

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, COLLEGE OF THE CITY OF NEW YORK.]

A STUDY OF CERTAIN CONFIRMATORY TESTS FOR TIN.

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I. The Iron Nail Reduction Test Followed by Treatment with Mercuric Chloride.—This well-known test for tin, which consists in reducing the stannic chloride in acid solution with iron and subsequently treating the stannous chloride formed with mercuric chloride, was proposed by A. H. Allen in 1872.¹ It is mentioned in nearly every text-book on qualitative analysis. Despite its general use, nothing very definite appears to be known concerning the conditions under which this test may be relied upon to give constant results. The frequent failure of students to report this metal indicated the need for further investigation. It was therefore the object of this work to ascertain the best conditions for this test and also to determine its limit under these discovered conditions.

The standard solution employed throughout this work was prepared in the following manner: Ten grams of C. P. tin foil were treated in a 500 cc. Erlenmeyer flask with an excess of hydrochloric acid (sp. gr. 1.19) and solution was hastened by heating on a steam bath. The solution was saturated with chlorine to completely oxidize the tin to the stannic condition. It was then boiled for some time to expel the last traces of free chlorine as well as to reduce the quantity of hydrochloric acid present. After cooling, the solution was diluted to 500 cc. in a volumetric flask. A portion, thoroughly mixed, failed to react with a saturated mercuric chloride solution, showing that all the tin was completely oxidized.

To determine whether any stannic chloride had been lost by volatilization while the excess of chlorine was being boiled off, the solution was analyzed for tin by the method given by Treadwell.² Two well agreeing determinations made on twenty cc. portions of the solution gave as the average result 19.9 mg. Sn in one cc.

To determine the quantity of free hydrochloric acid in the solution, separate portions of it were titrated with standard potassium hydroxide solution, by the method described by Treadwell.³ The acidity was found to be 0.0063 gram of anhydrous hydrochloric acid per cc., which, in the diluted solutions used in the tests, was reduced to such an extent as to be neglected without any appreciable error.⁴

¹ *J. Chem. Soc. (London)*, 25, 274.

² Treadwell, "Quant. Anal.," trans. by W. T. Hall, pp. 243, 4, 5.

³ *Ibid.*, pp. 495, 60, 1.

⁴ Upon dilution to 1-1 the amount of free acid becomes 0.0031 g. per cc., which in consideration of the final acidity of the solutions employed in the tests, may be neglected without any appreciable error, particularly so, since the volume of the standard tin solution used never exceeded one cc.

This solution was not used directly, but one hundred cc. of it were diluted with an equal quantity of water, giving a solution of 9.95 mg. Sn in one cc. In nearly all the sets of experiments performed the largest volume used was 0.5 cc., equivalent to 4.97 mg. Sn. This is practically 5 mg. Sn and was so assumed in all experiments, for the reason that the error resulting from this assumption is too small to be detected by this test, as will be shown later. The smallest volume of this solution used was 0.1 cc. containing 0.995 mg. Sn, which for the reason stated above was considered one milligram. When smaller quantities of tin were required, a portion of the second solution was again diluted so that one cc. was equivalent to 0.1 mg. Sn. In this dilution it was found that hydrolysis took place very rapidly; to prevent this, a new solution of similar strength was prepared to which were added five cc. of conc. hydrochloric acid to every fifty cc.¹ This proved to be satisfactory.

The general procedure was as follows: To definite amounts of conc. hydrochloric acid pipetted into test tubes, were added varying quantities of a standard tin solution. After dilution to five cc. one or two nails were added, the tubes placed in a boiling water bath² and the reduction was allowed to continue for from two to five minutes; the contents of the test tubes were then immediately filtered into two cc. of saturated mercuric chloride solution. The filtrates were examined after five minutes and the results recorded. In all cases where less than one mg. of tin was used the results were controlled by one, two or even three blanks. This was necessary because it was found that under certain conditions a cloudy filtrate was obtained from the blanks. To determine whether this cloudiness in the blank was due to an interaction between a substance resulting from the action of the acid on the iron, and the mercuric chloride, the following experiments were performed. In separate test tubes, one, two and three 1½-inch cut nails were heated for five minutes with five cc. of hydrochloric acid (1-1) in the boiling water bath and the solution was then filtered into distilled water. The water in each case became slightly cloudy. The experiments were repeated except that the reaction product was filtered into mercuric chloride instead of distilled

