The last example I give is the result on an alloy sent me by the Pittsburg Section of the American Chemical Society for analysis. The alloy contained, as reported to me after I had sent in my report, the following: 4.98 to 5.02 per cent. copper, 14.70 per cent. antimony, and the balance tin. My report by this method was 14.73 per cent. antimony, the average of two determinations.

NATIONAL LEAD CO.,
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THE ETCHING TEST FOR SMALL AMOUNTS OF FLUORIDES.

BY A. G. WOODMAN AND H. P. TALBOT.

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IN THE course of some work on the detection of fluorides in malt liquors it was found necessary to make a study of the etching test on glass as commonly employed, both from its standpoint as a qualitative test and with a view to making it approximately quantitative.

As a qualitative test, the etching method was found eminently satisfactory, as regards delicacy and reliability, if carried out under proper conditions. The procedure employed was the same in principle as that proposed by Blarez,[1] later modified by Leach,[2] and adopted as a provisional method by the Association of Official Agricultural Chemists.[3] It may be described briefly as follows: To 150 cc. of the liquid to be tested add 10 cc. of potassium sulphate (33 grams per liter), heat the solution to boiling and while boiling add slowly from a burette or pipette 10 cc. of a 10 per cent. barium acetate solution. Continue the boiling for a moment and then set the beaker aside for the precipitated barium sulphate and fluoride to settle. In most cases, unless the precipitate settles very readily, it is preferable to let it stand over night. The clear supernatant liquid is decanted, the precipitate transferred to a filter, washed and ignited in a platinum crucible. An alternative method which is more rapid and has the added advantage of avoiding the use of filters, is to decant off the clear liquid and wash the precipitate into one of the tubes of a centrifugal machine. The sedimented material is then washed directly into a platinum

[1] Chem. News, 91, 39 (1905).

[2] Ann. Rept. Mass. State Board Health, 1905.

[3] U. S. Dept. Agr., Bur. Chem., Circular 28.

crucible. This is placed in the centrifugal machine and whirled again, after which the precipitate can be ignited over a flame.

Meanwhile a small glass plate, clear and free from scratches, is thoroughly cleaned and coated on one side with a mixture of equal parts paraffin and carnauba wax. This can readily be done by pouring a little of the melted wax on the warmed plate. If the excess is drained off and the glass held level, a thin uniform wax coating will result. While the coating is still warm make a characteristic mark, such as a small cross (+), in the wax with a pointed instrument, taking care that the glass is laid bare but not scratched. The precaution should be taken to have the cross of approximately the same size in the different tests; for example, with arms about 4 mm. long and 1 mm. wide. On the uncoated side of the plate locate the cross by marks placed at the ends of the arms with a diamond or file.

To the precipitate in the crucible add 2 to 3 cc. of concentrated sulphuric acid, hold the crucible in the tongs, and heat its upper edge cautiously and quickly in a small flame. Press the glass plate quickly down on the warm crucible, having the cross nearly in the center, and hold it a moment to seal the glass securely to the crucible. The crucible should be embedded in the wax so firmly that it can be lifted by the plate. Support the crucible in a piece of heavy asbestos board in which a hole has been cut so that the crucible fits closely, put two or three drops of water on the glass plate and press down on it a condenser, the lower end of which is closed by a piece of thin sheet rubber such as is employed by dentists. Heat the crucible for an hour by a small flame about 9 mm. long placed 6 mm. below the bottom of the crucible. At the end of this time remove the plate, scrape off the wax and clean the glass on both sides, with "bon-ami" or other polishing material which will not scratch the glass. Examine it by reflected light for an etching. A test should not be considered positive unless the cross can be seen when viewed from either side of the glass.

Several times during the hour it may be necessary to put a drop of water on the plate around the edge of the condenser, to keep the wax from melting.

It is hardly necessary to speak of the need for using the purest reagents obtainable and testing them carefully by blank tests. The barium acetate has given the most trouble from traces of fluorides and it has been found best to prepare it from recrystallized barium nitrate by precipitating with ammonium carbonate, dissolving the washed carbonate in acetic acid, and recrystallizing the barium acetate.

