THE SEPARATION AND DETERMINATION OF RUBIDIUM AND CESIUM BASED ON ION EXCHANGE

Thesis for the Degree of Ph. D.

MICHIGAN STATE COLLEGE

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1954

THE SEPARATION AND DETERMINATION OF RUBIDIUM AND CESIUM BASED ON ION EXCHANGE

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A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1954

ACKNOWLEDGMENT

Appreciation is most gratefully extended to Doctor Elmer Leininger under whose kind and efficient supervision this work was effected.

The author also wishes to express his gratitude to Doctor Verne Stenger of the Dow Chemical Company for the rubidium bromide concentrate.

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ABSTRACT

The conditions for the ion exchange separation of rubidium and cesium have been established.

A preparative procedure for high purity rubidium chloride using an ion exchange separation has been developed. It consists essentially of eluting one gram quantities of commercial rubidium chloride from a column containing a resin bed 81 cm. high and 3.8 cm. in diameter of 200-400 mesh Dowex 50 with 0.7 normal hydrochloric acid at a flow rate of 4.4 ml. per minute. The rubudium chloride is recovered from the proper volume of eluate by evaporation and precipitation with hydrogen chloride. Flame-photometric analysis of the purified product shows the rubidium chloride content to be approximately 99.7 per cent.

Cesium chloride was prepared from pollucite by treating the mineral with a mixture of hydrofluoric and sulfuric acids and then recrystallising the resulting cesium alum. The sodium and potassium content appears to remain constant after several recrystallizations. For final purification the cesium alum was converted to the iododichloride and recrystallised. The purified product was analyzed flamephotometrically and the cesium chloride content is approximately 99.7 per cent.

Flamephotometric determination of rubidium and cesium is described. The flame intensities at 780 and 852 mu were measured for the estimation of rubidium and cesium respectively. The enhancement effect of large amounts of rubidium on other alkalies is demonstrated and methods proposed for their approximation in the purified rubidium chloride.

A method for the quantitative determination of rubidium and cesium based on ion exchange has been developed. The procedure involves separating samples of the mixed chlorides by elution from a column containing a resin bed of Dowex 50, minus 400 mesh, 87 cm. high and 2.2 cm. in diameter with 0.7 normal hydrochloric acid at a flow rate of 2.7 ml. per minute. After elution the appropriate fractions of effluent were evaporated to dryness and the alkali metal content determined by weighing the ignited rubidium and cesium sulfates. A small blank correction, obtained by evaporating portions of eluate and weighing the ignited sulfate residues, was found necessary. An accuracy of two per cent was obtained for 100-200 mg. samples of the chlorides when rubidium and cesium are present in approximately equal proportions.

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INTRODUCTION

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In the determination of the alkalies a separation is frequently made which divides the family into two groups. One group consists of lithium and sodium; the other, potassium, rubidium and cesium. This separation is accomplished by the use of either the chloroplatinate or perchlorate method, both of which remove the potassium, rubidium and cesium leaving the lithium and sodium in solution (19). With certain precautions, the chloroplatinate method reportedly gives quantitative separation (20,28). In the perchlorate method, the mixed chlorides of the alkalies are converted to the perchlorates and then sodium and lithium are extracted with a mixture of anhydrous n-butyl alcohol and anhydrous ethyl acetate. Quantitative separation is obtained (21).

There are several methods available for the separation and determination of potassium, rubidium and cesium. Although these methods are somewhat empirical, under limited conditions they give good results (19).

In one method for the separation of potassium from rubidium and cesium, 9-phosphomolybdic acid serves to precipitate rubidium and cesium while potassium remains in solution. Although some potassium is co-precipitated O'Leary and Papish (28) report good results for certain concentration ranges of potassium, rubidium and cesium.

Before rubidium and cesium can be separated, the phosphomolybdate precipitate must be dissolved in sodium hydroxide, the molybdenum

removed with hydrogen sulfide and the alkalies converted to chlorides after a chloroplatinate separation.

The separation of rubidium from cesium can be brought about by precipitating cesium from the mixed chlorides with silico-tungstic acid. Rubidium is determined in the filtrate as the perchlorate or chloroplatinate.

To determine cesium, the silico-tungstic acid precipitate is dissolved in sodium hydroxide, mecureous nitrate added to remove the silico-tungstate and cesium is determined as the chloroplatinate or perchlorate after oxidation of the excess mercury (19).

Another method for the separation of cesium from rubidium involves the formation of a precipitate with ferric chloride and antimony chloride which removes cesium. Cesium is determined as the chloroplatinate or perchlorate after the precipitate is dissolved and the iron and antimony removed (12).

Wells and Stevens (42) report a method for the separation of potassium, rubidium and cesium. An extraction of the mixed chlorides with absolute alcohol, which has been saturated with hydrogen chloride gas, serves to remove rubidium and cesium from potassium. The separation of cesium from rubidium depends upon the greater solubility in alcohol of cesium sulfate. This method is quite empirical and the conditions, as well as the number of extractions, are dependent upon the amount of potassium, rubidium and cesium present.

More recently Sato (37) described a method for the determination of the alkali metals based on the difference in the solubilities of the

hexyl dipicrylamine salts in mixed organic solvents. An accuracy of five percent was reported.

Another method for the separation and determination of rubidium and cesium based on the formation of the alkali polyhalides is given by Yamatera (44). In this method, the tri-iodides are formed and upon treatment with carbon tetrachloride only the rubidium salt decomposes.

A method for the quantitative determination of cesium and its separation from rubidium and potassium has been proposed by Dutt (11). In this method cesium is precipitated as $Cs_2NaLa(NO_2)_6$ and determined either by weighing the precipitate, $Cs_2NaLa(NO_2)_6$, or by titrating the nitrite content with ceric sulfate. Both the gravimetric and volumetric procedures have been adapted to the microdetermination of cesium.

Several workers have used spectrographic and flamephotometric procedures but these in general are limited to small amounts and are more frequently used for qualitative identification rather than quantitative determination (5,6,10,13,15,41,45).

The methods discussed here are representative procedures and many more are found in the literature. Fresenius and Jander (12) have reviewed the methods through 1940 and a discussion of some of the methods is given by Hillebrand (19).

There appears to be no truly specific reagent for either rubidium or cesium ions (19). The chemical methods of determining rubidium and cesium are either rather long and involve a number of operations, or the separations are incomplete, giving rise to errors as large as five percent.

In the hope of finding a method which would give accurate results but also have a maximum of simplicity, it seemed advisable to try another approach. Rieman and co-workers (7,39) developed an ion exchange method for sodium and potassium that gives excellent results but does not involve the tedious procedures of the chemical methods.

A review of the literature indicated that the ion exchange separation of rubidium and cesium had been accomplished by Kayas (23). No quantitative results were given for rubidium and cesium but 99 percent recovery is claimed for sodium.

It seemed that for an ion exchange method to be successful, it should be capable of resolving macro quantities while giving adequate intervals of separation between the various ions and yet not involve unlimited volumes of eluant. It was toward this end that the following work was directed.

HISTORICAL

HISTORICAL

One of the first attempts to separate the alkali metals employing the ion-exchange technique was carried out by Cohn and Kohn (9). A column containing a resin bed 1.0 sq. cm. in area and 10.4 cm. high of colloidal agglomerates of Dowex 50 and a recording counter to assay the relative activity in the effluent solution was employed. A neutron activated mixture containing 1.0 mg. of sodium, 10 mg. of potassium, 8 mg. of rubidium and 13 mg. of cesium was dissolved in water and absorbed on the resin. Elution was then begun with 0.15 normal hydrochloric acid at a flow rate of 0.3 ml. per minute and completed with 0.3 normal hydrochloric acid. The effluent from the column was collected in a number of fractions, each of which was radiometrically analyzed for Na^{24}, K^{42}, Rb^{86} and Cs^{134}. Sodium was recovered in one fraction which also contained one per cent of the cesium. The remainder of the sample was recovered in the other fractions with incomplete separation. The total elution required 160 ml.

The first fairly complete separation of sodium, potassium, rubidium and cesium by ion exchange was accomplished by Kayas (23). A glass column 1 cm. in diameter and 50 cm. high, fitted at the lower end with a sintered glass disc, was filled to a height of 40 cm. with Amberlite IR 100 resin having a mesh size of 80-120. The samples consisted of mixtures of Na^{24}, K^{42}, Rb^{86} and Cs^{134}. The separation was followed with

a specially constructed Geiger tube which indicated the movement of the ions down the column. Another tube was placed so as to measure the activity of the eluate as it passed from the column. The separation obtained, as read from the elution curves, is approximately 25 ml. between sodium and potassium, 15 ml. between potassium and rubidium and 10 ml. between rubidium and cesium for a mixture containing 15.2 mg. sodium, 24.0 mg. potassium, 28.3 mg. rubidium and 25.5 mg. of cesium. The initial elution was carried out with 0.15 normal hydrochloric acid but after the last of the potassium was removed the acid strength was increased to 0.3 normal. The complete elution required approximately 825 ml. of eluant. No quantitative data are given for rubidium and cesium but as an example of the results obtainable by evaluation of the area under the elution curves 99 percent recovery was claimed for sodium.

A method for the separation and determination of sodium and potassium employing an ion-exchange separation has been proposed by Rieman (7). The method consists of two steps: a separation of the sodium and potassium by means of elution through a cation exchanger, and a titration of the chloride in the alkali chloride residues obtained from the evaporation of the separate fractions of eluate to dryness.

For the ion-exchange separation a column 3.80 sq. cm. (2.2 cm. in diameter) by 59.0 cm. containing 59.5 g. of colloidal Dowex 50 resin was employed. Samples containing up to 500 mg. of the mixed chlorides were separated by elution with 0.7 normal hydrochloric acid at a flow rate of 0.60 ml./min./sq. cm. from this column. In this elution the first 370 ml. of eluate were discarded. The next 160 ml. contained

the sodium and the following 190 ml. contained the potassium.

The evaporations were carried out on a steam bath and the residues heated in an oven to 140°C. The residual hydrogen chloride was determined by titration with standard base and the chloride content by the Mohr titration. The alkali chloride content was then calculated from the difference in these two titrations. Excellent results are reported.

