).

CaF₂ present.	F found.	F found.	F theor.
0.1052 g.	0.0425 g.	40.4%	48.52%
0.1298	0.0570	43.9	...

Determinations employing acid prepared by heating the above acid in a retort till about one-tenth of the volume had passed over (method of Daniel) (analysis = 98.6% H_2SO_4). This corresponds to "constant boiling" acid.

CaF₂ present.	F found.	F found.	F theor.
0.0930 g.	0.0436 g.	46.9%	48.52%
0.1418	0.0678	47.8	...

Seemann has shown that an acid of higher percentage formed by the addition of sulfur trioxide gives off the trioxide on heating, and is difficult to condense.

TABLE II.—VARIATIONS IN TEMPERATURE.

	Temperature.	CaF₂ present.	F found.	F found.	F theor.
1	180°	0.0930 g.	0.0436 g.	46.9%	48.52%
2	180	0.1418	0.0678	47.8	...
3	200	0.1243	0.0589	47.4	...
4	220	0.1211	0.0570	47.1	...
5	230	0.1225	0.0583	47.6	...
6	280	0.1245	0.0564	45.3	...
7	310 (b. p.)	0.1100	0.0393	35.7	...
8	310 (b. p.)	0.1002	0.0327	32.6	...

The results shown in Table II would indicate a temperature of 200–220° as most desirable. In Experiments 4 and 5, after titrating the solution in K, the acid in the decomposition flask was raised to the boiling point for 15 minutes and the air current continued for 1 hour longer. It was hoped in this way to obtain any fluorine which might not be expelled at 220°, but which might be driven over by boiling the acid. The water in K still showed neutral reaction. This would seem to contradict Daniel[1] and Hileman,[2] who maintained the formation of an intermediate compound which was only completely broken up into gaseous silicon tetrafluoride on boiling the sulfuric acid.

Repeatedly in later determinations, toward the close of the operation, the temperature of the decomposition flask was raised to the boiling point of sulfuric acid, but no increase in the amount of silicon tetrafluoride evolved was indicated.

It was also noted that when heated over 280° the contents of the decomposition flask (which included always 1 g. of anhydrous copper sulfate) changed from white to a blue color, undoubtedly indicating that at this temperature even "constant boiling" sulfuric acid decomposes thus:

$$H_2SO_4 = H_2O + SO_3$$
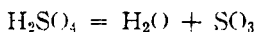
One of the most important conditions for the success of the method, where silicon tetrafluoride is evolved, has been the exclusion of every trace of moisture from the apparatus. However, it cannot be overlooked that water is one of the products of the reaction and is just as influential a factor as the concentration of the sulfuric acid used. The introduction of a dehydrating agent to take up this water is an obvious step. Drawe[3] suggested the use of anhydrous copper sulfate. Quantitative measurements showed:

CaF₂ present.	Quartz present.	Dehydrating agent.	Time. Hours.	F found.	F found.	F theor.
0.1019 g.	0.33 g.	None	3	0.0484 g.	47.5%	48.52%
0.1243	0.50	2 g. CuSO₄	5	0.0589	47.4	...
0.1211	0.50	2 g. CuSO₄	3¹/₂	0.0570	47.1	...
0.0799	0.30	1 g. P₂O₅	3¹/₄	0.0380	47.5	...

The form of silica used in the formation of silicon tetrafluoride is another factor strangely affecting the reaction. Daniel found quartz preferable to precipitated silica and showed that it is more easily attacked by hydrofluoric acid than other varieties of silica. Drawe suggested the use of powdered feldspar as a "more easily combinable form" of silica. Measurements with varying quantities of each showed the results given in Table III.

[1] Z. anorg. Chem., **38**, 257 (1904).

[2] Am. Jour. Sci., [4] **22**, 329, 383 (1906).

[3] Z. angew. Chem., **25**, 1371 (1912).

TABLE III.

Quartz.

CaF$_2$ present.	Gram added.	Time. Hours.	F found.	F found.	F theor.
0.1243 g.	0.50	5	0.0589 g.	47.4%	48.52%
0.1211	0.50	3$^1/_2$	0.1570	47.1	...
0.1225	0.23	4	0.0583	47.6	...
0.0900	0.08	3$^1/_2$	0.0413	45.9	...

Precipitated silica present.

0.0859	0.20	8	0.0378	44.0	48.52

Feldspar present.

