there is more than one root, as I have already intimated, and then to apply the appropriate remedies.

It is most important that the educators of future generations of chemists ponder these matters and endeavor to devise ways for improvement, if not by concerted action, then by the efforts of single colleges.

WASHINGTON, D. C.

METHODS FOR THE COMPLETE ANALYSIS OF REFINED COPPER.

BY GEORGE L. HEATH.

Received December 29, 1904.

In 1894 Dr. H. F. Kellar[1] presented a paper on the analysis of copper as practised by him at that time, and similar condensed accounts on Montana methods appeared from the pen of Titus Ulke,[2] in 1899. In response to invitation, the writer will present the principal methods now employed in large technical laboratories, giving preference to those which are personally believed to be most delicate and accurate, condensing the account by references wherever possible.

Great accuracy, both in sampling and in chemical manipulation, is especially necessary in the case of copper on account of the precious metals it frequently contains, and on account of the marked effect which traces, even, of some impurities, have on its physical properties, and because of the liability of those impurities to segregation on cooling from a fluid to a solid state.

No technical chemist would now go through the tedious extraction of vast quantities of sulphide of copper as originally proposed by Fresenius. The present tendency is to take separate samples for the estimation of each group of foreign elements by some special method of isolation. Analytical results are usually carried out to 0.0001 per cent.

SAMPLING.

When copper is to be assayed for gold and silver, the material should be sampled direct from the molten furnace charges after thoroughly mixing and agitating the bath by the refining process.

A thin square plate, 6 x 6 x ½ inches, to represent the lot, is carefully poured from a full ladle. The size might be increased to 9 x 9 x ¾ inches for very rich material. A set of five ($^5/_{16}$ inch) holes, drilled through the half-inch plate, will furnish an assay-ton (29 grams) sample for assay for silver and gold. The drillings from one hole of ¼ inch diameter will give one sample for electrolytic copper assay. Duplicates are generally taken.

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[1] *J. Frank. Inst.*, July, 1894; this Journal, 16, 784 (1894).

[2] *Eng. Min. J.*, 68, 727 (1899); "Mineral Industry," 1901, pp, 223 *et seq.*

The holes should be bored at a distance from the edges of at least three times the thickness of the plate.

Edward Keller's[1] admirable research fully explained the principles of sampling in detail and proves the foregoing to be the rational method of procedure. Commercial reasons, however, make it necessary for custom works to sample an immense amount of western metal in the form of pigs, slabs and anodes. These are sampled by drilling holes in sample castings from each car-load, according to some fixed mathematical routine, established at each plant. Sometimes a set of five bars are taken and one hole drilled half way through each, but in different positions. The bars are then turned bottom up and drilled half way through again so as to bring the holes "staggering," or in reverse order.

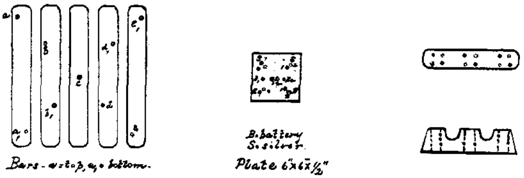

Fig. 1.

In some refineries templets of sheet-metal are made to fit each size of casting received. These templet plates are perforated with uniform rows of numbered holes, which are used, one on each pig, in a fixed system of rotation to secure a good average sample of a car-load in spite of the marked segregation of precious metals in any individual casting of the copper.

When refined cakes or bars for rolling are to be tested, it is the purity of the clean metal itself that is required, and the surface oxides should be accordingly removed before drilling.

In the case of ingots which are to be placed directly in the pots at the brass foundry, the fairest way to sample a lot, is to bore, in each of two or three sample ingots, six holes ($^5/_{16}$ inch diameter) half way through from the top and then half way from the bottom, including the surface oxides, and let the mixed drillings constitute the sample. This would not hold exactly true, however, in the case of very deep, wedge-shaped ingots in which the greater part of the weight is contained in the upper half of the vertical section.

The following tests are now made upon the finished metal at all large refineries and foundries: I. Mechanical, II. Electrical, III. Chemical. The first two are described in a paper presented to the Lake Superior Mining Institute,[2] and the third, only, is considered here.

Practical men often object to the small scale of laboratory re-

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[1] *Trans. A. I. M. E.*, **27**, 106 (1897).

[2] Proc. Lake Superior Mining Inst., **7**, 68–82 (1901).

SPECIFIC GRAVITY OF COPPER.

