On the Determination of Cesium with KBiI$_4$ or NaBiI$_4$ Reagent*

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It has been thought that the determination of cesium with HBiI$_4$ reagent is impossible because exact results can not be obtained by this method. Therefore, the determination of cesium with HBiI$_4$ and similar reagents has never been tried. However the author has established gravimetric and volumetric methods for the determination of cesium in which the cesium salt is produced in concentrated acetic acid instead of water as in the conventional HBiI$_4$ method. The results are excellent and are interfered only when a large amount of rubidium is present. In this paper, the gravimetric and volumetric methods for analysis of a cesium sample in which no other substance are present, are discussed.

INTRODUCTION

It has already been reported that the composition of the cesium salt produced by KBiI$_4$ or NaBiI$_4$ reagent is Cs$_3$Bi$_2$I$_9$ or 3CsI·2BiI$_3$. The purpose of this research is to establish a method for the determination of cesium using these reagents. N. A. Tananaeff and E. P. Harmasch[1] have reported that the amount of cesium can be easily estimated with HBiI$_4$ reagent not only in the case of cesium alone but also even in the case where rubidium is present. Thereafter, R. W. Feldmann[2] pointed out that previous experiments using HBiI$_4$ were all false and that the exact estimation of cesium with this reagent was not possible. Since then, no attempts have been made to estimate the amount of cesium with HBiI$_4$ or similar reagents.

The author studied both conventional methods and found that the largest defect in the conventional method consists in the preparation of the cesium salt in an aqueous solution and that under this condition, the quantitative procedure for the determination of cesium is impossible because the solubility of the cesium salt is extremely large. For instance, in R. W. Feldmann's experiment, the cesium salt is produced by adding HBiI$_4$ reagent to a concentrated aqueous solution of cesium chloride, and it is filtered, washed, dried and weighed. With this method, experimental values for a sample with a definite amount of cesium are short by about 6% when the sample contains cesium alone, and the error increases rapidly with an increase in the amount of accompanying rubidium.

At any rate, it is concluded that the quantitative method using HBiI$_4$ reagent is unsuitable for the determination of cesium. However the author has found

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that the defect in the conventional HBiI₄ method can be easily removed by using concentrated acetic acid instead of water and that even a small amount of cesium in the solution can be exactly estimated by this method. Advantages of the quantitative method using NaBiI₄ or KBiI₄ reagent are as follows :

  1) The percentage content of cesium in the precipitate is the smallest among the quantitative methods which have been reported.

Compound	Cesium content (%)
$CsClO_4$	57.20
$CsIO_4$	41.05
$CsB(C_6H_5)_4$	29.42
$C_6H_2(NO_2)_3 \cdot N(\cdot Cs) \cdot C_6H_2(NO_2)_3$	23.29
Cs_2SO_4	73.48
Cs_2PtCl_6	39.45
$Cs_2NaCo(NO_2)_6 \cdot H_2O$	41.43
$Cs_3Bi_2I_9$	20.38

  2) The cesium salt is a red crystalline precipitate, and therefore filtering and washing are easy.

  3) The cesium salt is considerably stable to heat and is not hygroscopic.

  4) The cesium salt is difficultly soluble in cold concentrated acetic acid.

  5) The precipitation reaction is specific for cesium except for thallous thallium.

  6) The amount of the cesium is indirectly determined by titrating the iodide from the cesium salt with a standard iodate solution.

  7) The preparation of the reagent is simple.

GRAVIMETRIC ANALYSIS

(1) **Reagents and Appratus**

  KBiI₄ Reagent : 9 grams of powdered bismuth trioxide is dissolved in 300 ml. of a saturated solution of potassium iodide in concentrated acetic acid. After heating for some time, the solution is rapidly filtered through a glass-filter equipped with a foot and the filtrate is stored in a glass-stoppered bottle in a cold dark place.

  NaBiI₄ : This reagent is prepared by the same procedure as that for the KBiI₄ reagent except using sodium iodide.

  Rubidium Chloride and Cesium Chloride : These salts are spectroscopically pure and standard solutions of these salts are all prepared by weight. In order to take a definite amount of cesium or rubidium, an injector and a chemical balance are used. A semimicro-balance is also used for weighing the cesium salt.

