On the Purification of Cesium Chloride[*]

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For the purification of cesium chloride, two methods have been developed. One of them is the improved iodine mono-chloride method and the other is the same method combined with the KBiI₄ method. Furthermore, several separation factors necessary for the purification have been found and the relationships between the time for recystallization and the purity are also discussed.

INTRODUCTION

The chemical composition of the lepidolite produced in Korea and the extraction of the rarer alkali elements from it have been already reported by M. Ishibashi and T. Ishihara[1],[2]. The present study was made in order to purify further the previously obtained cesium chloride, which still contained a lot of impurities such as rubidium, potassium, sodium and so on. It has been reported that the purification of cesium chloride in the presence of a considerable amount of potassium and rubidium *etc.* is not satisfactory even by the use of an ion exchange-resin[3]. The present paper deals with the purification by means of reagents.

The methods for the purification of cesium chloride are divided into two, that is to say, the ICl method and the KBiI₄ method which contains the ICl method. The former has been used for samples containing a considerable amount of cesium and the latter for samples with a much samaller amount. With these methods, the cesium chloride in various kinds of samples can be easily purified.

APPARATUS AND CHEMICALS

Iodine monochloride : The preparation of this reagent by the conventional method[4] is comparatively troublesome, but the following method has been found to be very simple and satisfactory enough for this study. To a flask as indicated in Fig. 1, 50 ml. of concentrated hydrochloric acid and 200 grams of purified iodine are added. Then washed and dried chlorine gas from a tank is passed into it. At this time, the outside of the vessel is cooled with cold water. The treatment with chlorine gas is continued until all of the solid iodine has just disappeared, and then the contents are transferred to a brown colored bottle for use as a reagent.
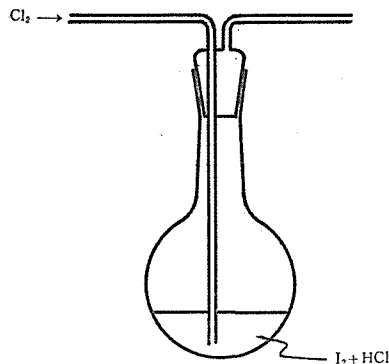

Fig. 1.

KBiI$_4$ reagent: 45 grams of potassium iodide are dissolved in 78 ml. of water and after adding 18 grams of powdered bismuth trioxide and 225 ml. of concentrated acetic acid, the bismuth trioxide is dissolved by heating, keeping the solution out of contact with the air as far as possible. Then the solution is rapidly filtered through a glass-filter and the filtrate is stored in a colored bottle for use.

Sample: Crude cesium chloride was used as a starting material for the purification and it was found to have an approximate composition such as shown in Table 1.

Table 1. The composition of the sample.

Constituent	Percent
CsCl	89.7
RbCl	9.2
KCl	0.4
NaCl	Trace
Insol. substance	Trace

The Quartz spectrometer, Middle Type of Adam Hilger Co. Ltd. was used for the identification of trace impurities. The auxiliary electrodes were copper for the identification of the alkali elements and carbon for the other elements. The method of excitation depended on the cathode layer method. Fuji Process and Oriental Hyper-Panchromatic dry plates were used together.

<center>CONSIDERATION</center>

a) Characteristics of Cesium Salts

It is nearly impossible to separate cesium only by one process from mixtures including cesium, rubidium, potassium and sodium etc. because the efficiency of the practical separation is much worse than that expected from the solubility differences between the individual salts. With respect to this, the following statement can be generally made as to the characteristics of rubidium and

cesium salts, those salts in which the efficiencies of the separation by one process are good, can not be easily recrystallized, but on the contrary, those salts in which the efficiencies of the separation are bad, can be easily recrystallized. The situation where the efficiency of the separation is not very good, though the recrystallization of the salt can be easily done, will still be useful for the purification of certain kinds of sample. The situation where the efficiency of the separation is good, but the recrystallization of the salt is difficult, of course, will be more useful for purification.

b) Separation Factor

In order to indicate more quantitatively whether the separation is good or not, the separation factor instead of the efficiency of the separation should be used, for then the various separation factors which are significant of the purification of cesium chloride will be found. The separation factor is applicable whenever a mixture of two elements has been divided into two fractions. This term is then the ratio of one element to the other in one fraction divided by the corresponding ratio in the other fraction.

$$\text{Separation factor} = Fs = \frac{\dfrac{A_1}{B_1}}{\dfrac{A_2}{B_2}} = \frac{A_1}{B_1} \times \frac{B_2}{A_2} .$$

A_1, B_1 : the amount of A and B in one fraction.

A_2, B_2 : the amount of A and B in the other fraction.

It does not involve an analysis of the initial material and is mathematically independent on the original ratio, the presence of other elements, the extent to which a separation process has taken place or the units of measurement employed. If any separation should not take place between two substance,

$$A_1/B_1 = A_2/B_2 \text{ and therefore } Fs = 1.$$

If the ratio of the two fractions is always so written as to be greater than one whenever there is separation between the two substances, the larger the value of Fs the better the efficiency of the separation. The values of Fs for the several significant methods for separating cesium from rubidium are shown in Table 2. As the Table shows, the value of Fs for the KBiI$_4$ method is much larger than that for the triple salt method which has been used for the purification of cesium.

