

## THE ELECTROLYTIC ASSAY OF COPPER CONTAINING ARSENIC, ANTIMONY, SELENIUM, AND TELLURIUM.

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THE percentage of the principal metal in matte, pig, anodes and refined copper is determined in technical laboratories either by titration or electrolysis, and the methods should be suited to the character of the material treated. Although a quick titration may be preferred for low-grade ores and mattes, it does not permit as close work, according to the writer's experience, on 99 to 100 per cent. copper. The margin of difference between the standard and sample is too narrow, and possible errors in titration are too large to permit results accurate within a limit of error of 0.05 per cent. on "converter" or 0.01 per cent. on "refined" copper.

The complete deposition of copper may be proved by testing 1 cc. of the copper solution with hydrogen sulphide water on a porcelain tile.

0.005 mg. of dissolved metal in 1 cc. will impart a distinct brown tint and electrolysis is thus theoretically and practically an *absolute* method, yielding the total metal in metallic form for exact weight.

The impurities commence to deposit generally after some hours, when the solution has become colorless, while the deposition of the last traces of copper, particularly from the solution of a 5-gram sample, is not complete for several hours, until some hydrogen is evolved from the cathode and most of the free nitric acid present has been converted to ammonium sulphate.

From this fact the old, oft quoted test, which directs that the dish or beaker shall be filled up a little and the color of the upper portion of the plate noted after a short interval, must be condemned as not accurate, at least for concentrated solutions.

If the electrolytic assay can be made applicable to impure copper, it will permit closer agreement and more absolute work, if accuracy is desired rather than saving of time.

A. H. Low<sup>1</sup> devised a method for the volatilization of arsenic only, from ores by means of a solution of sulphur in bromine.

<sup>1</sup> Peters' "Copper Smelting," 7th edition, p. 52.

The writer<sup>1</sup> succeeded in removing antimony with the same reagent, applied to the chlorides, and by subjecting the residue to a high heat. The operation is too tedious and offensive to be practical.

It is very unfortunate that the many experimenters on electrolytic separations have taken such small quantities for their published researches. In practical technical work the necessity of securing a fair sample makes the selection of at least 0.5 gram of matte and generally from 1 to 5 grams of copper an imperative necessity.

Duplicate 5-gram samples of refined metal ought to check within 0.02 per cent., and the allowable error in the weighing alone may be assumed as 0.01 per cent., and 0.0001 gram on the scales.

In theory this requires a sample of 5 grams to permit work within the above specific limits of error.

E. F. Smith<sup>2</sup> describes a method for the electrolysis of arsenical copper in ammoniacal solution. The principle has been variously modified by Smith, Oettel, Rüdorff and McCay.

The writer will describe another modification and three original methods, devised in order to adapt the principle of electrolysis to any class of copper produced by refineries.

The beaker is 5.4 cm. ( $2\frac{1}{8}$  inches) in diameter and about 12.7 cm. (5 inches) high, and is always kept covered with split glasses to prevent loss by spattering.<sup>3</sup> The writer always deposits the silver with the copper. Before weighing a sample of drillings a strong magnet should always be passed carefully through the drillings to remove iron.

Annoying discrepancies between chemists may have been partly due to neglect of this precaution.

#### METHOD I.

*Details.*—The following process is adapted to the assay of metal containing arsenic and antimony, but less than 0.01 per cent. of nickel plus cobalt plus zinc, which would be at least partially deposited.

Dissolve 5 grams of refined metal (or 1 gram of low-grade material) in 20 cc. of strong chemically pure nitric acid (or

<sup>1</sup> *Trans. A. I. M. E.*, 27, 962, 978 (1899).

<sup>2</sup> "Electrochemical Analysis," edition 1890, page 93.

<sup>3</sup> All directions apply to assays made with a long-stemmed cylindrical cathode, made by bending a sheet, 5 cm. (2 inches) high and 10 cm. (or 4 inches) wide, into a cylindrical form, and for calculation of current density both sides of plate are included.

10 cc. for 1 gram copper) and evaporate at a gentle heat with 10 cc. concentrated sulphuric acid until the residue is white and smells sweet, or free from nitric acid. Dissolve in 70 cc. of distilled water, add 1 cc. nitric acid and just sufficient excess of ammonia to redissolve the basic copper and form a clear alkaline solution. Cover the beaker and electrolyze. As soon as the solution is colorless, wash down covers and sides of the beaker with a fine jet. When the cathode commences to show bubbles of hydrogen, remove 1 cc. of solution with a medicine dropper to a porcelain tile and test, first acidifying with a drop of dilute sulphuric acid. The time may be much shortened by the employment of a very high initial voltage, 3.8, and amperage,  $N.D._{100} = 2.5$ , for about six hours, or until the solution takes a paler purple color and the copper starts to rapidly deposit. Then lower current gradually to  $N.D._{100} = 0.35$ ;  $V = 2.5$ .<sup>1</sup> The check results given are on a copper (A) containing 0.260 per cent. of arsenic and traces of antimony and show the agreement which can be obtained in spite of the segregation of impurities possible in such material: 99.63 per cent.; 99.64 per cent.; copper (+ silver). Time, sixteen to eighteen hours.

The chemists of the International Nickel Co. are understood to have proved that the platinum anode spirals will not be appreciably attacked by ammonia if old, very soft, and pure wires are selected.

#### METHOD II.

This method may be used for copper containing only traces of antimony and less than 0.02 per cent. arsenic, but large amounts of selenium or tellurium.