¹ As the volume of this tin solution employed in any test never exceeded 0.5 cc., the quantity of additional acid was 0.05 cc. This amount when compared with the quantity added in any test is so small as to be neglected without any apparent difference in the result.

² The water bath employed throughout this work consisted of a 500 cc. beaker half filled with water and covered with a lead plate having six perforations large enough to accommodate the ordinary size of test tubes. The water was heated to boiling in each case before inserting the tubes and the boiling thereafter continued for the full time that the tubes were in the bath. This form of water bath was found very convenient in this work, since it enabled us to perform six tests at one time. The glass beaker was preferred to the usual copper bath, for the reason that the former permitted us to observe the progress of the reaction.

water. The same results were obtained, showing that the cloudiness was due to very fine particles of carbon which passed through the filter.

It was the object of the first experiments to determine the effect of heating for two minutes in the presence of a one-quarter inch brad in a volume of five cc. containing two cc. (1-1) HCl.

The results of sixteen experiments with diminishing amounts of tin under these conditions showed that with one mg. of tin the results were inconsistent, the final results of three tests being a fair cloud in the first case, a faint cloud in the second case and a practically negative result in the third. In two tests where two mg. of tin were used, the results were also discordant. Prolonging the time of heating as well as increasing the concentration of the acid did not give uniform results. It was, however, observed that in every series of experiments the reducing action in the water bath was not uniform. As the conditions in each set of experiments were kept constant, it appeared that the irregular results obtained were due to a lack of uniformity in the nails employed. To test this point, four blank tests were run under the conditions mentioned for the first tests, with one and one-quarter inch brads selected at random. The action in the water bath was decidedly not uniform. At the conclusion of three minutes the acid was poured off. The nails were then washed, treated with fresh acid and again subjected to the same test. This was done to see whether the first treatment had eliminated any differences which might be due to variations in the surfaces of the brads. The action of the acid during the second treatment was also not uniform. Finally, the brads were examined and it was found that the acid had so energetically attacked one of them that it was about one-half the diameter of any of the others. These results verified the conjecture that the inconsistencies in the previous tests were due to the variations in the iron nails which caused the stannic chloride to be reduced at different rates in the water bath.

The brads employed in these preliminary tests were therefore rejected and the previous experiment was repeated with one and one-half inch wire nails. The results were also found to be very irregular. Accordingly, one and one-half inch cut nails, or four-penny nails, were used. These gave uniform results and were employed in all further experiments, unless otherwise specified. The results of all further tests were classified as good or negative: good when they could readily be distinguished from the blanks run at the same time, negative in all other cases.

Having found nails to act with a fair degree of uniformity, it was the purpose of the next series of experiments to determine the separate and combined effects of the various factors which influence the delicacy of the test. These are: first, the acid concentration; second, the time of heating; and third, the number of nails employed. As a result of a

large number of experiments, the conditions which were most favorable for the test were found; these, together with the results obtained in the final tests, are given in the table below:

TABLE I.

Conditions: Time of heating, 3 min. Acidity, 2.5 cc. conc. HCl. Volume, 5 cc. One $1\frac{1}{2}$ inch cut nail.

Number.	Mg. Sn.	Result.
1-13	20.0-1.0	Good
14-18	0.5-0.3	"
19-26	0.2	"
27-29	0.1	Negative

Under the above conditions, the results show that the smallest quantity of tin which may be detected is 0.2 mg. in a volume of 5 cc. The blanks obtained were practically perfect and the results of the limit tests were very striking when compared with the blanks run at the same time. Under no circumstances could the results be mistaken.