Table 2. The values of separation factor.

Purification method	Fs
ICl	29.1
CsCl-SbCl$_3$-FeCl$_3$	1780
KBiI$_4$	44580

c) Recrystallization

When the value of Fs in the separation method is rather small, many re-

petitions of the same recrystallization process will be necessary to purify the cesium chloride. Therefore the relationship between the number of times of recrystallization and the resulting purity can be expressed mathematically. If it is supposed that the separation process has started from a grams of a cesium sample which includes a considerable amount of rubidium and after one process, *i.e.*, the solid phase, the cesium salt, still contain x_1 grams of rubidium, the solution will contain $(a - x_1)$ grams of rubidium. Therefore

$$\frac{x_1}{a - x_1} = k \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1)$$

$$x_1 = \left(\frac{k}{1+k}\right) \cdot a \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$

Then if the same separation process is applied to the first solid phase-cesium salt and x_2 is the amount of rubidium in the second solid phase, x_2 is represented as follows when k is constant.

$$x_2 = \left(\frac{k}{1+k}\right)^2 \cdot a \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots(3)$$

Therefore the amount of rubidium in the "n"th solid phase after "n" times of precipitation is shown by equation (4).

$$x_n = \left(\frac{k}{1+k}\right)^n \cdot a \qquad \cdots\cdots\cdots\cdots\cdots\cdots(4)$$

Equation (4) shows the number of times of recrystallization necessary in order to obtain a definite purity of cesium salt when the values of a and k are known. In equation (4), the value of k has been considered constant, but it can be expected vary considerably. Therefore, equation (4) is only approximate.

d) Limit of Identification

The following spectral lines (the unit of wave lenghth is the Angstrom) were used to indentify the various elements. Na : 3302.3, 3302.91, K : 4044.2, 4047.2, Rb : 4201.8, 4215.6, Cs : 4555.3, 4593.2, Si : 2881.6, 2516.1.

The limits for identification of alkali elements in various samples have been found as follows : Rubidium chloride in the presence of 20 mg of cesium chloride — 0.016 mg. Cesium chloride in the presence of 20 mg of rubidium chloride — 0.020 mg, Potassium chloride in the presence of 20 mg of rubidium chloride — 0.030 mg.

e) Last Stage of the Purification Process

Though the last stage of the purification process seems to be insignificant, it is very important for the actual process because it is especially desirable that the purified salt can be easily transformed into the desired form of the salt. Of course, various impurities must not enter into the purified salt during such a transformation. As a matter of fact, it is not too much to say that the value of the purification method depends chiefly on the last stage of the purification process.

IODINE MONOCHLORIDE METHOD

As seen from Table 2, the value of Fs by the iodine monochloride method is not very large. So the efficient separation of cesium from rubidium cannot be expected. However this method has been found to have following strong points :

1) The recrystallization process is very easy,

2) The conversion at the last stage of purification process is easy and it is represented as follows : $CsICl_2 \longrightarrow CsCl + ICl \uparrow$,

3) As the solubility of the cesium dichloroiodide in 9N-HCl is comparatively small, the procedure for the purification can be carried out with a good yield in this acid concentration. Table 3 shows the solubility of dichloroiodides of rubidium and cesium[6].

Table 3. The solubility of dichloroiodides.

Concn of HCl (N)	$CsICl_2$ (g.-salt/100 ml. soln.)		$RbICl_2$ (g.-salt/100 ml. soln.,)	
	0°C	25°C	0°C	25°C
0.8805	3.783	9.805	—	—
1.998	3.745	9.052	31.68	64.92
2.989	3.577	8.236	—	—
4.909	3.187	6.824	21.50	38.20
6.987	2.877	5.746	—	—
8.989	2.691	5.142	12.98	22.17
10.75	2.604	4.841	—	—
12.48	2.591	4.697	10.83	17.16
15.29	2.652	4.700	—	—

For these reasons, the iodine monochloride method has been chosen as the one for the purification of cesium samples in which the concentration of cesium is considerably large.

Procedure : The sample is dissolved with the minimum of water necessary to dissolve it and the solution is filtered with a glass-filter No. 4. After the filtrate has been vaporized to a small volume, a definite amount of concentrated hydrochloric acid is add to make a nine normal hydrochloric acid solution and then a measured quantity of iodine monochloride solution is added while the solution is hot. After the vessel has been adequately cooled with ice, the contents are filtered through a glass-filter and the precipitate is allowed to drain. The precipitate is transferred into the previous vessel containing a definite amount of water, covered with a watch-glass and warmed on a steambath and dissolved as much as possible. Then a definite amount of concentrated hydrochloric acid and a small amount of iodine monchloride are added to it and it is again cooled with ice. The same procedure is repeated until the impurities can not be identified. At the last stage of the purification process, the cesium dichloroiodide is drained as completely as possible, transferred into

a quartz beaker and decomposed by gradual heating. As the iodine monochloride is incompletely removed by a single ignition, the residue is dissolved in a small amount of distilled water and the solution is filtered through a purified glass-filter. Then the filtrate is vaporized to dryness and the residue is ignited to dull red. The obtained cesium chloride is cooled in a desiccator containing phosphorus pentaoxide and stored in a glass-stoppered bottle. By means of seven recrystallizations about 71% of the cesium chloride in the sample has been obtained at a purity of 99.9% or more.

