The Determination of Cesium in the Presence of
Other Alkali Elements*

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This study was made to estimate cesium in the presence of various amount of other alkali elements especially rubidium. The amount of cesium is found directly by the $KBiI_4$ or the $NaBiI_4$ method when the amount of the rubidium accompanying the cesium is less than one-half of the cesium in the sample, but in the presence of a much larger amount of rubidium, the exact determination of the cesium must depend on the reprecipitation of the cesium salt. Moreover, a method for the determination of cesium in the presence of a large amount of sodium and potassium is also reported.

INTRODUCTION

The gravimetric and volumetric methods for the determination of a small amount of cesium have already been reported, but the determination of cesium in the presence of other alkali elements, especially rubidium, has not been reported at all. So this study was made to estimate the amount of cesium in the presence of other alkali elements.

While no precipitate is formed from a saturated solution of rubidium chloride by the $NaBiI_4$ or the $KBiI_4$ the reagent, a considerable amount of rubidium coprecipitates with the cesium salt when the cesium salt is thus precipitated in the presence of rubidium. This phenomenon is thought to be a typical post-precipitation, or a kind of coprecipitation.

When the amount of the rubidium accompanying the cesium is less than one-half of the cesium in the sample, the amount of the coprecipitated rubidium is small and therefore the amount of the cesium can be directly and exactly found with the $KBiI_4$ or the $NaBiI_4$ reagent.

However, in the presence of a much larger amount of rubidium, the amount of the coprecipitated rubidium rapidly increases, and therefore the exact determination of the cesium can not be made by the $KBiI_4$ or the $NaBiI_4$ method.

Fortunately, it has been found that the amount of the coprecipitated rubidium with cesium salt is less than one-half that of cesium present. This fact suggests that by the reprecipitation of the cesium salt the exact determination of the cesium in the presence of a large amount of the rubidium may be possible. As a matter of fact, a small amount of cesium in a large amount of rubidium has been determined by the reprecipitation of the cesium salt. As it

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is impossible to reprecipitate in the form of $Cs_3Bi_2I_9$, this salt is destroyed and the cesium is again precipitated by adding the $KBiI_4$ or the $NaBiI_4$ reagent after removal of the bismuth.

For the determination of a small amount of cesium in an extremely large amount of rubidium, potassium and sodium, the larger part of the impurities are preliminarily separated from the cesium and then the cesium is determined by the reprecipitation method.

CHEMICALS AND APPARATUS

Hexanitrodipicrylaminate Solution : 0.1N-Hca solution.
Metal Iodides : Sodium iodide, magnesium iodide, stannic iodide, cobalt iodide, nickel iodide and ferric iodide.
All other reagents and the experimental apparatus are the same as in the previous report.

EXPERIMENT

Table 1. Determination of cesium in the presence of rubidium.

CsCl (mg.)	RbCl (mg.)	$KBiI_4$ (ml.)	Total volume (ml.)	Cooling (hours)	$Cs_3Bi_2I_9$ (mg.)	CsCl (mg.)	Error (mg.)
2.00	—	1	2	1	7.70	1.99	−0.01
5.00	—	1	3	1	19.26	4.97	−0.03
10.00	—	1	3	1	39.10	10.08	+0.08
20.00	—	1	3	1	77.38	19.95	−0.05
30.00	—	2	5	1	116.75	30.01	+0.01
2.00	1	1	2	1	7.81	2.01	+0.01
5.00	2.5	1	3	1	19.50	5.04	+0.04
10.00	5	1	3	1	39.06	10.04	+0.04
20.00	10	1	3	1	78.22	20.16	+0.16
30.00	15	2	5	1	117.41	30.27	+0.27
2.00	2	1	2	1	7.95	2.05	+0.05
5.00	5	1	3	1	19.92	5.13	+0.13
10.00	10	1	3	1	39.78	10.25	+0.25
20.00	20	1	3	1	79.62	20.54	+0.54
30.00	30	2	5	1	118.90	30.65	+0.65
2.00	5	1	2	1	8.41	2.18	+0.18
5.00	10	1	3	1	21.25	5.48	+0.48
10.00	20	1	3	1	43.20	11.14	+1.14
20.00	40	1	3	1	83.45	21.51	+1.51
30.00	60	2	5	1	124.58	32.10	+2.10
2.00	50	1	3	2	9.18	2.35	+0.37
5.00	100	1	7	2	24.30	6.26	+1.26
10.00	100	1	7	1	46.76	12.02	+2.02
20.00	100	1	7	1	87.57	22.55	+2.55
30.00	100	2	7	1	129.58	33.40	+3.40
5.00	150	1	7	2	27.81	7.17	+2.17

