

On a New Method for Separating Rubidium and Cesium from Potassium

Masayoshi ISHIBASHI, Toshio YAMAMOTO and Tadashi HARA

(Ishibashi Laboratory)

Received February 4, 1959

In order to separate rubidium and cesium from potassium, a new reagent, $\text{Na}_2\text{AgBi}(\text{NO}_2)_6$, was proposed and a method using it was established. As this reagent reacts selectively with rubidium and cesium, the amounts of rubidium and cesium in a large amount of potassium can be accurately determined by this method. This method is also convenient for the identification of rubidium and cesium since a yellow precipitate is formed even when only small amounts are present. The amounts of rubidium contained in several kinds of potassium salts were also found.

INTRODUCTION

There are a lot of reagents which have been used for the separation of rubidium and cesium from potassium, but it is not an exaggeration to say that there is no satisfactory reagent because none of them involve any selective reaction with rubidium and cesium and therefore their exact separation from potassium is not only incomplete but also very difficult.

The authors have already studied the reagents for the separation of potassium, rubidium and cesium, and $\text{Na}_2\text{AgBi}(\text{NO}_2)_6$ reagent has been reported as an excellent one for the separation of rubidium and cesium from Potassium. With this reagent, no precipitate is produced even in a saturated solution of a potassium salt, but 20 p.p.m. of rubidium can be identified as the yellow crystalline precipitate. In addition to these facts, this reagent produces more difficultly soluble salts of rubidium and cesium than those salts produced with the well known $\text{Na}_3\text{Bi}(\text{NO}_2)_6$ reagent¹⁾. Based on these experimental facts, the separation of rubidium and cesium from potassium has been studied, and a new method has been established. The distinctive characteristic of this method consists in the fact that rubidium and cesium are selectively separated from potassium. This paper deals with the study of the conditions which are necessary for the separation of rubidium and cesium from potassium with the $\text{Na}_2\text{AgBi}(\text{NO}_2)_6$ reagent and its application for the determination of the amount of rubidium in potassium salts.

REAGENTS AND APPARATUS

Potassium Nitrate : Potassium chloride is purified by dropping its hot satu-

* Read at the First Annual Congress, Japan Society for Analytical Chemistry, October 1952.

** 石橋雅義, 山本俊夫, 原 正

rated solution into concentrated hydrochloric acid and recrystallizing it. Then the chloride is converted into the nitrate²⁾ by treating with concentrated nitric acid. The purity of the dried potassium nitrate was tested with the $\text{Na}_2\text{AgBi}(\text{NO}_2)_6$ reagent, but no rubidium was found.

Rubidium Nitrate Solution : Purified rubidium chloride is converted into the nitrate, and standard solutions of 2.00 mg. and 4.86 mg. respectively of rubidium per one gram of solution were prepared.

Cesium Nitrate Solution : Purified cesium chloride is converted into the nitrate and two solutions which contain 2.00 mg. and 4.92 mg. respectively cesium per one gram of solution were prepared. A definite amount of rubidium and cesium was taken from these solutions, the amount determined by weight.

$\text{Na}_2\text{AgBi}(\text{NO}_2)_6$ Reagent : This reagent consists of (a) and (b) which have the following compositions.

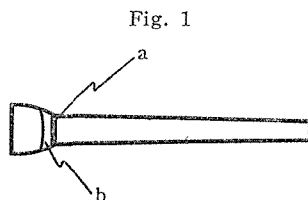
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| (a) | { | Bi $(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ | 20.5 gr. |
| | | AgNO ₃ | 2.0 gr. |
| | | 6 <i>N</i> -CH ₃ COOH | 100 ml. |
- (b) 9*N*-NaNO₂ solution

As a mixture of (a) and (b) is unstable, they are separately added to the sample solution. The above composition of each reagent has been found experimentally, and the reagent has been found to be best when they are used in ratio of two parts of (a) to three parts of (b). The mixture of (a) and (b) is unstable when it stands in the open air, but when it is placed in a glass-stoppered bottle and stored in a cold place, it is stable for a much longer time. It is doubtful whether the proposed chemical formula of the reagent is right or not, but it will be used for simplicity.

Washing solution : A washing solution which has the following composition was prepared, placed in a glass-stoppered bottle and cooled with ice for an hour before its use.

- | | | | |
|------------------|---|-------------------|---------|
| Washing Solution | { | Reagent (a) | 2 parts |
| | | Reagent (b) | 3 parts |
| | | Water | 3 parts |

Filter-Stick : The filter-stick equipped with a platinum spiral and purified asbestos as shown in Fig. 1 were prepared.



