water has been found to retard growth, and 1 part in approximately 800,000 was fatal to the growth of corn.

(3) One part of copper per million of water should condemn the water for irrigation purposes.

(4) Copper salts are not rendered entirely insoluble when brought into contact with solutions containing carbonates and bicarbonates, and there may be held in solution under such conditions sufficient copper to be toxic to plants.

(5) That the solubility of copper in solutions of bicarbonates probably explains the observed injury produced by irrigating waters carrying copper, even when applied to soils containing large amounts of carbonates and bicarbonates.

THE DETERMINATION OF SMALL QUANTITIES OF COPPER IN WATER.

(Published by permission of the Director of the U. S. Geological Survey.)

BY EARLE B. PHELPS.

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DURING the past few years the question of the addition of small quantities of copper salts to water supplies as a preventative of algal growths and as an emergency disinfectant against typhoid fever germs, has received much discussion and led to many important investigations in this country as well as abroad. One result of all this work has been to indicate the need of some simple yet accurate method for the determination of the small amounts of copper with which the investigator has to deal. The method recommended by the Committee on Standard Methods of Water Analysis of the Laboratory Section of the American Public Health Association,[1] is essentially that of Clark and Forbes.[2] It involves the concentration of a sufficient amount of the water to yield a weighable amount of copper, the precipitation of the copper as well as of certain other metals which may be present, as sulphides, and the separation from the mixed sulphides of the lead and iron by the usual methods. The copper is then deposited electrolytically and weighed. Quantities of copper as small as 2 or 3 mg. are thus determined by Clark and Forbes with a mean probable error of about 5 per cent., while the de-

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[1] "Report of the Committee on Standard Methods of Water Analysis," Jour. Inf. Dis. 1905, Sup. No. 1, p. 1.

[2] Mass. State Board of Health, 32d Ann. Rep. for 1900, p. 487.

termination of 1 mg. obviously cannot be made with a probable error of less than 10 per cent. The disadvantages of the process are, first, the necessity for boiling down a large volume of water in order to get sufficient copper to weigh with accuracy, and, second, the length of time required and the liability of error introduced by the precipitations and separations involved.

Colorimetric methods, while generally much more sensitive than the gravimetric, are greatly influenced by the presence of other substances, especially other metals and organic coloring-matter.

The writer has had occasion to make a number of such copper determinations and was moreover limited by the experimental conditions to quantities of one liter for each determination. Since the water contained at times only a few tenths of a milligram of copper per liter, the standard method of procedure was obviously out of the question. As a result of a study of various possible methods for the determination, a procedure was devised which seemed to combine to a satisfactory degree the requisite sensitiveness, accuracy and simplicity. The method consists in the evaporation of a given volume of the water to about 100 cc. the electrolytic separation of the copper from the acidulated solution, the solution of the deposited copper in dilute acid, and its neutralization and colorimetric determination as sulphide, by comparison with standard tubes of known copper content. By this procedure it is easily possible to determine 0.1 mg. of copper, or if this amount were derived from a liter of water, 0.1 part per million. The accuracy is fully as great as with the gravimetric method using ten times as much of the same water.

The detailed procedure is as follows:

Apparatus.—Platinum dishes of about 100 cc. capacity to serve as anodes. Connection with the circuit is most conveniently made by placing the dish in a little mercury, contained in a shallow metal dish. To the latter is soldered a wire leading to the positive binding post.

A stout platinum wire, about 50 cm. long, 40 cm. of which is coiled into a flat spiral and whose end is fastened directly to the negative binding post. The spiral constitutes the cathode.

A convenient source of electrical current. The character of the current is not so important in this case as in gravimetric processes, since only small amounts of copper are dealt with and

SUMMARY OF COPPER DETERMINATIONS.