EXPERIMENTAL

EXPERIMENTAL

Conditions for the Ion Exchange Separation of Rubidium and Cesium

The theory of the ion exchange process has been extensively investigated and much of the work is summarized by Kunin and Myers (24) and Samuelson (32).

In practice, however, the final experimental conditions for a given separation are mainly found by trial and error methods. From experience it has been learned that certain factors greatly influence separation. The most important of these are:

1. Nature of the resin
2. Sample-resin ratio
3. Concentration and nature of eluant
4. Flow rate
5. Exchange affinity of the ions involved
6. Shape of column
7. Temperature

Choice of Resin

Two different resins have been employed in the separation of the alkalies. Kayas (23) used Amberlite IR100 which is a phenolic methylene sulfonic acid type. Cohn and Kohn (9) and Rieman (7,39) used Dowex 50 which is a nuclear sulfonic acid exchanger. Dowex 50 appeared to have two advantages over Amberlite IR100. In general the nuclear sulfonic acid type is less subject to attack by acid and having a greater capacity per gram (25) should give better resolution per unit volume of resin bed. For these reasons Dowex 50 was chosen.

Dowex 50 is produced by the polymerization of styrene with divinylbenzene, followed by sulfonation. The percentage of divinylbenzene determines the degree of cross linkage and consequently the density. It has been shown that the degree of crosslinkage influences selectivity (26) and the degree of swelling of the resin (33). Insufficient data are available to determine the per cent crosslinkage at which maximum selectivity for the alkalies exists but it has been found that the twelve per cent divinylbenzene resin is satisfactory. This crosslinkage, maximum for the Dowex series, also gives a maximum capacity per gram and a minimum of swelling within the Dowex 50 series.

In the choice of resin one further factor needed to be considered, the size of the resin particles. The smaller the particle size the greater the resolution (36). At extremely small particle sizes the resistance of the column to eluant flow becomes appreciable. For a column containing a resin bed 45 cm. high and 2.2 cm. in diameter of colloidal Dowex 50 a flow rate of 1.7 ml. per minute required a pressure of over 20 inches of mercury.

The resin finally chosen was Dowex 50, 12% divinylbenzene crosslinkage with a particle size of 200-400 mesh for the preparative column and a particle size of minus 400 mesh for the analytical column.

Preparation of Resin for Use

The commercial grade of Dowex 50 as received from the manufacturer requires rather extensive preparation before it is suitable for use. The first step in the preparation involves the removing of the so-called

"fines" (7). The "fines" are extremely small particles of resin that have been produced during synthesis and subsequent handling. If these small particles are not removed they will migrate through the column and eventually obstruct the porous disc in the bottom. To remove these particles the crude resin is mixed with about three times its volume of water, the resin permitted to settle, and the supernatant liquid decanted. This process is repeated until the solution above the resin is clear after a few minutes of settling. This process may consume more than 25 per cent of the resin. In one attempt to use a batch of colloidal Dowex 50 that had been insufficiently washed, the fine particles diffused through six feet of Tygon tubing into the reservoir containing the eluant.

The removal of iron from the crude resin is also important. Samuelson (35) recommends treatment with five normal hydrochloric acid. Goudie and Rieman (18) recommend the passage of diammonium citrate through the resin. The procedure followed was a combination of these in which the resin was given several treatments in a beaker with five normal hydrochloric acid, and then, after being washed with distilled water and placed in the column, one molar diammonium citrate passed through the column until the remaining iron was removed.

Filling the Column

The filling of the column is very important; if not done properly channeling will occur and instead of receiving full efficiency from the column the eluant only comes in contact with part of the resin. The

first method attempted was that of pouring the dry resin into the column. After wetting, the resin swelled leaving channels.

The most satisfactory method appears to be that of first filling the column with water and then slurrying in small portions of resin through a funnel that dips below the water level in the column (29). As the resin-water slurry enters the column the particles gradually settle giving a uniform bed. A large beaker is placed under the column to catch the displaced water and resin that overflows. The slurry should be added at such a rate that the extremely fine particles do not have a chance to settle but are carried over the top of the column. If the rate of addition of resin-water slurry is too slow bands of fine particles will develop which may migrate through the column and obstruct the porous disc. A properly filled column has a uniform color and exhibits no channeling.

Choice of Acid

When a solution of a salt is placed on an ion exchange resin, such as Dowex 50, the cation exchanges with the hydrogen ion of the sulfonic acid groups in the resin. This may be pictured as a reversible reaction where R^- represents the sulfonic acid group of the resin.

$$RH + Na^+ \rightleftharpoons RNa + H^+$$

That this is an equilibrium process has been demonstrated, the final equilibrium being dependent upon the concentrations of the two cations and the relative cation-resin bond strength (40).

Thus when a solution containing a mixture of the alkalies is placed on the acid form of the column, hydrogen ions are replaced since the affinity of the alkalies for the resin is greater than that of hydrogen ions. When elution begins the rate of migration of the various alkalies will depend upon their relative affinities for the resin and the hydrogen ion concentration of the eluant. The relative order of affinities of the alkalies for the sulfonic acid type exchangers are Cs > Rb > K > Na and consequently their order of elution will be Na, K, Rb and Cs (22,23, 40).

It was found in ion-exchange studies with the rare earths that the equilibrium existing in a column could be shifted by the use of complexing agents which varied the effective concentration of the metal ions and enhanced separation.

It was thought that the differences in solubility existing between certain compounds in the alkali metal family may exert an influence upon their separation in a manner similar to that exhibited by the differences in the stability of the rare earth-citric acid complexes.

Hydrochloric (7) and perchloric acids (22) both have been used for the separation of sodium and potassium but due to the different experimental conditions involved no comparison between the degree of separation obtained was possible. It was felt that if an anion effect is important a comparison of the elution of sodium and potassium with hydrochloric and perchloric acids should demonstrate it since a twenty fold difference exists between the molar solubilities of the sodium and potassium chlorides and perchlorates (38).

To determine if an anion effect exists two runs were made, identical, except in one case elution was carried out with perchloric acid and in the other hydrochloric acid. The column contained a resin bed 31 cm. high and 2.2 cm. in diameter of 200-400 mesh Dowex 50. Twenty-five milligram samples of Mallinckrodt reagent grade sodium chloride and Baker Analyzed Reagent potassium chloride were taken and eluted at a flow rate of 3 ml. per minute with 0.75 normal hydrochloric acid in one run and 0.75 normal perchloric acid in the other. The elution was followed flamephotometrically. The results are shown in Table I.

TABLE I

SEPARATION OF SODIUM AND POTASSIUM WITH HYDROCHLORIC AND PERCHLORIC ACIDS

Acid	Volume Containing Sodium (ml.)	Volume Representing Separation (ml.)	Volume Containing Potassium Fraction (ml.)
HCl	480-580 ± 15	580-1130 ± 15	1130-1420 ± 15
$HClO_4$	480-580 ± 15	580-860 ± 15	860-1030 ± 15

Evidently the replacing of chloride ion with perchlorate ion has little influence upon the elution of sodium from the column, however, the interval of separation between sodium and potassium has been reduced by 270 ml. or nearly one-half the original separation. The volume of eluate containing potassium has been reduced from 290 ml. to 170 ml.

These data indicate that the more insoluble the salt formed between the cation on the column and the anion in the eluant the more easily that

cation is removed from the column. As for the magnitude of this effect it can only be said that a large difference in solubility seems necessary for any appreciable influence upon separation.

Undoubtedly the absolute solubilities as well as the difference in solubilities is a factor.

A review of the solubilities of the chlorides of sodium, potassium, rubidium and cesium reveals that the chlorides are all quite soluble (Table II).

TABLE II

SOLUBILITIES OF ALKALI CHLORIDES
(Moles Per 100 Grams Water at 25°C) (38)

Alkali Chloride	Solubility
NaCl	0.615
KCl	0.476
RbCl	0.730
CsCl	1.130

Potassium chloride is the least soluble (on a molar basis) while rubidium chloride is intermediate between potassium and cesium chlorides; cesium chloride is the most soluble. Thus, if there is an anion effect at this level of solubility it should enhance separation. The perchlorates of potassium, rubidium and cesium all have low solubilities with a slight decrease from potassium to cesium. It was felt that this

low solubility in addition to the slight difference in solubilities gave perchloric no advantage over hydrochloric acid.

Since the elutions were to be followed flamephotometrically hydrochloric acid offered the further advantage that the chlorides of the alkali metals are the most sensitive for flame analysis.

From these considerations hydrochloric acid was chosen as the eluant.

Construction of Column and Pressure System

Figure 1 shows a typical column and the pressure system used to deliver eluant (29). Pressure is supplied by tank oxygen. Two regulators are included to control the system pressure and consequently the flow rate. One is a diaphragm type on the oxygen tank. The other (B) consists of a length of 6 mm. glass tubing dipping into a column of mercury whose height is determined by positioning the leveling bulb (C). An exit tube is provided to carry the excess oxygen and mercury fumes from the regulator into a container of six normal nitric acid (A) which is fitted with an exit tube containing ascarite.

The mercury manometer (D) permits reading of the system pressure. This is convenient for reproducing flow rates and checking the condition of the system at various times.

A 12 liter reservoir is included at (E) to minimize pressure fluctuation and help maintain a constant flow rate as the volume of eluant in bottle (F) decreases.