EXRERIMENT

1) Composition of the Precipitate

The precipitate produced with the $\text{Na}_2\text{AgBi}(\text{NO}_2)_6$ reagent determined in

that form since no suitable washing solution has been found, and the precipitate is also apt to hydrolyze in a neutral or alkaline aqueous medium. In addition, the precipitate is easily dissolved in various mineral acids, and the composition of this precipitate is not thought to be constant, considering that the composition of the precipitate produced by the $\text{Na}_3\text{Co}(\text{NO}_2)_6$ and AgNO_3 reagent³⁾ is not constant. Therefore, in this method, the rubidium and the cesium in a sample are precipitated and separated from potassium and then they are determined by an other method.

2) Separation of Rubidium and Cesium from Potassium

In order to find the optimum conditions for separating rubidium and cesium from potassium, various studies have been made in detail. These studies were made under the assumption that a procedure by which rubidium can be quantitatively separated from potassium should be also conveniently applicable for the separation of cesium from potassium since cesium salts are more difficultly soluble than rubidium salts. This assumption has been substantiated by the results of this study.

a) **Procedure.** A definite amount of rubidium is weighed and taken into a vessel and to it are added distilled water, reagent (b) and (a). The vessel is covered with a watch-glass and cooled. The yellow rubidium salt is immediately precipitated, and it is filtered with the filter-stick charged with asbestos after cooling with ice. The precipitate is washed four to five times with 0.6 to 1.0 ml. of the washing solution each time. The platinum spiral and the asbestos in the filter-stick are taken off by pushing at the opposite side with a platinum wire and washed down into the vessel with distilled water. The filter-stick is washed with 0.5 ml. of concentrated nitric acid in another vessel. The solution is brought to about 10 ml. and a few drops of concentrated hydrochloric acid are added to it. By passing hydrogen sulfide gas into it, the sulfide is precipitated and filtered off. The filtrate is vaporized to dryness and dried at 150°C. Then the residue is dissolved in a little water and the solution is transferred into a vessel which has been preliminarily weighted with a filter-stick, followed by the determination of the rubidium using 0.1 *N*- HCl_a reagent.

Table 1. Determination of potassium by HCl_a reagent.

K taken (mg.)	0.1 <i>N</i> - HCl_a (ml.)	Total volumm (ml.)	HK found (mg.)	K fonnd (mg.)	Error (mg.)
1.04	0.7	1.7	13.21	1.08	+0.04
1.04	0.7	1.7	13.10	1.07	+0.03
1.04	0.5	1.5	12.72	1.04	±0.00
2.08	1.5	3.5	25.52	2.09	+0.01
2.08	1.0	3.0	25.73	2.11	+0.03
5.19	3.0	8.0	63.95	5.24	+0.05
5.19	2.0	7.0	62.80	5.15	-0.04
10.46	6.0	16.0	127.02	10.41	-0.05
10.46	4.0	14.0	127.36	10.43	-0.03

b) **Determination of potassium and rubidium by H_{Ca} reagent⁴⁾.** In order to examine the procedure for the separation of rubidium and cesium from potassium, it is indispensable that the amounts of these elements be exactly estimated. For these reasons, cesium was determined by the $KBiI_4$ method which has been already reported, and potassium and rubidium were determined by means of 0.1 N - H_{Ca} reagent. In the latter case, special care has to be taken of the reagent concentration in the supernatant liquid when H_K and H_{Rb} are precipitated and the various accompanying elements have valencies of two or three. It is necessary for the exact determination of potassium and rubidium that the reagent concentration in the supernatant liquid be 0.01~0.03 N . Tables 1 and 2 show the results obtained in the determination of potassium and rubi-

Table 2. Determination of rubidium by H_{Ca} reagent.

Rb taken (mg.)	0.1 N - H_{Ca} (ml.)	Total volume (ml.)	H_{Rb} found (mg.)	Rb found (mg.)	Error (mg.)
1.76	0.5	1.5	10.90	1.77	+0.01
1.76	0.5	1.5	10.90	1.76	± 0.00
1.76	0.5	1.5	10.82	1.76	± 0.00
4.00	2.0	4.0	24.82	4.04	+0.04
4.00	2.0	4.0	24.38	3.97	-0.03
8.02	4.0	8.0	49.10	8.00	-0.02
8.02	4.0	8.0	49.42	8.05	+0.03
17.61	8.0	18.0	107.37	17.50	-0.11
17.61	8.0	18.0	107.84	17.58	-0.03

dium by 0.1 N - H_{Ca} reagent. As seen from the tables, these elements can be determined satisfactorily by this method.

c) **Recovery of rubidium.** The results obtained with regard to definite amount of rubidium by the above procedure are shown in Table 3 and Table

Table 3. Determination of rubidium after precipitation (1).

