

# On Concentrating Rubidium and Cesium from a Large Volume of Aqueous Solution\*

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A method for concentrating a small amount of rubidium and cesium from a large volume of aqueous solution has been proposed in which the rubidium and the cesium are coprecipitated with potassium cobaltinitrite which is produced at temperatures below 10°C by adding sodium cobaltinitrite reagent.

By this method, the accuracy in the determination of one to ten milligrams of rubidium and cesium in 10 liter is about  $\pm 10\%$ .

This method has also been applied to the determination of the amount of rubidium dissolved in sea-water.

## INTRODUCTION

Concerning the amount of rubidium dissolved in sea-water, there have been several reports,<sup>1)</sup> but they have many defects and therefore their results differ markedly from each other.

With the ultimate objective of estimating the amounts of rubidium and cesium dissolved in sea-water, this study was made concerning the concentration of a small amount of these elements from a large volume of aqueous solution. For the determination of the amount of rubidium, difficulties are expected to arise in concentrating it from a large volume of aqueous solution and in the exact separation of rubidium from a large amount of potassium.

The latter problem has already been discussed in a previous paper. As for the former, the vaporization method has been chiefly employed as the conventional method. However, in this method, the salts produced during the vaporization must be removed and at the same time a certain amount of rubidium and cesium are probably lost. The following facts have been found during the course of an investigation of the concentration of rubidium and cesium from a large volume of aqueous solution. Most of the potassium in ten liters of solution are carried down at a solution temperature of less than 10°C with  $\text{Na}_3\text{Co}(\text{NO}_2)_6$  reagent and a large amount of potassium cobaltinitrite is also precipitated from ten liters of sea-water under the same conditions. Therefore it was thought that most of the rubidium and cesium would be carried down with the potassium cobaltinitrite, and this would be an available method for the efficient concentration of them. Accordingly, the recoveries of rubidium

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and cesium have been studied in detail and as a result, rubidium and cesium have been found to be almost quantitatively precipitated from an artificial sea-water. Then the amount of rubidium dissolved in sea-water was also found.

### REAGENT AND APPARATUS

$\text{Na}_3\text{Co}(\text{NO}_2)_6$  Reagent : Prepared by Ishibashi-Kagi's method.<sup>2)</sup>

$\text{H}_{\text{Mg}}$  Reagent : Hexanitrodipicrylamine is added to the suspended solution of excess magnesia and it is warmed on a steam-bath until the reagent is completely dissolved. Then the solution is filtered and about 0.15 mole per liter solution is obtained.

Bottle : A bottle of which the content is 20 liters is used for the production of potassium cobaltinitrite. It is rather a new one.

### EXPERIMENT

In order to precipitate rubidium and cesium from a large volume of solution, a study was made of such methods as phosphotungstate, dipicrylamine and cobaltinitrite. As a result, sodium cobaltinitrite reagent has been found to be the best when it is used at lower solution temperatures. The composition of potassium cobaltinitrite produced at lower temperatures is thought to be like  $\text{KNa}_3\text{Co}(\text{NO}_2)_6 \cdot n\text{H}_2\text{O}$ , and its particle size is very fine. If a definite amount of sodium cobaltinitrite reagent is added to the solution which is cooled to less than  $10^\circ\text{C}$  and contains 3.8 grams of potassium, an orange-yellow precipitate would be found throughout the solution. After standing for three hours, the precipitate is completely carried down to the bottom of the vessel and the supernatant liquid is clear. For this type of salt, the solubility of the salt is expected to decrease with an increase in the atomic weight of the alkali element, and therefore most of the rubidium and cesium are expected to be coprecipitated with the potassium salt by this method.