0.1013	0.59	2$^3/_4$	0.0466	46.0	48.52
0.1168	0.50	2$^1/_4$	0.0540	46.3	...
0.0696	0.45	2$^1/_2$	0.0325	46.7	...
0.0781	0.40	2$^1/_2$	0.0361	46.2	...
0.0641	0.35	2	0.0293	45.7	...
0.1547	0.20	3$^1/_2$	0.0719	46.4	...

The results in using quartz were the most satisfactory, while the application of silica in the form of feldspar evolved the gas in a manner which was more easily swept along to the absorption tube, with a consequently much shorter time required for the determination. When quartz was employed, a continued agitation of the decomposition flask was necessary to break up the small bubbles of gas remaining collected on the surface of the sulfuric acid, while with feldspar the silicon tetrafluoride was evolved on heating almost as readily as is carbon dioxide from a carbonate on treatment with acid.

The Details of the Offermann Method.—The standardized procedure which the above experiments seemed to recommend, and which was used in all the subsequent determinations follows: The sample of calcium fluoride weighing 0.1–0.2 g. was mixed in a mortar with three times its weight of powdered quartz. (The quartz had been strongly ignited and kept in a desiccator.) This was placed in F, about 1 g. of anhydrous copper sulfate was added and 25 cc. of concentrated sulfuric acid introduced. (The sulfuric acid was prepared by the method of Daniel.) With the stopcock at E closed, the air bath was heated gradually till in $^1/_2$ hour the temperature had risen to 220°. E was then opened to let an air current of about three bubbles per second pass through the apparatus and the temperature kept at 220°. Occasional shaking of the evolution flask was found desirable. When the bubbles of silicon tetrafluoride had disappeared from F, the flame was removed, the air current continued, and after about $^1/_2$ hour the solution in K was titrated with 0.1 N KOH. The entire determination for fluorspar required about 2$^1/_2$ hours. A single vessel at K containing 50 cc. of water was found sufficient for the complete absorption of the evolved gas. Another tube attached after K gave always a blank test. The apparatus employed, at the specified

temperature, succeeded in completely condensing all sulfuric acid before reaching K. After twenty successive determinations, the apparatus was taken apart and the tubes H, I and J tested by washing out with a little water. That from H showed a distinct acid reaction with litmus, I was very slightly acid, while J showed a neutral reaction. A total of fifty determinations was made by this method.

As the addition of feldspar to the contents of the evolution flask showed an interesting behavior, observations were made upon other minerals. In each case the mineral was finely powdered and intimately mixed with the calcium fluoride before this was placed in the decomposition flask.

TABLE IV.

	Form of silica present.	CaF_2 present.	Time. Hours.	F found.	F found.	F theor.
Calamine	0.59 g.	0.1153 g.	$2^{1}/_2$	0.0522 g.	45.3%	48.52%
Calamine	0.41	0.0919	3	0.0418	45.5	...
Leucite	0.38	0.0824	4	0.0366	44.5	...
Powdered glass	0.135	0.1321	5	0.0612	46.3	...
Sodium silicate	0.37	0.0961	6	0.0219	22.8	...
Wollastonite	0.46	0.1138	$2^{1}/_2$	0.0366	32.1	...
Wollastonite	0.56	0.1072	$2^{1}/_2$	0.0317	29.6	...
Pyroxene	0.50	0.0691	$2^{1}/_2$	0.0316	45.7	...

These measurements are interesting in showing the manner in which different forms of silica, or at least different forms of silicate combinations, may affect this reaction.

Since different forms of silica presented a varying behavior, it was sought to determine whether mineral fluorspar behaved in the same manner as precipitated calcium fluoride. The following results were obtained (Table V):

TABLE V.

Fluorspar present.

Wt. taken.	Quartz.	F found.	F found.	F theor.
0.1256 g.	0.50 g.	0.0592 g.	47.2%	48.50%
0.1130	0.50	0.0537	47.5	...
0.0783	0.50	0.0371	47.3	...

CaF_2 artificial.

0.0243 g.	0.50 g.	0.0589 g.	47.4	48.52
0.1211	0.50	0.0570	47.1	...
0.1225	0.23	0.0583	47.6	...

Apparently there was no difference in the behavior of these two forms of calcium fluoride.

The fact that the best determinations by the Offermann method are low is still to be explained. The general belief has been that there is formed in the course of the reaction an oxyfluoride of silicon, perhaps of the formula $SiOF_2$, which is not decomposed by sulfuric acid. The varied behavior of the several silicates in the reaction as shown above is probably explained

by the formation of such a compound. The aim, therefore, should be to get conditions least favorable to the formation of this oxyfluoride. The solid residue remaining in the decompositon flask at the conclusion of each determination was repeatedly tested for fluorine, but the methods employed failed to detect it.

