

where M represents the alkali metal. This conclusion is in accord with that of Henderson, concerning the action of the tartrates on arsenious oxide.

Ion migration test of the oxalate solution also showed that the metals migrate as anions. According to Russ<sup>2</sup> the oxides dissolve in oxalic acid forming definite compounds to which he assigned formulas. He did not test for the complex nature of these compounds. Since this investigation revealed the fact that the metals migrate as anions, it must be concluded that they are joined with the oxalate ions, forming complexes. It may be that columbium and tantalum form complexes with oxalic acid similar to chromium. According to Werner,<sup>3</sup> chromium forms with oxalic acid the complex chromo-oxalic acid,  $H_6Cr_2(C_2O_4)_6$ , where the chromium is united with the oxalate ion forming a complex anion. In agreement with this theory, columbium and tantalum would form the compound,  $H_5M(C_2O_4)_5$ , where M represents the metal.

### Summary

The freshly precipitated hydrated oxides of columbium and tantalum were found to be appreciably soluble in a hot aqueous solution of tartaric acid, forming compounds of the tartar emetic type.

Also it was found that the compounds formed when the oxides were dissolved in oxalic acid were not simple salts, but instead there were formed complexes. Ion migration tests showed that the metals united with the oxalate ion to form complex anions.

The oxalate and tartrate solutions of columbium and tantalum showed no activity toward various organic acids.

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[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

## THE PREPARATION OF IODINE-FREE BROMINE

BY GEORGE M. KARNS AND H. C. DONALDSON

RECEIVED AUGUST 25, 1931

PUBLISHED FEBRUARY 5, 1932

The purification of most of the reagents used in the preparation of large samples for analysis for small amounts of iodine has been discussed at length by von Fellenberg<sup>1</sup> and Reith.<sup>2,3,4</sup> Some of the reagents used in smaller amounts, however, have not been dealt with so completely by these or other authors. Bromine, which is used as an oxidizing agent in one titrimetric method for the final determination, offers considerable chance for the introduction of iodine into the blank, *c. p.* bromine being frequently listed as containing 0.1% of that element. Saturated bromine water

<sup>1</sup> Von Fellenberg, *Ergebnisse Physiol.*, **25**, 194 (1926).

<sup>2</sup> Reith, Dissertation, Utrecht, July, 1929.

<sup>3</sup> Reith, *Biochem. Z.*, **216**, 250 (1929).

<sup>4</sup> Reith, *ibid.*, **224**, 223 (1930).

prepared from such bromine would contain a minimum of 40 gammas of iodine per cc. and if the bromine water used were prepared, as is often the case in the laboratory, by adding an excess to a bottle containing water, it could contain considerably more.

If iodine in bromine is present as iodine bromide, it should be possible to convert it to water-soluble iodic acid by treatment with water. Upon this assumption, an investigation was made of the effectiveness of successive washings in removing iodine from bromine. A sample of bromine, treated with iodine to bring its iodine content to 0.1% (the iodine content of C. P. bromine was usually found to be considerably below the manufacturer's figure), was washed successively with 500 cc. portions of water, using a mechanical shaker. Data obtained from iodine determinations upon the washings from a typical run are given in the accompanying table.

TABLE I  
IODINE DETERMINATIONS

Initial weight of bromine, 453 g.		Purified bromine obtained, 246 g.		
		Iodine per 100 cc. washings (gammas)	Total iodine removed (gammas)	Iodine to be removed subsequently
1st washing	after 1 hour	9320		
	after 3 hours	9640	48132	
2d washing, after 3 hours		16.6	83.0	31.4
3d washing	after 1 hour	1.8		
	after 3 hours	4.2	18.6	12.8
4th washing, after 3 hours		1.0	4.9	7.9
5th washing, after 6 hours		0.7	3.8	4.1
6th washing, after 24 hours		0.5	2.5	1.5

Iodine remaining in bromine sample as estimated by the method described in the following paragraph less than 1.5 gammas.

That oxidizing agents other than bromine were being removed by the first washings was indicated by the fact that, upon boiling to remove bromine, cooling and adding excess potassium iodide, a shifting end-point was obtained when the solution was titrated with thiosulfate. This difficulty would be carried over to the actual determinations if the bromine water examined had been used and may account in part for the difficulties that have caused numerous investigators to abandon the oxidation titrimetric method for the colorimetric method in the micro-determination of iodine. Determinations were made on such samples by boiling off the bromine, reducing with acidified sodium sulfite, evaporating to dryness after the addition of potassium carbonate, and extracting with alcohol. The final determination of iodine was then made titrimetrically, as described above, using water from purified bromine as an oxidizing agent. As the washing was continued determinations made directly, and after reduction and extraction as described above, became identical. In the determination of iodine in the purified bromine sample, 100 cc. of bromine

was allowed to evaporate through a layer of water containing a small amount of sodium hypobromite. This method was chosen in preference to one which would introduce considerable amounts of other reagents after a control determination showed good recovery of iodine.

From the data in the table it is evident that bromine of sufficient purity for microchemical work can be prepared by the washing method. It is also evident from data on the third washing at the end of one and three hours, respectively, that considerable time must be allowed for the reaction between iodine bromide and water to take place. Water from the third washing, if separated from the bromine residue, would introduce less than 0.04 gamma of iodine into the sample per cc. of bromine water used. Saturated bromine water prepared from the bromine obtained at this stage would contain approximately one-twentieth of that amount.

### Summary

A method for the preparation of iodine-free bromine for use in the micro-analytical determination of iodine is described.

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[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE MICHIGAN COLLEGE OF MINING AND TECHNOLOGY]

## THE SURFACE RELATIONS OF POTASSIUM ETHYL XANTHATE AND PINE OIL. I

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RECEIVED AUGUST 27, 1931

PUBLISHED FEBRUARY 5, 1932

During recent years the froth flotation method for the concentration of ores has made great progress, but an actual knowledge of the mechanism of the formation of the froth and the flotation of the metallic values by the admixture of potassium ethyl xanthate and pine oil is still lacking. A program of research has been instituted from which, it is hoped, a satisfactory explanation of the phenomena may result. This paper is a brief exposition of the methods used and the results obtained in the first stage of the investigation. Generalization in the field as a whole is reserved for later papers, when more complete data on the surface relations of these materials will be available. In this report data on the surface relations of solutions of potassium ethyl xanthate and pine oil are presented, the relative values of the various data are discussed, and problems are suggested for future solution.

The surface tension of the potassium ethyl xanthate solutions was measured by the methods of Ferguson and Dowson and the interfacial tension of the xanthate-pine oil system by the method of Bartell and Miller. A series of parallel determinations was carried out on sodium car-