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On the Composition of the Cesium Salt by $KBiI_4$ Reagent*

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It has been reported that there are three kinds of compounds, $CsBiI_4$, Cs_2BiI_5 and $Cs_3Bi_2I_9$, in the cesium salt produced by $KBiI_4$ reagent. The composition of that cesium salt has been studied, and been found to be $Cs_3Bi_2I_9$.

INTRODUCTION

The reagents for the separation and determination of potassium, rubidium and cesium have been studied, and the regularities[1] between the solubilities of the salts of these elements have already been reported, $KBiI_4$ or $NaBiI_4$ being recommended as excellent reagents for the separation of cesium from rubidium. Moreover these reagents are also expected to be appropriate for the determination of cesium.

However, the composition of the cesium salt produced by these reagents have been reported as follows: $CsBiI_4$, Cs_2BiI_5[2),5)] and $Cs_3Bi_2I_9$.[3),4)] Therefore, this study was made to clarify the composition of the cesium salt as the first stage in applying this reagent to the quantitative determination of cesium. Among these cesium salts, Cs_2BiI_5 is very similar to $Cs_3Bi_2I_9$ in the percentage of each component, so the determination of the composition of the cesium salt is rather difficult and must be done with great care. The amounts of each component in the precipitate have been determined as follows. The amount of the cesium is estimated by the hexanitrodipicrylamine method after removal of the bismuth. The amount of the bismuth is estimated by iodometry after the separation of the addition compound consisting of 8-hydroxyquinoline and $HBiI_4$. The amount of the iodine is estimated by iodometry.

By these methods, the composition of the cesium salt produced by the $KBiI_4$ reagent has been found to be $Cs_3Bi_2I_9$.

CHEMICALS AND APPARATUS

Solution (A): The saturated solution of potassium iodide in cold concentrated acetic acid is diluted with an equal volume of comcentrated acetic acid and the solution is kept in a glass-stoppered bottle.

$KBiI_4$ reagent: To 225 ml. of a cold saturated solution of potassium iodide, 75 ml. of concentrated acetic acid and purified bismuth trioxide are added. After heating, the solution is filtered through a glass-filter and the filtrate is kept in

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a glass stoppered bottle in a cold, dark place.

Hca reagent : 0.1*N*-calcium hexanitrodipicrylaminate solution. The vessel and the filter-stick as shown in Fig. 1 are used for the preparation, filtering and washing of the precipitate.

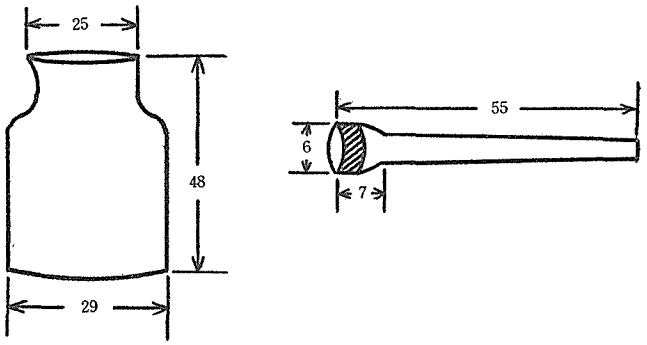

Fig. 1. (Unit : mm)

EXPERIMENT AND RESULTS

Preparation of the cesium salt: The composition of the cesium salt has been examined for the compounds obtained under three different conditions, samples (A), (B) and (C).

For sample (A), a definite amount of cesium chloride, which is spectroscopically pure, is dissolved in solution (A) and to its hot solution, a definite volume of $KBiI_4$ reagent is added. After cooling, the cesium salt is filtered with a glass-filter-stick, washed sufficiently with cold concentrated acid dried at 142°C for an hour. Then the cesium salt is cooled in a desiccator containing calcium chloride and is used as the sample (A).

For sample (B), the procedure is the same as for sample (A) except that the cesium salt is produced in the concentrated acetic acid.

For sample (C), the procedure is the same as in the sample (A) except that the cesium salt is produced in a saturated solution of potassium iodide in concentrated acetic acid.