Starck[1] in estimating fluorine takes advantage of the double halide formed on adding lead chloride to a solution of soluble fluoride, PbFCl. It is unfortunately only applicable to soluble fluorides and to those in neutral solutions. Lead chlorofluoride is quite appreciably soluble in water, but insoluble in a saturated solution of lead chloride. A number of other soluble lead salts and other soluble chlorides were examined, but none found which would render the chlorofluoride insoluble to the same degree. The real difficulty of the method lies in the washing of the precipitate, which is a delicate matter even with the use of a Gooch crucible, and requires the very least amount of wash water. The precipitate is dried and weighed as such in a Gooch crucible. It was found desirable to wash with ice-cold water. Satisfactory results may be obtained under carefully standardized conditions. An obvious advantage of the method is the fact that the precipitate weighed is about fourteen times the weight of the fluorine it contains. A solution of sodium fluoride was employed and treated according to the original directions.

F present	0.0344 g.	0.0344 g.	0.0492 g.	0.0863 g.
PbFCl found	0.4757 g.	0.4738 g.	0.6743 g.	1.1941 g.
F found	0.0345 g.	0.0344 g.	0.0490 g.	0.0867 g.

These figures are typical of a larger number of analyses which confirm those reported by Starck.[1]

An "alundum" filter cone was substituted for the Gooch crucible. The washing of the precipitate on the cone was found to require a greater amount of wash water and the results were correspondingly low. It was then thought possible to use in washing the precipitate, instead of pure water, a saturated solution of lead chlorofluoride itself. This was employed and gave more satisfactory results as follows:

F present	0.0344 g.	0.0344 g.	0.0344 g.	0.0344 g.	0.0344 g.
PbFCl found	0.4641 g.	0.4712 g.	0.4744 g.	0.4816 g.	0.4773 g.
F found	0.0337 g.	0.0342 g.	0.0344 g.	0.0350 g.	0.0347 g.

Guyot[2] and Greeff[3] have evolved a volumetric method based on the precipitation of the salt Na_3FeF_6 upon the addition of standard ferric chloride to a solution of a soluble fluoride. This precipitation is complete in the presence of alcohol and an excess of sodium chloride. The end point is read by the use of thiocyanate as indicator and absorption of the red

[1] Z. anorg. Chem., 70, 173 (1911).

[2] Compt. rend., 71, 274 (1870).

[3] Ber., 46, 2511 (1913).

thiocyanate color in an ether layer. A standard solution of ferric chloride was used, of such value that 1 cc. = 0.00267 g. of fluorine. Bellucci[1] has shown the effect of varying the quantity of pure sodium chloride present. The method was applied to a solution of sodium fluoride according to the recommendations of Greeff, and gave reliable results.

F present	0.0344 g.	0.0344 g.	0.0993 g.	0.0585 g.
NaCl present	1 g.	1 g.	2 g.	1 g.
F found	0.0339 g.	0.0339 g.	0.0995 g.	0.0582 g.

In several determinations the ordinary sodium chloride found in the laboratory was substituted for the c. p. salt, giving results as follows:

F present	0.0344 g.	0.0543 g.	0.0688 g.	0.0866 g.	0.1094 g.
NaCl present	2 g.	2 g.	2 g.	2 g.	3 g.
F found	0.0331 g.	0.0281 g.	0.0585 g.	0.0643 g.	0.1057 g.

These values serve to show that the influence of slight amounts of impurities in the sodium chloride was considerable.

In the place of sodium chloride, pure potassium chloride was used, giving:

F present	0.0301 g.	0.0343 g.	0.0344 g.	0.0387 g.	0.0585 g.	0.0619 g.
KCl present	4 g.	4 g.	4 g.	4 g.	4 g.	4 g.
F found	0.0304 g.	0.0341 g.	0.0347 g.	0.0387 g.	0.0587 g.	0.0630 g.

Hence, potassium chloride recommends itself quite as well as sodium chloride.

Attempts were made to apply this volumetric method to the analysis of fluorspar. The powdered mineral was fused with silica and sodium-potassium carbonate. The silica was precipitated by ammonium carbonate and ammoniacal zinc oxide. The resulting solution was neutralized, diluted to 30 cc., 4 g. of potassium chloride added, and titrated with standard ferric chloride solution. No satisfactory end point could be obtained.