Equation (4) may also be applied to this case. Since the spectral lines of rubidium were not seen after seven recrystallizations of the cesium dichloroiodide, n is equal to 7 and x_n is 0.08%. If 9.2% is substituted for "a" in $=\left(\dfrac{k}{1+k}\right)^n \cdot a$, k is found to be 1.036 and equation (5) is obtained.

$$x = 0.509^n \cdot a \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(5)$$

From equation (5), the number of recrystallizations necessary for the desired purity can be easily calculated. For instance, the necessary recystallizations of cesium dichloroiodide in order to obtain 99.99% pure cesium chloride, with respect to rubidium chloride is found to be just ten in the case of the sample used.

KBiI$_4$ Method

When the concentration of cesium in the sample is rather small, it seems wiser that all the cesium be precipitated by such a method in which various impurities are also removed as much as possible and then that the small amount of impurity in the cesium precipitate be removed by some othe method. Therefore the KBiI$_4$ method has been chosen for purification of such a sample.

As the reaction between the KBiI$_4$ reagent and cesium is specific for cesium and the solubility of the precipitate is rather small, almost all the cesium in a sample is precipitated as $Cs_3Bi_2I_9$. After the bismuth in the precipitate has been removed, the cesium is purified by the previous iodine monochloride method. When the amounts of sodium and potassium in a sample are markedly large, the purification process is carried out as mentioned above after most of the sodium and potassium have been removed.

Though the solubility of the cesium salt by a KBiI$_4$ reagent is especially small in concentrated acetic acid, the solubility of the rubidium salt at the same conditions is extremely large and no precipitate of rubidium is produced even from saturated solutions. However, a considerable amount of rubidum is coprecipitated with the cesium salt when the cesium salt is produced in the presence of rubidium and the amount of the coprecipitated rubidium abruptly increases with an increase in the amount of the accompanying rubidium. As for the amount of the coprecipitated rubidium for a definite amount of the cesium, there seems to be a maximum value where the amount of the coprecipitated rubidium is almost as much as one-half of the cesium.

When the cesium in a sample contains a large amount of rubidium, the larger part of the rubidium is expected to be removed. These phenomena are

Table 4. The precipitate of cesium in the presence of rubidium.

CsCl taken (mg.)	RbCl taken (mg.)	Cs₃Bi₂I₉ (mg.)		Rb–salt (mg.)
		Experimental	Theoretical	
5.0	0	19.3	19.4	—
〃	10	19.4	〃	±0
〃	20	20.8	〃	+1.4
〃	50	22.1	〃	+2.7
〃	100	24.6	〃	+5.2
〃	200	28.1	〃	+8.7*

* It contains rubidium chloride.

explained by the results shown in Table 4. In order to remove bismuth from the cesium precipitate, hydrogen sulfide is used.

Procedure : All the filtrates which have been obtained during the purification of cesium chloride by the iodine monochloride method are collected and used as a starting material for this procedure. This sample is no longer treated by the iodine monochloride method. The sample solution is evaporated to dryness and ignited to the chlorides. Then, concentrated acetic acid is added to it at the rate of 30 ml. of acid per 10 grams of sample and after being covered with a watch-glass, it is warmed on the steam bath for half an hour. The solution is filtered through a glass-filter while hot and to the hot filtrate, KBiI₄ reagent is added. After being cooled by ice, the precipitate is filtered with a glass filter. The precipitate is washed several times by using small amounts of concentrated acetic acid and then it is dissolved in $2N$–HNO₃ by heating. The bismuth in the solution is precipitated as its sulfide by passing hydrogen sulfide gas into the solution and after filtering off the precipitate, the filtrate is vaporized to dryness. The residue is recrystallized five times by the iodine monochloride method. The cesium chloride obtained thus has been found to have a purity of 99.9% or more and the amount of it has corresponded to about 4% of the orginal cesium chloride sample.

SUMMARY

In order to obtain pure cesium chloride starting from cesium sample in which the concentration of cesium varies, two methods have been proposed. One is the iodine monochloride method. The other is the KBiI₄ method including the iodine monochloride method. It has been shown that the cesium in a wide range of samples can be easily purified if these methods are suitably adopted in accordance with the nature of the sample. Moreover, the several separation factors which seem to be necessary for the study of the purification of cesium chloride, have been found. The approximate equation which represents the relationship between the number of recrystallization and the purity was applied to the purification of cesium chloride.

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