Name of specimen.	Specific gravity at 60 F. (15.5° C.).	Specific gravity at 15.5° C. referred to water at 4° C.
Quincy mine, native mass copper 0.015 per cent. silver, solid bar planed 2 x 2 x 8 inches	8.93	8.922
Wire (0.104 inch diameter) from same—annealed.[1] A button from same native mass[2]—melted in charcoal cup. This oxidized button drawn into wire and annealed[3].........	8.925[1] 8.950[2] 8.950[3]	8.917 8.942 8.942
Pure cathode copper (Lake Superior) direct from vats, sheet drawn into wire and annealed—somewhat porous........	8.890 8.900	8.887
"Lake"-cast metal from furnaces; each test is from a separate lot of refined ingot or bar. This metal contains 10 to 12 ounces of silver per ton, but only traces of impurities.........	8.67 8.66 8.657 8.67 8.674 8.638 8.648 8.618	
Average,	8.654	8.646
Cast copper—low set—contains more Cu$_2$O........	8.543	8.535
Annealed wire from the same refined cast metal........	8.916 8.895 8.898 8.903 8.900	8.892
Deoxidized metal produced by melting the refined "Lake" copper in a covered charcoal cup and cooling under the charcoal........	8.950	8.942

searches. A valid objection can be made to some of the figures taken as standards for the strength, ductility, electrical resistance and specific gravity of copper. The values, were in most cases, deduced from experiments with copper remelted and cast from crucibles. Commercial copper, melted under charcoal, is nearly deoxidized by the charcoal and does not crystallize like that refined in reverberatory furnaces.

To eliminate this objection, some determinations of specific gravity were made from the native mass copper, the refined product (both cast and rolled) and metal remelted in contact with charcoal.

Copper, deoxidized by melting and cooling under charcoal in a charcoal cup, compares, not only in density, but in the large size of its crystals, as revealed by the microphotograph, with the native mass copper direct from the mines.

ASSAY OF GOLD AND SILVER.

At the suggestion of Dr. Le Doux[1] the "wet" and "all-fire" methods were discussed by several assayers in the *Trans. A. I. M. E.* for 1894. A later account of the work at the Mint was given by Whitehead and Ulke.[2] Ulke described the "all-fire" method in the same form in which the writer employs it. Ten samples of 0.1 assay ton are each scorified with 50 grams of lead, and the assays are finally combined into two for final cupellation. Assayers agree that the results are a little higher in gold than by the combination method, which is too well known, also, to need explanation. With any copper fairly free from silica and sulphur much time and chance for error may be saved by cupelling the gold and silver chloride directly without scorification. The details will be found in another paper.[3] This short-cut method is in regular use in at least three American refineries.

Estimation of Pure Metallic Copper in Commercial Metal.—The principle of electrolysis is the only one to be depended upon. In the titration methods, usually employed for low-grade material, the margin of difference in the case of refined copper between standard and sample is too small, and the liability to appreciable error is too great to permit as exact work as the battery assay. For the electrolytic assay, 4 to 5 grams of metal is the least quanity which will theoretically produce results accurate within a limit of error of 0.01 per cent.

A strong magnet should always be passed through the drillings before weighing. Neglect of this precaution has probably been the cause of some discrepancies in the results of different laboratories.

The electric current for the work can be very easily furnished, where a direct current system is used for electric lights, by re-

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[1] *Trans. A. I. M. E.*, 1894, 250.

[2] *Eng. Min. J.*, February, 1898, pp. 189, 223, 250.

[3] *Trans. A. I. M. E.*, **31**, 484 (1901).

ducing the current with a bank of incandescent lamps. All the lamps are placed parallel with each other, but the whole bank is in series with the electrolytic assays. Where a continuous day current is not available, two sets of storage cells are very convenient, with disk rheostats for regulation.

In other papers[1] by the writer, a full description is given of the assay of pure metal and of copper containing arsenic, antimony, selenium and tellurium. Copper will deposit better from a solution of dilute sulphuric acid with a little nitric acid than from either acid alone.