To determine whether two nails would not give better results under the conditions of the last tests, another series of experiments was performed with the following results:

TABLE II.

Conditions same as those of Table I, except that two $1\frac{1}{2}$ inch cut nails were used instead of one.

Number.	Mg. Sn.	Result.
1-12	3.0-0.3	Good
13-14	0.1	Negative

The blanks in these tests were not as good as those obtained under the conditions as in Table I. The results therefore were not so striking and conclusive. The conditions for the test as given in Table I are therefore to be preferred.

As increasing the number of nails did not improve the test, it was thought worth while to see if prolonging the time of heating to five minutes would not give better results. To this end the following experiments were made:

TABLE III.

Conditions same as in Table I, except that the time of heating was increased to 5 minutes.

Number.	Mg. Sn.	Result.
1-14	3.0-0.3	Good
15-18	0.2-0.1	Negative

The above results show that extending the time to five minutes does not increase the sensitivity of the test.

Before concluding this work it was thought desirable to carry out one more set of experiments in which the conditions given in Table I were varied both as to the time of heating as well as to the number of nails employed. The results are embodied in the table below:

TABLE IV.

Conditions: Time of heating 5 min. Acidity, 2.5 cc. conc. HCl. Volume, 5 cc.
Two 1½ inch nails.

Number.	Mg. Sn.	Result.
1-13	0.1-0.2	Good
14-18	0.1	Negative

The results show that the sensitivity of the test under these conditions is greater than that given in Table III; the limiting test is, however, the same as that given in Table I. There is, however, an important difference in the quality of the blanks obtained under these different sets of conditions and correspondingly in the decisiveness of the results. The blanks obtained under the conditions of Table I are clearer and as a consequence the limit tests are more readily distinguished than those of Table IV. The conditions given in Table I are, therefore, to be recommended.

Influence of Antimony on the Test.—Having determined the best conditions for the iron-nail reduction test for tin when this metal alone is present, it was desirable to ascertain whether these conditions would hold good in the presence of antimony, for in most schemes of analysis the test for tin is made in the presence of antimony. Since the maximum amount of this metal in any given solution seldom exceeds 500 mg., and since it is customary to divide the solution containing antimony and tin into two equal portions before testing for each of these metals, 250 mg. of antimony¹ were employed in each of the following tests:

TABLE V.

Conditions: Time of heating, 3 min. Acidity, 2.5² cc. HCl. Volume, 5 cc.
One 1½ inch cut nail.

Number.	Mg. Sn.	Mg. Sb.	Result.
1-8	20.0-0.3	250	Good
9-12	0.2	250	Good

The above conditions are the same as those which afforded the maximum delicacy of the test when tin alone was present (see Table I).

To control the results of Table V, two sets of blanks were run: one of the usual kind containing neither antimony nor tin, and the other containing only antimony. The latter were perfectly clear and thus facilitated the detection of small quantities of tin; the former were practically clear and could readily be distinguished when compared with the tubes containing tin. Comparison of the tubes is best made by holding them at arm's length against a dark field such as the floor. The difference can then be very readily seen.

¹ The solution used was made by dissolving 18.8 grams SbCl₃ in HCl (1-1) and making the volume up to 100 cc. in a volumetric flask by the addition of more HCl (1-1). The strength of this solution was 100 mg. Sb. in one cc.

² The 1.25 cc. conc. HCl contributed by the antimony solution is included in this total of 2.5 cc.

All the blanks which might contain any unreduced antimony were largely diluted. No precipitate formed, indicating that even after reduction there was enough free acid present to keep the antimony in solution, thus obviating the danger of mistaking a precipitate of antimony oxychloride for the test for tin.

Summary and Conclusions.

1. That certain nails are unsuitable because of the irregularity of their action.

2. That in a total volume of 5 cc. with one $1\frac{1}{2}$ inch cut nail the best conditions are: time of heating, three minutes in boiling water bath; acidity, 2.5 cc. conc. HCl.