The condenser may be made from a piece of wide glass tubing arranged so that a constant current of cold water may be kept flowing through it and with a piece of thin sheet rubber (dental dam), stretched tightly over the bottom. The diameter of the tube should be somewhat greater than that of the platinum crucible. A "carbon funnel," as shown in the figure, has been found to answer well.

The electric stove, as recommended by Leach, has not given good results in our hands for furnishing a uniform source of heat, it being our experience that different stoves, and even different sides of the same stove, vary considerably in temperature. On account of the larger surface radiating heat it is more difficult to prevent the melting of the wax than when the small flame is used.

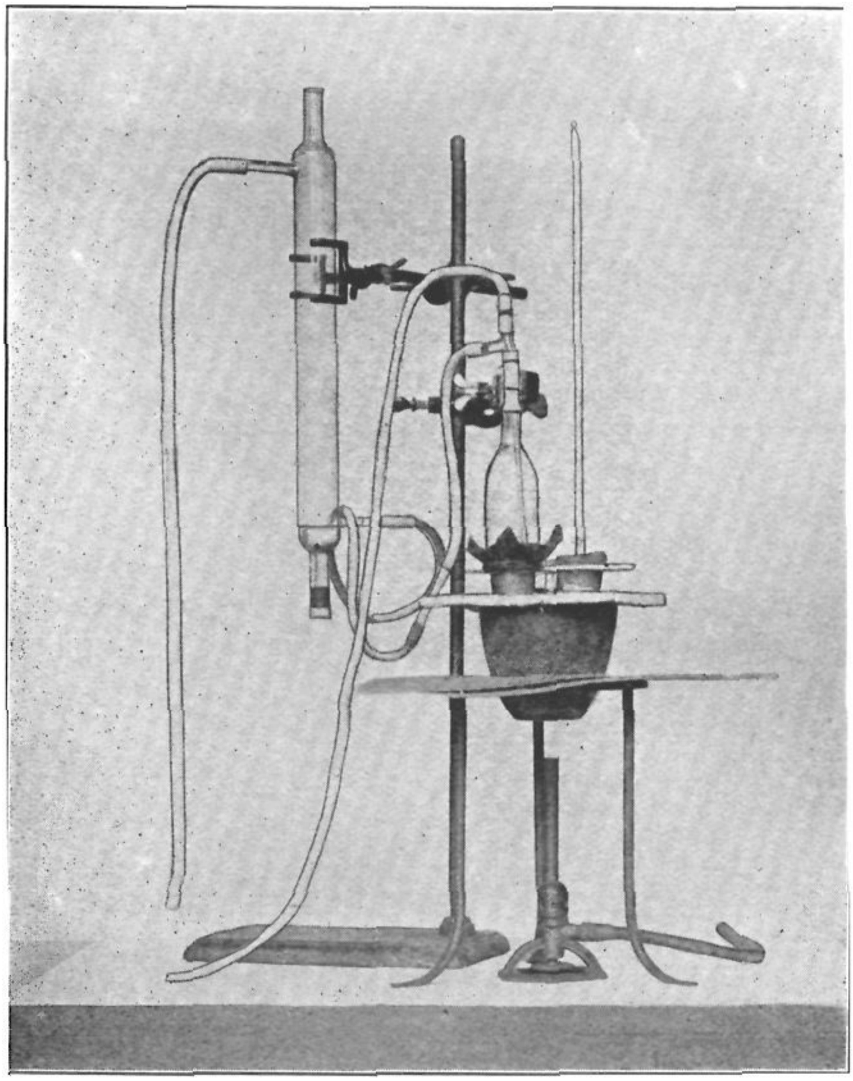
The delicacy of the procedure above described, as tested on aqueous solutions of potassium fluoride, is rather surprising. A perfectly distinct etching is readily obtained from 150 cc. of solution containing 1 : 10,000,000 of fluorine, and by careful working it is possible to get a recognizable test from 1 : 50,000,000. By a recognizable test is meant one which is visible from either side of the glass and does not have to be brought out by breathing on the glass. Care should be taken to clean the glass with "bon-ami" before examining it, since sulphuric acid alone will give a "stain" which can be brought out by breathing on it, and might easily be mistaken for an etching. The scouring will always remove this, however.