Exp. No.	1	2	3	4	5	6	7
Rb taken (mg.)	4.97	4.97	4.97	4.97	4.97	4.97	4.97
H_2O (ml.)	1	2	3	4	5	6	7
Reag. (b) (ml.)	3	3	3	3	3	3	3
Reag. (a) (ml.)	2	2	2	2	2	2	2
Cooling (hrs)	3	3	3	3	3	3	3
H_{Rb} found (mg.)	30.91	30.63	29.84	30.76	29.94	29.75	29.82
Rb found (mg.)	5.04	4.99	4.88	5.03	4.89	4.86	4.88
Error (mg.)	+0.07	+0.02	-0.09	+0.06	-0.08	-0.11	-0.09

4. As seen from these tables, it is desirable that the volume of the aqueous sample solution be less than 7 ml. before the reagent solutions are added. The results also indicate that a certain range of change in the ratio of reagent (a) to reagent (b) does not extremely affect the results.

New Method for Separating Rubidium

Table 4. Determination of rubidium after precipitation (2).

Exp. No.	1	2	3	4	5	6	7
Rb taken (mg.)	4.97	4.97	4.97	4.97	4.97	4.97	4.97
H ₂ O (ml.)	0.5	1	2	3	4	5	6
Reag. (b) (ml.)	3	3	3	3	3	3	3
Reag. (a) (ml.)	1	1	1	1	1	1	1
Cooling (hrs)	3	3	3	3	3	3	3
HR _b found (mg.)	29.35	29.64	30.70	29.68	29.20	30.72	29.78
Rb found (mg.)	4.78	4.83	5.00	4.85	4.76	5.04	4.87
Error (mg.)	-0.19	-0.14	+0.03	-0.12	-0.21	+0.07	-0.10

d) **Washing of the precipitate.** The precipitate produced from 4.97 mg. of rubidium was washed various times with one ml. of washing solution each time and the recoveries of the rubidium in each case were determined. The data is nearly constant for less than six washings.

e) **Determination of rubidium in the presence of potassium.** The results obtained in the presence of various amounts of potassium are shown in Table 5. As seen from the table, the values of rubidium increase with an increase in

Table 5. Determination of rubidium in the presence of potassium.

Exp. No.	1	2	3	4	5	6	7
Rb taken (mg.)	4.97	4.97	4.97	4.97	4.97	4.97	4.97
K taken (mg.)	0	5	10	20	50	250	500
H ₂ O (ml.)	3	3	3	3	3	3	3
Reag. (b) (ml.)	3	3	3	3	3	3	3
Reag. (a) (ml.)	2	2	2	2	2	2	2
Tot. vol. (ml.)	9	9	9	9	9	9	9
Cooling (hrs)	2	2	2	2	2	2	2
Washing (times)	5	5	5	5	5	5	5
HR _b (mg.)	30.82	30.60	34.93	44.58	56.24	55.06	50.26
Rb found (mg.)	5.03	5.00	5.69	7.27	9.16	8.97	8.19
Error (mg.)	+0.06	+0.03	+0.72	+2.30	+4.19	+4.00	+3.22

the amount of the accompanying potassium, but the amount of the potassium coprecipitated with rubidium is less than that of rubidium. Also, rubidium can be directly determined in the presence of potassium if the amount is less than that of the rubidium. Therefore, if the precipitate produced by the Na₂AgBi (NO₂)₆ reagent can be recrystallized, an exact result for rubidium can be expected to be obtained by that procedure.

3) Separation by Reprecipitation

It has been tried to separate rubidium from potassium by recrystallizing by the Na₂AgBi (NO₂)₆ reagent. The procedure is as follows :

The precipitate obtained in accordance with the method of (2)·(3) is filtered, washed and taken off together with the asbestos and the platinum spiral by

pushing them at the opposite side with a platinum wire. The residual precipitate on the filter-stick is washed down into the vessel by the washing solution which is contained in a microwashing-bottle and the volume is brought to about 7 ml. The vessel is covered with a watch-glass and warmed for about five minutes on a steam-bath. Then the vessel is cooled with ice for an hour and a half. The precipitate is filtered and washed three times with the washing solution. The precipitate is treated by the same procedure as that in (2)·(a) and the amount of the rubidium is found.

The results obtained by these methods are shown in Tables 6 and 7. It is

Table 6. Determination of rubidium by reprecipitation.

Exp. No.	1	2	3	4	5	6	7
Rb taken (mg.)	4.86	4.86	4.86	4.86	4.86	4.86	4.86
K taken (mg.)	0	5	10	20	50	250	500
Reag. (b) (ml.)	2	2	2	2	2	2	2
Reag. (a) (ml.)	3	3	3	3	3	3	3
H ₂ O (ml.)	4	4	4	4	4	4	4
Tot. vol. (ml.)	10	10	10	10	10	10	10
Cooling (ml.)	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Washing (times)	5	5	5	5	5	5	5
Precipitant (ml.)	7	7	7	7	7	7	7
Cooling (hrs)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Washing (times)	3	3	3	3	3	3	3
HR _b (mg.)	29.92	29.55	29.86	29.74	29.88	30.02	29.64
Rb found (mg.)	4.88	4.82	4.87	4.85	4.86	4.89	4.84
Error (mg.)	+0.02	-0.04	+0.01	-0.01	+0.00	+0.03	-0.02

Table 7. Determination of rubidium in the presence of a large amount of potassium.

