

produced with the color shown by the doubled tubes. The slightest acidity or alkalinity of the citrate is at once shown by difference of tint; the test is very sensitive. The amount of acid or alkali needed to bring it right, can then be easily obtained by adding one-half normal sulphuric acid or ammonia; then by calculating to the five cc. taken, the necessary addition to the "stock" solution can be found and when made the solution re-tested with remainder of the colored water. The operation is very rapidly performed and the results surprisingly exact. Solutions so neutralized, when tested by Huston's method, have always been found exactly correct. The litmus solution should be prepared from the alcohol extracted litmus, as directed by Sutton.

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### THE COPPER ASSAY BY THE IODIDE METHOD.

BY ALBERT H. LOW.

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THE last edition of Dr. Peters' Modern Copper Smelting contains a description of the writer's modification of the copper assay by the iodide method. The following description of the same method embodies whatever changes have been deemed desirable up to date as the result of almost daily work upon copper ores and products. For the most accurate technical work I prefer it to all other methods. For practical work it exceeds the electrolytic method in accuracy, notwithstanding that the latter, when every precaution is taken, is perhaps theoretically more accurate.

#### COPPER ASSAY BY THE IODIDE METHOD.

Prepare a solution of sodium hyposulphite containing about nineteen grams of the pure crystals to the liter. Standardize as follows: Weigh accurately about 0.200 gram of pure copper foil and place in a flask of about 250 cc. capacity. Add five cc. of a mixture of equal volumes of strong nitric acid (1.42 sp. gr.) and water, and thoroughly boil off the red fumes,—a very essential point. Now remove from the lamp and add six to seven grams of crystallized zinc acetate, roughly weighed, and about fifteen cc. of water. Instead of adding the zinc acetate in this way, a cold saturated solution may be kept on hand and about twenty

cc. taken, the additional fifteen cc. of water being then unnecessary. Heat to boiling for a moment and then cool to ordinary temperature, and dilute to a bulk of about fifty cc. Now add about three grams of potassium iodide and shake it about gently until dissolved. Cuprous iodide will be precipitated and iodine liberated according to the following reaction:  $2(\text{Cu} \cdot 2\text{C}_2\text{H}_3\text{O}_2) + 4\text{KI} = \text{Cu}_2\text{I}_2 + 4(\text{K} \cdot \text{C}_2\text{H}_3\text{O}_2) + 2\text{I}$ . The free iodine colors the mixture brown. Titrate at once with the hyposulphite solution until the brown tinge has become weak and then add sufficient starch liquor to produce a marked blue coloration. Now continue the titration cautiously until the blue tinge has entirely vanished. When almost at the end allow a little time after the addition of each drop to avoid passing the point. One cc. of the hyposulphite solution will be found to correspond to about 0.005 gram of copper. In the assaying of ores, etc., when half a gram is taken, one cc. of the standard hyposulphite would then equal about one per cent. copper. The reaction between the hyposulphite and the iodine is:  $2(\text{Na}_2\text{S}_2\text{O}_3) + 2\text{I} = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$ . Sodium iodide and tetrathionate are formed. The starch liquor may be made by boiling about half a gram of starch with a little water and diluting with hot water to about 250 cc. It should be used cold and must be prepared frequently for regular work, as it does not keep very well. The hyposulphite solution made of the pure crystals and distilled water appears to be very stable, showing no appreciable variation at the end of a month, when kept under reasonable conditions.

#### TREATMENT OF ORES.

Treat half a gram of the ore in a flask of 250 cc. capacity with five or six cc. of strong nitric acid and boil gently nearly to dryness. Then add five cc. of strong hydrochloric acid and again boil. As soon as the incrustated matter has dissolved add five cc. of strong sulphuric acid and heat strongly, best by manipulating the flask in a holder over a small naked flame, until the more volatile acids are expelled and the fumes of the sulphuric acid are coming off freely. Allow to cool and then add twenty cc. of cold water and heat the mixture to boiling to thoroughly dissolve any anhydrous sulphates of iron, etc. Now