No.	Water.	Parts per million.		Characteristics of the water.	Substances added.	Mg. of copper.	
		Total solids.	Loss on ignition.			Taken.	Found.
1	Boston tap water....	40	15	Soft, colored, surface.	None.	0.54	0.52
2	Boston tap water....				None.	0.27	0.27
3	Boston tap water....				None.	0.27	0.24
4	Boston tap water....				None.	0.14	0.12
5	Boston tap water....				None.	0.14	0.12
6	Boston tap water....				Fe as $FeCl_3$, 5 mg.; Pb as acetate, 40 mg.	0.54	0.54
7	Boston tap water....				Ag as $AgNO_3$, 0.5 mg.; Sn as $SnCl_3$, 1.0 mg.	0.54	0.57
8	Chattahoochee, Ga..	300	50	Soft; solids are red iron clay.	None.	0.54	0.57
9	Pecos, N. Mex.......	2000	100	Hardness of 840 parts; turbid.	None.	0.54	0.54
10	Milk, Mont...........	750	.....	Hardness of 620 parts; clear.	None.	0.54	0.55
11	Colorado, Tex........	300	.....	Hardness of 128 parts; turbidity of 110.	None.	0.54	0.52
12	Boston sewage..	4000	810	Chlorine abnormal, about 1500.	None.	0.54	0.50
13	Hay infusion.........	.....	.....	Color about 300.	None.	0.54	0.55
14	Straw board waste..	7000	4000	High in CaO and organic acids.	None.	0.54	0.51

the deposit need not be washed or dried. In the present experiments the current was supplied by two "gravity cells" in series, yielding a current through the solution of about 0.02 ampere. The current density at the cathode was about N. D_{100} = 0.3 ampere.

Nessler jars of the short type holding 100 cc.

Reagents.—Standard copper solution. About 0.8 gram of clean copper sulphate crystals are dissolved in water and, after the addition of 1 cc. concentrated sulphuric acid, the volume is made up to one liter. In 100 cc. of this solution the copper is determined in the usual way by electrolytic deposition and weighing and the solution is diluted so that 1 cc. contains 0.2 milligram copper. This solution is permanent.

Potassium sulphide reagent. An alkaline solution of potassium sulphide made by mixing equal volumes of 10 per cent. potassium hydroxide solution, and a saturated solution of hydrogen sulphide in water.

Nitric acid one to three and sulphuric acid one to one, both tested for copper.

The Determination.—Of waters carrying from 0.1 to 1.0 part copper one litre is taken. For other concentrations take proportionate amounts. Evaporate to about 75 cc. and wash into the platinum dish. Add 2 cc. of the dilute H_2SO_4 for clear and soft waters. For alkaline waters an additional amount is used to offset the alkalinity. For waters carrying much organic matter or clay, 5 cc. of acid are added to assure the formation of a soluble copper salt. The dish is then placed in position, the cathode suspended in the solution so that it is parallel to and about half an inch from the bottom, and the circuit is closed. Electrolyze for about four hours with occasional stirring, or over night, if convenient. Lift out the cathode without previously having opened the circuit, and immerse the spiral in a small amount of the dilute nitric acid, previously heated to boiling. Wash off the wire and evaporate the nitric acid solution to dryness on the water-bath. If silver is suspected to be present, add a few drops of hydrochloric acid before evaporation. Take up in water and wash into the Nessler jar. Make up to the mark and add 10 cc. of the sulphide reagent. The color of the copper sulphide develops at once and is fairly permanent, lasting for several hours, at least. A similar tube is prepared by adding 10 cc. of the reagent to a tube of distilled water and then adding standard copper solution in 0.2 cc. portions until the colors of the two tubes match. If one litre of water were originally taken, each cubic centimeter of standard solution used represents 0.2 part per million of copper.

The method has been carefully tested as to the completeness of the separation and as to the influence of other substances in the water. Particular care has been taken to separate small amounts of copper from large amounts of organic matter (sewage and industrial wastes), coloring-matter in surface waters, and from salts of iron, lead, silver and tin. As will be seen from the appended table of results the separation is in all cases satisfactory. Silver and tin appear to be, according to the authorities, the only metals which will separate out under the conditions used. Neither will be commonly met with. The silver may be converted into the chloride as indicated and does not interfere with the determination. The tin is only partially dissolved by the nitric acid and during the evaporation is converted into metastannic acid. In the alkaline solution used in the test the tin in this form does not interfere in the least.

In the accompanying table are given the results obtained in testing this method. In all cases except those in which Boston sewage and straw-board liquor (the waste liquor of a straw-board mill) were used, one litre of water was taken and the necessary solutions added to it. In the two cases mentioned only 100 cc. were taken.

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SOME INVESTIGATIONS ON SALTS OF CASEIN.[1]

BY J. H. LONG.

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THE question of the identity of caseins from different kinds of milk is an old problem for which the complete solution appears to be still some distance in the future. Even superficial observation suggests that in the milks from different animal species the peculiar coagulating substance is characteristic. From cow's milk, for example, by acid or rennet coagulation what is loosely termed "casein" is thrown down in large flakes. From

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[1] Read at the New Orleans Meeting of the American Chemical Society.