(1) Effect of the Rubidium on the Cesium Salt

Table 1 shows the results obtained in the determination of cesium in the presence of rubidium by the $KBiI_4$ method. As seen from the Table, the cesium can be directly determined by the $KBiI_4$ method when the amount of the accompanying rubidium is less than one-half of the amount of the cesium, but the experimental results in the presence of a much larger amount of rubidium show larger positive errors.

(2) Preventing the Coprecipitation of Rubidium with the Cesium Salt

The following fact suggests the possibility of preventing the co-precipitation of rubidium with the cesium salt. It is well known that the double salt composed of cesium chloride and antimony chloride carries down a considerable amount of rubidium but that the triple salt composed of cesium chloride, antimony chloride and sodium chloride or ferric chloride carries a much smaller amount of rubidium in the presence of rubidium. Moreover, antimony and bismuth are known to produce similar double salts, $3CsCl \cdot 2SbCl_3$ and $3CsI \cdot 2BiI_3$. From these considerations, various metal iodides were added and studied as to their ability to prevent the coprecipitation of rubidium with the cesium salt. The added iodides were as follows: NaI, MgI_2, CaI_2, SrI_2, BaI_2, SnI_4, CoI_2, NiI_2, FeI_3.

However, the results obtained were all negative and no desirable effects were observed.

(3) Relationships between the Amount of the Coprecipitated Rubidium and the Amount of the Cesium Salt

The attempt to prevent the coprecipitation of rubidium by adding various metal iodides ended in failure. So the relationships between the amount of the coprecipitated rubidium and the amount of the cesium salt have been studied in detail and as a result, several useful data for the determination of a small amount of cesium in the presence of alkali elements have been found.

The amount of the coprecipitated rubidium was determined as follows: A definite amount of the cesium salt containing rubidium is dissolved in acid and the sum of the dipicrylaminate of rubidium and cesium (H_{Rb+Cs}) is estimated. Then the amount of the coprecipitated rubidium is counted from the difference between H_{Rb+Cs} and H_{Cs} which is the theoretical amount of the cesium. The

Table 2. The amount of coprecipitated rubidium.

CsCl taken (mg.)	RbCl taken (mg.)	$Cs_3Bi_2I_9$ (mg.) Experimental	$Cs_3Bi_2I_9$ (mg.) Theoretical	Coppted Rb–salt (mg.)	H_{Rb+Cs} (mg.)	H_{Cs} (mg.)	H_{Rb} (mg.)	RbCl coppted (mg.)
10.00	100	47.25	38.79	8.46	41.25	33.88	7.37	1.70
20.00	100	88.10	77.58	10.52	76.85	67.76	9.09	2.10
30.00	100	130.20	116.37	13.83	113.20	101.64	11.56	2.53
40.00	100	176.40	155.16	21.24	154.65	135.52	19.13	4.42
10.00	150	48.85	38.79	10.06	42.20	33.88	8.32	1.92
	(sat. soln)							

results obtained by this method are shown in Table 2. From the table, it is seen that the amount of the coprecipitated rubidium is less than one-half of the amount of the cesium even in the saturated solution of rubidium. Therefore it can be expected that the amount of cesium can be exactly estimated by re-precipitation of the cesium salt.

(4) Determination of Cesium in the Presence of Rubidium

Two kinds of procedure have to be considered according to whether the amount of the accompanying rubidium is more than 200 mg. or not. Those procedures are as follows :

(A) RbCl < 200 mg : The cesium salt containing a small amount of rubidium is obtained by the previous KBiI₄ method and the salt is dissolved in 3 to 4 ml. of dilute nitric acid. The filter-stick is thoroughly washed with dilute hot nitric acid and the filtrate is added to the previous solution.