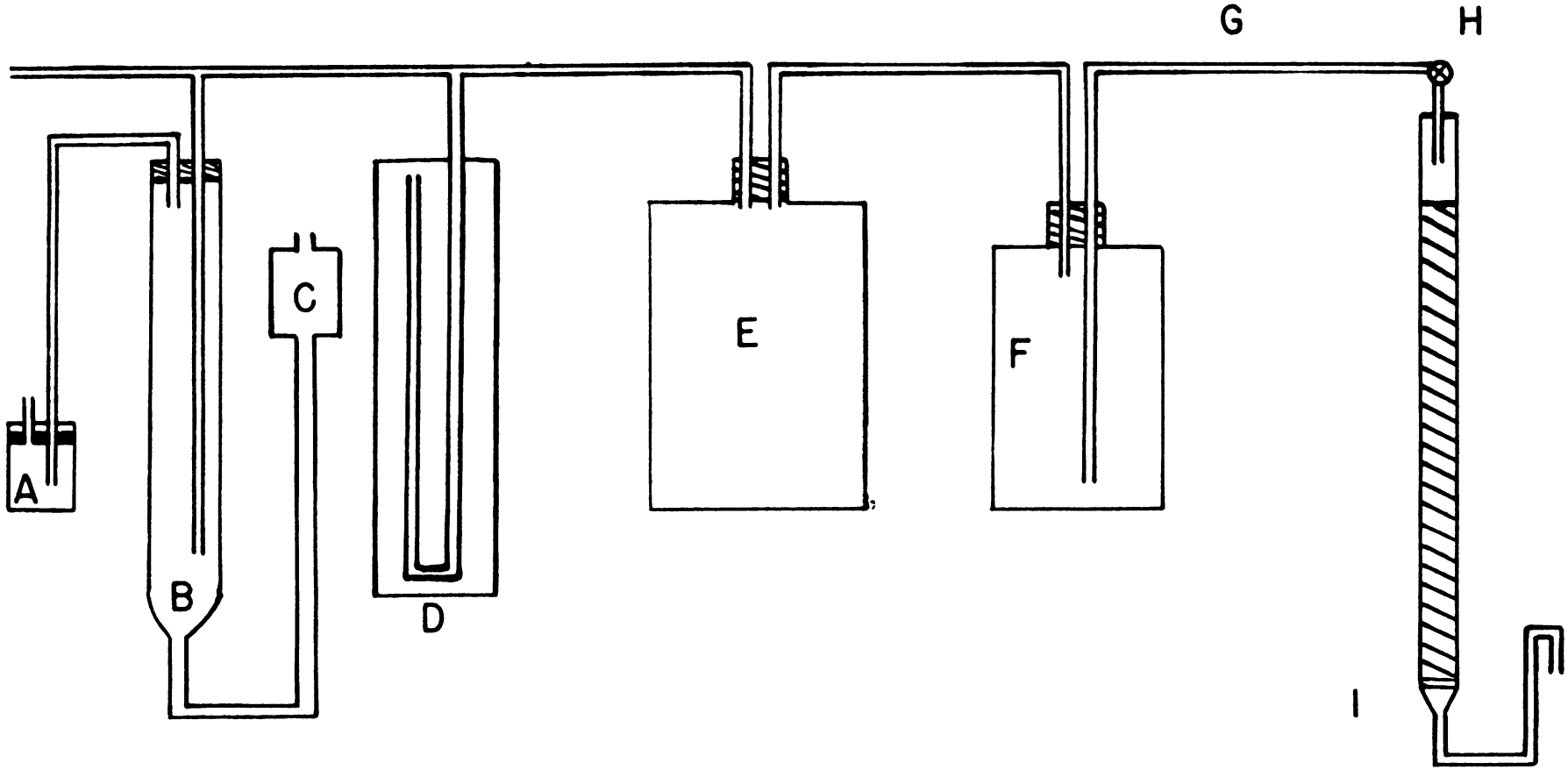

FIGURE 1

ION EXCHANGE COLUMN AND PRESSURE SYSTEM

All connections from the pressure tank to the eluant bottle are pressure tubing. The tube (G) carrying the eluant from the eluant bottle to the column is Tygon.

A stopcock (H), which is fitted with a Wenzel stopcock clamp, number 14-631, facilitates controlling the flow of eluant during column loading. It is held in place by a rubber stopper which is secured in the top of the column with a wire clip.

The various columns used were constructed of Pyrex tubing with a porous glass disc (I) incorporated in the lower end. Discs of two porosities, fine and medium, were used but no difference in performance was observed in respect to the amount of resin passing from the column. The exit tube from the column is 6 mm. in outside diameter and delivers the effluent so that it flows down the side of the beakers in the fraction collector thus preventing splashing.

The fraction collector employed was one supplied by the Microchemical Specialties Company, 1834 University Avenue, Berkeley, California. It is capable of cutting fractions at time intervals from 3 minutes to 20 hours. The turn-table accommodates 24 tall form, 150 ml. Pyrex beakers. The entire turn-table of the fraction collector and the exit tube from the column were protected by a transparent cover.

Loading the Column

In order to load the column, aliquot portions of the standard alkali solutions were evaporated to dryness on a steambath and then, with the aid of a stirring rod, were transferred to the column by washing

with portions of eluant delivered from a polyethylene wash bottle. The eluant bottle was replaced with an empty one, the rubber stopper inserted in the top of the column and pressure was applied to the system. This forces the solution which contains the sample into the resin bed. Pressure was applied until the sample solution was nearly even with the top of the resin bed; then more eluant added to the column and pressure applied until the solution was nearly even with the top of the resin bed. The eluant bottle was again placed in the system, pressure applied, a few ml. of eluant run onto the top of the column, the rubber stopper replaced and elution begun.

ION EXCHANGE SEPARATION OF RUBIDIUM AND CESIUM

From reviewing the work of Kayas (23) and Cohn and Kohn (9) it appeared that in order to separate macro quantities of rubidium and cesium it would be necessary to use a column with greater capacity than that employed by Kayas (23). It was thought that if a column similar to the one used by Riesman (7) to separate 0.5 g. samples of sodium and potassium chlorides were used, but the sample size reduced, separation might be accomplished. In choosing the acid strength it was decided to increase it over that used by Riesman (7) since it is known that rubidium and cesium are more firmly held than sodium and potassium (22,23).

A sample containing 0.12 g. of rubidium chloride (approximately 95 per cent pure) obtained from Fisher Scientific Company and 0.10 g. of pure cesium chloride (page 27) were placed on a column containing a resin bed of colloidal Dowex 50, 45 cm. high and in diameter. Elution was carried out at a flow rate of 1.5 ml. per minute with 1.55 ± 0.05 normal hydrochloric acid prepared by diluting Baker Analyzed Reagent concentrated hydrochloric acid. The hydrochloric acid used in this run and following ones was standardized with standard sodium hydroxide.

The progress of the elution was followed flamephotometrically. Fractions of 26 ml. were collected, evaporated to dryness in platinum dishes, diluted to 75 ml. and analyzed in a Beckman flamephotometer as described under "Flamephotometery of Rubidium and Cesium." The results are shown in Figure 2. Rubidium appears in the fractions from 530 ml.

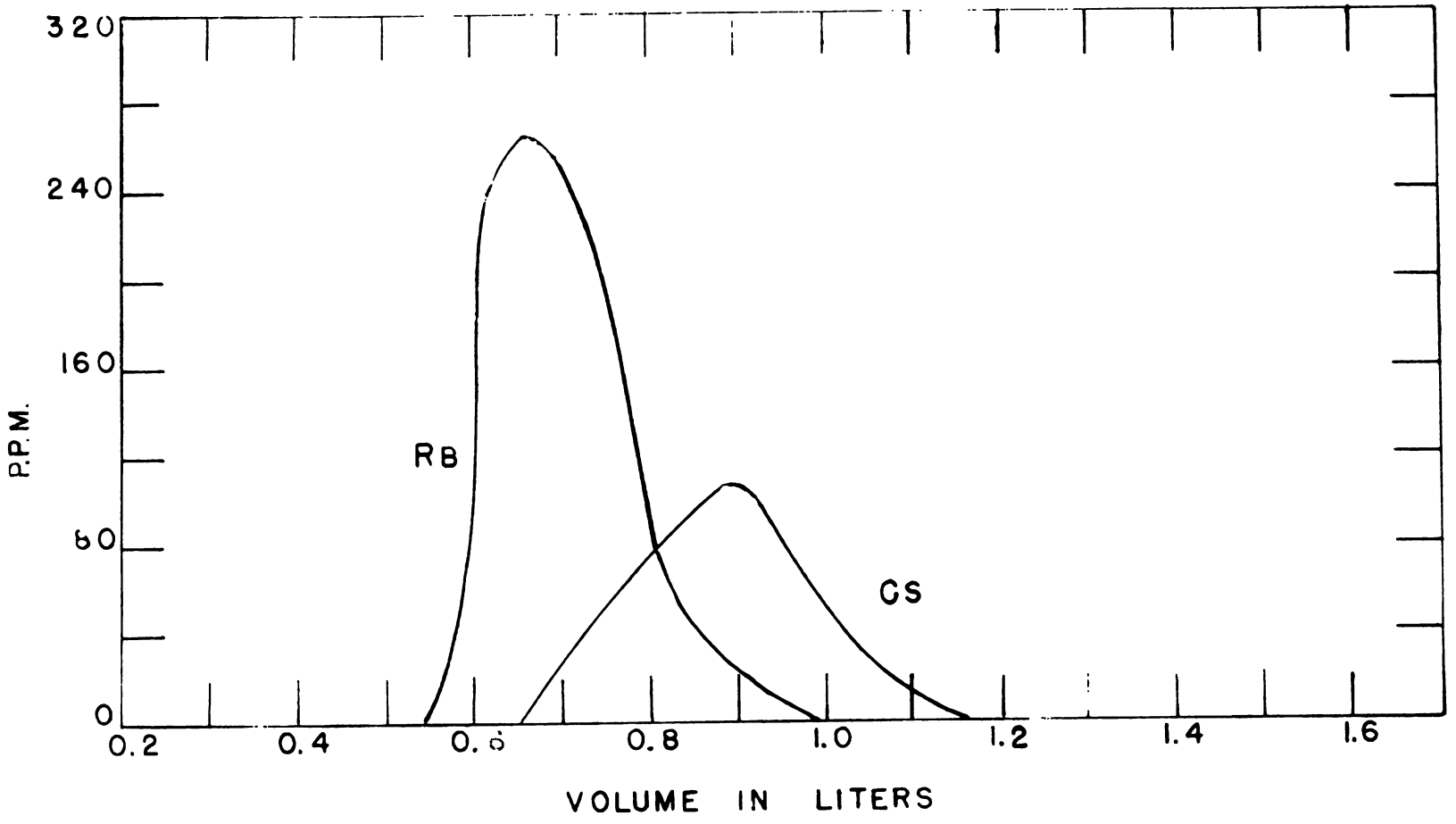

FIGURE 2 ELUTION OF RUBIDIUM AND CESIUM WITH 1.55 NORMAL HYDROCHLORIC ACID

SAMPLE: 0.12 G. RUBIDIUM CHLORIDE AND 0.10 G. CESIUM CHLORIDE
RESIN BED: 45 CM. HIGH AND 2.2 CM. IN DIAMETER, COLLOIDAL DOWEX 50
FLOW RATE: 1.5 ML. PER MIN.

to 1000 ml. and cesium in the fractions from 660 to 1180 ml. with an overlap in fractions from 660 to 1000 ml. The variables that could be changed without resorting to a different resin bed were the sample size, acid concentration and flow rate. Another run was carried out using the same resin bed but the sample size decreased to 0.05 g. of rubidium chloride and 0.07 g. of cesium chloride with 1.03 normal hydrochloric acid used for elution. Fractions of 26 ml. were collected and analyzed as in the previous run. As seen from Figure 3 rubidium appears in the fractions from 930 to 1440 ml., cesium in the fractions from 1185 to 1800 ml. with both being present from 1185 to 1440 ml. In comparison with the previous run it can be seen that complete elution required a larger volume in Figure 3 and that separation is somewhat improved as judged by the difference in overlap areas in Figures 2 and 3.