filter to remove more especially any lead sulphate and receive the filtrate in a beaker about two and one-half inches in diameter. Wash the flask and filter with hot water and endeavor to keep the volume of the filtrate down to about fifty or sixty cc. Place in the beaker two pieces of sheet aluminum, which, for the sake of convenience in subsequent washing, may be prepared as follows: Stout sheet aluminum, say about one-sixteenth of an inch in thickness, is cut into pieces an inch and a half square, and then the four corners are bent, for about a quarter of an inch, alternately up and down at right angles. This scheme prevents the pieces from lying flat against each other or upon the bottom of the beaker, and their washing is thus facilitated. The same pieces of aluminum may be used repeatedly, as they are but little attacked each time. Add five cc. of strong sulphuric acid, cover the beaker and heat to boiling. Boil strongly for about seven minutes. Unless the bulk of the solution is excessive this will be quite sufficient with all percentages of copper. Ordinarily the aluminum will be found to be clean and nearly or quite free from precipitated copper. If, by chance, the copper adheres to any considerable extent, it will usually become loosened by a little additional boiling, or it may be removed by the aid of a glass rod. Transfer the solution back to the original flask, and, by means of a wash bottle of hot water, rinse in also as much of the copper as possible, leaving the aluminum behind. Drain the beaker as completely as possible and temporarily set it aside with the aluminum which may still retain a little copper. Allow the copper in the flask to settle and then decant the liquid through a filter. Again wash the copper similarly two or three times with a little hot water, retaining it as completely as possible in the flask. Finally wash the filter once or twice and endeavor to rinse all metallic particles down into the point. Now pour upon the aluminum in the beaker five cc. of a mixture of equal volumes of strong nitric acid (1.42 sp. gr.) and water and warm the beaker gently, but do not heat to boiling, as the aluminum would be thereby unnecessarily attacked. See that any copper present is dissolved and pour the warm solution through the filter last used, thus dissolving any contained particles of copper, and receive the filtrate in the flask containing the main

portion of the copper. At this stage do not wash either the aluminum or the filter, but simply remove the flask and set the beaker in its place. Heat the mixture in the flask to boiling and see that all the copper is dissolved. Then add about half a gram of potassium chlorate and again boil for a moment. This is to oxidize any arsenic present to arsenic acid and is a very important point. Remove the flask from the lamp and again place it under the funnel and wash the beaker, aluminum and filter with as little hot water as possible. Again boil sufficiently to remove every trace of red fumes. All the copper is now in the flask as nitrate. Add the zinc acetate and proceed from this point precisely as described with the original nitrate of copper solution in the standardization of the hyposulphite, finally calculating the percentage of copper present from the amount of standard hyposulphite required. One point, however, remains to be further explained. According to the equation previously given, half a gram of pure copper requires 2.62 grams of potassium iodide. While direct experiment shows this to be apparently true, yet it is found that with small percentages of copper, the reaction, when only the theoretical amount of potassium iodide is taken, is slow and in fact does not appear to proceed to completion until during the titration, which is thereby unduly prolonged. It is therefore best to use not less than three grams of potassium iodide in any case. An excess does no harm. Silver does not interfere with the method. Lead and bismuth are without effect, except that by forming yellowish iodides they may mask the end-point before adding starch. Lead is practically removed as sulphate at a previous stage. If bismuth is suspected in any appreciable amount, simply add the starch earlier in the titration. Arsenic when oxidized as described has no influence. The return of the blue tinge in the liquid by long standing after titration is of no significance, but a quick return of the color, which an additional drop or two of the hyposulphite does not permanently destroy, may indicate either an incomplete combination of all the nitric acid with zinc, or a failure to completely boil off the red fumes when dissolving the copper in nitric acid. The assay in such a case is spoiled. This trouble may be avoided by carefully following the directions

given and not guessing at strengths or quantities. The amount of zinc acetate recommended is a safe excess. Sodium acetate does not appear to work as satisfactorily.

For the assay of alloys, etc., the necessary modifications of the foregoing scheme are obvious.

The foregoing scheme directs the use of five cc. of dilute nitric acid for dissolving the copper previous to titration and prescribes six to seven grams, or about twenty cc. of a saturated solution of zinc acetate as a safe excess of neutralizing agent. It is obvious that if most of the nitric acid be boiled away the amount of zinc salt necessary is greatly reduced. In such a case, however, it is perhaps best, for safety's sake, not to use less than one-half the prescribed quantity. Half the zinc salt may thus be saved at the expense of a little more time. This is the ordinary practice in my own laboratory.

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## ON TWO SOURCES OF ERROR IN SUGAR HOUSE ANALYSES.

BY EDMUND C. SHOREY.

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**I**NCIDENTAL to the study of the action of water of different temperatures on bagasse, I have had occasion to make some determinations which throw some light on a source of error in fiber determinations.

Finely cut cane was washed with cold water until the polariscope reading in a twenty cm. tube was 0; the excess of water squeezed out in a press, and three portions of fifty grams each taken. In one the moisture was determined by drying to constant weight in an air bath at 105° C.; the two others were treated with boiling water; one for five minutes and the other for two hours. The quantity of water used was in each case just sufficient to cover the cane chips, and at the expiration of the time the water and the chips were poured on a filter and washed four times with cold water, using each time the same quantity of wash water as was used in the original treatment. The filtrate so obtained was evaporated to dryness over a water-bath, dried at 105° C., and calculated to percentage of dry sub-