Then the vessel is covered with a watch-glass, and hydrogen sulfide gas is passed into the solution using a glass capillary. The deposited bismuth sulfide is filtered through a glass-filter equipped with the foot, and the filtrate is received in another vessel which has been preliminarily weighed together with a filter-stick. The filtrate is evaporated to dryness and dried in an oven to drive off the nitric acid. Then, a definite amount of the saturated solution of potassium iodide in concentrated acetic acid is added and heated, followed by the determination of the cesium by the KBiI₄ method.

Table 3. Determination of cesium by reprecipitation (1).

CsCl taken (mg.)	RbCl taken (mg.)	KBiI₄ (ml.)	Total volume (ml.)	Cooling (hrs.)	KBiI₄ (ml.)	Total volume (ml.)	Cs₃Bi₂I₉ (mg.)	CsCl (mg.)	Error (mg.)
2.00	50	1	3	2	1	2	7.70	1.98	−0.02
5.00	100	1	5	2	1	3	19.26	4.96	−0.05
10.00	100	1	5	1	1	3	38.52	9.92	−0.08
20.00	100	1	5	1	1	3	77.24	19.92	−0.08
30.00	100	2	5	1	2	5	116.25	29.97	−0.03

The results obtained are shown in Table 3 and it is seen from the Table that the cesium can be exactly estimated by this method.

(B) RbCl > 200 mg : Mixtures containing each 5 and 10 mg. of cesium chloride in 1000 mg. of rubidium chloride which was spectroscopically pure were used as the samples. A sample is dissolved in 20 ml. of 10N-HCl and 40 ml. of 96% ethyl alcohol is added to the hot solution. After cooling with ice, the precipitate (Pɪ) is filtered off and washed with 96% ethyl alcohol. The filtrate is evaporated just short of dryness and 10 ml. of 10N-HCl and 20 ml. of 96% ethyl alcohol are added. Then the precipitate (Pɪɪ) is filtered off. The filtrate is evaporated just short of dryness and 5 ml. of 10N-HCl and 10 ml. of 96% ethyl alcohol are added. The precipitate (Pɪɪɪ) is filtered off, and the filtrate is evaporated to dryness on the steam-bath.

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Table 4. Determination of cesium by reprecipitation (2).

Exp. No.	1	2	3	4	5	6
RbCl (mg.)	1000	1000	1000	1000	1000	1000
CsCl (mg.)	5.00	5.00	5.00	10.00	10.00	10.00
P_I (mg.)	439.0	451.0	457.3	429.0	462.0	443.0
P_{II} (mg.)	375.3	357.8	332.8	388.5	353.8	368.9
P_{III} (mg.)	70.8	82.5	90.0	85.7	73.7	83.3
$P_I+P_{II}+P_{III}$ (mg.)	885.1	891.3	880.1	903.2	889.5	895.2
CsCl+RbCl (mg.)	119.9	113.7	124.9	106.8	120.5	114.8
$KBiI_4$ (ml.)	1	1	1	1	1	1
Tot. vol. (ml.)	5	5	5	6	6	6
P_{Cs+Rb} (mg.)	24.35	26.90	25.45	46.20	47.80	47.25
$KBiI_4$ (ml.)	1	1	1	1	1	1
Tot. vol. (ml.)	3	3	3	4	4	4
$Cs_3Bi_2I_9$ (mg.)	19.25	19.10	19.31	38.40	38.66	38.05
CsCl (mg.)	4.96	4.92	4.98	9.90	9.96	9.81
Error (mg.)	−0.04	−0.08	−0.02	−0.10	−0.04	−0.19

Table 5. Determination of cesium in the presence of LiCl, NaCl and KCl.