It appeared from the comparison of Figures 2 and 3 that a closer approach to equilibrium conditions would be necessary before complete separation would be possible. In the next run samples containing 0.05 g. of rubidium chloride and 0.05 g. of cesium chloride were eluted from the same column with 0.38 normal hydrochloric acid at a flow rate of 1.5 ml. per minute. Figure 4 shows the results. Rubidium appears in the fractions from 3250 to 4320 ml. and cesium in the fractions from 4300 ml. on with only a 20 ml. portion containing both alkalies.

From these results it became evident that if macro samples were to be successfully separated greater resolution would be necessary. It did not seem feasible to further reduce the acid strength of the eluant since the volume containing the alkalies was already appreciable.

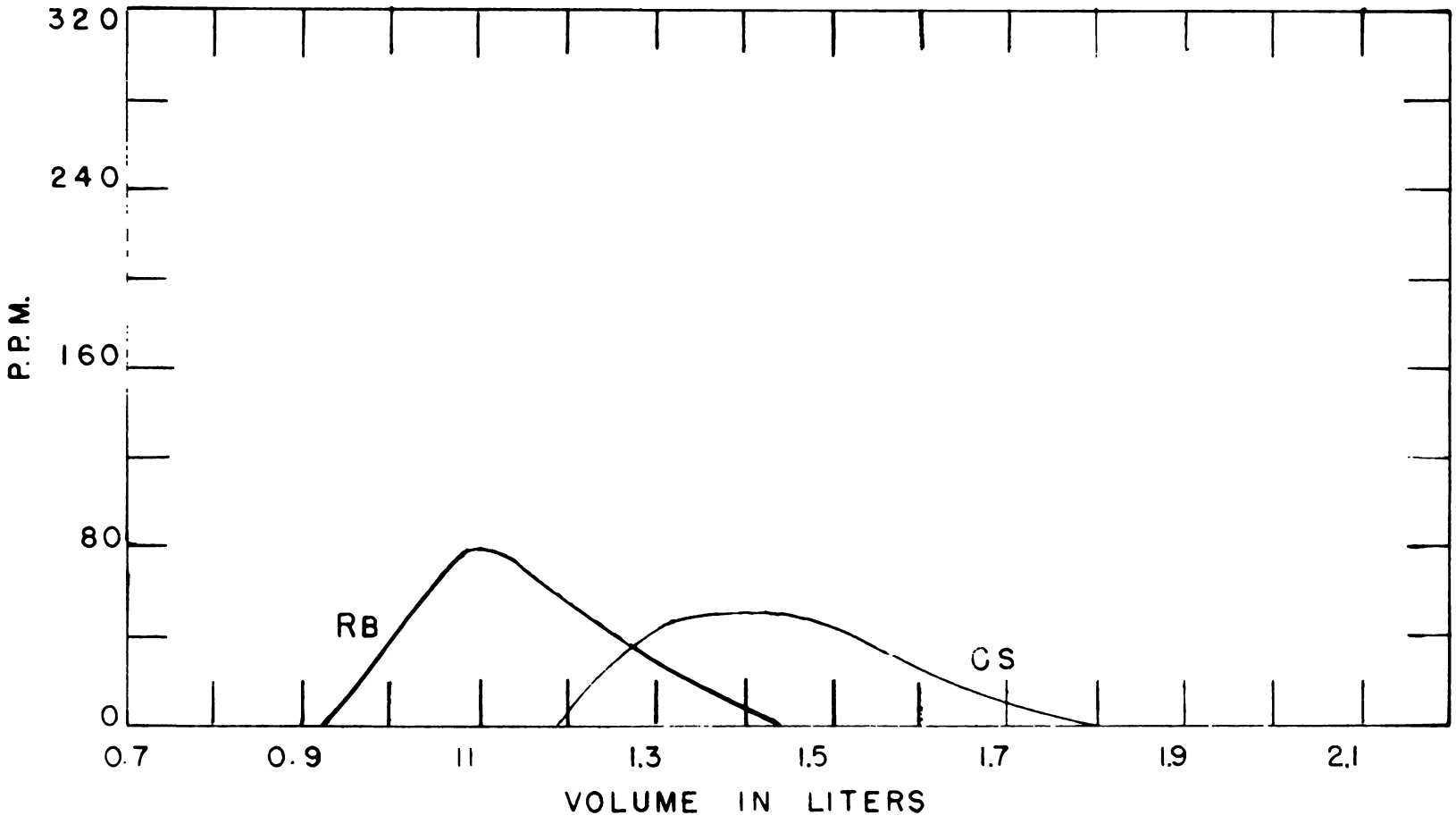

FIGURE 3 ELUTION OF RUBIDIUM AND CESIUM WITH 1.03 NORMAL. HYDROCHLORIC ACID

SAMPLE: 0.05 G. OF RUBIDIUM CHLORIDE AND 0.07 G. OF CESIUM CHLORIDE
RESIN BED: 45 CM. HIGH AND 2.2 CM. IN DIAMETER OF COLLOIDAL DOWEX 50
FLOW RATE: 1.5 ML. PER MIN.

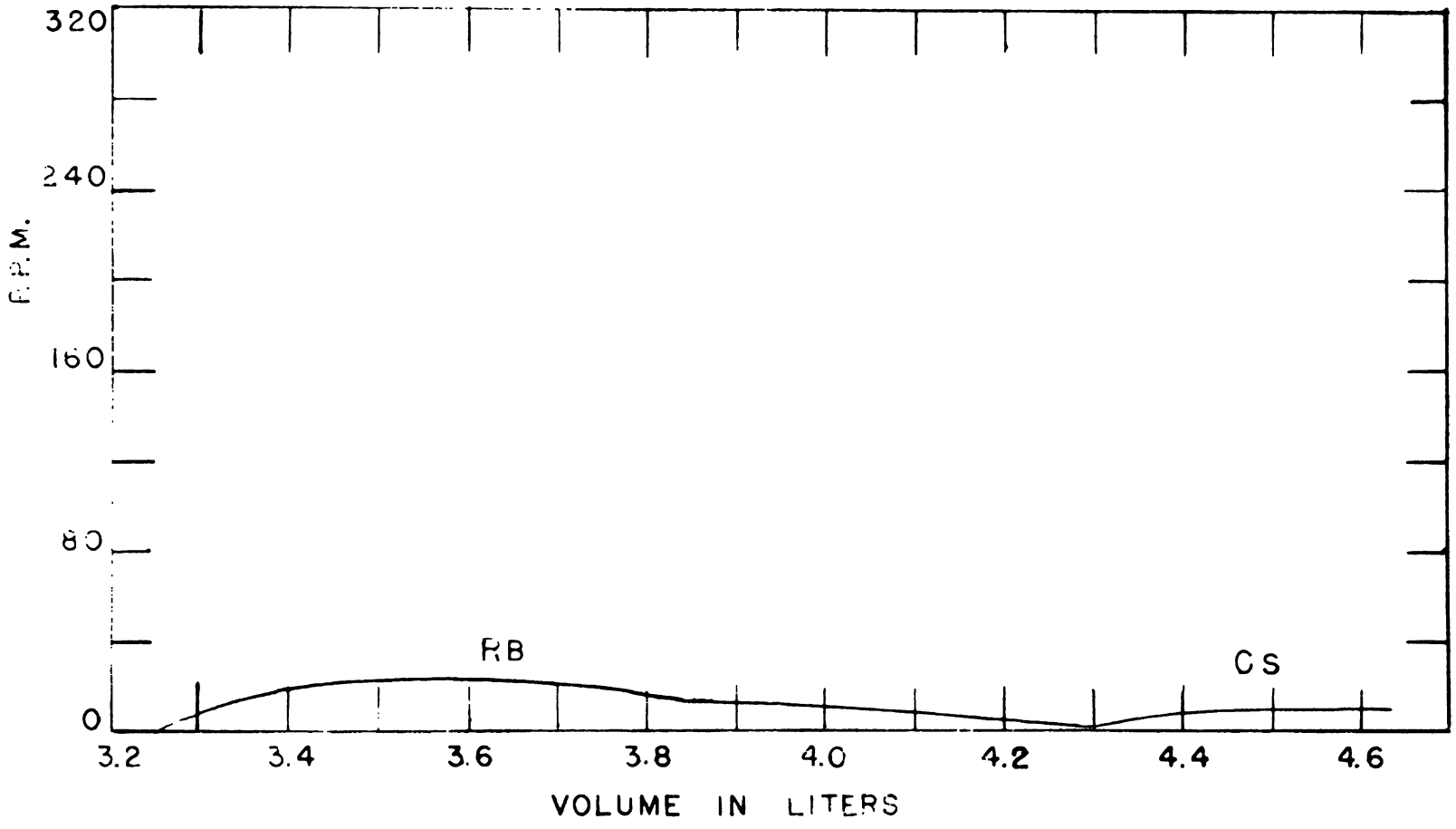

FIGURE 4 ELUTION OF RUBIDIUM AND CESIUM WITH 0.38 NORMAL HYDROCHLORIC ACID

SAMPLE: 0.05 G. OF RUBIDIUM CHLORIDE AND 0.05 G. OF CESIUM CHLORIDE
RESIN BED: 45 CM. HIGH AND 2.2 CM. IN DIAMETER OF COLLOIDAL DOWEX 50
FLOW RATE: 1.5 ML. PER MIN.