In the account of a process recently devised for the direct electrolysis of copper, containing traces of antimony, and a heavy percentage of arsenic, the saturation of the solution with nitrate of ammonia was recommended. I now find it more convenient to prepare a saturated stock solution of this salt and to proceed as follows: To the solution of 5 grams of the arsenical copper in 20 cc. of nitric acid add 50 cc. of the saturated solution of ammonium nitrate, neutralize the copper solution with ammonia till slightly basic and then add 1.0 cc. of strong sulphuric acid, or enough to make the liquid slightly acid. Fill up with the ammonium nitrate solution until the body of the cylindrical platinum electrode is just covered. Loss from spattering is prevented by split watch-glasses. Current, $N.D_{100} = 0.7$ ampere, counting both sides of the cathode. As soon as the solution becomes colorless wash down the cover and the walls of the beaker with a fine jet, and reduce the current to 0.5 ampere. $N.D_{100} =$ the density in amperes per square centimeter of cathode surface.

The waste solutions can be preserved and the ammonium nitrate recovered by treating the neutralized solution with hydrogen sulphide, evaporating to a jelly and re-solution.

Oxygen.—The estimation of oxygen by solution of the copper in neutral nitrate of silver is an uncertain reaction. The well-known German authority, Dr. Hampe,[2] has developed the most accurate method, that of ignition of the finely divided material in a current of dry, pure hydrogen gas, and the determination of the resulting loss of weight of the metal. Archbutt,[3] Hofmann,[4] and others have somewhat shortened and improved the process, doing away with a preliminary heating or drying in carbonic acid gas.

According to personal experience, however, the apparent loss of weight is not all oxygen, and must be corrected for any arsenic or sulphur driven off. Any oil is removed from the copper filings (or very fine chips) with pure petroleum ether (completely volatile below 60° C.), or according to Archbutt with ethyl ether. The metal is then carefully dried and transferred to a dried

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[1] *Trans. A. I. M. E.*, **27**, 390 and 962–970 (1897); This Journal, **26**, 1120 (1904).

[2] Fresenius: "Quantitative Analysis," B. II, p. 519; *Ztschr. anal. Chem.*, **13**, 202.

[3] *Analyst*, **25**, 253 (1900).

[4] *Trans. A. I. M. E.*, **34**, October, 1904.

and weighed bulb tube, or to a porcelain crucible, to be enclosed within a Shimer combustion apparatus.

The newer form of apparatus, made by E. H. Sargent & Co., Chicago, is even more convenient for a quick approximate ignition, as the crucible is flanged and clamped, and can be withdrawn without disturbing the tube connections. The air is first driven out by a current of hydrogen, then the bulb tube is heated to a red heat with a flat-flame Bunsen burner for one hour, and cooled in the current of hydrogen. The hydrogen is finally replaced by dry air and the tube weighed. The writer absorbs the hydrogen sulphide evolved in an ammoniacal solution of cadmium salt and weighs the cadmium sulphide formed.

Chemists differ somewhat in the means they employ for the purification of the hydrogen gas. As investigators on atomic weights have recently observed, strong sulphuric acid should not be used as a drying agent, since hydrogen has a slight reducing action upon it.

It is best to purify the gases in separate trains of tubes as follows: Air train— (1) elevated pressure bottle; (2) concentrated sulphuric acid tube; (3) potassium hydroxide solution in absorption bulbs; (4) long, gently-inclined tube of concentrated sulphuric acid. Hydrogen train—(1) automatic generator; (2) Liebig tube with saturated solution of mercuric chloride to remove hydrocarbons; (3) Potassium hydroxide bulbs; (4) bottle of silver nitrate; (5) large tube filled with fused stick potassium hydroxide cut into small pieces; (6) drying tube of fused, granulated calcium chloride. The air and gas "trains" are led to one three-way glass stop-cock so that a positive pressure is always maintained at this point (see Fig. 2).

Beyond the ignition tube is a small bent tube for the partial condensation of water, etc., and another three-way stop-cock. One tube from the stop-cock leads to a calcium chloride drying tube and hydrogen jet, the other to the bottle of cadmium solution. The objection to the employment of a crucible apparatus, instead of the less convenient bulb tube, lies in the difficulty of saving any volatilized arsenic, lead oxide, or sulphur.

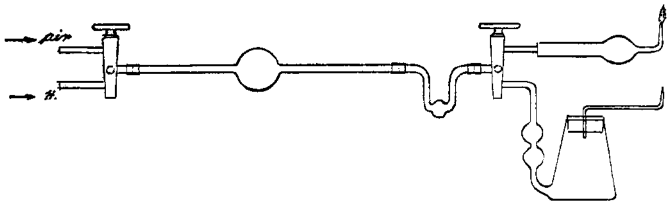

Fig. 2.