Dissolve the sample of copper in nitric acid, as previously directed, and evaporate with 6 cc. of sulphuric acid until the residue is white. Dissolve in 60 cc. of water and wash into a lipped beaker, placing the first beaker under a funnel fitted with a 3 cm. filter. Heat solution nearly to boiling and saturate with a current of sulphur dioxide for ten minutes. The gas must be free from chlorine, generated from refined copper and pure sulphuric acid. Settle over night, filter into the original beaker and wash with a

<sup>1</sup> A peculiar condition is produced by the passage of a strong current for several hours through a saturated ammoniacal copper solution.

The copper will not deposit to any extent until the metal is apparently reduced to a colloidal condition or metallic solution.

At this stage, if the solution is acidified with sulphuric acid, a heavy precipitate of red, metallic copper is immediately thrown down.

little hot water. Boil off the sulphurous acid. Ignite the filter in a porcelain crucible to a red heat, redissolve the residue in 1.5 cc. nitric acid, wash into the copper solution and electrolyze. Have the final volume of the solution sufficient to cover the electrode—about 120 cc. Current N.D.<sub>100</sub>, 0.3 to 0.4 ampere; voltage, 2.2; time, thirty hours; results are accurate; check samples (B) of a seleniferous pig copper assayed 99.78 and 99.79. A sample of only 1 gram will evidently require much less time for electrolysis.

## METHOD III.

*For Metal Carrying Over 0.01 Per Cent. Antimony and Other Elements.*—The details of this method were worked out by Mr. A. W. Senter and involve more personal manipulation, but will accomplish the removal of much antimony in addition to the other impurities.

Dissolve the copper and evaporate with sulphuric acid as usual. Redissolve in 70 cc. water and add a measured quantity of a solution of pure nitrate of iron (1 cc. = 0.01 gram of metallic iron). For 1 gram of copper use 1 cc. ferric nitrate, or 3 cc. for 5 grams of metal. Wash into a lipped beaker and place original beaker under a funnel, fitted with a small paper filter. Precipitate the iron from the hot solution with ammonia, filter and wash out salts. Place the solution on a hot plate to concentrate, reprecipitate iron from dilute sulphuric acid solution, preserving the filtrate, dissolve the iron again and pass hydrogen sulphide gas. Filter on the same filter, extract with a very little hot, dilute sodium sulphide, pouring it back and forth through the filter. Ignite filter and contents in a porcelain crucible, redissolve in 1.5 cc. of strong nitric acid and add to the main solution, which has been acidified with sulphuric acid and diluted, or concentrated, to the proper final volume. Results: Sample (A), 99.64; sample (B), 99.78. Current N.D.<sub>100</sub>, 0.35 to 0.45 ampere. Voltage, 2.2 to 2.4. Time, about thirty hours for 5 grams of metal.

## METHOD IV.

The principle of this has just been discovered as the result of various experiments to find a salt which would prevent deposition of arsenic and antimony.

It is rapid and accurate in its proper field and peculiarly adapted

to several commercial brands of copper containing much arsenic, but not over 0.005 or, at most, 0.01 per cent. of antimony. In the latter case, to avoid contamination of the large cathode, the last traces of copper had better be taken out with a narrow 1 inch cathode, if antimony commences to show on the copper. If much selenium or tellurium are present with the excessive arsenic, remove them first by Method II. Dissolve 5 grams of copper in nitric acid, dilute to 50 cc., and add only 3 cc. of concentrated sulphuric acid. Add ammonia until a slight permanent precipitate forms and redissolve this by exactly 1 cc. of sulphuric acid (sp. gr. 1.84) to prevent deposition of nickel or zinc. Now stir in dry, powdered, chemically pure ammonium nitrate (free from traces of chlorine) until the solution is thoroughly saturated and a little remains undissolved. Electrolyze with a current  $N.D._{100} = 0.7$  ampere, and 2.7 to 2.8 volts for twelve hours, then reduce to 0.5 ampere. The total time for a 5-gram sample is about thirty hours. Test as usual with hydrogen sulphide water. Any trace of copper will show at once; arsenic a little later. Results: Sample (A), 99.64 per cent. In presence of 0.1 per cent. antimony, black plate, 99.88 per cent.

After removing the large cathode, test the solution with a small cathode, if the end-point is doubtful. If the solution is too acid, the copper will not deposit properly, but a trace of free acid is necessary.

Less time and chemicals should be allowed for in any of these methods, if only 1 gram of copper is taken for the assay.

One or the other of the plans devised may be selected so as to permit accurate control work with any brand of metallic copper.

HUBBELL, MICHIGAN.

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## RESULTS OBTAINED IN ELECTROCHEMICAL ANALYSIS BY THE USE OF A MERCURY CATHODE.<sup>1</sup>

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IT HAS been clearly demonstrated in recent years<sup>2</sup> that valuable

<sup>1</sup> From the author's thesis for the Ph.D. degree.

<sup>2</sup> Gibbs: *Chem. News*, **42**, 291; Gibbs: *Am. Chem. J.*, **13**, 571; Luckow: *Ztschr. anal. Chem.*, **25**, 113; Vortmann: *Ber. d. chem. Ges.*, **24**, 2749; Drown and McKenna: *J. Anal. Chem.*, **5**, 627; Smith: This Journal, **25**, 883; Coehn and Kettenbeil: *Ztschr. anorg. Chem.*, **38**, 198; Kettenbeil: *Ztschr. anorg. Chem.*, **38**, 213.