Increasing the height of the resin using colloidal Dowex 50 was prohibited by the increased pressure that would be necessary to obtain a feasible flow rate.

Another column containing a resin bed of 200-400 mesh Dowex 50, 68 cm. high and 3.8 cm. in diameter, was prepared. After placing a mixture of 0.056 g. of sodium chloride, 0.083 g. of potassium chloride 0.056 g. rubidium chloride and 0.0841 g. of cesium chloride on the column elution with 0.70 normal hydrochloric acid was begun at a flow rate of 1.8 ml. per minute. Fractions of 45 ml. were collected, evaporated to dryness, diluted to 100 ml. in volumetric flasks and analyzed flamephotometrically. The results are given in Table III. The separation between sodium and potassium is nearly 8000 ml., between potassium and rubidium, nearly 2600 ml. and between rubidium and cesium approximately 2700 ml. Only enough of the cesium was eluted to determine its position in the elution sequence.

TABLE III

ELUTION OF 0.056 G. SODIUM CHLORIDE, 0.083 G. POTASSIUM CHLORIDE, 0.056 G. RUBIDIUM CHLORIDE, 0.084 G. CESIUM CHLORIDE WITH 0.70 NORMAL HYDROCHLORIC ACID WITH A FLOW RATE OF 1.8 ML. PER MINUTE

Resin Bed = 68 cm. high x 3.8 cm. in diameter
200-400 mesh Dowex 50

Volume in Ml. Containing Sodium	Volume in Ml. Containing Potassium	Volume in Ml. Containing Rubidium	Volume in Ml. Containing Cesium
4650-5430	13410-16110	18710-21360	24060-

A series of runs was conducted with the purpose of obtaining conditions that would provide separation of rubidium and cesium chlorides on a preparative scale.

In the first of this series a 2.08 g. sample of a chloride mixture containing approximately 70 per cent cesium chloride and 30 per cent rubidium chloride with small amounts of sodium and potassium chlorides was placed on the column described in Table III. This mixture was prepared from a rubidium bromide concentrate supplied by Dr. V. Stenger of the Dow Chemical Company, Midland, Michigan and is referred to as the Dow mixture. Elution was carried out with 1.0 normal hydrochloric acid at a flow rate of 4.4 ml. per minute. Figure 5 gives the results. These conditions give some separation but the greater part of the rubidium fractions contain cesium.

Kayas (23) in his separation of the alkali metals carried out the initial elution through sodium and potassium with 0.1 normal hydrochloric acid and then completed elution with 0.3 normal. As shown in Figure 4, 0.3 normal hydrochloric acid removes cesium very slowly from a column of Dowex 50. Although it effects a near separation, the volume of eluate in which rubidium or cesium appears is too large to make the use of 0.3 normal hydrochloric acid practical. However, from Figure 3 it can be seen that 1.0 normal hydrochloric acid satisfactorily removes rubidium and cesium from a column of Dowex 50 but the separation is incomplete. It was thought, following the approach of Kayas (23), that perhaps an initial elution with 0.5 normal hydrochloric acid followed by an elution with 1.0 normal hydrochloric acid would give an adequate

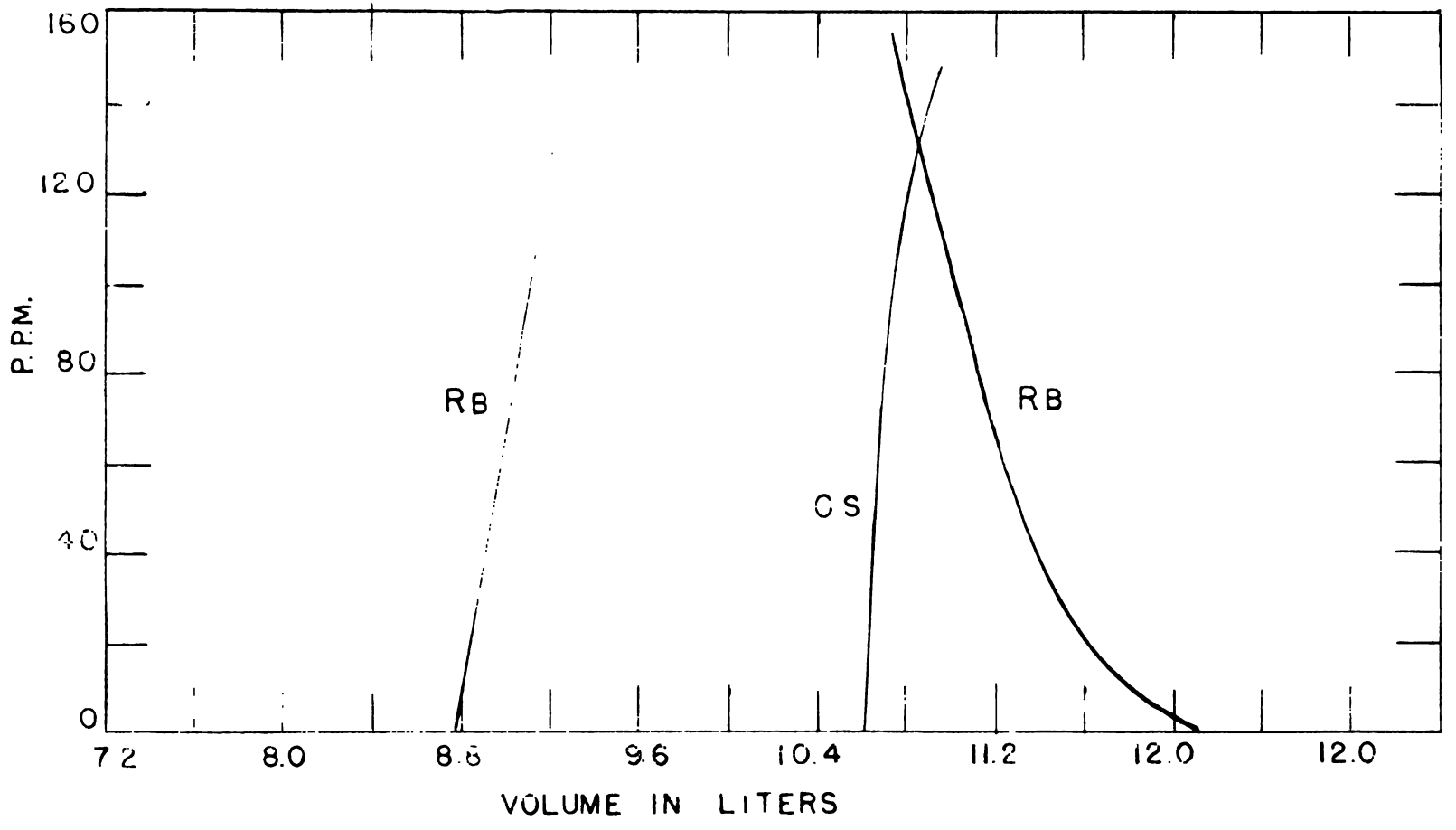

FIGURE 5 ELUTION OF RUBIDIUM AND CESIUM

SAMPLE: 2.08 G. OF DOW MIXTURE
RESIN BED: 68 CM. HIGH AND 3.8 CM. IN DIAMETER OF 200-400 MESH DOWEX 50
ELUANT 10 NORMAL HYDROCHLORIC ACID
FLOW RATE 4.4 ML PER MIN.

separation with the respective alkalies appearing in volumes that would be practical.

A sample containing 2.19 g. of the Dow mixture was placed on the same column as in Table III and with a flow rate of 4.4 ml. per minute 19 l. of 0.5 normal hydrochloric acid were passed through the column. No rubidium or cesium appeared in the effluent. Elution was completed with 1.0 normal hydrochloric acid. Figure 6 shows that the separation of rubidium and cesium is not improved.

Another run was carried out with the same column, identical flow rate and a 2.11 g. sample of the Dox mixture, but the eluant changed to 0.7 normal hydrochloric acid. Figure 7 represents the separation obtained. Although considerable cross contamination exists a greater percentage of the eluate containing rubidium is free from cesium.

From Figures 5, 6 and 7 it appeared that a more favorable sample-resin ratio would be necessary if a satisfactory separation were to be attained. Figure 8 shows the results of using the conditions as in Figure 7 but decreasing the sample size to 1.05 g. The separation is complete except for a small amount of tailing of rubidium into the cesium fractions.

To further increase separation the height of the resin bed in the column was increased to 81 cm. A 1.02 g. sample was taken and elution carried out as in Figure 8. Complete separation was obtained as is evident from Figure 9. Rubidium is separated from cesium by a volume of over 600 ml.