Determination of Cesium

Though there are several methods for the determination of cesium in the cesium salt, the hexanitrodipicrylamine method by Hh, has been chosen because in this method, the chemical factor and the solubility of the salt are both small, and the filtering and washing are very easy. The procedure used is as follows :

A definite amount of the cesium salt is weighed and put in a 100 ml. beaker. Then, dilute nitric acid is added, and it is covered with a watch-glass and warmed on a steam bath to destroy the salt. Then hydrogen sulfide gas is passed into the solution and the bismuth is precipitated as the sulfide. The bismuth sulfide is filtered through a small glass-filter fitted with a foot and the filtrate is vaporized to dryness. To the residue, a definite amount of water is added and the solution is warmed on a steam-bath. Then the solution is made slightly

alkaline with diluted hydrochloric acid and sodium hydroxide after adding a small amount of bromthymol blue, and the solution is again filtered through the same glass-filter as before. The filtrate is received in the vassel which has been preliminarily weighed together with a glass-filter-stick and a definite amount of 0.1*N*-Hca reagent is added. The vessel is cooled by ice and the precipitate is filtered, washed five times with each 0.8 ml. of ice-cooled water and then dried at 110°C for an hour. After cooling in a desiccator, the weight of the Hcs is determined. It seems to be especially important for this HH method that the concentration of the Hca reagent in the supernatant solution must be 0.01~0.03 *N*[6] when the precipitate is produced. The results are shown in Table 1.

Table 1. The content of cesium in the precipitates.

Sample		Hcs	Cs found	Content of cesium	
Kind	Weight (mg.)	(mg.)	(mg.)	(%)	Mean value
A	100.0	86.5	20.15	20.15	20.29
A	〃	87.7	20.42	20.42	
B	〃	87.2	20.31	20.31	20.48
B	〃	88.6	20.64	20.64	
C	〃	86.4	20.03	20.03	20.18
C	〃	87.2	20.32	20.32	

Determination of Bismuth[7]

a) Procedure: A definite amount of cesium salt is dissolved in dilute sulfuric acid and the solution is further diluted with water. Then, an excess of 5% 8-hydroxyquinoline in 0.2*N*-H_2SO_4 and about 10 ml. of 0.1*N*-KI solution are added to it. An addition compound which consists of $HBiI_4$ and 8-hydroxyquinoline is produced, filtered through the glass-filter equipped with the foot and washed five to six times, using each time one to two ml. of a washing solution which contains 50 ml. of 2*N*-H_2SO_4, 25 ml of 0.1*N*-KI solution, 1.8 grams of 8-hydroxyquinoline and a small amount of hydroxylamine hydrochloride per liter. The washed precipitate is dissolved in 10 ml. of 10% hydrochloric acid containing 0.5 grams of potassium cyanide and after adding one to two ml. of starch solution, the solution is titrated with 0.1*N*- or 0.02*N*-standard solution of potassium iodate until the iodine-starch reaction disappears. One ml. of 0.1*N*-potassium iodate solution corresponds to 0.002613 grams of bismuth.

b) Preliminary experiment: The previous procedure has been examined

Table 2. Preliminary experiment of bismuth.

Bi taken	KIO_3 solution (ml.)		Bi found	Error
(mg)	0.1*N*	0.02*N*	(mg.)	(mg.)
1.00	—	2.15	1.02	+0.02
2.00	—	4.10	2.04	+0.04
5.00	—	9.80	5.02	+0.02
20.00	7.50	—	20.02	+0.02
30.00	11.81	—	29.93	−0.07

by using known amounts of bismuth. The standard solution of bismuth is prepared by dissolving 1.114 grams of bismuth trioxide in a small amount of concentrated nitric acid and diluting it to one liter of $0.2N$-H_2SO_4 solution with sulfuric acid after removal of an excess nitric acid. One ml. of this solution contains one mg. of bismuth. The results obtained for known amounts of bismuth are shown in Table 2. As shown in Table 2, the amount of bismuth can be satisfactorily found by this method. Therefore, the amount of bismuth in the cesium compound has been estimated and the results obtained have been shown in Table 3.

Table 3. The content of bismuth in the precipitates.

