

On the Purification of Rubidium Chloride*

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There being no reliable method for the purification of rubidium chloride, three methods were devised for this purpose, the method used depending on the type of a sample. By these methods, it was shown that spectroscopically pure rubidium chloride can be easily obtained from various samples.

INTRODUCTION

As the rubidium stands at the middle of potassium and cesium in the periodic table and, moreover, since potassium, rubidium and cesium are very similar in their chemical properties, it is very difficult to purify the rubidium chloride in a sample containing potassium and cesium. A few methods have been already reported for the purification of rubidium chloride, but they seem still to be incomplete. Therefore, three simple methods : A, B and C for the purification of rubidium chloride have been proposed, based on knowledge obtained during the investigation of the conventional method for the analysis of rubidium.

Method A is appropriate for a sample in which the concentration of rubidium chloride is large. The small amount of cesium in the sample is completely removed by dropping the concentrated solution of the alkali sulfate into a hot ethyl alcohol solution and repeating this crystallization process. Then the other impurities such as potassium and sodium *etc.* are easily removed by recrystallizing rubidium dichloriodide which can be obtained by treating the previous rubidium sulfate with iodine monochloride in a concentrated hydrochloric acid.

Method B is appropriate for a sample containing a considerable amount of cesium. The cesium in the sample is precipitated by HBiI_4 reagent and removed. The filtrate is then treated by the iodine monochloride method or by Method A.

Method C is suitable for a sample which contains a large amount of potassium. The larger part of the potassium is first removed by treating the sample with ethyl alcohol and concentrated hydrochloric acid, and the rubidium chloride in the filtrate is then purified by the method A or B.

CONSIDERATION

While the factors considered in the purification of cesium chloride are helpful also in this case, the following points must be especially considered.

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1) Solubility Characteristics

Generally, the solubilities of the salts of the alkali elements which are called difficultly soluble, are larger than those of the other difficultly soluble salts, so it is not desirable that the impurity be removed as a precipitate, because the purified substance will always contain an amount of the impurity corresponding to the solubility of the impurity under the given conditions. Therefore, purification will not be accomplished by a procedure in which the impurity is only removed as a precipitate. However, this procedure is useful for removing a large fraction of the impurity rapidly from a sample in which a large amount of the impurity is contained.

2) Relative Amount and Line Intensity

It has been confirmed that the purity of the rubidium chloride changes with a relative amount of rubidium to cesium or potassium. As a matter of fact, the spectral lines of cesium appear again when the potassium is removed from a rubidium sample from which the cesium had already been removed and in which no spectral lines of cesium had been found previous to that treatment. Therefore in order to obtain rubidium chloride of spectroscopic purity it is necessary that the cesium, should be more completely removed at first or that the sample be purified further after the removal of the potassium. The above-mentioned phenomenon is believed to depend not only on the change in the relative amounts of the elements but also on interference among the spectral lines of these elements. The interference among the spectral lines of the alkali elements is generally stated as follows : The presence of an element which shows a higher ionization voltage weakens the line intensity of the element which shows a lower ionization voltage, and the presence of an element which shows a lower ionization voltage strengthens the line intensity of an element which shows higher ionization voltage.

This was confirmed during the spectroscopic investigation of the identification limit of potassium, rubidium and cesium.

3) Removal of Cesium

There are various conventional methods for the separation of cesium from rubidium. As is well known, a triple salt¹⁾ consisting of cesium chloride, antimony chloride and ferric chloride can be used for this purpose. However, as this salt is rather soluble, the complete separation of rubidium from cesium is impossible by this method alone. Therefore the conventional method for separating rubidium from cesium by this triple salt method is unsatisfactory. There is also a modified triple salt method in which the rubidium in the filtrate is precipitated as the perchlorate, and after being converted into the sulfate, is recrystallized as the bitartrate²⁾. Unfortunately, this method has several defects such as the great length of the procedure, the ignition of the bitartrate which is accompanied by violent bubbling, and the removal of the carbon due to the incomplete combustion of the tartrate. There is also another method in which

the separation of rubidium from cesium are carried out by the solubility difference between their bitartrates. However it has the same defects as those in the previous methods.