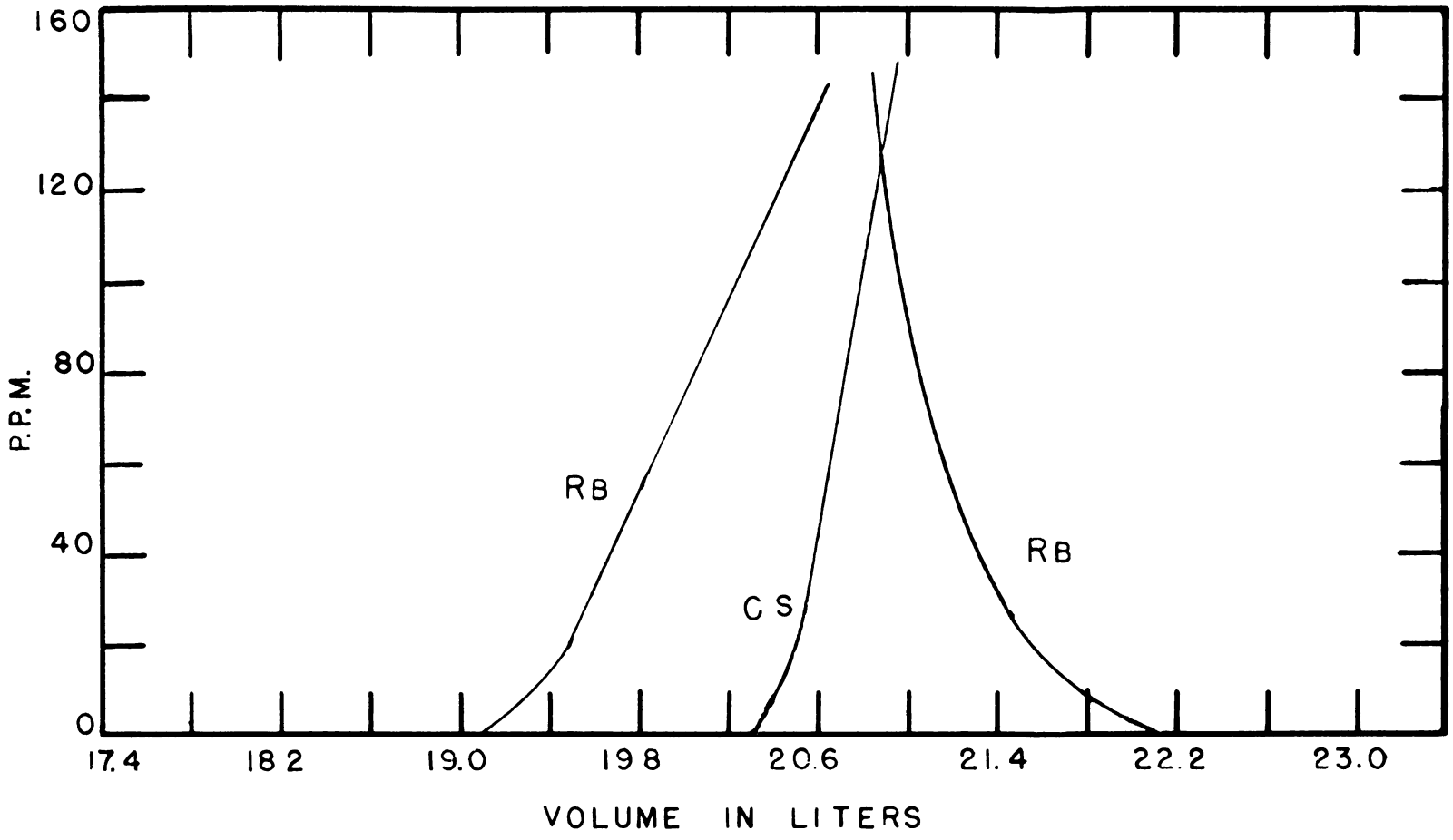

FIGURE 6 ELUTION OF RUBIDIUM AND CESIUM

SAMPLE: 2.19 G. OF DOW MIXTURE
RESIN BED: 68 CM. HIGH AND 3.8 CM. IN DIAMETER OF 200-400 MESH DOWEX 50
ELUANT: 0.0-19 L. 0.5 NORMAL, 19-23 L. 1.0 NORMAL HYDROCHLORIC ACID
FLOW RATE 4.4 ML. PER MIN.

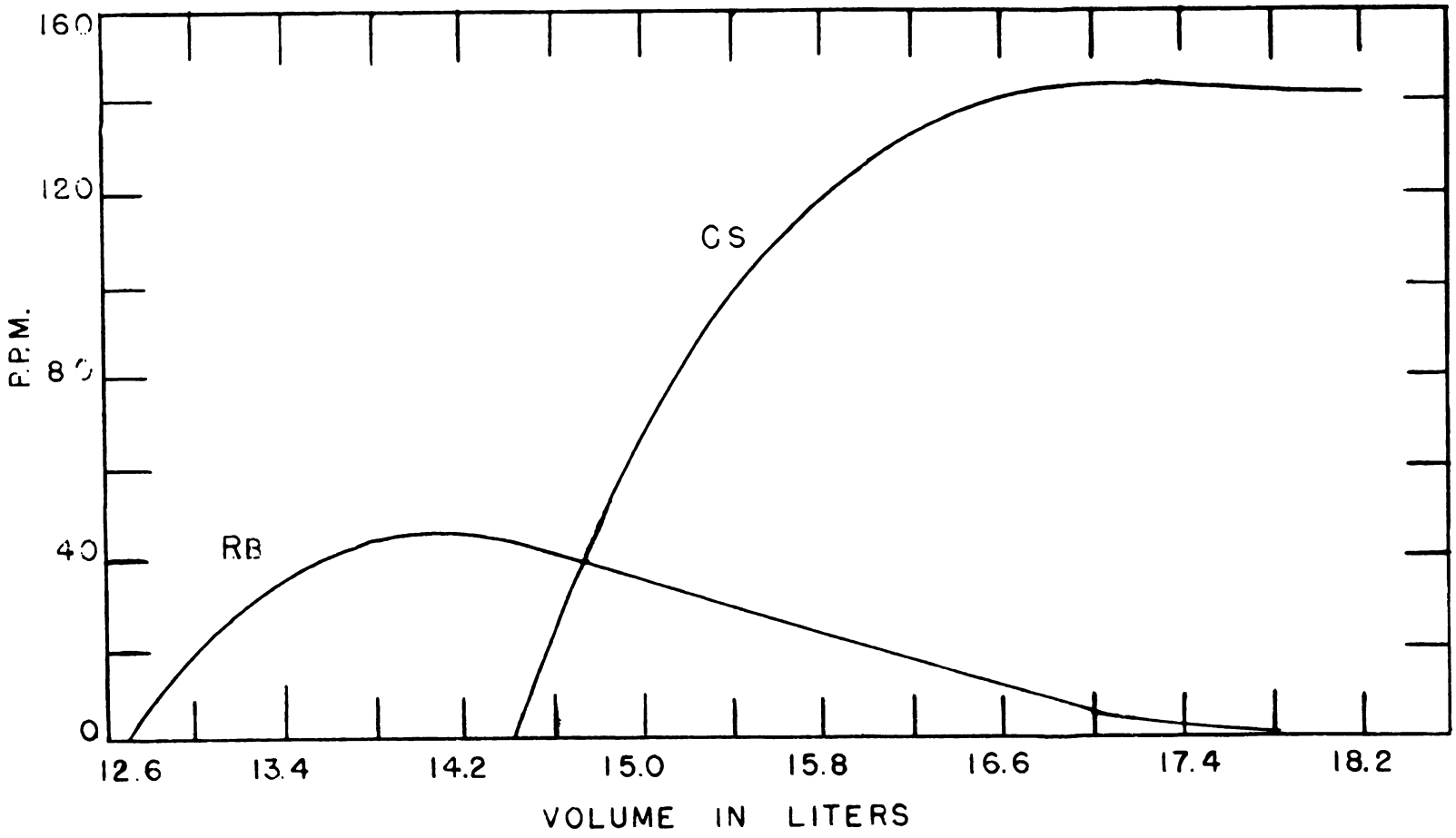

FIGURE 7 ELUTION OF RUBIDIUM AND CESIUM

SAMPLE: 2 11 G. OF DOW MIXTURE
RESIN BED: 68 CM. HIGH AND 3.8 CM. IN DIAMETER OF 200-400 MESH DOWEX 50
ELUANT: 0.7 NORMAL HYDROCHLORIC ACID
FLOW RATE: 4.4 ML. PER MIN.

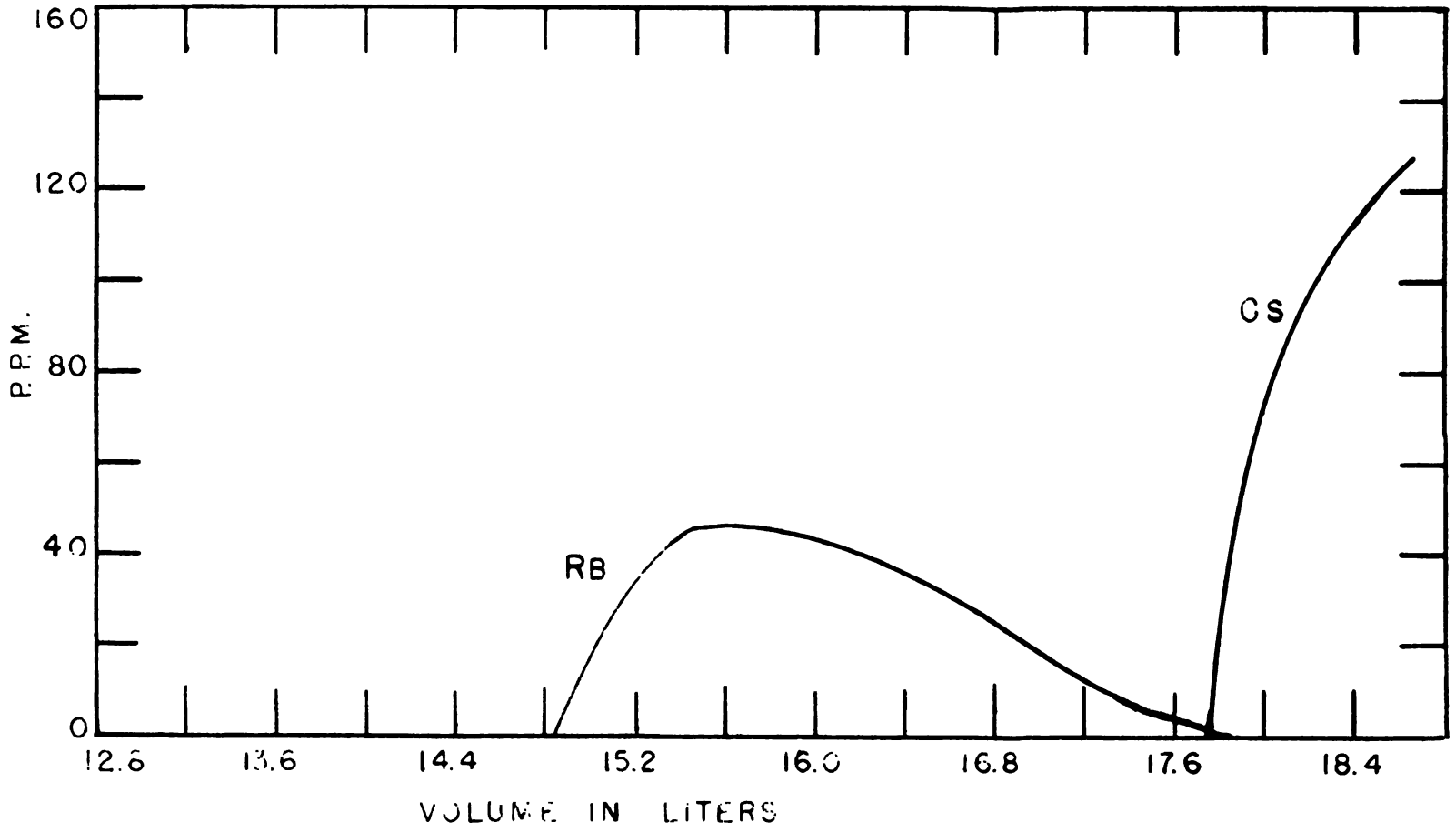

FIGURE 8 ELUTION OF RUBIDIUM AND CESIUM

SAMPLE 1.05 G. OF DOW MIXTURE
RESIN BED 68 CM. HIGH AND 3.8 CM. IN DIAMETER OF 200-400 MESH DOWEX 50
ELUANT. 0.7 NORMAL HYDROCHLORIC ACID
FLOW RATE: 4.4 ML. PER MIN.