3. That under these conditions the smallest amount of tin that can be detected either alone or in the presence of 250 mg. of antimony is 0.2 mg. in a volume of 5 cc.

4. That it is imperative to run a blank when the quantity of tin present is small.

II. Instead of reducing the tin with an iron nail, some analysts prefer to reduce the tin to the metallic state by means of zinc in an acid solution and then test the solution of the precipitated tin in hydrochloric acid, with mercuric chloride. This test has recently been investigated by Noyes and Bray,¹ who found that it possesses a delicacy of 0.5 mg. Our experiments confirmed their work.

III. *The Test Based upon the Reduction of Ammonium Molybdate*—This test was first proposed by Longstaff,² who states that it is delicate to one part in 1,500,000 when directly applied to a freshly prepared stannous solution. In the application of this test to qualitative analysis Baskerville³ finds that it is easily sensitive to one part of tin in five thousand. As diligent search of the literature failed to disclose a record of systematic experiments performed to establish the conditions which would afford the greatest delicacy to the test when applied to stannic solutions as the starting point, the following work was undertaken. In our work, stannic solutions were exclusively employed, for the reason that it is in this form that tin is encountered in the course of systematic analysis.

The method of reducing the tin with an iron nail in acid solution was found inapplicable, because of the reducing action of the ferrous salt, formed in the reaction, upon the ammonium molybdate. Accordingly reduction by means of zinc was tried.

After a number of preliminary experiments the following procedure was finally adopted: To definite amounts of conc. hydrochloric acid run

¹ THIS JOURNAL, 29, 181.

² Chem. News, 80, 282.

³ J. Elisha Mitchell Scientific Society, 16, Part II, Feb., 1900.

into test tubes from a buret, varying quantities of standard stannic chloride solution were added and the volume was then made up to 5 cc. After the addition of a scant one-half gram of c. p. granular zinc,¹ the tubes were put into the boiling water bath and allowed to remain therein until the action practically ceased; another definite quantity of conc. hydrochloric acid was then added.² As soon as the second reaction was completed,³ the solution was diluted to ten cc. and immediately filtered into one cc. of saturated ammonium molybdate solution. The results were immediately compared with a blank run simultaneously.

In the following series of experiments the total quantity of acid used in the test was gradually reduced in order that the best conditions of acidity might be found. The results are given below:

TABLE I.

Total quantity of acid, 4 cc. Two cc. added each time.		
Number.	Mg. Sn.	Result.
1	1.0	Fair blue
2	0.2	Faint blue
3-4	0.1-0.05	Negative

TABLE II.

Total quantity of acid, 3 cc. Two cc. added first time. One cc. added second time.		
Number.	Mg. Sn.	Result.
1	0.1	Faint blue
2-4	0.05-0.03	Very faint blue
5-6	0.02-0.01	Negative

TABLE III.

Total quantity of acid, 2.5 cc. One and one-half cc. added first time. One cc. added second time.		
Number.	Mg. Sn.	Result.
1-2	0.1-0.05	Faint blue
3-6	0.04-0.01	Very faint blue

A comparison of the results of Tables I, II, and III shows that the conditions given in Table III are the best, since the test becomes delicate to one part in a million. The blanks obtained throughout the work were found to possess a slight greenish blue color which could readily be distinguished from the pure faint blue of the limit test.

¹ A very granular form of zinc reduced the time of the reaction by reason of its readiness to dissolve in the acid.

² In the above procedure the acid was added in two portions, the first to aid in the reduction of the tin by the zinc and the second to redissolve the spongy tin which separated out. This method gave a rapid solution of the tin. If instead of adding the acid in two portions as just described, the total quantity was added at the outset, it was found that the tin did not readily go into solution on further heating.

³ In a few of the many experiments tried, an intense blue coloration was obtained, which was out of proportion to the small quantity of tin present. These results were due to the presence of minute particles of metal which passed through the filter. Hence care must be exercised in filtering.