As these conventional methods are not satisfactory, the authors have studied the separation of rubidium from cesium by dropping their sulfate solution into a hot alcohol solution. This method is similar to the Well-Stevens method³⁾ in which the separation of rubidium sulfate from cesium sulfate is carried out in a concentrated alcohol solution (about 80% by volume) by adding ammonium sulfate solution to their chloride solution, but the former is better than the latter in such points as the efficiency of the separation and the absence of the ammonium salt. By this method, the spectral line of cesium has not been found after seven recrystallizations, but on the contrary, the cesium line has been still seen after thirteen recrystallizations by the Well-Stevens method under the same condition. In the Well-Stevens method, the greater part of the cesium is easily removed by the first several recrystallizations, but the residual cesium is difficult to remove. Generally speaking, as the conversion of the sulfate into the chloride is difficult, the separation of rubidium from cesium as their sulfate has never been used. However it has been found that rubidium sulfate can be easily converted into the dichloroiodide which involves the complete separation of rubidium from potassium and sodium. That is the reason why this method has been applied for the separation of rubidium from cesium.

4) Removal of Potassium

The Strecker-Diaz-Fresenius method¹⁾ using chloro-stannic acid is well known as the method for separating potassium from rubidium. However it has been ascertained chemically and spectroscopically that this method is quite unsuitable for quantitative analysis and the purification of rubidium because the efficiency of the separation of potassium from rubidium is very bad. The separation of potassium from rubidium can be done effectively using chloroplumbic acid but it also has defects such as the instability of the reagent and the rather large solubility of rubidium salt. There is also another separation method using a mixture of hydrochloric acid and ethyl alcohol. This method is appropriate for a rough separation of rubidium from potassium, but not for their complete separation.

The iodine monochloride method, in which rubidium is precipitated as the dichloroiodide and potassium remains in the solution, has been studied. As the dichloroiodide of potassium is very soluble, no precipitate is produced even from a saturated solution in the concentrated hydrochloric acid. The rubidium dichloroiodide is difficultly soluble if it is cooled enough in the concentrated hydrochloric acid and the efficiency of the separation by this method is much better than that of the separation of cesium from rubidium. It has been confirmed spectroscopically that the spectral line of potassium is only faintly seen after three recrystallizations of the rubidium dichloroiodide in a saturated solution of potassium, but the line is hardly noticeable after four recrystallizations. The conversion of the dichloroiodide into the chloride is as easy as in the case of

cesium dichloriodide.

REAGENT AND APPARATUS

HBiI₄ Reagent : Hydrogen sulfide is passed into a solution which contains 20 grams of purified iodine and 100 ml of water. Hydroiodic acid is produced in accordance with the following reaction : $I_2 + H_2S \longrightarrow 2HI + S$. The hydrogen sulfide gas is stopped just before the yellow color of the iodine disappears, and the solution is filtered after it has been warmed on a steam-bath for some time. 8 grams of the powdered bismuth trioxide is added to the filtrate, and it is completely dissolved by adding a small amount of concentrated acetic acid and heating. The color of the solution is dark red and the solution is kept in a cold place after filtering through a glass-filter.

Sample : Crude rubidium chloride is used as the starting material and its composition is as follows : rubidium chloride, 56 % ; cesium chloride, 19 % ; potassium chloride, 23 % ; and the other : sodium, silica *etc.*

Anion exchange resin : Amberlite IRA-410.