It has been found best to continue the heating for at least an hour. The etching obtained with a small amount of fluorine, say 1 : 5,000,000, is distinctly less after fifteen or thirty minutes than if the heating is continued for the longer period. There seems to be, however, no advantage in prolonging the test above an hour.

It is best to have the area of glass exposed approximately the same in different tests, because the intensity of the etching produced evidently depends somewhat upon the area of glass exposed. Tests made with 1 : 100,000 of fluorine showed that a test in one case indicating apparently 25 or 30 times as much fluorine as in another could be obtained by simply exposing that much more glass. The presence of organic matter or of traces of water during the etching does not seem to make much difference except in the character of the mark obtained. In the absence of organic matter, and when the contents of the crucible are perfectly dry, the resulting etching is usually a "matt" etching, resembling ground glass. If moisture is present, either originally or resulting from the action of organic matter on the sulphuric acid, the etching is clear and transparent and somewhat more difficult to detect.

It was noticed early in the investigation that the test would not infrequently fail to give a positive result even when fluorides were known to be present. This led to a somewhat detailed study of the conditions during the precipitation and the etching in order to see if in any part of the procedure a lack of strict adherence to minor detail was the reason why a successful test could not be obtained. Without giving a minute description of the numerous experiments, it may be said that considerable variations in the manner of carrying out the precipitation made no apparent difference in the result. The precipitate settles better and slightly more uniform results are obtained when the precipitation is made slowly and at the boiling temperature, although good results have been obtained repeatedly by adding the reagents in the cold and then heating to boiling. The experiments showed, however, that one factor is extremely important—essential in fact,—namely, the temperature during the etching. This one factor was found sufficient to explain the failures experienced, a difference of 15° or 20° in temperature being enough to prevent the obtaining of a test with a given amount of fluoride.

The differing results obtained at varying temperatures led to an attempt to base an approximately quantitative method on the temperature factor, since something more than a qualitative test is necessary to distinguish between natural and added fluorides. Traces of fluorine are widely distributed in food products and the mere fact that an etching can be obtained is not evidence that fluorides have been added as a preservative. It is essential to know approximately the proportion of fluoride present and the temperature-effect seemed to offer a simple means of determining this. The usual methods for determining fluorine in minerals are, of course, not applicable to the minute quantities that have to be considered here. The objection of lack of delicacy applies also to the various methods based on the loss in weight sustained by



glass of known composition when subjected to the action of hydrofluoric acid. A comparison of the etchings obtained in different tests as regards their apparent intensity has not proven satisfactory in our experience and the same has been found true by others.[1] In order to render such comparisons reliable the etchings must be made by the use of special apparatus to maintain exact conditions, whereas in a test of this kind, if it is to be available for use in general analytical practice, simplicity of apparatus is an important consideration.

With this idea in view, a series of experiments have been carried out on known fluoride solutions in order to determine the temperature corresponding to a definite amount of fluorine. In all cases the fluorine has been precipitated from 150 cc. of solution by means of barium acetate and potassium sulphate, as described above. In fact, up to the point of making the etching test, the procedure is exactly the same as in making a qualitative test.

The apparatus used for heating the crucible during the etching was a simple form of air-bath consisting of a large nickel or iron crucible provided with an asbestos cover in which two platinum crucibles are inserted at equal distances from the center. These two crucibles should be similar in size and shape. One crucible, as shown in the figure, is provided with a waxed plate and condenser, the other with an asbestos lid through which projects a thermometer reaching to the bottom. This control crucible contains 2–3 cc. of concentrated sulphuric acid. The heat is furnished by a burner centrally placed beneath the large crucible. After the apparatus is once adjusted and in working order it should be kept intact and undisturbed. The platinum crucibles should always occupy the same positions and it is necessary to determine, by means of two thermometers whose relative values are known, what temperature on the control thermometer corresponds to the desired temperature in the "etching crucible." This should be done for each of the "etching temperatures" stated below.