(2) **Procedure**

  The sum of the weight of a vessel and a filter-stick is preliminarily found,

and the filter-stick is kept free from dust. A definite amount of the cesium solution is taken into the vessel and vaporized to dryness. Then, a solution of equal volumes of the saturated solution of potassium iodide or sodium iodide in concentrated acetic acid and concentrated acetic acid is added to the residue and the vessel is warmed for some time. The hot solution of $KBiI_4$ or $NaBiI_4$ reagent is added to it and the vessel is cooled with ice for half an hour or more. Then the precipitate is filtered with the previous filter-stick and washed five times with 0.5 to 0.8 ml. of cold concentrated acetic acid until the orange-yellow color of the filtrate disappears. The precipitate is dried at 142°C for an hour, cooled in a desiccator containing calcium chloride and weighed together with the filter-stick. Then the amount of the cesium or the cesium chloride is found by the following equations,

$$Cs = W \times 0.2038$$

$$CsCl = W \times 0.2578$$

where W represents the weight of the precipitate.

(3) Fundamental Examination of the Procedure

As the procedure for the determination of cesium with $KBiI_4$ or $NaBiI_4$ reagent has never been reported, the fundamental conditions for it have been examined.

a) **Proportionality**: The experimental results obtained with 2 to 100 milligrams of cesium chloride are shown in Table 1, and it is seen from the table that a satisfactory proportionality exists among them.

Table 1. The proportionality of cesium salt.

CsCl taken (mg.)	KBiI₄ (ml.)	Total volume (ml.)	Cs₃Bi₂I₉ found (mg.)	CsCl found (mg.)	Error (mg.)
2.00	1	3	7.70	1.99	−0.01
5.00	1	3	19.26	4.97	−0.03
10.00	1	3	39.10	10.08	+0.08
20.00	1	3	77.40	19.96	−0.04
100.00	4	9	389.30	100.40	+0.40

b) **The amount of the reagent and the volume of the solution**: Table 2 shows the results obtained for various volumes of the reagent and the solution. It shows that a change of the amount of the reagent hardly affects the result but that the data obtained for a large volume of solution gives a negative error. When the volume of the solution is large, the cesium salt seems to deposit with difficulty. Therefore it is necessary for the exact determination of cesium to cool the vessel containing the cesium salt with ice for a longer time. The relationships between the amount of the cesium chloride and the cooling time have been found experimentally, and they are as follows: The necessary cooling time for 5 to 50 mg. of cesium chloride is an hour for seven ml. of the solution and half

Table 2. Influence of the amount of reagent and the volume of solution on the weight of cesium salt.

CsCl taken (mg.)	KBiI₄ (ml.)	Total volume (ml.)	Cs₃Bi₂I₉ (mg.)	CsCl found (mg.)	Error (mg.)
2.00	2	3	7.71	1.99	−0.01
5.00	2	3	19.25	4.96	−0.04
10.00	2	3	38.60	9.96	−0.04
20.00	2	3	77.30	19.94	−0.06
5.00	5	6	19.30	4.98	−0.02
10.00	5	6	38.55	9.94	−0.06
2.00	2	10	7.02	1.81	−0.19
5.00	2	10	19.30	4.98	−0.02
10.00	2	10	38.80	10.01	+0.01
20.00	2	10	75.50	19.91	−0.01
100.00	4	10	390.20	100.63	+0.63

an hour for five ml. Similarly, for 2 to 5 mg. of cesium chloride it is an hour for 3 ml. and for 50 to 100 mg. of cesium chloride, half an hour for 3 ml. and for 50 to 100 mg. of cesium chloride, half an hour for 10 ml. To sum up these data, the relationships between the necessary cooling time and the concentration of the cesium chloride solution are represented as follows : it is necessary for the exact determination of cesium to cool the vessel with ice for an hour in the case of a solution containing more than 0.7 mg. of cesium chloride per ml. and for half an hour in cases of more than 2 mg. per ml.

c) **Washing of the precipitate** : Here a study was made concerning the number of times of washing and the amount of washing solution necessary. The optimum conditions for washing the cesium salt were found to be, to wash the precipitate five to six times using each time 0.5 to 0.8 ml. of the washing solution. These weshing conditions were found to be satisfactory for the determination of 2 to 100 mg. of cesium chloride.

d) **Drying temperature** : As for the same cesium salt, the relationship between the weight of the salt and the temperature was found by drying the salt at each temperature for an hour and the results obtained are shown in Table 3. From the table, it is clearly seen that the cesium salt would indicate a definite weight at 140° to 145°C. The previous procedure for the determination of cesium has been devised by combining these conditions.