The Guyot-Greeff volumetric method seems admirable for simple solutions of sodium fluoride, but fails when other substances are present.

Starck and Thorin[2] have suggested the addition of a known volume of standard ammonium oxalate before precipitating with calcium chloride, with the idea that the presence of oxalate would render the calcium fluoride precipitate more insoluble and at the same time aid in its filtration. The combined precipitates were brought upon a Gooch crucible, dried and weighed according to the original directions. The known weight of the calcium oxalate was subtracted from the total. Results:

F present.	CaC_2O_4 present.	$CaF_2 + CaC_2O_4$ found.	CaF_2 found.	F found.
0.0344 g.	0.1097 g.	0.1787 g.	0.0690 g.	0.0336 g.
0.0344	0.1097	0.1786	0.0689	0.0335
0.0344	0.1097	0.1796	0.0699	0.0340

[1] Ann. chim. appl., 1, 441 (1914).
[2] Z. anal. Chem., 51, 14 (1912).

It was found preferable to determine the strength of the ammonium oxalate solution by precipitation and weighing as calcium oxalate, rather than by titration with permanganate. The numerical results of Starck and Thorin are verified, but the combined precipitate of calcium fluoride and oxalate was found extremely difficult to filter and handle, contrary to the observations of the original proposers of this modification. The method is obviously limited to the estimation of fluorine in neutral solutions of soluble fluorides in the absence of most other substances.

Precipitation as Thorium Fluoride.—Thorium fluoride is precipitated in gelatinous form, but becomes rapidly granular and easy to filter on standing. A further advantage lies in the fact that simple ignition transforms it to dioxide, in which form it may be weighed. The fluoride must be precipitated, moreover, in strictly neutral solutions. The best results obtained were far from satisfactory.

F present............	0.0688 g.	0.0344 g.	0.0344 g.
F found.............	0.0661 g.	0.0368 g.	0.0329 g.

Some doubt was felt whether simple ThF_4 could be precipitated from a solution of sodium fluoride without being accompanied at the same time by Na_2ThF_6. A solution of about 0.5 g. of sodium fluoride was treated with an excess of thorium nitrate in neutral solution. The washed precipitate was dissolved in acid, the thorium precipitated by ammonia, and from the filtrate a small amount of sodium chloride was obtained.

A number of characteristic reactions for the metals are known, upon which the presence of fluorine exercises an inhibitory influence. Steiger's[1] method, improved by Merwin,[2] takes advantage of the color produced on treating a titanium solution with hydrogen peroxide. Fluorine tends to destroy this color. This "fading" effect can be readily measured by comparing the depth of color of two equivalent titanium solutions, one of which contains the fluorine, while the other does not. This indirect method was worked out in the U. S. Geological Survey for analysis of fluorine-containing minerals and, as pointed out by the authors, is only applicable to fluorine in very small amounts. They also emphasize the necessity of each analyst carefully setting for himself standard conditions and developing a factor which shall satisfy his own conditions of operation.

To calculate the factor: About 0.02 g. of calcium fluoride was taken, fused with silica and 1 g. of sodium carbonate, extracted with water and the silica precipitated with ammonium carbonate. To the solution were added 3 cc. of hydrogen peroxide, 10 cc. of titanium sulfate (= 0.01 g. TiO_2), 6 cc. of sulfuric acid and the whole diluted to 100 cc. Its depth of color was compared by means of a Duboscq colorimeter with another titanium solution prepared under the same conditions, but containing no

[1] This Journal, **30**, 219 (1908).

[2] Am. Jour. Sci., [4] **28**, 119 (1909).

fluorine. A blank reading to provide for the influence of sodium sulfate gave the number 103. Substituting in the formula, $\dfrac{R - 103}{X} = $ grams of fluorine, the following readings gave:

Calcium fluoride.	F preseent.	Ratio R.	Factor X calculated.
0.0142 g.	0.0068 g.	120	2500
0.0182	0.0088	125	2500

Using this formula, $\dfrac{R - 103}{2500}$, the following results were obtained:

Calcium fluoride.	F present.	Ratios.	F calculated.
0.0230 g.	0.0115 g.	132	0.0116 g.
0.0389	0.0188	150	0.0188

These figures show that under standardized conditions reliable results can be expected. A less-concentrated titanium solution provides for still smaller amounts of fluorine. On a qualitative basis alone, the method stands as probably the only satisfactory means of detecting in a silicate amounts of fluorine less than a milligram.

