(2) Large volumes of water can be used, thus reducing the error when computing to milligrams per liter.

(3) The results can be found to check and can be obtained much more quickly by having a residue free from an excess of sodium and potassium chlorides.

(4) The method involves the use of calcium hydrate instead of barium hydrate for the precipitation of magnesium. This procedure does not introduce another substance which has to be removed by ammonia and ammonium oxalate because we have our calcium in common and have a precipitate of calcium oxalate which is less soluble and more easily washed than barium oxalate.

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A NEW VOLUMETRIC METHOD FOR TIN.

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Numerous methods for the determination of tin have been tried out in this laboratory with various degrees of success. Gravimetric methods giving results of the required accuracy are too lengthy and tedious for ordinary use in laboratories where it is required to complete a large number of determinations in a short time. Shorter schemes, such as weighing the combined oxides of antimony and tin, determining antimony in a separate sample, and calculating tin by difference, cannot be used for alloys containing lead, copper, or numerous other metals which are to be found in some commercial alloys, unless the amount of these impurities contaminating the oxides be determined and taken into consideration.

The volumetric methods proved to be rather unsatisfactory, especially if the titrating solution was standardized against a standard reducing solution in preference to C. P. tin. The authors found that determinations on quantities as small as 5% were unreliable, and that on high percentages it was almost impossible to obtain consistently accurate results even if the oxidizing solution was standardized against an equivalent amount of metal treated in an exactly similar manner.

Endeavoring to overcome these difficulties, the following method was finally adopted. The results obtained are consistent and correct to within 0.2 per cent. on amounts of 50 per cent. or over and considerably more accurate on smaller percentages. As large percentages of copper, lead, nickel, and perhaps other metals not experimented with, interfere, it has been found expedient to modify the method somewhat in the presence of these elements. Both determinations will be described.

REGULAR METHOD.

The following scheme of analysis is available where no more than 5 per cent. of either lead or copper is present in the alloy. Where the percentages of these elements exceed this limit a modification of the method is necessary.

Place an amount of sample corresponding to 0.5 gram or less of tin in a 500 cc. Jena Erlenmeyer flask

and add 0.15 gram C. P. metallic antimony if as much or more is not already present in the alloy. If the sample contains less than this amount it is necessary to make up the deficiency. Add 10 cc. of concentrated sulphuric acid and heat to effect solution. Remove from the hot plate and cool. Dilute the cold sulphuric acid solution with 10 cc. of water, add 60 cc. of concentrated hydrochloric acid, and then 40 cc. more of water. Prepare a four-hole rubber stopper that fits the neck of the flask. Through one hole pass a glass tube bent at right angles reaching to the bottom of the flask and through the hole diagonally opposite insert another tube bent in a similar manner but extending only a short distance below the bottom of the stopper. Through the third hole pass a long thin glass rod fitted with a 2" piece of platinum wire. This rod should fit rather snugly without, however, giving any difficulty to the operator in raising or lowering it during the determination. The platinum wire is now bent into the shape of a hook and a piece of very nearly C. P. iron wire attached. Swedish iron in plates of $\frac{1}{8}$ " thickness cut

Volumetric Tin Apparatus

into strips of $\frac{1}{8}$ " in width and four inches in length, curled up in the form of a spiral, will suit the purpose well. Through the fourth hole pass a $\frac{1}{2}$ " tube 4" long and drawn out at the lower end to an opening small enough to enable the operator to introduce iodine solution in sufficiently small quantities to obtain the starch iodide reaction within one drop of titrating solution. The tapered end is bent slightly in the di-

