[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY.]

THE PREPARATION AND STUDY OF THE RARER ALKALI BROMATES. CESIUM BROMATE.

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Introduction.

The literature affords no reference to the preparation of the bromates of cesium and rubidium. Since it seemed plausible to expect that these salts could exist, as well defined crystalline bodies, it was thought worth while to attempt their preparation, and then to study some of their physical and chemical properties.

The preparation of cesium bromate is taken up in this paper. Later an effort will be made to prepare and study the properties of rubidium bromate.

Preparation of Bromic Acid.

This acid was made by the action of bromine upon silver bromate. Potassium bromate was dissolved in water, and silver nitrate added. The silver bromate precipitated from the warm saturated solution in the form of a fine white powder. This was well washed with water to free it from nitrates of potassium or silver and then treated, in a large amount of water, with liquid bromine as long as the color disappeared. Due to the slight solubility of silver bromate, amounting to 0.158 part in 100 parts of water, and also to the formation of the still more insoluble silver bromide, 0.000026 part in 100 parts of water, the reaction mixture was stirred constantly for 2 days or longer with the addition of bromine from time to time. The bromic acid solution was then decanted from the silver bromide and the excess bromine expelled by bubbling air through the solution.

According to Kammerer[1] the reactions indicated above proceed as follows:

$$KBrO_3 + AgNO_3 = AgBrO_3 + KNO_3$$

$$5AgBrO_3 + 6Br + 3\ H_2O = 5AgBr + 6HBrO_3.$$

One would conclude from Kammerer's work that all of the free bromine could be expelled, leaving pure bromic acid. But in our experience this was found impossible, the solution still being colored with a little bromine after bubbling pure air through it for 24 to 48 hours. It was apparent that there was a slow decomposition of the bromic acid. At any rate, the reaction proceeds slowly, and in expelling the excess bromine, only a small amount of bromic acid was lost.

Preparation of Cesium Hydroxide.

Cesium chloride was treated with an excess of sulfuric acid and the mixture heated until the fumes of sulfur trioxide ceased to come off.

[1] Gmelin-Kraut, Vol. I, ii, 262 (1870).

The cesium hydrogen sulfate was dissolved in water, and a saturated solution of barium hydroxide added until a drop gave no precipitate of barium sulfate. The clear cesium hydroxide solution was kept in a platinum container.

Preparation of Cesium Bromate.

Cesium hydroxide was neutralized with bromic acid and then an excess of the acid added. The solution was evaporated somewhat and allowed to crystallize. Several yields of crystals were obtained each time the mother liquors were concentrated, and even the last yield of crystals showed no test for a bromide. As the mother liquor became concentrated, the liberation of bromine became quite pronounced, as only a 4.28% solution of bromic acid is stable under ordinary conditions.[1]

Examination of the Product.—The product was recrystallized from water and the resulting crystals were small but well defined. The crystals were dried at different temperatures, and each time the temperature was raised there was a slight loss in weight, without, however, any apparent loss of crystalline structure. Some of the substance was heated in a test-tube, whereupon marked decrepitation occurred, which indicated that water was held between the crystals, and probably accounted for the loss in weight when dried slowly. There was no visible deposit of water on the cold portion of the test-tube, thus indicating the absence of water of crystallization. Further heating caused the substance to melt and then decompose with the evolution of large quantities of oxygen. The residue gave the bromide test.

From the position of cesium in the periodic table the melting point of the bromate ought to be above that of potassium bromate, 434°. No comparison could be made between the chlorate, bromate, and iodate of cesium, as the melting points of the first and last salts mentioned apparently have not been determined. An apparatus for determining a temperature above 360° was not on hand, and only a rough estimation could be obtained. It was found that in melted anhydrous zinc chloride[2] potassium bromate fused several seconds before the cesium bromate.

Analysis of the Substance.—The samples of the salt were ground finely in an agate mortar. They were then dried for about 36 hours at 115° and at the end of that time became constant in weight.

Two methods of analysis were employed, the iodometric and a gravimetric method used by Harkins[3] and by Baxter.[4] The latter is based upon the reducing action of hydrazine hydroxide and the determination of the bromine as silver bromide.

The following set of results (Tables I and II) establish the identity of the

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[1] Gmelin-Kraut, Vol. I, ii, 262 (1870).

[2] McCrosky, THIS JOURNAL, 40, 2 (1918).