Exp. No.	1	2	3	4	5	6	7
Rb taken (mg.)	1.96	9.92	19.44	1.96	4.86	9.92	19.44
K taken (mg.)	500	500	500	750	750	750	750
H ₂ O (ml.)	7	7	7	7	7	7	7
Reag. (b) (ml.)	3	3	3	3	3	3	3
Reag. (a) (ml.)	2	2	2	2	2	2	2
Tot. vol. (ml.)	13	13	13	13	13	13	13
Cooling (hrs)	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Washing (times)	5	5	5	5	5	5	5
Precipitant (ml.)	7	7	7	7	7	7	7
Washing (times)	3	3	3	3	3	3	3
HR _b found (mg.)	11.96	61.02	120.2	11.66	29.48	60.53	119.8
Rb found (mg.)	1.95	9.95	19.60	1.90	4.81	9.86	19.52
Error (mg.)	-0.01	+0.03	+0.16	-0.06	-0.05	-0.06	+0.08

seen from these tables that the recrystallization method must be adopted in order to separate rubidium from potassium quantitatively.

4) Determination of Cesium in Potassium

For the determination of a small amount of cesium in a large amount of potassium, the cesium is separated from most of the potassium by (2)·(a) and determined by the KBiI_4 method. The results obtained are shown in Table 8

Table 8. Determination of cesium in the presence of a large amount of potassium.

Exp. No.	1	2	3	4	5	6	7	8
Cs taken (mg.)	1.98	1.98	1.98	1.98	4.92	4.92	9.84	9.84
K taken (mg.)	50	100	250	500	250	500	250	500
H ₂ O (ml.)	7	7	7	7	7	7	7	7
Reag. (b) (ml.)	3	3	3	3	3	3	3	3
Reag. (a) (ml.)	2	2	2	2	2	2	2	2
Tot. vol. (ml.)	12	12	12	12	12	12	12	12
Cooling (hrs)	3	3	3	3	3	3	3	3
Washing (times)	5	5	5	5	5	5	5	5
Cs ₃ Bi ₂ I ₉ (mg.)	9.70	9.75	9.68	9.80	24.22	23.90	48.21	48.53
Cs found (mg.)	1.97	1.98	1.97	1.99	4.92	4.87	9.80	9.87
Error (mg.)	-0.01	±0.00	-0.01	+0.01	+0.00	-0.05	-0.04	+0.03

and indicate that cesium can be accurately determined by this method.

5) Application of this Method

A small amount of rubidium and cesium in a large amount of potassium have been satisfactorily determined by the above methods, so these methods have been applied to the determination of rubidium in several samples.

Determination of Rubidium in analytical grade Potassium chloride. 10 grams of a potassium chloride sample are dissolved in hot water and one part of potassium chloride is deposited by adding concentrated hydrochloric acid. The precipitate is filtered while the mother liquor is hot and washed with concentrated hydrochloric acid. The filtrate is condensed until a crystal begins to deposit on the vessel wall and 96% ethyl alcohol is added. The chloride is immediately filtered and washed with 96% ethyl alcohol. The filtrate is again condensed until a crystal begins to deposit on the vessel wall and 96% ethyl alcohol is added to it. The precipitate is filtered off and the filtrate is vaporized to dryness. Here the amount of potassium chloride will be one gram or so. The chloride is converted into the nitrate by treating with concentrated nitric acid and the amount of rubidium in the potassium nitrate has been determined by this method. As a result, the amount of rubidium chloride in this potassium chloride has been found to be 0.00057%. The amount of cesium in a common potassium salt is very minute compared with that of the rubidium in it, so the amount found in this study has been considered to be approximately equal to the true amount of rubidium in the sample.

b) Determination of rubidium in potassium nitrate. The purity of this salt is inferior to the previous potassium chloride. 10 grams of a potassium

nitrate sample are taken and converted into the chloride by treating with concentrated hydrochloric acid. Then, the amount of rubidium in the chloride is determined by the same procedure as that in (5)·(a) and the amount of rubidium nitrate in potassium nitrate has been found to be 0.0012%.

SUMMARY

Though there has not been hitherto any suitable method for the separation of rubidium and cesium from potassium, a new method in which $\text{Na}_2\text{AgBi}(\text{NO}_2)_6$ reagent is used and reacts selectively with rubidium and cesium to separate them from potassium has been proposed. It was also shown that a small amount of rubidium and cesium in a large amount of potassium can be quantitatively separated and determined by this method.

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