A New Colorimetric Method for the Determination of a Small Amount of Cesium*

Tadashi Hara**
(Ishibashi Laboratory)

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A new method using HBiI₄ reagent has been established for the colorimetric determination of a small amount of cesium. By this method, 10 to 45 µg of cesium can be determined in the presence of less than 4 mg. of potassium and rubidium.

INTRODUCTION

In order to determine a microgram order of cesium in a large amount of rubidium, it has been necessary to depend upon the spectrographic method since the chemical separation of cesium from the above-mentioned sample has been next to impossible. Moreover, it has been found that the identification limit of cesium using the visible spectral lines is 20 µg or so at the most and the intensity of the spectral lines are considerably affected by the presence of other elements. During the course of an investigation of the reaction between the KBiI₄ reagent and a small amount of cesium, a possible method for the determination of cesium in the above-mentioned sample has been found. The principle of the method is as follows: To the dried cesium sample, the HBiI₄ reagent is added and the resulting cesium salt, Cs₃Bi₂I₉, is washed with cold concentrated acetic acid. Then the precipitate is dissolved in dilute nitric acid and the amount of the cesium is indirectly found by the colorimetric determination of bismuth using dithizone-chloroform. This method owes its development to the following experimental facts.

1) The identification limit of cesium is 0.2 µg when 0.03 ml. of HBiI₄ reagent is added to a solid cesium sample.
2) Under the same procedure as the above mentioned one, even 0.5 µg of cesium can be obtained as a red precipitate.
3) Similarly, 5 µg of cesium in 2 mg. of rubidium can be obtained as a red precipitate.
4) Apparently, the amount of the cesium salt obtained is proportional to the amount of the cesium.
5) In the quantitative semi-micro analysis of cesium, it has been reported that the amount of coprecipitated rubidium with a definite amount of cesium salt increases only gradually with a rapid increase in the amount of the accompanying rubidium in the sample.
6) The cesium salt in the presence of a large amount of potassium is ob-

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**Hara, T.
Tadashi Hara

tained more easily than that in the case with rubidium.

7) The cesium salt is less soluble in concentrated acetic acid than in water, and washing with concentrated acetic acid is easier than with water.

REAGENT AND APPARATUS

HBI$_4$ reagent: 4 grams of purified bismuth trioxide was dissolved in hydroiodic acid which was obtained by passing hydrogen sulfide gas into 100 ml. of water containing 20 grams of purified iodine. The filtered solution was stored in a glass-stoppered bottle in a cold place avoiding light. It is good for about three months.

Dithizone-chloroform solution: 60 mg. of dithizone was dissolved in dilute ammonium hydroxide solution (1:200) and impurities were extracted with chloroform. The aqueous dithizone phase was filtered through a pledget of cotton inserted in the stem of a separatory funnel into another funnel. The filtrate was carefully acidified with metal-free hydrochloric acid (1:1) to precipitate dithizone, which was then reextracted with purified chloroform. The chloroform layer was filtered as before and diluted to 500 ml. with purified chloroform for future use.

Standard bismuth solution: 100 p.p.m. of bismuth solution was prepared by using purified bismuth trioxide.

Rubidium nitrate: The rubidium nitrate was purified by the previously reported method. The cesium which might be minutely present in the rubidium nitrate, could not be identified with HBI$_4$ reagent which is capable of detecting as little as 0.2 µg of cesium. Moreover, it was confirmed that there is no interference even in the determination of cesium in large amounts of rubidium.

Rubidium nitrate solutions of 10, 100 and 1000 p.p.m. were prepared.

Cesium nitrate: Cesium nitrate solutions of 2, 5 and 10 p.p.m. were prepared.

Nitric acid: 1% and 3% solutions.

Concentrated ammonium hydroxide: Redistilled.

Potassium cyanide: Special grade reagent.

A Hitachi filter photometer Model EPO-A equipped with 1 cm. cells and filters of approximately 30 mp band width was used for all photometric measure-

Graduated Line.

2.5 mm 

30 mm

Fig. 1. Glass apparatus.
Determination of a Small Amount of Cesium

A Beckman Model H-2 pH meter was utilized to measure the pH values. The glass apparatus shown in Fig. 1 was used. (A) is a graduated 10 ml. vessel and (B) a filter-stick with a sintered glass-filter-plate.

EXPERIMENT

(1) Absorption Curve of Bismuth Dithizonate

According to the literature, the absorption curve of bismuth dithizonate is said to have its maximum peak at 490 to 505 μm wave length. The author also found that the absorption curves of the bismuth dithizonates from which 10 and 20 μg of bismuth were extracted respectively with chloroform-dithizone solution, showed their maximum absorption at 500 μm. For the determination of bismuth dithizonate with a filter-photometer, “Filter C” was found to be appropriate because the concentration of bismuth and the absorbance are proportional with it.

