ply houses, but not graduated, the graduation must be done in the laboratory. The supports F F can be made of rather heavy walled glass tubing, about 1 cm. outside diameter.

The mirrors are made of a good grade of looking glass, the lower and top edges blackened, and cemented to the ground ends of the glass tubes with Canada balsam, after which the backs are coated with paraffin. Paraffin answers well as a coating for a large number of colorimetric solutions. In case a liquid is to be used which attacks paraffin, a substitute must be employed which is unaffected by the liquid in question. It will be found necessary to replace the mirrors from time to time, as it is not possible to so protect the silvered surfaces as to prevent the gradual eating in from the edges by the various solutions used.

The comparison is made by pouring a solution of known strength into one of the cells. The unknown solution made up to a definite volume, is put into the other. The left-hand cell is then placed at a convenient point, which should be determined by the depth of color of the solution it contains. The right-hand cell is then moved back and forth till, on looking in the end M of the apparatus, Fig. 1, the two mirrors appear to be of the same shade.

The strengths of the two colorimetric solutions being inversely proportional to the thickness of the liquids looked through, by substituting in the following equation the amount of the material to be determined may be found.

Let R equal the reading of the cell containing the known solution with a concentration C, and r the reading of the cell containing the unknown solution, which has a concentration c, then

$$c = \frac{RC}{r}.$$

CHEMICAL LABORATORY,
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THE ESTIMATION OF SMALL AMOUNTS OF FLUORINE.

BY GEORGE STEIGER.

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The estimation of fluorine in such substances as rock mixtures, which require a carbonate fusion to bring the fluorine into a soluble form, is not only a long and difficult operation, but also the final results are far from being satisfactory.

When as much as one tenth of one per cent. is present, a negative result will often be obtained by the Berzelius method, the one usually employed.

The method to be described is based on the well known fact, that the presence of fluorine has a powerful bleaching effect on the yellow color, which is produced by the oxidizing of a titanium solution with hydrogen peroxide. A solution of definite volume is made containing the fluorine to be estimated, also having a known amount of titanium present; this is compared in a colorimeter with a second solution containing an equivalent amount of titanium per cc., and the bleaching effect recorded. From the extent of this bleaching, the percentage of fluorine can be calculated.

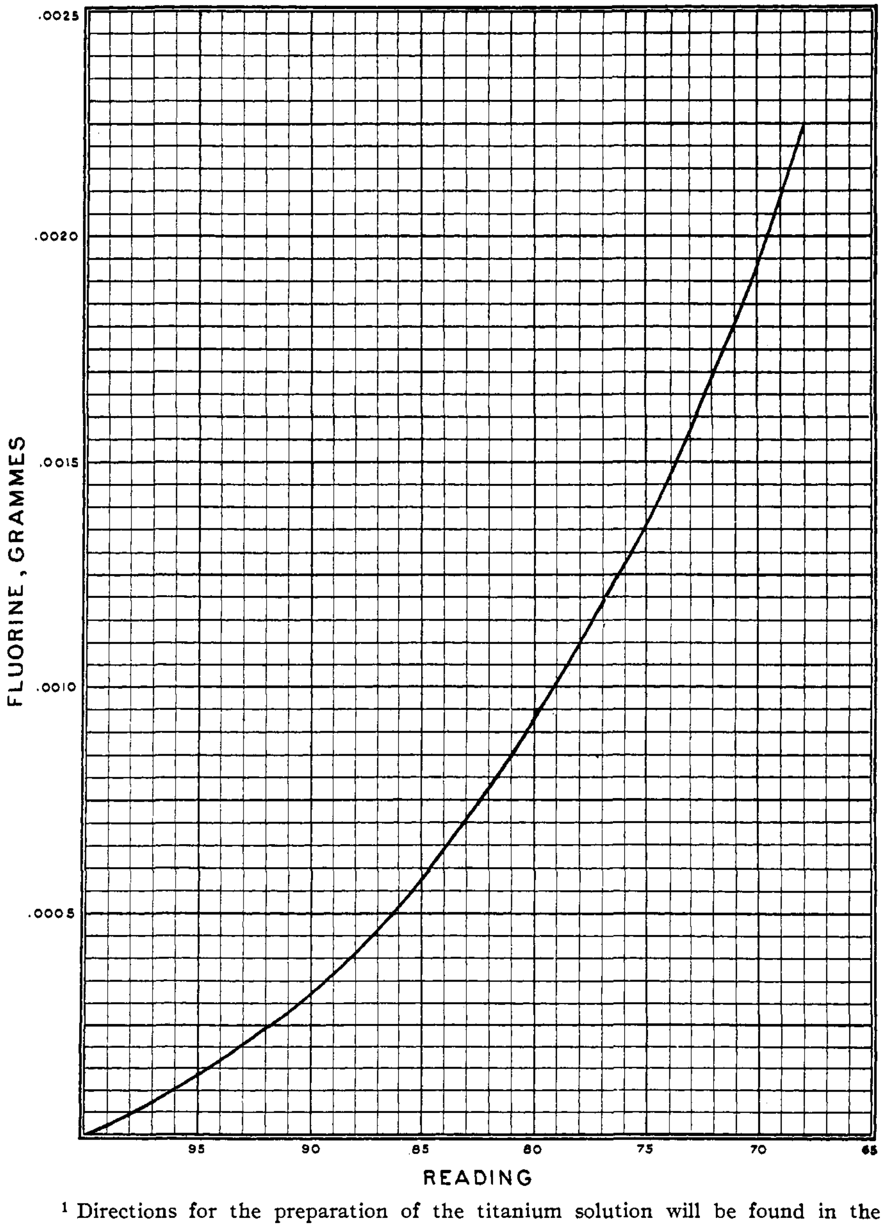
Although the results obtained are not so accurate as those given by many methods for the estimation of other elements, yet considering the difficulty of the fluorine determination, and the time and labor required by methods now in use, the present one may well be employed, where small quantities of fluorine are to be determined. The operations require not only less skill to carry out, but are fewer in number and take much less time.