Sulphur.—The completeness of removal of this harmful element from the copper of commerce depends on the care with which the final rabbling and poling process is carried out. The best refined copper contains hardly a trace. It is perhaps not sufficiently understood, or appreciated, that hot copper absorbs both oxygen and sulphurous gases with great avidity when considerably below the melting-point in the annealing furnace.

The only rapid and exact method for the estimation of traces of sulphur in the refined product which has appeared in print is one presented by the writer to the Society in 1895.[1] This depends on the removal of the copper from its solution in pure nitric acid by electrolysis. The solution, freed from copper, is gradually transferred to a No. 3A casserole and evaporated to dryness over an alcohol flame with the addition of a little sodium carbonate to retain the sulphuric acid. The remaining nitric acid is removed by two evaporations with hydrochloric acid. If any lead sulphate is found on the filters, they are boiled with a little sodium carbonate to render the sulphuric acid soluble, and ready for precipitation by barium chloride. A blank analysis must be performed with the acids and distilled water, which will show usually about 1 mg. of barium sulphate. When the copper contains much sulphur it is necessary to use aqua regia for its solution, and remove the hydrochloric acid by subsequent evaporation with nitric acid.

Other Foreign Metals in Copper.—In the determination of metallic impurities we find, among chemists, considerable divergence of methods.

When a complete analysis is to be made, the filtrate from the 50-gram assay for gold may be taken for the determination of the arsenic, antimony and tin group, or for selenium and tellurium. Technical chemists, as far as I know, employ some modification of Dr. Hampe's[2] original processes for the separation of the bulk of the copper when a complete test is to be made. As routine refinery tests are often only partial, the daily practice is to determine single elements by special tests.

Arsenic, Antimony and *Tin.*—Arsenic may be determined by: (A) The Fischer or Lundin[3] distillation of the copper with ferrous sulphate and hydrochloric acid.

(B) By Aller's[4] method, or distillation of the arsenic in hydrochloric acid solution, using an aliquot part (two-fifths) of the copper to reduce the solution of the remainder. The arsenic is obtained from the distillate, and the material in the flask is then evaporated almost to fusion with 75 cc. of a saturated solution of zinc chloride to distil off the antimony. The residue is cooled, treated with 20 cc. of hydrochloric acid and evaporated again. I have no experience with this scheme.

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[1] This Journal, 17, 714 (1895); Abstract *Eng. Min. J.*, 1896, p. 202.

[2] *J. Soc. Chem. Ind.*, 1894, p. 421 ; Fresenius' "Quantitative Analysis," B. II.

[3] Classen : "Analysis by Electrolysis."

[4] Ulke : *Eng. Min. J.*, 78, 727 (1899).

(C) Heberlein's method[1] removes 98 per cent. of the copper from the refined product (or 90 per cent. from the crude) by electrolysis in a mixture of nitric and sulphuric acids containing 2.5 grams of ammonium nitrate, as in Hampe's original method. The solution is then treated with hydrogen sulphide, the arsenic and antimony separated as sulphides by sodium sulphide, and dissolved in hydrochloric acid (2 : 1) by the aid of a little potassium chlorate. Hydrochloric acid is added until the solution contains enough to prevent the precipitation of antimony (3 acid : $1H_2O$) and the arsenic precipitated by hydrogen sulphide. The liquid, after filtration, is diluted to four times its original bulk so that the antimony may be precipitated.

(D) The Baltimore method for arsenic and antimony depends on the separation of impurities by precipitation with ferric sulphate and excess of ammonia. This principle was said to be due to Lehman, Mager and Johns, and was also used by Keller.

I perform this separation as follows: Fifty grams of clean copper are dissolved in 200 cc. of strong nitric acid and diluted to 1 liter. If the metal is known to contain less than 0.05 per cent. arsenic, add 1.5 grams of crystallized ferrous sulphate ($FeSO_4 + 7H_2O$), or about 1 gram of the anhydrous $FeSO_4$. If the material is rich in arsenic, use 2.5 grams of the crystals. Heat the solution to boiling and add strong ammonia until basic salts of copper are redissolved. If antimony and bismuth are to be determined, add (as soon as the ferric hydroxide is down) 0.75 gram of ammonium carbonate and a few cubic centimeters of a saturated solution of sodium phosphate. After three minutes' boiling and ten minutes' settling, in a warm place, pour through a 15 cm. filter, keeping the solution hot to prevent crystallization. Wash two or three times with dilute ammonia (1 : 20) wash the precipitate back into the beaker and clean the paper with a little dilute sulphuric acid, finally treating it with dilute ammonia. Dissolve the iron completely, reprecipitate, filter and wash as before. Finally redissolve in dilute sulphuric acid and pass hydrogen sulphide gas, filter and extract the arsenic group with a little hot dilute sodium sulphide (sp. gr. 1.1).