It will be realized that an apparatus so simple has its limitations, and in the work which has been done it has not been attempted to control the temperature closer than 5° on either side of the desired point.

As the result of numerous tests, the following temperatures

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[1] Ost: Ber. 26, 152.

have been fixed, the corresponding amounts of fluorine being stated in each case.

Temperature.	Distinguishes between.
79°-82°	1 : 25,000 and 1 : 100,000.
113°	1 : 100,000 and 1 : 1,000,000.
136°	1 : 1,000,000 and 1 : 5,000,000.
173°-178°	1 : 5,000,000 and 1 : 25,000,000.
213°-218°	1 : 25,000,000 or less.

This statement means that by running the test for an hour at 136° (131-141°), for example, a distinct etching will be obtained with one part of fluorine in 1,000,000; no test whatever will be given by a dilution of 1 : 5,000,000. Each of these temperature points has been fixed as the result of numerous tests with the apparatus described and they are believed to be definite. It is probable that by more closely regulating the temperature during the etching, the results could be made more nearly quantitative, but it was felt undesirable to attempt this at present on account of the necessary complication of apparatus.

In making a test on a solution containing an unknown amount of fluorine the precipitation is made in the usual manner and the etching carried on for an hour at the lowest temperature (79-82°), counting from the time when the corresponding temperature is reached in the control crucible. At the end of the hour the plate is removed, the crucible taken in the tongs, its upper edge gently warmed, and a fresh plate applied. If upon examining the plate just removed no etching is apparent, the test is continued for an hour at the next higher "etching temperature," and so on until a test is obtained or the absence of fluorides is shown. This has been done with a number of unknown solutions with very satisfactory results.

If it can be shown as a result of the examination of pure samples that the fluorine present naturally in a given food material is not above a certain maximum amount, then for the purpose of indicating the presence of added fluorides the test could be materially shortened, it being necessary to make the test at only one temperature. It is hoped to continue the investigation along this line in the future and to examine numerous samples of food and raw products with a view to determining the limiting values for their fluorine content.

In conclusion, it gives us much pleasure to record our indebtedness to Mrs. L. C. Krueger, to whom the credit for the analytical work is largely due.

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DETERMINATION OF URANIUM AND VANADIUM.

BY A. N. FINN.

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A STUDY of the ore carnotite; which is a potassium uranyl vanadate, repeatedly required the determination of uranium and vanadium. This led to a comparison of the various titration methods that have been suggested.

Bĕlohoubek[1] refers to the reduction of uranium in solution by zinc and sulphuric acid and titration with potassium permanganate. Sutton, in the sixth edition of his "Volumetric Analysis," states that this method is very accurate if care is taken to insure complete reduction which requires from one-quarter to one-half an hour.

Determinations of uranium by this method in solutions of uranyl sulphate gave very satisfactory results provided the potassium permanganate solution was not more than twentieth-normal. When, however, uranium is to be determined from a complex mixture or an ore, great difficulty is found in securing the uranium in a form sufficiently pure for the titration. This is especially true in the presence of vanadium.

The general method of separating the uranium and vanadium from each other and from the various other elements in the ore, is to treat an acid solution of the ore with an excess of sodium carbonate, which precipitates the iron, aluminum, etc., and filter. The filtrate containing the uranium and vanadium is acidified, the carbon dioxide expelled by boiling and the solution is made alkaline with sodium, potassium or ammonium hydroxide. This precipitates the uranium as the corresponding uranate, while the vanadium remains in solution. The uranate is dissolved in sulphuric acid, reduced with zinc and titrated with permanganate. The solution of vanadium is acidified, reduced with sulphur dioxide and titrated with permanganate.

The precipitated uranate is gelatinous and it was found impossible to wash this precipitate free from vanadium, and since

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[1] J. pr. Chem. 99, 231.