Traces of fluorine amounting to several hundredths of one per cent. are easily detected, and an approximation to the quantity can be made. In amounts up to a few tenths of a per cent. the method seems to be more reliable, and if not more than two per cent. is present, the results compare favorably in accuracy with the standard methods. It is hardly to be expected, however, to find a colorimetric method using only a few milligrams of the material to be determined, that will compare in accuracy with the gravimetric methods using much larger quantities, where considerable percentages of fluorine are concerned.

Description of the Method.—In rock mixtures containing only a few tenths of a per cent. of fluorine, two grams of the finely ground rock powder are fused with four or five times its weight of a mixture of sodium and potassium carbonates. It may be necessary in the case of a subsilicic rock, to add silica, 50 per cent. of which should be present.

From the aqueous leach of the fusion, all of the alumina, and most of the silica, are separated by adding ammonium carbonate, heating on the water bath for fifteen or twenty minutes, allowing to cool an hour or more and filtering. The filtrate is evaporated to small bulk (25 or 30 cc.) and filtered a second time to insure a perfectly clear solution, a condition absolutely necessary for a satisfactory comparison of the color. After this treatment the solution should be entirely free from alumina, and contain no more than 25 milligrams of silica. This amount of silica is not sufficient to interfere with the reaction.

The solution is now put into a 100 cc. measuring flask, sulphuric acid added to almost neutral reaction with care not to add an excess, and well shaken to free from the excess of carbon dioxide, and then fully acidified. Care should be taken not to have an excess of acid present before shaking, for the reason that the escaping gas will carry off some fluorine; even under the above conditions a slight loss occurs. If a considerable amount of fluorine is present, an aliquot part of the solution should be used containing not more than 2 or 3 milligrams. 20 cc. of standard titanium sulphate solution[1] (1 cc. of which contains 0.0001



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[1] Directions for the preparation of the titanium solution will be found in the second part of this paper.

gm. TiO_2) are now added, together with 2 or 3 cc. of hydrogen peroxide, and the flask filled to the mark with water. The solution is now ready to be compared with the standard. The latter is prepared by using 20 cc. of the standard titanium solution, 2 or 3 cc. of H_2O_2 and bringing the volume up to 100 cc. with water.

These two solutions containing the same amount of titanium per cc. should be of the same depth of color, but the one having the fluorine present will be found to be of a lighter shade, owing to the bleaching effect which that element has on a solution of titanium oxidized by H_2O_2. The extent of this bleaching is not directly proportional to the amount of fluorine present, but by reference to the curve below, the quantity corresponding to a given bleaching can be found.