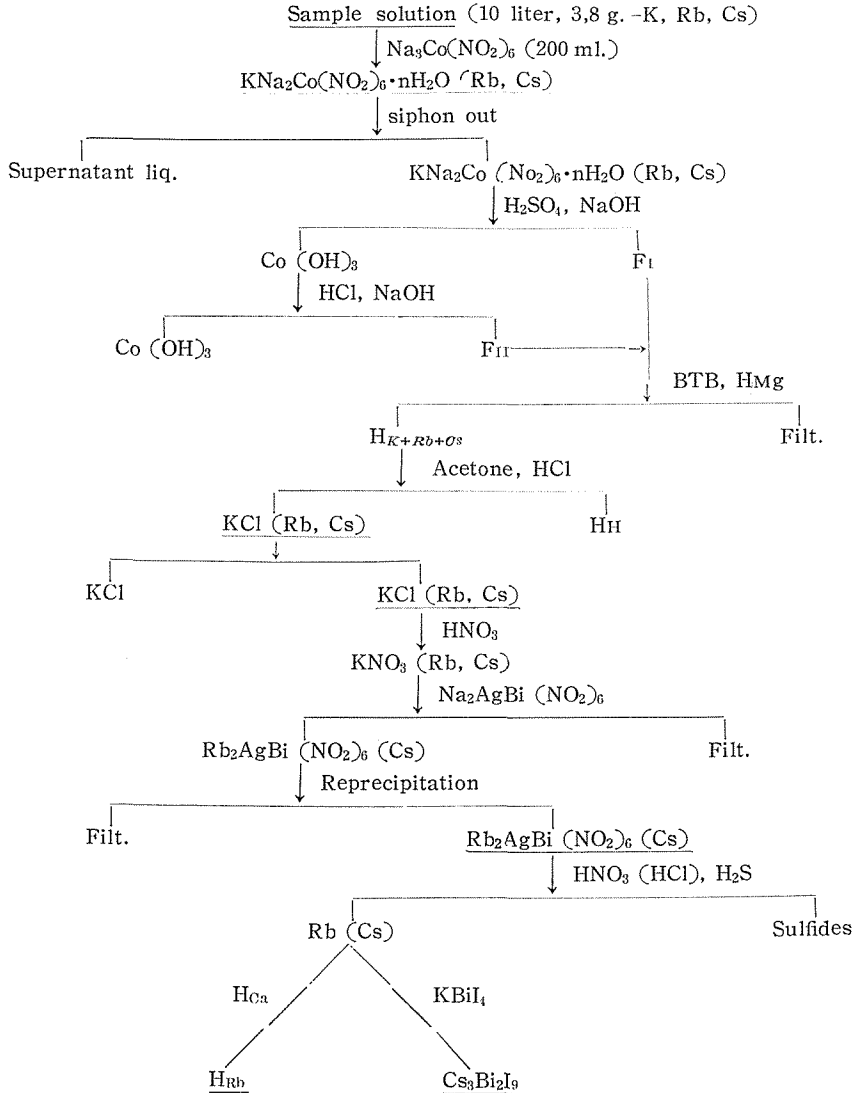
#### 1) Outline of the Procedure

The outline of the procedure is shown in Table 1.

#### 2) Procedure

The determination of the amount of rubidium and cesium was made as follows : 10 liters of a sample solution is put in a 20 liter bottle and the solution temperature is brought below  $10^\circ\text{C}$ . Then 200 ml. of sodium cobaltinitrite reagent is added to it, stirred and allowed to stand quietly. After the salt has been completely carried down to the bottom, the supernatant liquid is siphoned out until the volume of the residual solution is 300 to 400 ml. The precipitate is taken off from the vessel by stirring and transferred into a one liter beaker. After adding a little distilled water, concentrated sulfuric acid is carefully added and the residual precipitate is thoroughly transferred to the previous beaker. Then the precipitate in the beaker is dissolved by heating, and cobalt

Table 1.



hydroxide is precipitated by adding sodium hydroxide solution. The precipitate is filtered off with a glass-filter equipped with a foot and the filtrate (F<sub>I</sub>) is stored. The precipitate is dissolved in a little hydrochloric acid and again treated with sodium hydroxide. The filtrate (F<sub>II</sub>) is added to F<sub>I</sub> and they are concentrated. After a pH adjustment by using an indicator BTB, H<sub>Mg</sub> reagent is added to it and it is cooled with ice. Then the precipitate is filtered through a glass-filter equipped with a foot and washed several times using cool water. After the precipitate has been drained as much as possible, it is completely transferred into the previous beaker by using acetone and the precipitate is thoroughly dissolved in acetone. Immediately a little 6N-hydrochloric acid is added and the red dipicrylamines are completely destroyed into yellow dipi-