CsCl taken (mg.)	Accompanined salt		$KBiI_4$ (ml.)	Total volume (ml.)	$Cs_3Bi_2I_9$ (mg.)	CsCl (mg.)	Error (mg.)
	Kind	Weight (mg.)					
2.00	KCl	1	1	2	7.75	2.00	±0.00
5.00	〃	2.5	1	3	19.35	4.99	−0.01
10.00	〃	5	1	3	38.75	9.99	−0.01
20.00	〃	10	1	3	77.80	20.06	+0.06
30.00	〃	15	2	4	116.25	29.97	−0.03
2.00	〃	2	1	2	7.80	2.01	+0.01
5.00	〃	5	1	3	19.30	4.98	−0.02
10.00	〃	10	1	3	38.55	9.94	−0.06
20.00	〃	20	1	3	77.65	20.02	+0.02
30.00	〃	30	2	4	116.50	30.03	+0.03
2.00	〃	20	1	3	7.70	1.99	−0.01
5.00	〃	40	1	4	19.40	5.00	±0.00
10.00	〃	50	1	4	38.48	9.91	−0.09
20.00	〃	50	1	4	77.90	20.08	+0.08
30.00	〃	50	2	5	117.20	30.21	+0.21
2.00	NaCl	20	1	2	7.80	2.01	+0.01
5.00	〃	20	1	3	19.32	4.98	−0.02
10.00	〃	30	1	4	38.65	9.96	−0.04
20.00	〃	50	1	4	77.85	20.06	+0.06
30.00	〃	50	2	5	116.75	30.10	+0.10
2.00	LiCl	20	1	2	7.65	1.97	−0.03
5.00	〃	20	1	3	19.25	4.97	−0.03
10.00	〃	30	1	4	38.55	9.94	−0.06
20.00	〃	50	1	4	77.60	20.01	+0.01
30.00	〃	50	2	5	116.45	29.92	−0.08

After the residue was dried in an air oven, the amount of the cesium was found by method (A) and the results are shown in Table 4. It is found from the Table that a small amount of cesium in a large amount of rubidium can be exactly determined by this method. The blank test was made using a sensitive $HBiI_4$ reagent on the residue obtained by separating P_I, P_{II} and P_{III} from one gram of rubidium chloride, but no cesium was found.

(5) Determination of Cesium in the Presence of Other Alkali Elements

Two procedures have to be considered according to the amount of LiCl, NaCl and KCl in the sample. Procedure (A) is appropriate for a sample in which the amount of LiCl, NaCl and KCl is not too large and Procedure (B) is appropriate for a sample in which the amount of these elements is much larger.

Procedure (A): In this case, the cesium in the sample is directly determined by the $KBiI_4$ method. The results obtained are shown in Table 5. As seen from the Table, the values are satisfactory.

Procedure (B): A sample which does not contain rubidium chloride is dissolved in the minimum water necessary for dissolving it and to the hot solution, a mixed solution composed of one part of concentrated hydrochloric acid and two parts of ethyl alcohol is added.

While the solution is hot, precipitates are filtered off and the filtrate is evaporated to dryness. A definite amount of the previous mixed solution is added to it and the residue is filtered off after thirty minute's heating. The residue is washed with 96% ethyl alcohol, and the filtrate is evaporated to dryness. From the residue, the cesium is directly determined by the $KBiI_4$ method. The results obtained are shown in Table 6, and it is seen from the Table that a small amount of cesium in a large amount of rubidium can be exactly determined by this method.

Table 6. Determination of cesium in the presence of a large amount of NaCl and KCl.

NaCl (mg.)	KCl (mg.)	CsCl (mg.)	$Cs_3Bi_2I_9$ (mg.)	CsCl (mg.)	Error (mg.)
1000	—	5.00	19.22	4.96	−0.04
1000	—	10.00	39.10	10.08	+0.08
1000	—	20.00	77.96	20.10	+0.01
—	1000	5.00	19.14	4.94	−0.06
—	1000	10.00	39.43	10.15	+0.15
—	1000	20.00	78.12	20.14	+0.14

SUMMARY

The cesium in a sample in which the amount of the rubidium is less than one-half of the cesium can be directly determined by the $KBiI_4$ method. However in order to estimate the cesium in a sample in which the amount of the rubidium is much larger than the amount of the cesium, the first cesium salt has to be reprecipitated for the exact determination of cesium.

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The cesium in a sample in which the amounts of LiCl, NaCl and KCl are not too large can be directly determined by the KBiI₄ method. If the amounts of NaCl and KCl are extremely large, the cesium can be determined by the KBiI₄ method after the preliminary removal of the larger part of NaCl and KCl.

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