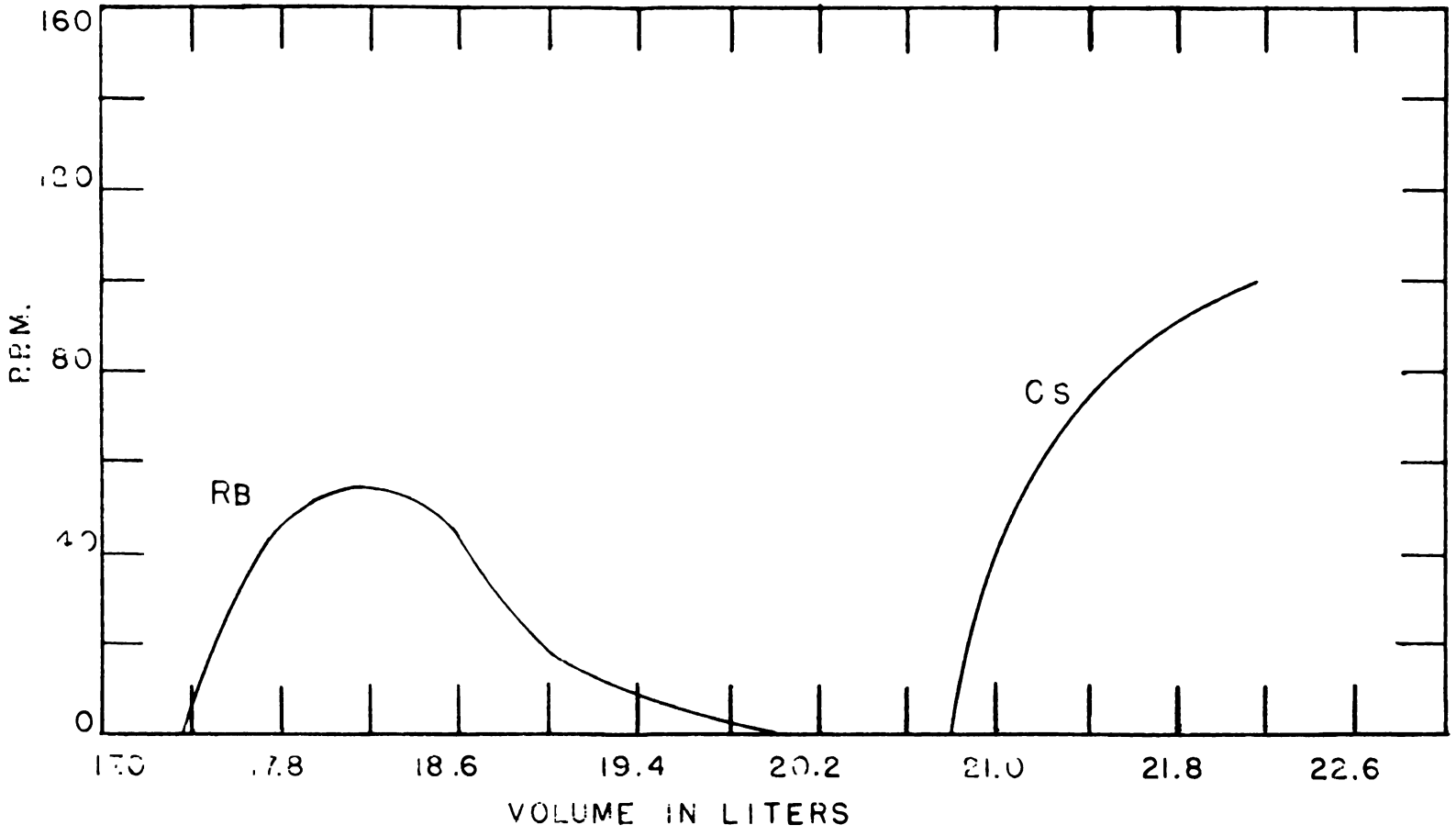

FIGURE 9 ELUTION OF RUBIDIUM AND CESIUM

SAMPLE: 1.02 G. OF DOW MIXTURE.
RESIN BED: 81 CM. HIGH AND 3.8 CM. IN DIAMETER OF 200-400 MESH DOWEX 50
ELUANT: 0.7 NORMAL HYDROCHLORIC ACID
FLOW RATE: 4.4 ML. PER MIN.

PREPARATION OF RUBIDIUM CHLORIDE BY ION EXCHANGE

The principal impurities in commercial rubidium chloride are potassium and cesium with a somewhat smaller amount of sodium. Rubidium compounds are intermediate in solubility between potassium and cesium so that any chemical scheme for purification must include at least two series of recrystallizations. Archibald (1) recommends recrystallizing the iododichlorides for removal of sodium and potassium, and crystallizing the tartrates to remove cesium.

To remove the amounts of impurities present in commercial rubidium chloride an ion exchange method offered the possibility of being more efficient for small quantities. To accomplish this it would only be necessary to elute a sample from the proper column and recover the purified rubidium chloride from the appropriate fractions.

It has been shown (page 18) that a one gram sample of the Dow mixture could be completely separated with a column containing a resin bed 81 cm. high and 3.8 cm. in diameter of 200-400 mesh Dowex 50 by eluting with 0.7 normal hydrochloric acid at a flow rate of 4.4 ml. per minute. A run was made using these conditions but the sample of Dow mixture was replaced by a 1.0 g. sample of commercial rubidium chloride (the Fisher Scientific Company). Rubidium appeared in the eluate fractions from 16.3 liters to 22.2 liters. Potassium was not detected in the 600 ml. of eluate preceding the rubidium fractions nor was cesium found in the 400 ml. of eluate immediately following the rubidium fractions.

For recovery of the purified rubidium chloride the fractions from 16.2 liters through 22.2 liters were combined in Vycor beakers protected by Pyrex cover glasses which were supported on Pyrex beaker hooks. The combined fractions were evaporated on a hot plate at 120°C which was surrounded by a protective netting of cheese cloth. It is desirable to use an evaporating temperature below that at which the resin decomposes since on decomposition the resin would introduce sulfate ions into the purified material. The final combined residues contained considerable amounts of resin and some silica, as well as the rubidium chloride.

To remove the silica the combined residues were dissolved in a minimum amount of distilled water and filtered.

For removal of the resin rubidium was precipitated as the chloride. This was accomplished by making the combined filtrate and washings from the silica removal 6 normal with respect to hydrochloric acid, evaporating until just before crystallization began and then passing in hydrogen chloride.

The hydrogen chloride was supplied by a generator consisting of a suction flask, a separatory funnel and an exit tube.

Concentrated sulfuric acid was placed in the suction flask and then the separatory funnel, which was held in place by a rubber stopper, inserted so that the tip of the stem was below the surface of the sulfuric acid. The separatory funnel was filled with concentrated hydrochloric acid and then as the hydrogen chloride was needed the hydrochloric acid was added by positioning the stopcock.

The solution containing the purified rubidium chloride was cooled with an ice bath and hydrogen chloride passed through the solution until no further precipitation occurred. The supernatant liquid was decanted and the precipitated rubidium chloride washed three times with anhydrous ethyl alcohol. A second crop of crystals was obtained from the decanted mother liquor and washings. The rubidium chloride was dried in an oven at 120°C, transferred to a muffle furnace, and heated to 300°C. The dried product was dissolved in distilled water, filtered, and again carried through the precipitation and drying procedures. The final product was entirely white, leaving no visible evidence of the resin, but a slight odor of hydrogen chloride was detectable.

Flame analysis of a solution containing 1000 p.p.m. of the purified rubidium chloride showed a small flame intensity at 767 mu which was not detected during elution. Evidently at the dilution used for analysis in the original separation procedure the amount of the constituent responsible for this flame intensity was below the detection limit of the flamephotometer under the operating conditions used.

In an attempt to determine the source of this flame intensity at 767 mu a 0.5 g. sample of the purified rubidium chloride was again carried through the elution process under the same conditions. The elution was followed by taking aliquots from the middle of the fractions containing rubidium. These were evaporated on a steam bath, dried at 120°C, weighed, and an appropriate amount of distilled water added to give a 1000 p.p.m. solution. In every sample the flame intensity remained

constant, and, within experimental error, equal to that found in a solution containing 1000 p.p.m. of the purified rubidium chloride.

Since a second pass through the column with a smaller sample did not reduce the flame intensity at 767 mu it seemed that a further adjustment of operating conditions was not necessary.

The expected impurities, due to incomplete separation, are sodium, potassium and cesium. The amounts of these present are discussed under "Flamephotometry of Rubidium and Cesium."

Flame analysis showed the rubidium chloride content to be approximately 99.7 per cent. Two other possible impurities, contributed from the resin, are sulfate and iron ions. The amounts of these present are less than 0.002 per cent for iron and 0.005 per cent for sulfate (30).

PREPARATION OF CESIUM CHLORIDE FROM POLLUCITE

The methods for the extraction of cesium from pollucite have recently been reviewed and several specific procedures given (43). In the various methods there are four reagents used in the initial treatment of the mineral. They are hydrochloric acid, sulfuric acid, hydrofluoric acid and sodium carbonate. Except in the case of hydrofluoric acid the solutions obtained from this initial treatment contain silica which is removed by filtration before recovery of the cesium.