The two solutions are now compared in a colorimeter and their ratio recorded. Suppose a ratio for example, of 100 to 85, that is, the fluorine present has caused a bleaching of the solution equivalent to 15 per cent. of the titanium present; then by finding the point on the abscissa marked 85, with the help of the curve the amount of fluorine (0.00055) can be directly read off on the ordinate.

It is necessary to employ a colorimeter[1] whose error is not more than two or three per cent.

Experimental Work.

Directions for the preparation of the solutions used in the experimental part of this work:

Titanium Solution.—A quantity of potassium-titanium-fluoride was dissolved in water, a large excess of sulphuric acid added and the solution evaporated till fumes of sulphur trioxide came off, then cooled, more water added and the operation repeated. This was done several times to insure the entire removal of fluorine; the solution was then largely diluted with water, and its contents of titanium determined by precipitating a portion of it with ammonia, and weighing the titanium directly as its oxide. The solution was next so diluted as to contain 0.0001 g. TiO_2 per cc., at the same time adding enough sulphuric acid to make a 3 per cent. solution.

Fluorine Solution.—1.236 gm. of potassium-zirconium-fluoride were dissolved in one liter of water. One cc. of this solution contained 0.0005 gm. of F.

Silica Solution.—Five grams of silica and 10 gm. of sodium carbonate were fused together, dissolved in water, filtered, and made up to 500 cc. This solution contained 0.01 gm. SiO_2 per cc.

Aluminum Solution.—Common alum was dissolved in water sufficient to make a solution containing 0.01 gm. Al_2O_3 per cc.

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[1] A description of the colorimeter used in this work will be found in the preceding article.

Phosphorus Solution.—A solution of microcosmic salt was made, one cc. of which contained 0.005 gm. P_2O_5.

Iron Solution.—A solution of ferric sulphate containing 0.005 gm. Fe in each cc.

In the method described, after fusing the rock with carbonates and leaching with water, there will be in solution besides the fluorine, silicates and aluminates of sodium and potassium, and the excess of sodium and potassium carbonates, all in large amounts, a small quantity of iron, and all of the phosphorus, chlorine, vanadium, and some other elements usually found in very small quantities. The effect of silicon, aluminum, sodium, and iron salts, and the phosphorus, has been determined; the possible effect of traces of such salts as vanadates, tungstates, and chlorides, has not.

In all the following experiments 20 cc. of the titanium solution and 1½ cc. of the fluorine solution were used, oxidized with 2 or 3 cc. of hydrogen peroxide and made up to 100 cc. A large number of comparisons were made of this solution with one of the same composition, excepting that it contained no fluorine. The average ratio found was 100 to 82.5, that is, 1½ cc. of fluorine solution (0.00075 g. F) should cause a bleaching effect equivalent to 17.5 per cent. of the titanium present, when the solution contains no interfering substances.

The following results were obtained, when the several salts were introduced into solutions containing the above quantities of titanium and fluorine.

The figures given under the head of "reading" denote the ratio of the color of the solution containing the fluorine, etc., to that of the standard titanium solution, the latter being taken as 100.

Effect of Sodium Salts.—The sodium carbonate was dissolved in water, the solution acidified with sulphuric acid and well shaken to free it from dissolved gas, the titanium, fluorine, and hydrogen proxide added, and made up to 100 cc. with water.

Na_2CO_3, gms	8.	8.	8.	8.	8.	8.
Reading	85.2	85.7	83.7	86.4	85.2	84.4
Na_2CO_3, gms	8.	8.	8.	8.	8.	8.
Reading	82.9	83.5	83.3	83.4	83.1	86.3

Effect of Silica.—

Silica solution, cc. added	1.	2.	5.	5.	5.
Reading	84.4	83.5	83.8	85.7	84.2
Silica solution, cc. added	5.	10.	30.	50.	....
Reading	84.2	84.9	85.9	88.8	....

Effect of Aluminum.—

Alum solution, cc. added	1.	3.	5.	5.	20.
Reading	92.	96.3	97.3	96.6	99.3

Effect of Iron.—

Iron solution, cc. added	5.	5.	....	....	....
Reading	90.	89.9	....	....	....

Effect of Phosphorus.—

P_2O_6 solution, cc. added	5.	25.	....	....	....
Reading	84.5	80.3	....	....	....

The following experiments were made having phosphorus present but no fluorine.

P_2O_5 solution, cc. added	5.	25.	....	....	....
Reading	98.4	94.3	....	....	....