PROCEDURE

Method A

10 grams of the crude rubidium chloride is dissolved in 30 ml. of water and the solution is filtered through a glass-filter. After adding an excess of sulfuric acid, it is vaporized to dryness and the chloride is converted into the sulfate by igniting it. The resulting sulfate is dissolved in 15 ml. of water, and the solution is added drop by drop to a 96 % alcohol solution which is warmed to about 70°C. The sulfates of potassium and rubidium will deposit on the bottom of the vessel as a large crystalline precipitate. Here the final concentration of the alcohol should be about 82 %. The precipitate is filtered by a glass-filter and washed with 85 % alcohol solution. Then the precipitate is dissolved in a definite amount of water, and the same procedure as before is repeated until the spectral line of cesium disappears.

In this case, the spectral line of cesium disappeared after seven recrystallizations. Then the sulfates of potassium and rubidium are dissolved in a minimum of concentrated hydrochloric acid and to it the iodine monochloride is added. After a thorough cooling with ice, the dichloriodide of rubidium is filtered through a glass-filter and washed with a small amount of cold concentrated hydrochloric acid. Then the dichloriodide is dissolved in a minimum of hydrochloric acid and recrystallized five times after adding a little iodine monochloride solution. The purified dichloriodide is dissolved in a considerably large volume of 9*N*-HCl and the small amount of the dichloriodide which will deposit after ice-cooling is filtered off. Then the filtrate is vaporized to dryness in a quartz-beaker and the residue is ignited to the chloride. The chloride is dissolved in a little water and the solution is filtered through a glass-filter. The filtrate is vaporized to dryness in a platinum-dish and the residue is ignited to dark red.

Purification of Rubidium Chloride

The rubidium chloride thus obtained is spectroscopically pure and the yield is about 57 % of the rubidium chloride in the original sample.

Method B

In this case, the residual solution obtained in the purification of cesium chloride by the iodine monochloride method is used as the starting material. The above solution is vaporized to dryness and the dichloroiodides are obtained after adding the iodine monochloride and concentrated hydrochloric acid. After three recrystallizations of the dichloroiodides, they are converted into the chlorides by igniting in a quartz beaker. The chlorides are powdered and HBiI_4 reagent is added. The contents are stirred violently for some time and then the precipitate is filtered with a glass-filter. The HBiI_4 reagent is destroyed by adding nitric acid and hydrogen sulfide gas is used to precipitate bismuth sulfide. The filtrate following the removal of the sulfide is vaporized to dryness and ignited after adding sulfuric acid. The sulfates contain only a little potassium and cesium, and therefore they are dealt with Method A. However in this case, it has been found necessary for the preparation of the spectroscopically pure rubidium salt to have five recrystallizations of the sulfate and three of the dichloroiodide. When the cesium is removed as $\text{Cs}_3\text{Bi}_2\text{I}_9$ by the reaction between the solid sample and the HBiI_4 reagent, the spectral line of the cesium in the filtrate is faint and moreover, $\text{Cs}_3\text{Bi}_2\text{I}_9$ is available as the starting material for the purification of cesium chloride.

Method C

The residual iodine monochloride solution obtained in the purification of rubidium chloride, was used as the starting material for this method. As this sample solution contains the sulfate ion in addition to the chloride ion, the solution is vaporized to dryness and ignited to the sulfate. The sulfate is dissolved in water and the solution is passed through a column of the chloride form of the IRA-410. The effluent is concentrated until the salt slightly deposits on the wall of the vessel. Then, equal volumes of ethyl alcohol and concentrated hydrochloric acid are added to it and the resulting salt is filtered with a glass-filter while the solution is warm. The filtrate is vaporized to dryness and from the residue, the rubidium chloride is purified by the iodine mono-chloride method. As the starting material does not contain any cesium, there is no need to take into account the removal of cesium. By this method, spectroscopically pure rubidium chloride has been easily obtained.

SUMMARY

Though there have been no reliable methods for the purification of rubidium chloride, three methods are proposed for this purpose. By these methods, the rubidium chloride in various kinds of sample can be easily obtained at spectroscopic purity.

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