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crylamine ( $H_H$ ). After the solution has been brought to about 200 ml. with water, it is warmed on a steam-bath and the acetone is driven off as much as possible. Then the  $H_H$  is filtered off and the filtrate is concentrated until a salt begins to deposit. After adding concentrated hydrochloric acid, the precipitate is filtered off and washed with a concentrated hydrochloric acid. To the filtrate, 5 ml. of 80% ethyl alcohol is added and the deposited salt is filtered off. The precipitate is washed with 80% ethyl alcohol, and the filtrate is vaporized to dryness. The residue is converted into the nitrate by treatment with nitric acid. The nitrate is thoroughly dried in an oven to remove excess nitric acid and dissolved in water. The solution is transferred into a 30 ml. vessel and the volume is brought to 5 to 7 ml. Then 3 ml. of 9*N*-sodium nitrite and 2 ml. of Reagent (a) are added to it, and after covering with a watch-glass, it is cooled with ice for two hours and half. The precipitate is filtered with a filter-stick charged with asbestos and washed four times with washing solution. Then the precipitate is recrystallized as described in the previous paper. The precipitate is filtered after 90 minutes of cooling and washed 3 times with the washing solution. To the precipitate, 0.5 ml. of concentrated nitric acid and a little hydrochloric acid are added and the solution obtained is saturated with hydrogen sulfide gas. The precipitates of bismuth and silver are filtered off, and the filtrate is vaporized to dryness. The residue is dissolved in a little water, and the solution is transferred into a weighing bottle which has been preliminarily weighed together with a glass-filter-stick. After a pH adjustment of the solution, the amount of rubidium is found by use of 0.1*N*- $H_{Ca}$  reagent. For the determination of the cesium, the  $KBiI_4$  reagent is used.

3) Results

The solution temperature and the amount of the reagent which seem to influence the recoveries of rubidium and cesium in the coprecipitation method using sodium cobaltinitrite reagent have been studied in detail.

(a) **Solution temperature.** The experiments have been made with solutions of about 10 liters in which the solution temperature is respectively 9°C and 18°C, and in which 3.8 grams of potassium and a definite amount of rubidium and cesium are contained. The results obtained are shown in Tables 2 and 3. As they indicate, the recoveries of rubidium and cesium get poorer with an

Table 2. Recovery of rubidium.

Soln Temp.		9°C					18°C		
Rb taken	(mg.)	2.00	4.98	4.98	4.98	9.96	2.00	4.98	9.96
K	(g.)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
$Na_3Co(NO_2)_6$	(ml.)	50	50	50	50	50	50	50	50
Tot. vol.	(ml.)	10.05	10.05	10.05	10.05	10.05	10.05	10.05	10.05
$H_{Rb}$	(mg.)	7.67	25.26	24.03	24.78	49.04	4.78	14.72	30.76
Rb found	(mg.)	1.25	4.12	3.92	4.04	8.00	0.78	2.40	5.02
Recovery	(%)	62.5	82.7	78.7	81.1	80.3	39.0	48.2	50.4

Table 3. Recovery of cesium.

Soln temp.	9°C			18°C		
	CaCl taken (mg.)	5.02	10.04	15.06	5.02	10.04
K (g.)	3.8	3.8	3.8	3.8	3.8	3.8
Na <sub>3</sub> Co(NO <sub>2</sub> ) <sub>6</sub> (ml.)	50	50	50	50	50	50
Tot. vol. (ml.)	10.05	10.05	10.05	10.05	10.05	10.05
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>6</sub> (mg.)	16.70	35.70	53.73	10.72	24.39	35.42
CsCl found (mg.)	4.30	9.19	13.83	2.76	6.28	9.12
Recovery (%)	86	91.5	91.8	55	62.6	60.5

increase in the solution temperature, and in any case, the recovery of cesium is better than of rubidium.

(b) **The Amount of reagent.** Under such condition as those described in (a), the recoveries of both elements are not satisfactory, but it is expected that a good recovery may be obtained by lowering the solution temperature or using a larger volume of reagent. Tables 4 and 5 indicate the results obtained for various amounts of reagent and show that the rubidium and the cesium in 10 liters of solution are quantitatively precipitated if 200 ml. of sodium cobaltinitrite is added to the solution at temperatures less than 9°C.