Fluorine likewise produces a fading effect upon the color produced between a ferric salt and ammonium thiocyanate. The red color is more suitable for comparison than the titanium color and it was thought would lend itself to the detection of larger amounts of fluorine. A preliminary study was made into the extent to which the thiocyanate color would be affected by reagents other than fluorides.

Solutions were prepared as follows: A solution of alum (1 cc. = 0.01 g. of Al_2O_3), a solution of sodium silicate (1 cc. = 0.01 g. of SiO_2), a solution of microcosmic salt (1 cc. = 0.005 g. of P_2O_5). The effect of each of these common constituents of rocks, i. e., Al_2O_3, SiO_2, P_2O_5, was tried in turn upon a solution containing 10 cc. of ferric chloride (= 0.03 g. Fe_2O_3) and 5 cc. of 5% solution of ammonium thiocyanate, diluted to 50 cc. and compared with a standard prepared under similar conditions.

TABLE VI.

Al_2O_3.		SiO_2.		P_2O_5.		Na_2CO_3 neutr. w. HCl.		NaF.	
Amount.	Ratios.	Amount.	Ratios.	Amount.	Ratios.	Amount.	Ratios.	Amount.	Ratios.
1 cc.	112	3 cc.	100	1 cc.	114	1 g.	102	0.0004	124
2	150	10	140	2	226	3	113	0.0007	128
5	271	20	148	3	decolor-	5	125	0.0010	142
10	350	..	...		ized	..	...	0.0014	161
..	...	..	...	..	...	..	...	0.0018	166

These values with NaF arrange themselves along a curve which could be used in reading the unknown amount of fluorine present necessary to produce a given fading effect, but the decided deleterious influence of the phosphorus, alumina, etc., which usually accompany fluorine in minerals shows the reaction not well adapted to such a field. It was further de-

termined that the thiocyanate color is not a permanent one. Exposed to light, a solution was found to lose one-half its depth of color in 48 hours.

The halogens, chlorine, bromine and iodine when passed through a tube over samples of fluorspar heated to redness in a boat produced no reaction with the mineral. It is known that hydrochloric acid gas will transform sodium fluoride to sodium chloride. The effect of this gas was tried upon fluorspar.

The powdered mineral was placed in a platinum boat and heated in a fairly rapid stream of hydrogen chloride for 5 hours. To determine if the decomposition was complete, the contents of the boat after the operation were treated with water, when the calcium chloride formed dissolved. A high temperature was found necessary. At 350° the mineral was only very slightly decomposed. The amount of decomposition increased with higher temperature. At 500° after most of the mineral had been acted upon the resultant calcium chloride fused, occluding in the fused mass undecomposed mineral and the action ceased. At 450° the action was extremely slow and after 8 hours showed still only partial decomposition. None of eight different samples, weighing 0.1 to 0.2 g. subjected to hydrogen chloride gas were more than partly acted upon. Apparently that temperature could not be found, high enough to cause complete reaction with hydrochloric acid, and low enough to prevent fusion of the calcium chloride.

The mineral cryolite behaved in a different manner. A sample of 0.1380 g. heated at 600° in hydrogen chloride for $6^{1}/_{2}$ hours left a residue weighing 0.0875 g. which dissolved in a few drops of water to a clear solution. A second sample of 0.1252 g. at 650° for 6 hours left a residue of 0.0823 g. and dissolved completely. The aluminum chloride formed volatilized completely and carried with it some of the sodium chloride.

Lenz,[1] desiring to estimate the amount of fluorine in an organic compound, heated the substance with calcium oxide and after extraction with dilute acetic acid weighed calcium fluoride. Kessler[2] applied this method to sodium and ammonium fluorides. The principle employed recalled the J. Lawrence Smith method for alkalies; an attempt was made to use this to aid in the decomposition of fluorides not decomposable by sulfuric acid. A sample of topaz, finely powdered, was intimately mixed in a mortar with ten times its weight of calcium carbonate and three times its weight of ammonium carbonate. This was heated in a covered crucible for 15 minutes with a small flame, and for 15 minutes more to intense redness. The fluorine, it was thought, was now entirely transformed into calcium fluoride and the mass free from carbonate. It was powdered and placed with anhydrous copper sulfate and sulfuric acid in the apparatus

[1] *Ber.*, **12**, 580 (1879).
[2] *Monatsh.*, **28**, 163 (1907).

for estimating fluorine by the Offermann method. The conditions of preliminary ignition were varied in a number of trials, but the best results were always low.