(2) Procedure

A sample containing a small amount of cesium and additional elements such as rubidium and potassium is put in the vessel shown in Fig. 1 and evaporated to dryness on a steam-bath. After drying the residue in an air-bath at about 150°C for half an hour, it is cooled in a desiccator. Then, three drops (0.03-0.04 ml.) of HBil4 reagent which has been cooled in ice-water for more than an hour is added to the ice-cooled vessel and agitated so as to wet the vessel wall with reagent. As soon as the other salts accompanying the cesium—generally, potassium and rubidium salts—have dissolved, the precipitate is filtered through the filter-stick as shown in Fig. 1. This operation is generally done within four minutes after the addition of reagent and is satisfactory even in the presence of 4 mg. of potassium or rubidium. The precipitate is washed with 1 ml. of cold conc. acetic acid five to six times and treated with 3 ml. of 3% nitric acid. After heating it on a steam-bath for about 30 minutes, the filter-stick is washed with 1% hot nitric acid and the filtrate is put in the previous vessel. The solution is transferred into a separatory funnel and then, 20 ml. of potassium cyanide-ammonium hydroxide solution (10 g. KCN/1 NH4OH), 40 ml. of 1% nitric acid which has been treated with 8 ml. of dithizone-chloroform solution, and exactly 15 ml. of dithizone-chloroform solution are added to the solution. After shaking for about one minute, the chloroform layer is filtered through a filter paper and the absorbance is read in comparison with a blank solution.

(3) Results

a) Calibration curve : The calibration curve for cesium obtained by means of the above mentioned procedure is shown in Fig. 2. It was found that, in the absence of interfering ions, Beer’s Law holds for 2.3 to 45 μg of cesium.

b) Determination of cesium in the presence of potassium : The results obtained in the presence of 10, 100, 200 and 400 μg respectively of potassium are shown in Table 1. It is seen from the Table that up to 4000 μg, potassium does
Fig. 2. Calibration curve for cesium.

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

<table>
<thead>
<tr>
<th>K taken (µg.)</th>
<th>Cs taken (µg.)</th>
<th>Cs found (µg.)</th>
<th>Error (µg.)</th>
<th>K taken (µg.)</th>
<th>Cs taken (µg.)</th>
<th>Cs found (µg.)</th>
<th>Error (µg.)</th>
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<td>-0.2</td>
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<td></td>
<td>5</td>
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<tr>
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<td></td>
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<tr>
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<tr>
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<td>-2.8</td>
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</table>

not interfere with the determination of 10~45 µg of cesium, but in the presence of more than 2000 µg potassium, determinations of cesium of less than 10 µg give negative errors owing to the salt effect.

c) Determination of cesium in the presence of rubidium: The results obtained in the presence of rubidium are shown in Table 2, and the relations between the absorbance and the amount of existing rubidium are given in Table 3 for various amounts of cesium.
As can be seen from Table 2, it is obvious that the calibration curve (Fig. 2) can be used when the amount of rubidium present is less than that of cesium but it cannot be used in the presence of an amount of rubidium greater than that of cesium, because the values for cesium involve large positive errors with increasing amounts of rubidium. These results correspond to those obtained...
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in the gravimetric analysis of semi-micro quantities of cesium.

However, as Table 3 indicates, the absorbances change only gradually with an increase of rubidium, and good results can be obtained if we adopt the following groups with regard to rubidium and use the portions of the calibration curve for these given ranges of rubidium: 0—X, X—X+500, X+500—X+1000, X +1000—X+1500 µg etc. —here X denotes the amount of rubidium equal to that of cesium contained in a sample.

As a preliminary experiment for the determination of cesium dissolved in sea-water, a measurement was made for samples containing 2000 µg of rubidium with 10, 20, 30 µg of cesium respectively. The total weight of rubidium and cesium as their dipicrylaminates (HRb+Cs) was determined. After removal of amine, the amount of cesium was determined by the above mentioned procedure using the calibration curve obtained in the presence of 2000 µg of rubidium. The results are shown in Table 4. According to the results, interference due to the presence of potassium and rubidium is almost analogous to the case of rubidium alone. Thus, a small amount of cesium in the presence of potassium or rubidium or both can be easily estimated without separating it; We need only take into account the interference due to rubidium.

### Table 4. Determination of cesium in the presence of a large amount of rubidium.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<tbody>
<tr>
<td>Cs taken (µg.)</td>
<td>10</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Rb taken (µg.)</td>
<td>2000</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>Hrb+Cs (mg.)</td>
<td>12.10</td>
<td>12.23</td>
<td>12.35</td>
</tr>
<tr>
<td>Rb(=Rb+Cs) (mg.)</td>
<td>1.98</td>
<td>2.00</td>
<td>2.02</td>
</tr>
<tr>
<td>Absorbance</td>
<td>0.032</td>
<td>0.161</td>
<td>0.229</td>
</tr>
<tr>
<td>Cs found (µg.)</td>
<td>9.2</td>
<td>21.8</td>
<td>27.3</td>
</tr>
<tr>
<td>Error (µg.)</td>
<td>-0.8</td>
<td>+1.8</td>
<td>-2.7</td>
</tr>
</tbody>
</table>

SUMMARY

There has previously been no report by which a microgram quantity of cesium in a large amount of rubidium can be determined colorimetrically, but a new method using HBII4 reagent has been established for the colorimetric determination of cesium in such a sample. By this method, 10—45 µg of cesium can be determined in the presence of potassium and rubidium less than 4 mg. by using several corrected calibration curves.

ACKNOWLEDGEMENT

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REFERENCE