[3] Harkins, *ibid.*, 33, 1810 (1902).

[4] Baxter, *ibid.*, 31, 209 (1900).

salt prepared as cesium bromate. In the first column are given the weights of cesium bromate taken. The second column shows the amounts of cesium bromate obtained by analysis of the weighed samples of Column 1. The third column is the difference between the amount obtained by analysis and the weighed sample.

TABLE I.
Iodometric Method of Analysis.

Samples of $CsBrO_3$ weighed. G.	Amt. $CsBrO_3$ obtained by analysis. G.	Difference. G.
0.1022	0.1023	0.0001
0.1100	0.1103	0.0003
0.1010	0.1012	0.0003
0.0960	0.0961	0.0001
0.1054	0.1064	0.0010
0.0992	0.0982	0.0010
0.1052	0.1047	0.0005
0.1079	0.1077	0.0002
0.1106	0.1107	0.0001

TABLE II.
Precipitation Method of Analysis.
Reduction with Hydrazine Hydroxide.[a]

Samples of $CsBrO_3$ weighed. G.	Amt. $CsBrO_3$ obtained by analysis. G.	Difference. G.
0.2866	0.2871	0.0005
0.0934	0.0934	0.0000
0.1016	0.1013	0.0003

[a] *Ibid.*, **31**, 209 (1900). Hydrazine hydroxide was used by Baxter for reducing iodic acid in determining the atomic weight of iodine.

The Solubility of Cesium Bromate.

The solubility of cesium bromate was determined at 30°. The temperature of the bath in the thermostat varied from this only by 0.2° to 0.3° during the determinations. The method employed was essentially that used by Buchanan,[1] About 5 hours was allowed for the salt to come into equilibrium with the solvent, before the saturated solution was withdrawn for analysis. This solution was weighed and then carefully evaporated to dryness until constant in weight.

TABLE III.
Solubility of Cesium Bromate in 100 g. of Water at 30°.

	G.
	4.484
	4.573
	4.525
	4.549
	4.483
	4.577
Average	4.53

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[1] Buchanan, *J. Ind. Eng. Chem.*, **12**, 448 (1920)

Summary.

As a result of this investigation the following facts have been established.

The preparation of cesium bromate is probably best carried out in acid solution.

Cesium bromate is a definite crystalline salt with no water of crystallization. Occluded water causes decrepitation.

Its melting point (not as yet determined) is above that of potassium bromate. After melting, it soon decomposes, giving a large amount of oxygen, and leaves a bromide.

The solubility of cesium bromate is 4.53 g. in 100 g. of water at 30°.

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THE ELECTRO-ANALYTICAL SEPARATION OF NICKEL (COBALT) FROM ARSENIC.

BY N. HOWELL FURMAN.

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Introduction.

This investigation was undertaken at the suggestion of Dr. L. W. McCay, who first demonstrated the possibility of separating copper from quinquivalent arsenic in ammoniacal solution by means of the electric current.[1] A number of years ago he attempted the simultaneous separation of nickel and cobalt from arsenic by a similar method, but found that the results were always high, owing to the presence of arsenic in the deposits. The materials which he used in these investigations were specimens of smaltite and safflorite (arsenides of cobalt) which contained nickel.

The author has studied the action of the electric current upon ammoniacal solutions containing alkali arsenates and nickel alone, and finds that the nickel deposits are free from arsenic. On the other hand, when cobalt is deposited from an ammoniacal solution containing arsenates the deposit invariably contains arsenic in amounts ranging from 6.0–12.0 mg. per 0.1 g. of cobalt. If the 2 metals are deposited simultaneously they may or may not contain arsenic, for its presence depends upon the relative amounts of nickel and cobalt, and upon the absolute value of the concentration of the cobalt. For example, with a total volume of 100 cc. and a cathode surface of 55 $\overline{\text{cm}}^2$., the deposits were found to be free from arsenic when the relative amounts of the metals were 2.5 or more parts of nickel to one part of cobalt by weight, and the total weight of the mixed metals deposited was 0.1 g. When the 2 metals were present in a 1 : 1 ratio, from 0.5 to 1.0 mg. of arsenic was found in a 0.1 g. deposit of the mixed metals. If the concentration of the cobalt is increased, while the

[1] McCay, *Chem. Ztg.*, 14, 509 (1890).