Sample		$0.02N$-KIO_3	Bi found	Content of Bi
Kind	Weight (mg.)	(ml.)	(mg.)	(%)
A	40.0	16.5	8.62	21.6
B	39.5	16.0	8.36	21.1
C	39.5	16.3	8.49	21.5

Determination of Iodine[8]

The procedure is as follows: A definite amount of cesium salt is dissolved in 10% hydrochloric acid containing 0.5 grams of potassium cyanide and the solution is titrated with $0.02N$-standard solution of potassium iodate until the iodine-starch reaction disappears. One ml. of $0.02N$-potassium iodate solution corresponds to 1.269 mg. of iodine.

In the previous determination of bismuth, the amount of bismuth has been indirectly found by estimating the amount of iodine in the cesium salt. Threfore the reaction mechanism in the titrimetric determination of bismuth is the same as that of iodine and is explained as follows: Equation (1) is reversible, but the equilibrium shifts to the right with the presence of acid.

$$I_2+HCN \rightleftharpoons ICN+H^++I^- \quad \cdots\cdots(1)$$

On the one hand, the iodide ion in the solution loses its electron and is oxidized to I^+ ion as shown in equation (2). On the other hand, the iodate gets the electron from the iodide ion and it is reduced to I^+ in accordance with equation (3).

$$I^-+HCN-2e \longrightarrow ICN+H^+ \quad \cdots\cdots(2)$$

$$IO_3^-+HCN+5H^++4e \longrightarrow ICN+3H_2O \quad \cdots\cdots(3)$$

Table 4. The content of iodine in the precipitates.

Sample		$0.02N$-KIO_3	I found	Content of I
Kind	Weight (mg.)	(ml.)	(mg.)	(%)
A	16.6	7.70	9.78	58.9
B	15.4	7.10	9.02	58.5
C	19.5	8.92	11.30	57.9

Therefore, the iodine-starch reaction will be observed while the solution contains iodide ion, and the iodine is produced by the addition of the standard iodate solution. So the iodine-starch reaction will disappear at the end point of the titration. The results obtained by this method are shown in Table 4.

COMPOSITION OF THE PRECIPITATE

Table 5 shows the experimental results for each constituent in the cesium salt as well as the theoretical values of each constituent in the cesium salts—

Table 5. The composition of the precipitates.

Compound	Cs (%)	Bi (%)	I (%)
$CsBiI_4$	15.63	24.61	59.76
Cs_2BiI_5	23.94	18.84	57.22
$Cs_3Bi_2I_9$	20.38	21.25	58.37
A	20.29	21.6	58.9
B	20.48	21.1	58.5
C	20.18	21.5	57.9

$CsBiI_4$, Cs_2BiI_5 and $Cs_3Bi_2I_9$ which have been reported. It is seen from the table that the compositions of the samples (A), (B) and (C) are the same and are $Cs_3Bi_2I_9$ or $3CsI \cdot 2BiI_3$. This composition cause the composition of the double salt consisting of cesium chloride and antimony chloride to remember to be $3CsCl \cdot 2SbCl_3$ and both salts are thought to be isomorphous. The amount of cesium in the salt is 20.38% and is smaller than that of any other salts which can be available for the determination of the cesium. Moreover, the weights of the cesium salt produced by the $NaBiI_4$ reagent at the same conditions as those for the $KBiI_4$ reagent, except for sodium iodide, give nearly the same values as those for the $KBiI_4$ reagent. So the composition of the cesium salt with the $NaBiI_4$ reagent is thought to be the same as that for $KBiI_4$.

SUMMARY

The chemical composition of the cesium salt produced by $KBiI_4$ has hitherto been doubtful, but it has been found to be $Cs_3Bi_2I_9$ or $3CsI \cdot 2BiI_3$ by careful experiment. Also the composition of the cesium salt produced with the $NaBiI_4$ reagent is thought to be the same as that for the $KBiI_4$ reagent. As the chemical composition of the cesium salt has been determined and the content of the cesium in this salt is the smallest among the salts available for the determination of the cesium, it is expected that excellent quantitative methods for the determination of cesium with these reagents will be possible.

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