#### 4) Determination of the Amount of Rubidium in Sea-Water

(a) **Preliminary experiment.** By summarizing the data which have been

Table 4. Influence of the amount of reagent on the recovery of rubidium.  
(Solution temperature=9°C)

Exp. No.	1	2	3	4
Rb taken (mg.)	4.98	4.98	4.98	4.98
K (g.)	3.8	3.8	3.8	3.8
Na <sub>3</sub> Co(NO <sub>2</sub> ) <sub>6</sub> (ml.)	50	100	150	200
Tot. vol. (ml.)	10.05	10.10	10.15	10.20
H <sub>Rb</sub> (mg.)	25.27	27.55	28.78	29.58
Rb found (mg.)	4.12	4.49	4.69	4.82
Recovery (%)	82.7	90.3	94.2	96.8

Table 5. Influence of the amount of reagent on the recovery of cesium.  
(Solution temperature=9°C)

Exp. No.	1	2	3	4
CsCl taken (mg.)	5.02	5.02	5.02	5.02
K (g.)	3.8	3.8	3.8	3.8
Na <sub>3</sub> Co(NO <sub>2</sub> ) <sub>6</sub> (ml.)	50	100	150	200
Tot. vol. (ml.)	10.05	10.10	10.15	10.20
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> (mg.)	16.71	18.02	18.33	19.40
CsCl found (mg.)	4.30	4.84	4.93	4.99
Recovery (%)	86.0	96.4	98.2	99.6

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reported, the amount of rubidium in sea-water seems to be within a range of 50 to 500 micrograms. Therefore, as a preliminary experiment to estimate the amount of rubidium in sea-water, a definite amount of rubidium within the above range was added to ten liters of artificial sea-water and the recovery of the rubidium from it was studied. The results obtained are shown in Table 6.

Table 6. Determination of rubidium in artificial sea-water.

Exp. No.	1	2	3	4	5	6
Rb taken (mg.)	1.00	1.00	2.00	2.00	4.98	4.98
Art. sea-water (l)	10	10	10	10	10	10
Na <sub>2</sub> Co(NO <sub>2</sub> ) <sub>6</sub> (ml.)	200	200	200	200	200	200
H <sub>Rb</sub> (mg.)	5.88	5.76	11.90	12.45	29.05	29.40
Rb found (mg.)	0.96	0.94	1.94	2.03	4.74	4.79
Recovery (%)	96	94	97	101	95	96

It is seen from the table that the rubidium in an artificial sea-water can be satisfactorily determined by this method. The composition of one liter of artificial sea-water is as follow : NaCl=23,447 g, MgCl<sub>2</sub>=4.981 g, Na<sub>2</sub>SO<sub>4</sub>=3.917 g, CaCl<sub>2</sub>=1.102 g, KCl=0.742 g, NaHCO<sub>3</sub>=0.192 g.

(b) **The Amount of the rubidium in sea-water.** The sea-water used was sampled at the offing of Shirahama, Wakayama Prefecture and its chlorinity was 18.95‰. 200 ml. of sodium cobaltinitrite reagent was added to 10 liters of sea-water at 9°C and thereafter the same procedure as before was followed to estimate the amount of the rubidium. As a result of it, the weight of H<sub>Rb</sub> was found to be 11.65 mg. This means that 1.9 mg. of rubidium is contained in 10 liters of sea-water, and therefore 190 micrograms of rubidium in one liter of sea-water.

### SUMMARY

(1) A new method for the concentration of rubidium and cesium from a large volume of their solutions has been proposed.

(2) By this method, 1 to 10 mg. of rubidium and cesium in 10 liters of solution can be determined within an error of ±10%.

(3) The amount of rubidium in one liter of sea-water which was sampled at the offing of Shirahama, Wakayama Prefecture was found to be 190 micrograms.

### REFERENCES

- (1) Bunsen, *Phil. Mag.*, **22**, 347 (1861); M. Ishibashi and Y. Harada, *J. Chem. Soc. Japan*, **59**, 383 (1938); T. F. Borvik-Romanova, *Doklady Akad. Nauk, SSSR*, **42**, 221~3 (1944); K. N. Kovaleva and E. S. Bukser, *Dopovidi Akad. Nauk, URSR*, No. 5, 31~36 (1940); H. Wattenberg, *Z. anorg. u. allgem. Chem.*, **251**, 86 (1943).
- (2) M. Ishibashi and K. Kagi, *J. Chem. Soc. Japan*, **59**, 955 (1938).

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(3) H. Wattenberg, *Z. anorg. u. allgem. Chem.*, **236**, 339 (1938).

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