(E) This method consists in separating the arsenic from the copper[2] by methods (D) or (F), and then precipitating the arsenic with neutral silver nitrate from a solution of the *arseniate*, made neutral (according to the recommendation of Canby) with a slight, but permanent, excess of an emulsion of zinc oxide. To oxidize a minute amount of arsenic the ferric hydroxide precipitate is ignited, weighed, ground in an agate mortar to an impalpable powder, the remainder reweighed and fused with 8 parts of a mixture of sodium carbonate and potassium nitrate. If the arsenic is over 0.05 per cent., precipitation of sulphide is safer than any attempt at fusion.

By experiment with the process, as described,[1] using pure arsenic, results below the theory were obtained. By precipitating

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[1] *Trans. A. I. M. E.*, **27**, 962 (1897).

[2] Furman's "Manual of Assaying," last edition.

the arseniate of silver, however, in presence of an excess of suspended zinc oxide, stirring vigorously for five minutes to insure complete neutralization of the nitric acid set free by the reaction, the results have been more satisfactory. 25.0 parts of arsenic correspond to 107.93 parts of silver.

(F) The alternative method of Dr. Hampe,[1] which involves the saturation of the sulphuric acid solution of the copper with sulphurous acid gas, and the precipitation of the copper as cuprous sulphocyanate is accurate, but requires considerable personal attention and tedious manipulation.

If there is much antimony with the arsenic, Heberlein's scheme of precipitation by hydrogen sulphide in strong hydrochloric acid solution is the best for the subsequent separation of the two elements.

I do not think it safe to assume that the copper in crude material can be separated completely from the arsenic and antimony by electrolysis, unless a set of conditions which have been proved by experiment to give perfect results are rigidly adhered to. A large amount of ammonium nitrate will lessen or prevent trouble.

(G) The writer makes use of all the methods outlined, giving preference for accurate work to the precipitation with sulphate of iron and ammonia. The antimony and arsenic are separated, and the arsenic oxidized to arsenic acid for the final precipitation, (*a*) by fusing the ferric hydroxide precipitate, or (*b*) by filtering the sulphide on an asbestos felt, and dissolving the dry arsenious sulphide in red-fuming nitric acid. This acid must be full strength or the arsenic will not be completely oxidized. The solution is filtered and evaporated on the water-bath with the addition of 0.1 gram of sodium carbonate.

Where much arsenic is present I find that the arsenious sulphide is very apt to retain sulphur, even when precipitated in the cold and carefully extracted with absolute alcohol and carbon disulphide, and the sulphide should be redissolved and determined: (*a*) As arsenate of silver in the neutral solution of the nitrate, as described above under (E). (*b*) By precipitation as magnesium ammonium arsenate in a solution of very small bulk. The solution of purified arsenic acid in nitric acid, having been evaporated to dryness, the residue is treated with 0.5 cc. of hydrochloric acid, 5 cc. of water and 0.1 gram of tartaric acid. The solution is filtered, the filter washed with a very little water, made alkaline with ammonia and made up to 10 cc. in volume. It is then cooled, 3 cc. of magnesia mixture (Fresenius' formula) and 7 cc. of strong ammonia added and the solution stirred for five minutes, and allowed to settle over night.

The foregoing details apply to the precipitate obtained from a 50-gram sample of metal containing less than 0.1 per cent. of

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[1] *J. Soc. Chem. Ind.*, 1891, p. 421; Fresenius' "Quantitative Analysis," B II.

arsenic. If richer than this percentage, increase the volume of solution and the reagents one-half. Always test the filtrate for complete precipitation. Dry the precipitate and carefully char the small filter separately by repeated gentle heat and moistening with a saturated acid solution of ammonium nitrate.

If tin is present, it may be separated from antimony by a modification of F. W. Clarke's method[1] of precipitation by hydrogen sulphide gas in a hot solution, saturated with oxalic acid. The volume of the solution should not be over 25 to 50 cc.

Antimony sulphide is ignited in a porcelain crucible to the tetroxide.