This bleaching effect on the color of an oxidized titanium solution by phosphorus has been observed before.

These results show that sodium salts in large amounts have a slight effect in making the observed reading higher, but not enough to seriously alter the results. Silica in amounts up to 0.1 g. has but little effect. It is easy, however, by one precipitation with ammonium carbonate to leave not more than 30 milligrams of silica in solution. Aluminum, even in small quantities, has a very marked effect on the bleaching, but this base is entirely separated by the ammonium carbonate treatment. Phosphoric acid has the same effect as fluorine in bleaching the color, but as this is present in much smaller quantities than those used in the above experiments, its effect can be neglected. Iron prevents the bleaching, but as the quantity coming out in the leach water is hardly more than a trace, and even this small amount is probably separated by the treatment with ammonium carbonate it can also be neglected.

Various mixtures were made roughly representing commonly occurring rock mixtures, containing accurately known amounts of fluorine. Results of the fluorine determinations in these mixtures follow:

SiO_2.	Al_2O_3.	Fe_2O_3.	$MgCO_3$.	$CaCO_3$.	$NaHNH_4PO_4$.	TiO_2.	F calculated.	F found.
0.60	0.20	0.05	0.03	0.05	....	.....	0.0114	0.0102 Gm.
"	"	"	"	"	0.01	0.008	0.0052	0.00525 "
"	"	"	"	0.10	"	0.01	0.00284	0.0027 "
[1] 0,70	0.15	0.05	0.05	0.05	"	0.005	0.0005	0.0003 "
"	"	"	"	"	"	"	0.00526	0.0056 "
"	"	"	"	"	"	"	0.00526	0.0040 "
"	"	"	"	"	"	"	0.00253	0.0020 "
"	"	"	"	"	"	"	.0.01228	0.0089 "
"	"	"	"	"	"	"	0.00516	0.00486 "
"	"	"	"	"	"	"	0.00536	0.00530 "

To give an idea of the amount of silica in solution after the treatment with ammonium carbonate, several determinations were made in the above solutions after the colors had been compared. The results follow:

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[1] In this determination the fusion of the mixture was made as usual, and the fluorine added to the leach water before the treatment with ammonium carbonate.

SiO_2	0.0244	0.0740[1]	0.0268	0.0555[1]	0.0159	0.0298	0.0174	0.0113	0.0263 Gm.

The following determinations were made of fluorine in natural rocks and compared with the gravimetric results:

Gravimetric determination..................	0.15	3.01	3.01 per cent.
Colorimetric determination..................	0.21	2.58	3.20 per cent.

A number of determinations of fluorine were made in rocks containing quantities varying from 10 to 20 per cent., but the results were not satisfactory, being several per cent. out of the way.

Chemical Laboratory.
U. S. Geological Survey,
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VOLUMETRIC METHOD FOR THE DETERMINATION OF ZINC.

By Wm. Herbert Keen.

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Several schemes have been advanced for the estimation of zinc by titration with potassium ferrocyanide, but so far no one of them has found universal application. The methods which have found favor are either so complicated or so difficult in manipulation that a large personal error is always introduced and it seldom happens that very close checks are obtained by different operators, even when the same procedure is followed. Nearly a year ago I became interested in the volumetric determination of this metal with the idea of substituting it for the rather tedious gravimetric method which has always been in use in our laboratory.

At first, and for quite a long time in fact, I was not very successful and encountered numerous difficulties. The samples which I used in this preliminary work were spelters, the zinc content of which had been very carefully determined by difference. Finally, after a trial of all the methods which seemed reliable, with varying successes, I concluded that changes might be made to good advantage in nearly all of them, so with what experience I had already gained, I attempted to work up a scheme which would embody the good points of all of these methods and as far as possible none of the bad ones. The method which I am about to describe, therefore, is not new, but is rather a re-modeling of the older ones. The scheme is one which is identical in certain parts for almost every condition, but there are some slight variations which are necessary for different products and, if accuracy is desired, they should be observed. Accordingly, I will describe the method, applying it to typical cases.

Preparation of the Ferrocyanide Solution.—Dissolve crystals of c. p. potassium ferrocyanide in water in the proportion of 22 grams to the liter. If the solution is not clear, it should be filtered before it is diluted to the desired volume. It is a good plan to make up several liters at a

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[1] In these two cases the silica was filtered immediately after being precipitated with ammonium carbonate, which accounts for the large quantity found.