Influence of Antimony upon the Test.—Having determined the most favorable conditions for the test when tin alone is present, the next step was to ascertain the influence of the presence of antimony on the test under these conditions. For reasons given earlier in this paper, 250 mg. of antimony were used. The results follow:

TABLE IV.
Same conditions as in Table III.

Number.	Mg. Sn.	Mg. Sb.	Result.
1-4	1.0-0.4	250	Good blue
5-6	0.3-0.2	250	Fair blue
7-10	0.1-0.08	250	Faint blue
11-12	0.05	250	Very faint blue
13-16	0.04-0.02	250	Negative

The results show that the sensitivity of the test is lowered by the presence of large quantities of antimony and that under these conditions the limit is 0.05 mg. Sn.

Having found the test to work satisfactorily in the presence of the maximum amount of antimony, it was thought desirable to ascertain the influence of small quantities of this metal. The results of these tests showed that under the conditions given in Table III, 0.03 mg. of tin could be detected in the presence of 10 mg. of antimony, and that quantities of antimony up to 5 mg. are without influence on the test.

Longstaff states that an excess of acid vitiates the test by discharging the blue color, but supplies no experimental data on this point. As some preliminary work on our part had shown this statement to be true, it was thought worth while to run a series of experiments with the object of establishing definitely the influence of acidity on the test. In these experiments, the regular procedure already given was followed except that the quantity of acid added was varied in order to yield different acid concentrations after dilution to ten cc. The following results were obtained:

TABLE V.
Quantity of Sn, one mg.

Number.	Final acidity. Cc.	Results.
1	2.5	Dark blue
2	3.0	Lighter blue
3	3.5	Still lighter blue
4	4.0	Fair blue
5	4.5	Faint blue
6	5.0	Colorless or negative

The above results definitely show the influence of acidity on the delicacy of the test, and demonstrate the necessity for keeping the acidity within 4.5 cc. if a trustworthy test for one mg. of tin is desired.

Summary and Conclusions.

The investigation of the conditions under which the ammonium molybdate test for stannous tin might be applicable to stannic solutions after reduction by zinc, showed:

1. That with a total acidity of 2.5 cc. of conc. hydrochloric acid in a volume of 10 cc., the acid being added as directed, the test is delicate to 0.01 mg. Sn in the absence of antimony.
2. That in the presence of 250 mg. of antimony the test can be used to detect 0.05 mg. of tin.
3. That the presence of 5 mg. of antimony is without influence on the delicacy of the test.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

OBSERVATIONS ON THE RARE EARTHS.

YTTRIUM CHLORIDE AND THE ATOMIC WEIGHT OF YTTRIUM.

[PRELIMINARY PAPER.]¹

BY JAMES E. EGAN AND CLARENCE W. BALKE.

The results presented in this paper have been obtained in connection with a larger investigation upon the rare earths, which is being carried on in this laboratory.

Work is now in progress with material obtained from ten kilograms of gadolinite (from Norway), fifty-five kilograms of xenotime oxalate obtained from Drossbach & Company, Freiberg i. Saxony, fifteen kilograms of euxenite and ten kilograms of fergusonite, also large quantities of monazite residues furnished by the Welsbach Company, through the courtesy of Dr. H. S. Miner. The materials for the present work were obtained from the first two sources and the procedure for gadolinite and xenotime only will be given.

Ten kilograms of gadolinite were pulverized in a ball mill and then treated with an excess of concentrated hydrochloric acid with the addition of a little nitric acid from time to time. This was continued until decomposition was complete, and finally the mass was evaporated to dryness to dehydrate the silica. The residue was treated with water, the silica filtered off, and the rare earths precipitated from a slightly acid solution with oxalic acid. The oxalates were then washed by decantation.

Experience showed that the best and most rapid way to carry out an oxalic acid precipitation was to have both solutions hot. A small quantity of the acid was poured into the rare earth solution without stir-

¹ The work described in this paper furnished the basis for a thesis by Mr. Egan presented in partial fulfilment of the requirements for the Degree of Doctor of Philosophy at the University of Illinois.