Selenium and Tellurium.—These elements are usually determined in a separate sample by the method of Edward Keller.[2] The impurities are separated by precipitation with ferric hydroxide, which must be in large excess, and the selenium and tellurium are finally precipitated from a hydrochloric acid solution with sulphurous acid gas. Where a separation of the two is not desired, it is quicker and more convenient to precipitate them by stannous chloride. It is most accurate to filter and dry the selenium or tellurium on thin felts of the best asbestos, and, after weighing them, to ignite and determine the elements by loss as a check. Dr. H. F. Kellar[3] has recommended hydroxylamine as a precipitant.

Lead, Iron, Zinc, Nickel and Cobalt.—The bulk of the copper is removed by electrolysis and any deposit of lead peroxide on the anode is weighed. Fifty grams of copper are dissolved by a mixture of 50 cc. strong nitric acid, 80 cc. of sulphuric acid and 400 cc. of water. The solution is diluted with 600 cc. of water and the copper is precipitated on a large platinum cylinder, which may, with advantage, be perforated with narrow slits, as recommended by Heberlein. With a fixed anode the copper is deposited in about twenty hours, using a cathode 11 x 11 cm. and a current of 3 amperes. With a rotating anode (at 600 to 1000 revolutions per minute) the copper can be deposited in nine hours.

The following design for a rotating anode has been found satisfactory for use with platinum cylinders. A straight, stiff wire is bent back and forth at one end. A disc, the size of a quarter of a dollar, is cut from a sheet and is slit on radial lines to form ten propeller blades, and a small hole bored in the center through which the bent end of the wire is passed and clamped by pressure. This is revolved to generate downward pressure, which takes the weight off the spindle and greatly lessens the friction.

When the copper is deposited the solution is concentrated,

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[1] Fresenius' "Quantitative Analysis," 6th group separations.

[2] This Journal, **22**, 242 (1900).

[3] *J. Frank. Inst.*, July, 1894; This Journal, **16**, 785 (1894).

transferred gradually to a small casserole and evaporated to fumes to remove the free sulphuric acid and most of the ammonium salts. The residue is dissolved in water and any lead sulphate and silica are filtered off and saved. Hydrogen sulphide is then passed through the acid solution, the precipitate filtered off and washed with hydrogen sulphide. The precipitate is extracted with a little dilute hot sodium sulphide and the residue is combined with the other precipitates containing lead for the separation of that element as sulphate.

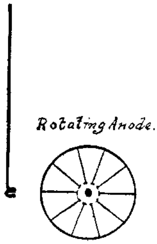

Fig. 3.

The main solution (volume = 30 to 50 cc.) is oxidized and the iron precipitated with ammonia.

The filtrate is acidified with acetic acid and one-fifth its volume of glacial acetic acid added. The zinc is then precipitated in the cold by hydrogen sulphide, and ignited and weighed as oxide. A trace of lead may make its appearance here. Formic acid (sp. gr. 1.2) is even better than acetic acid.

After removal of the acetic acid by evaporation, or if this is not convenient, after neutralization, the solution is heated to boiling and the cobalt and nickel precipitated by hydrogen sulphide.

The cobalt and nickel are separated in a small volume of solution by the potassium nitrite method, and after re-solution in sulphuric acid the metals are deposited from an ammoniacal solution by electrolysis.

Manganese.—This element is rarely present in refined copper. It would appear on the anode during electrolysis and could be weighed.

Bismuth.—A trace of this element is generally determined by a special method[1] unless it has been separated with the arsenic and antimony by precipitation with ferric hydroxide. It is usually estimated by adding excess of ammonia and some ammonium carbonate to the solution of 50 grams of metal and boiling. A little iron should be present. The precipitate is filtered off and purified from copper by repeated precipitation. The bismuth is then thrown down as sulphide and may be purified from a trace of copper by the well-known treatment with a little potassium cyanide. It can finally be weighed as oxide, or estimated by a color test.

To secure accurate and trustworthy results in copper analysis it is necessary not only to be very careful in manipulation, but to carry through blank analyses with all the reagents.

Even the distilled water will frequently show a trace of tin derived from the still in which it was condensed.

CALUMET AND HECLA SMELTING WORKS,
HUBBELL, MICH., December 23, 1904.

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[1] F. B. Stone: *J. Soc. Chem. Ind.*, **6**, 416; *J. Anal. Chem.*, 1887, p. 411.