Topaz present.	F found.	F found.	F present.
0.2380 g.	0.0414 g.	13.9%	17.48%
0.2487	0.0369	14.8	...
0.2240	0.0321	14.4	...
0.2449	0.0352	14.4	...

This procedure failed to produce a successful method for fluorine. The ignition with calcium carbonate evidently led to the formation of calcium silicate. It is interesting to note that strikingly low results were likewise obtained when this substance in the form of wollastonite was applied to the Offermann method.

Additional Observations.—It is possible that some other metallic fluoride than those usually used might be adapted to an analytical method. The existing data upon the properties and solubilities of the fluorides is extremely meager. The fluorides of most of the metals were examined. Many of those generally regarded as insoluble were found not quantitatively insoluble, while practically all were formed as gelatinous precipitates quite impossible to filter and wash. Barium fluoride has been used by Gautier[1] in a special method for fluorine in mineral water. Cerium fluoride seemed to recommend itself, since on ignition it is transformed to the dioxide. It was found necessary to precipitate the fluoride of cerium in a solution absolutely neutral. The precipitate formed was almost colloidal and the weights of cerium oxide obtained always low.

There are other volatile compounds which might be employed other than silicon tetrafluoride. Jannasch[2] expels as hydrofluoric acid and collects in alkali; an elaborate piece of platinum apparatus is required which is almost prohibitive. The fluorine is then precipitated and weighed as calcium fluoride. The "etch" methods likewise involve the evolution of hydrogen fluoride. The consequent measurement in some way of this etching effect is hardly to be favored as an analytical method.

Boron fluoride is formed upon treating a fluoride with sulfuric acid in the presence of boric anhydride. In attempting to carry this out under conditions corresponding to those of the Offermann method for silicon tetrafluoride, it was found that silicon fluoride was likewise formed in the glass decomposition flask, and carried along with the boron fluoride to the absorption tube forming both H_2SiF_6 and HBF_4, incapable of being estimated by a simple titration. Hydrofluoric acid likewise forms a volatile ethyl ester which might be applied if some simple method of forming it analytically could be found.

[1] *Compt. rend.*, **152**, 546 (1911); **154**, 1670, 1753 (1912); **154**, 1469 (1912).
[2] *Z. anorg. Chem.*, **9**, 267, 273 (1895).

Summary.

It may be concluded from the preceding experiments:

1. That by means of a refusion with carbonate all the fluorine in silicate minerals can be accounted for by the Berzelius-Rose method.

2. That the conditions have been indicated according to which the best results can be obtained in the volatilization of silicon tetrafluoride by the Offermann method.   This method is to be preferred for the direct estimation of fluorine in fluorspar.

3. That the soluble fluorides can be most accurately determined by precipitation as lead chlorofluoride.

4. That the only satisfactory method of determining and detecting fluorine in small quantities in minerals is the colorimetric method of Steiger-Merwin.

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AN ACID-RESISTING ALLOY TO REPLACE PLATINUM IN THE CONSTRUCTION OF A BOMB CALORIMETER.

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In the construction of an oxygen bomb for calorimetric purposes the necessity of providing an interior surface, such as is afforded by a platinum lining, is a recognized essential under all circumstances, but especially important in the combustion of Illinois and related coals, where the nitrogen and sulfur result in the formation of a mixture of nitric and sulfuric acids, equivalent on the average to about 30 cc. of 0.05 N nitric acid. If a solvent action with the metal of the bomb occurs, the error is twofold, in that a too low correction for the total acid is indicated, thus increasing the heat credited to the fuel, and besides, any heat of solution developed by such action goes as a false credit to the fuel also and cannot be corrected for.   The conditions as thus outlined would very naturally suggest the desirability of devising a metal or a complex which should be as resistant to the action of acids as platinum.

In arranging a working program where so little of the underlying principles have been developed, about the only method of procedure is the purely empirical one of trying many things.   If we look for suggestions toward the theories proposed for the passivity of metals, we are impressed with the fact that investigators in that field are far from agreed as to what causes passivity.   At best, however, passivity is only a transient condition and would seem not to be applicable to the problem in hand.

Another possible basis of procedure was formulated from reasoning somewhat after this fashion.   There are many combinations of metals and metalloids having solubility characteristics quite different from the