rection of the submerged wire for the purpose of conducting a stream of water to free the iron from adhering tin solution after it has been withdrawn from the liquid. This delivery tube should also be provided with a $\frac{1}{4}$ " hole about $\frac{3}{4}$ " above the lower opening to afford a means of escape for the carbon dioxide gas which is being rapidly introduced during the titration. A carbon dioxide generator is connected to the long tube while a piece of rubber tubing connects the short tube opposite to a 100 cc. pipette which dips into a reservoir of water. This automatically prevents any air from entering the system when a partial vacuum is formed in the flask during the determination, which cannot be taken care of by the entering carbon dioxide gas. Having attached the iron to the platinum wire, the rubber stopper is firmly placed in position in the neck of the flask and the rod lowered so that the spiral of wire rests on the bottom of the flask. The generator and water seal are attached as previously described, a cap is placed over the opening of the large delivery tube and a rapid stream of carbon dioxide gas passed through the system. After a few minutes it may safely be assumed that all of the air is expelled from the flask, whereupon heat is applied and the contents permitted to boil for 25 minutes. The solution when first placed in the flask appears a deep yellow or orange, depending, of course, upon the constituents present, but shortly before commencing to boil it becomes colorless and finally black, due to the liberated metallic antimony. After the reduction is complete, remove the burner, plunge the flask into a large container of cold water and allow to remain until thoroughly cold. The iron wire is then raised to a position directly below the end of the delivery tube. The cap of this tube is then removed and with all possible haste a stream of cold *freshly boiled* water permitted to play upon the spiral to free it from any adhering tin solution, after which the wire is raised so that the titrating solution will not come in contact with it. Freshly prepared starch is added and, without interrupting the passage of gas, standard iodine solution introduced into the flask as fast as the burette will permit. When near the end point, which is indicated by the reluctant disappearance of the blue, the titration can be carried on very slowly until completed. The blue of the starch iodide is not permanent, disappearing after a minute or two, which fact does not, however, detract from the accuracy of the determination.

It is not to be understood that the tin is completely reduced by the direct action of the iron alone, neither will the addition of pulverized metallic antimony bring about the desired result. However, this metal as deposited is in a state where its chemical activity is at a maximum, thus enabling it to fully complete the reduction.

Standardize the sodium thiosulphate, which serves to determine the strength of the iodine solution, very carefully against a bichromate or permanganate solution of known strength. It is essential that the utmost accuracy be employed in the above standard-

ization, since 0.1 cc. more or less of a $N/10$ oxidizing solution makes a considerable difference in the ultimate tin value of the iodine. It has been found advisable in finding the normality of a freshly prepared iodine solution to check the theoretical standardization against C. P. tin.

MODIFIED METHOD.

A modified method is used when 5 per cent. or more of copper or lead, or any other interfering element, is present in the specimen to be analyzed.

Place 0.5 to 1 gram of sample in a small casserole and add if necessary 0.15 gram of antimony as in the regular method. Cover the sample with 8-10 cc. of concentrated nitric acid and evaporate to dryness. It is advisable in order to facilitate the subsequent filtration to bake strongly for about 15 minutes. Cool and add 20 cc. of 1-1 nitric acid, and, after breaking up the lumps with a stirring rod, filter and wash several times with hot water. If the baking has been conducted properly no traces of oxides will be discernible in the filtrate. The precipitate with the filter paper is then placed in a 500 cc. Jena Erlenmeyer flask and treated with 20 cc. of concentrated sulphuric acid and 2 grams of potassium sulphate. Place the flask on a piece of asbestos over a medium hot burner and heat carefully till the first violent reaction is over, after which the heat can be increased. Towards the end of the oxidizing operation, while the liquid is still black however from the free carbon present, the flask and contents should be cooled and the sides of the container washed down with a stream of water. The particles adhering so firmly to the wall of the flask that the water does not loosen them should be brought back into the main solution with the aid of a "policeman." The removal of the carbon should by no means be hastened by the addition of an oxidizing agent, since this will cause the antimony to assume the pentavalent form, which must be avoided. The addition of the water will now have a tendency to again cause frothing when the heat is applied, making it necessary to conduct this operation very carefully. From 2-2½ hours are usually required, depending upon the intensity of heat employed, to rid the solution completely of the carbon. Cool, introduce the required amount of water, but add only 45 cc. of hydrochloric acid instead of 60 cc. as in the regular method.

If very large percentages of antimony are present, enough to obscure the end point obtained with the starch solution, it is well to treat in the usual manner up to the point where the metallic antimony separates out. The solution should then be rapidly cooled, filtered with suction and washed with hot water. About 0.10 gram of metallic antimony, which has previously been dissolved in a few cc. of sulphuric acid, is then added, the solution returned to the original container, and the reduction continued. The concentration of the solution after this operation should not be changed to any great extent, the additional acid introduced off-setting in a large measure the water used for washing. Antimony present up to 25 per cent. will not obscure the end point, provided a good light and white background are available.

