with solutions removed as much as possible by suction were analyzed for both copper and sulfate. The results are shown in Table II.

When these results are plotted on a triangular diagram the lines joining solution and residue form a very narrow pencil and the existence and position of a point of convergence cannot be proved satisfactorily by the usual method. Fortunately, the effect of water on the solids of the residues was negligible, for when the solids were washed with small portions of water, the third washing gave negative tests both with barium chloride and ammonium hydroxide. The solid which dried on standing at room temperature could, therefore, be safely analyzed and the result accords with the formula $4CuO.SO_3.4H_2O$.

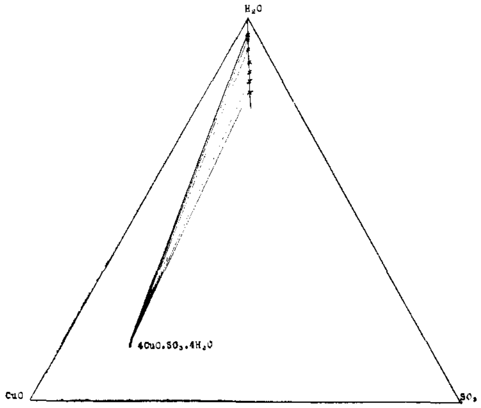

Fig. 1.—Equilibrium in the ternary system $CuO-SO_3-H_2O$ at 100°.

Anal. Calcd. for $4CuO.SO_3.4H_2O$: CuO, 67.7; SO_3, 17.0. Found: CuO, 67.8; SO_3, 17.7.

The tie lines in the diagram, therefore, converge on the point representing the above formula, which has probably the best status of all the formulas for the basic sulfates of copper.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE AGRICULTURAL COLLEGE]

DETERMINATION OF IODINE IN NATURAL WATERS

BY H. W. BRUBAKER, H. S. VAN BLARCOM AND N. H. WALKER

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About two years ago we began to make a survey of the principal water supplies of Kansas to determine the iodine content for the various communities of the state. Before doing this it seemed advisable to try out some of the most acceptable methods of making this determination in order to select one for both accuracy and ease of manipulation. We finally decided to try to adapt a method, used by Dr. Andrew Hunter,[1] for the determination of small amounts of iodine in thyroid tissue, to the determination of iodine in water. This method consists in oxidizing the iodine to iodate by boiling with a solution of sodium hypochlorite acidified with phosphoric acid. The boiling is continued until all of the free chlorine

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[1] Hunter, *J. Biol. Chem.*, **7**, 336 (1909).

is driven off. Potassium iodide is added from which the iodic acid liberates iodine. This iodine is then titrated with a standard solution of sodium thiosulfate using starch indicator, with the usual precautions.

The following reagents were used. (1) A solution of sodium hypochlorite of which the chlorine content was roughly known. (2) Phosphoric acid made by diluting the 85% acid with an equal volume of water. (3) A 1% solution of potassium iodide. (4) A standard solution of potassium biniodate for standardizing the thiosulfate solution. (5) A standard solution of sodium thiosulfate of the strength 0.00474 *N* or *N*/211. One cc. of this was equivalent to 0.1 mg. of iodine.

According to this method six times as much iodine was titrated as was originally present in the sample being analyzed. This made it possible to use much smaller samples, thus obviating the necessity of evaporating large volumes of water to concentrate the iodine. Generally we have found from 1 to 2 liters of water to be sufficient for a sample. This should be evaporated to about 200 cc. before the method is applied. For each determination 50 cc. of U.S.P. sodium hypochlorite should be used and 40 to 60 cc. of the phosphoric acid solution.

The Use of Phosphoric Acid.—Hunter[1] in describing the method as used for the determination of small amounts of iodine in thyroid says that the use of sulfuric acid gives uncertain results, perhaps because of the liberation of a small amount of sulfur dioxide, but that phosphoric acid gives reliable results. In addition to this, we have found that the presence of iron compounds in the water is a cause of high results when sulfuric acid is used. When, however, phosphoric acid is used in the amounts stated above, the iron has little or no effect up to 20 mg. which is equivalent to 20 parts per million in a 1-liter sample. Few waters contain as much as this amount of iron.

The Effect of the Presence of Bromides.—When the amount of bromine was large compared with the amount of iodine present, somewhat longer boiling was required in order to eliminate the bromine completely. In one case as much as 45 minutes of boiling were necessary when 50 mg. of potassium bromide was added to the 0.8 mg. of iodine being determined. Table I gives typical results. The errors caused by the presence of iron are very small, considering the large amount of iron present compared to the small amount of iodine to be determined.

TABLE I

TYPICAL RESULTS

Conditions of experiment	I_2 added, mg.	Iron added, mg.	I_2 found, mg.	Error, %
Using H_2SO_4	0.7644	..	0.9	+17.6
Using H_3PO_4	1.53	..	1.55	+ 1.3
Using 40 cc. of H_3PO_4, in presence of iron	0.7644	10.0	0.77	+ 1.3
Using 45 cc. of H_3PO_4, in presence of iron	.7644	20.0	.775	+ 1.95

The authors consider this a very satisfactory method for the determination of small amounts of iodine in natural waters.

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[Contribution from the Chemical Laboratory of Washington State College]

THE ACTIVITY COEFFICIENTS AND TRANSFERENCE NUMBERS OF BARIUM BROMIDE

By Ralph W. Gelbach and Walter F. Huppke

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Experimental

Electromotive forces of concentration cells of the following types have been measured.

(A) $Hg_xBa \mid BaBr_2, m_1, AgBr \mid Ag - Ag \mid AgBr, BaBr_2, m_2 \mid BaHg_x$
(B) $Hg_xBa \mid BaBr_2, m_1 \mid BaBr_2, m_2 \mid BaHg_x$
(C) $Ag \mid AgBr, BaBr_2, m_1 \mid BaBr_2, m_2, AgBr \mid Ag$
(D) $Ag \mid AgBr, BaBr_2, 0.03m \mid BaHg_x, 0.0424\%$

All measurements were made at 25 ± 0.01°.

Materials, Apparatus and Method.—Chemically pure barium bromide was twice recrystallized from distilled water and finally from conductivity water. A stock solution was made from this and the barium bromide content determined gravimetrically by the silver bromide method. Weighed portions of this solution were diluted to the approximate concentrations, boiled to remove oxygen and finally diluted with oxygen-free water to the desired molality. The dilutions were made with an accuracy of about 0.1%.

The mercury and amalgams were prepared in the manner previously described.[1]

The apparatus was essentially the same as used before. The amalgam electrodes were similar to those used by T. W. Richards[2] with the exception that the platinum contact was sealed in beyond the bend in the electrode so that the solution could not so easily come in contact with the platinum. This difficulty was further overcome by filling the tip with paraffin oil which formed a film on the inner wall and prevented the water from entering the capillary. The amalgam was permitted to flow from the tip at the rate of about one drop per second.

The silver bromide electrodes were prepared by heavily coating the platinum foil electrodes with silver and then electrolytically forming the silver bromide from a solution of potassium bromide. A rotating electrode was used which aided materially in the plating processes. Electrodes prepared in this way usually deviated among themselves by not more than 0.03 millivolt.

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[1] Pearce and Gelbach, *J. Phys. Chem.*, **29**, 1023 (1925).

[2] Richards and Conant, This Journal, **44**, 601 (1922).