Table 3. Influence of drying temperature on the weight of cesium salt (mg.).

Sample	135°C	140°C	145°C	150°C
1	19.76	19.50	19.50	19.48
2	38.82	38.40	38.35	38.28
3	77.10	76.45	76.45	76.35

(4) Determination of Cesium by NaBiI₄ Reagent

The procedure for the determination of cesium with NaBiI₄ reagent is the same as that for KBiI₄ reagent. The former is convenient for the determination of the rubidium in the filtrate after removal of the cesium precipitate, but the latter is quite unsuitable for this purpose because the separation of rubidium from a large amount of potassium in the filtrate is very difficult.

Therefore NaBiI₄ reagent is appropriate for the determination of potassium and rubidium in the mixture. The results obtained with NaBiI₄ reagent are shown in Table 4 which indicates that the determination of cesium by this method can be made with an accuracy similar to that with KBiI₄ reagent.

Table 4. Determination of cesium by NaBiI₄ reagent.

CsCl taken (mg.)	NaBiI₄ (ml.)	Total volume (ml.)	$Cs_3Bi_2I_9$ (mg.)	CsCl found (mg.)	Error (mg.)
2.00	1	2	7.72	1.99	−0.01
5.00	1	3	19.30	4.98	−0.02
10.00	1	3	38.65	9.96	−0.04
20.00	1	3	77.83	20.08	+0.08
2.00	2	3	7.64	1.97	−0.03
5.00	2	5	19.30	4.97	−0.02
10.00	2	5	38.90	10.03	+0.03
20.00	2	5	77.20	19.90	−0.10

5) Interfering Ions

Thallous thallium and rubidium ions interfere with this method. As the former is easily removed as the iodide, it is of no great concern but the presence of the latter is serious because it markedly influences the determination of cesium. This interference of rubidium will be reported in detail later on. The following ions do not interfere with this method: Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, I^-, Cl^-, NO_3^-, CH_3COO^-, SO_4^{2-} etc.

VOLUMETRIC ANALYSIS

The chemical composition of the cesium salt with KBiI₄ or NaBiI₄ reagent has already been reported as $Cs_3Bi_2I_9$. As the iodine in this precipitate can be easily estimated volumetrically, an indirect volumetric method for the determination of cesium can be expected. The procedure is as follows: The cesium salt is produced by the same procedure as that in the gravimetric analysis of cesium and the precipitate is filtered and washed. Then the precipitate is dissolved in 10% hydrochloric acid containing 0.5 grams of potassium cyanide and after adding 1 to 2 ml. of starch solution, the solution is titrated with a 0.02N-potassium iodate solution until the color of the iodine starch reaction has disappeared. The amount of the cesium chloride is found by the following equation,

$$CsCl(mg) = A \times 0.5606$$

where A refers to the volume of the 0.02N-potassium iodate solution. The results obtained by this method are shown in Table 5. It can be seen from the table that a small amount of cesium can be rapidly estimated by this method.

Table 5. Volumetric determination of cesium.

CsCl taken (mg.)	KBiI₄ (ml.)	Total volume (ml.)	0.02N-KIO₃ (ml.)	KCN-HCl (ml.)	CsCl found (mg.)	Error (mg.)
1.00	1	2	1.80	10	0.98	−0.02
2.00	1	2	3.54	″	1.98	−0.02
5.00	1	3	8.83	″	4.95	−0.05
10.00	1	3	17.80	″	9.98	−0.02
20.00	1	3	35.90	″	20.14	+0.14

SUMMARY

As for the determination of cesium by KBiI₄ or NaBiI₄ reagent, the optimum conditions have been found and by combinig them, a new gravimetric method has been established. This method is particularly excellent for the determination of a small amount of cesium. In addition, a volumetric method for the determination of cesium is also proposed.

ACKNOWLEDGMENT

REFERENCES

(1) N. A. Tananaeff and E. P. Harmasch, *Z. anal. Chem.*, **89**, 256 (1932).
(2) R. W. Feldmann, *Z. anal. Chem.*, **102**, 102 (1935).