The accompanying table gives a few results obtained on mixtures containing various amounts of copper, lead and nickel as noted. These figures are fairly representative of the results which may be obtained by the methods described in the preceding pages.

Method.	Approximate amount.			Tin taken. Gram.	Tin found. Gram.	Error. Mg.
	Copper. Gram.	Lead. Gram.	Nickel. Gram.			
Regular.....	..	..	..	0.4040	0.4038	0.2
Regular.....	..	..	..	0.0568	0.0575	0.7
Regular.....	0.03	..	..	0.4470	0.4478	0.8
Regular.....	0.05	0.05	..	0.1143	0.1153	1.0
Modified.....	0.25	0.30	..	0.4060	0.4065	0.5
Modified.....	0.03	0.66	0.03	0.1764	0.1763	0.1
Modified.....	..	0.30	0.05	0.4272	0.4261	1.1
Modified.....	0.15	0.80	..	0.0216	0.0214	0.2
Modified.....	0.08	0.80	..	0.1000	0.1000	0.0
Modified.....	0.50	..	..	0.4530	0.4526	0.4

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A NEW APPARATUS FOR THE VOLUMETRIC DETERMINATION OF CARBON DIOXIDE.

By HOWARD W. BRUBAKER.

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In THIS JOURNAL for March, 1912, appeared an account, by L. T. Bowser, of a volumetric method for the determination of carbon dioxide. In this method the carbon dioxide is liberated and then absorbed in a solution of potassium hydroxide. This solution is washed into a 100 cc. graduated flask, water added to the mark and an aliquot titrated, using phenolphthalein as the indicator to the disappearance of the red color, then methyl orange, the second part of the titration indicating the amount of carbon dioxide in the solution.

The writer had occasion to try out the method to see whether it could be used by a class of comparatively inexperienced students of chemistry. As a result of a little experience with the method some objectionable features were found with the apparatus used by Mr. Bowser which make it impracticable for use by students. Probably the most objectionable feature is the necessity of washing out the potassium hydroxide from the tall absorbing cylinder into a measuring flask. This process requires skilled manipulation, especially since it is necessary to wash the cylinder thoroughly and yet keep the whole volume of liquid and wash water down to 100 cc., which seems advisable, in order that a sufficiently large fractional portion of the solution may be titrated without using a very large volume.

Another objection lies in the fact that at the end of the decomposition of the carbonate when an attempt is made to distil over some of the liquid, in order to drive the last portion of carbon dioxide into the absorbing cylinder, there is a tendency for the potassium hydroxide solution to suck back into the condensing apparatus. In order to overcome these objections and to make the method applicable for the use of inexperienced students the writer devised the apparatus shown in the accompanying figure.

B is a standardized Erlenmeyer flask holding 100 cc. when filled to the mark.

C is a 10 cc. pipette half filled with glass beads, having a coil of copper wire at the bottom to prevent any of the beads from becoming wedged into the tapering part of the tube.

Eight cc. of the potassium hydroxide solution (50 grams KOH in 100 cc. water) are placed in the flask B which is then connected with the condenser as shown in the figure.

One gram of the material to be analyzed is placed in the flask A with about 50 cc. of water. The hydrochloric acid is run in from the funnel, drop by drop, until sufficient has been added to decompose the sample.

The carbon dioxide distils into the flask B, forcing the potassium hydroxide solution up into the pipette until it stands near the top of the broad portion where the bubbles break. There is left a thin layer of potassium hydroxide covering the bottom of the flask. The carbon dioxide which is not absorbed by this layer of potassium hydroxide passes up through the liquid in the pipette and is completely absorbed. After adding the hydrochloric acid the liquid in the distilling flask is heated and finally boiled for five minutes, the steam condensing and falling into the flask B. As can be seen by the construction of the apparatus, there is no backing up of the potassium hydroxide solution into the condenser even when the flame is entirely removed. This boiling drives the residual carbon dioxide into the absorbing flask where it is completely absorbed. If there is any doubt

as to the last portion of carbon dioxide in the flask B having been absorbed, the flask is shaken for a minute or two after disconnecting it and while holding a finger over the opening of the glass tube.

After distilling steam over for five minutes the writer