A procedure has been reported by Robinson (31) using hydrofluoric acid in which a mixture of finely ground pollucite and fluorspar was heated with sulfuric acid and cesium alum extracted with hot water from the resulting cake.

Since cesium alum can be obtained in a fairly pure state by recrystallization from water (8) a method using a combination of sulfuric and hydrofluoric acids for the initial treatment of the mineral followed by recrystallization of the resulting alum appeared very promising. This procedure would eliminate the silica filtration found in the hydrochloric acid and sulfuric acid treatments as well as the extraction of the calcium sulfate cake in the fluorspar procedure.

The selected pieces of pollucite, found to contain 46.5% SiO_2, 17.85% Al_2O_3, 32.76% Cs_2O(K,Rb) and 1.86% Na_2O(Li), were reduced to 170 mesh. Fifty gram quantities of the ground pollucite were placed in a platinum dish and enough distilled water added to form a slurry. Hydrofluoric acid was added in small portions and the mixture stirred

with a bakelite rod. The stirring was continued after each addition of acid until the reaction subsided. One milliliter of 50 per cent hydrofluoric acid for each gram of pollucite gave satisfactory removal of the silica.

After addition of the hydrofluoric acid the resulting mixture was heated on a sand bath until a paste formed. To this paste 30 ml. of concentrated sulfuric acid was added, the mass thoroughly mixed using a platinum rod, and the final mixture heated until nearly dry.

The platinum dish and contents were transferred to a large beaker, two liters of distilled water added, and the solution heated almost to boiling for one hour. After standing overnight the solution was decanted from the small amount of residue and evaporated to a small volume. On cooling the crystals of cesium alum formed.

For recrystallization the alum was dissolved in boiling water, 10 ml. taken for each gram of alum, and the beaker containing the dissolved alum transferred to a 95°C water bath. After 15 minutes the source of heat was removed from the water bath and the solution allowed to stand overnight. During the first five hours of the recrystallization period the solution was agitated with a mechanical stirrer. The crystals of cesium alum were collected on a Buchner funnel and washed with cold water. The yield from one recrystallization of 42 g. of cesium alum was 39 g. The alums were recrystallized ten times in this manner.

Flamephotometric analysis of solutions containing 1000 p.p.m. of cesium served to follow the progress of the purification. These solutions were prepared by dissolving 0.4275 g. of the air dried cesium alum

in 100 ml. of distilled water. Table IV shows that after the second recrystallization the flame intensities at 589, 767 and 780 mu become fairly constant.

TABLE IV

FLAME ANALYSIS OF CESIUM ALUM

N Number Recrystallizations	Sodium 589 mu s.w. 2 mm. Instrument Reading	Potassium 767 mu s.w. 1.3 mm. Instrument Reading	Rubidium 780 mu 0.08 mm. Instrument Reading
2	9	62	8
3	9	34	1
4	12	36	1
5	10	33	1
6	9	32	1
7	13	32	1
8	9	30	1
9	13	31	1
10	13	33	1

Cesium alum was converted to the chloride by precipitating aluminum with ammonium hydroxide and sulfate with barium chloride. Cesium chloride was recovered from the resulting solution by evaporation and ignition at 500°C.

For flame analysis a solution containing 1000 p.p.m. of cesium was prepared by dissolving 0.0317 g. of cesium chloride in 25 ml. of distilled water. The lines measured were those at 589 mu (sodium), 767 mu (potassium), and 780 mu (rubidium). The results are shown in Table V.

For further purification the method of Archibald (2) was used which takes advantage of the difference in solubility of rubidium and cesium iododichlorides. After seven recrystallizations the iododichlorides were converted to the normal chloride and a solution containing 1000 p.p.m. of cesium prepared for flame analysis. In Table V it can be seen that further purification has been obtained by recrystallizing the iododichlorides.

TABLE V

FLAME ANALYSIS OF CESIUM CHLORIDE

	Instrument Readings		
	589 mu	767 mu	780 mu
Cesium chloride Purified through alums	32*	10**	7*
Cesium chloride Purified through Iododi-chlorides	8*	1.0**	2*

*Instrument sensitivity of 0.1
**Instrument sensitivity of 1.0

No attempt was made to evaluate the effect of a large amount of cesium upon the flame intensities of the other alkalies. By comparing the flame intensities in Table V with the flame intensities obtained from solutions of the respective alkali chlorides the sodium, potassium and rubidium contents are less than 1 p.p.m. respectively thus giving a cesium chloride content of more than 99.7 per cent.

FLAMEPHOTOMETRY OF RUBIDIUM AND CESIUM

In considering the ion exchange experiments described in this thesis it was necessary to have a method of analysis for sodium, potassium, rubidium and cesium which would be rapid, simple and capable of detecting small amounts. In previous ion exchange studies of the alkalies two methods were used; one in which the activity of certain radioactive isotopes was measured (9,23), and another using a flamephotometric procedure (7). The flamephotometer was chosen to follow the ion exchange separations and to analyze the purified rubidium and cesium chlorides.

Recently the flamephotometer has found widespread use and many papers have appeared describing its adaptation to the determination of sodium and potassium (16). The literature dealing with the flamephotometry of rubidium and cesium, on the other hand, is very limited (3,4, 13,17,45) and procedures for the determination of small amounts of sodium, potassium and cesium in the presence of large amounts of rubidium are wholly lacking.

The flamephotometer employed was one supplied by Beckman Instruments Incorporated, South Pasadena, California, catalog number 10300. The instrument, as well as its operation, is described in Beckman Bulletin 193-B (3) and by Gilbert et al. (17).

The first considerations in developing a flamephotometric procedure for the alkali metals were those of selecting the proper wavelengths and flame conditions.

In selecting wavelengths those were chosen at which the least amount of the respective alkali metal could be detected in an oxygen-natural gas flame (17). These are respectively 589, 767, 780 and 850 mu for sodium, potassium, rubidium and cesium. In adjusting the instrument for the proper wavelength, the wavelength dial was initially set to these values and then, with a sample of the respective alkali metal spraying into the flame, a final adjustment made to give a maximum intensity reading.

The Beckman flamephotometer may be used with several combinations of gases for excitation of the elements (3,17). These are oxygen-natural gas, oxygen-acetylene and hydrogen-oxygen. Oxygen-natural gas was chosen since, (a) it is the most convenient and most economical to use, (b) the flame temperatures for exciting the alkali metals are comparatively low, and (c) it has a favorable flame background for those areas of the spectrum to be utilized (3,17).

The flame conditions, which are regulated by the relative gas, oxygen and air pressures, determine to a considerable extent the intensity of the emitted radiation. These pressures for the various elements were determined using the procedure recommended by the manufacturer (3).

In general potassium, rubidium and cesium emit more intensely in a cooler flame than that where sodium emits the most strongly. For fixed air and gas pressures the flame intensities of all four alkali metals go through a maximum as the oxygen pressure is increased.

In the case of fixed oxygen and gas pressures the flame intensity of sodium goes through a maximum as the air pressure is increased while the flame intensities of potassium, rubidium and cesium gradually increase. The particular flame conditions chosen are shown in Table VI.

TABLE VI

FLAME CONDITIONS FOR THE ALKALI METALS

Alkali Metal	Wavelength mu	Gas Pressure cm. Isopropyl Alcohol	Air Pressure Inches of Water	Oxygen Pressure p.s.i.
Sodium	589*	2	15	30
Potassium	767**	2	22	14
Rubidium	780**	2	22	12
Cesium	852**	2	22	12

*Blue sensitive phototube
**Red sensitive phototube

After having decided upon wavelength settings and flame conditions for the respective alkalies it was necessary to choose a slit width that would be wide enough to allow detection of small amounts yet be narrow enough to resolve the various spectral lines. The spectral lines that are the most subject to mutual interference are those of potassium at 767 and rubidium at 780. To determine the maximum slit width that could be used and yet resolve these two spectral lines the instrument wavelength dial was set at 780 mu and a solution containing 100 p.p.m. of potassium as the chloride sprayed into the flame. With the selector

switch of the Beckman DU Spectrophotometer in the 1.0 position and the variable sensitivity knob in its counterclockwise position, it was found that a slit width of 0.06 mm. could be tolerated without producing any flame intensity above distilled water background. After several ion exchange runs the slit width was reduced to 0.04 mm. and this value used for all the work reported.

The eluant used in the ion exchange separations was hydrochloric acid, varying in concentration from 0.7 to 1.5 normal. Due to the adverse effects of hydrochloric acid on the metal parts of the burner each sample was first evaporated to dryness in platinum ware.

The instrument conditions chosen for following the ion exchange separations were: flame conditions and wave lengths as shown in Table VI, slit width 0.04 mm., selector switch in the 1.0 position and the variable sensitivity knob in its full counterclockwise position.

The samples for flame analysis were placed in 5 ml. beakers and protected in a Petri dish until ready for actual analysis. The procedure for analysis, after instrument warm up and adjustment, consisted essentially of the following steps:

1) A sample of distilled water was sprayed into the flame and the background determined.
2) The sample beaker containing the sample for analysis was removed from the Petri dish and placed in position. The flame intensity was determined, the sample replaced by distilled water, the dark current and instrument gauges checked, and the flame intensity of the sample again determined.

3) If the first two flame intensities agreed within 0.5 of a unit no further measurements were made; if not, the procedure was repeated. In some samples of high concentration where the level of liquid in the sample beaker had an appreciable effect upon the reading the beakers were refilled for repeat measurements.

4) The final value for the flame intensity was determined by subtracting the background intensity of distilled water from the flame intensity of the sample.

If more than one measurement were to be made on a series of samples, for example both rubidium and cesium, all samples in the series would first be analyzed for rubidium or cesium, the instrument conditions changed, and then the series again analyzed for the next component.

Calibration curves for rubidium and cesium over the concentration range encountered are shown in Figures 10 and 11 respectively.

In these curves no correction for the effect of one alkali metal upon the other has been made. Since this is an enhancement effect the values obtained for the areas of cross contamination in the elution curves are maximum rather than minimum values.

In determining the purity of the rubidium chloride prepared by ion exchange it was necessary to determine small amounts of sodium, potassium and cesium in the presence of large amounts of rubidium. In choosing conditions for this determination two main factors needed to be considered; the minimum concentrations of sodium, potassium and cesium

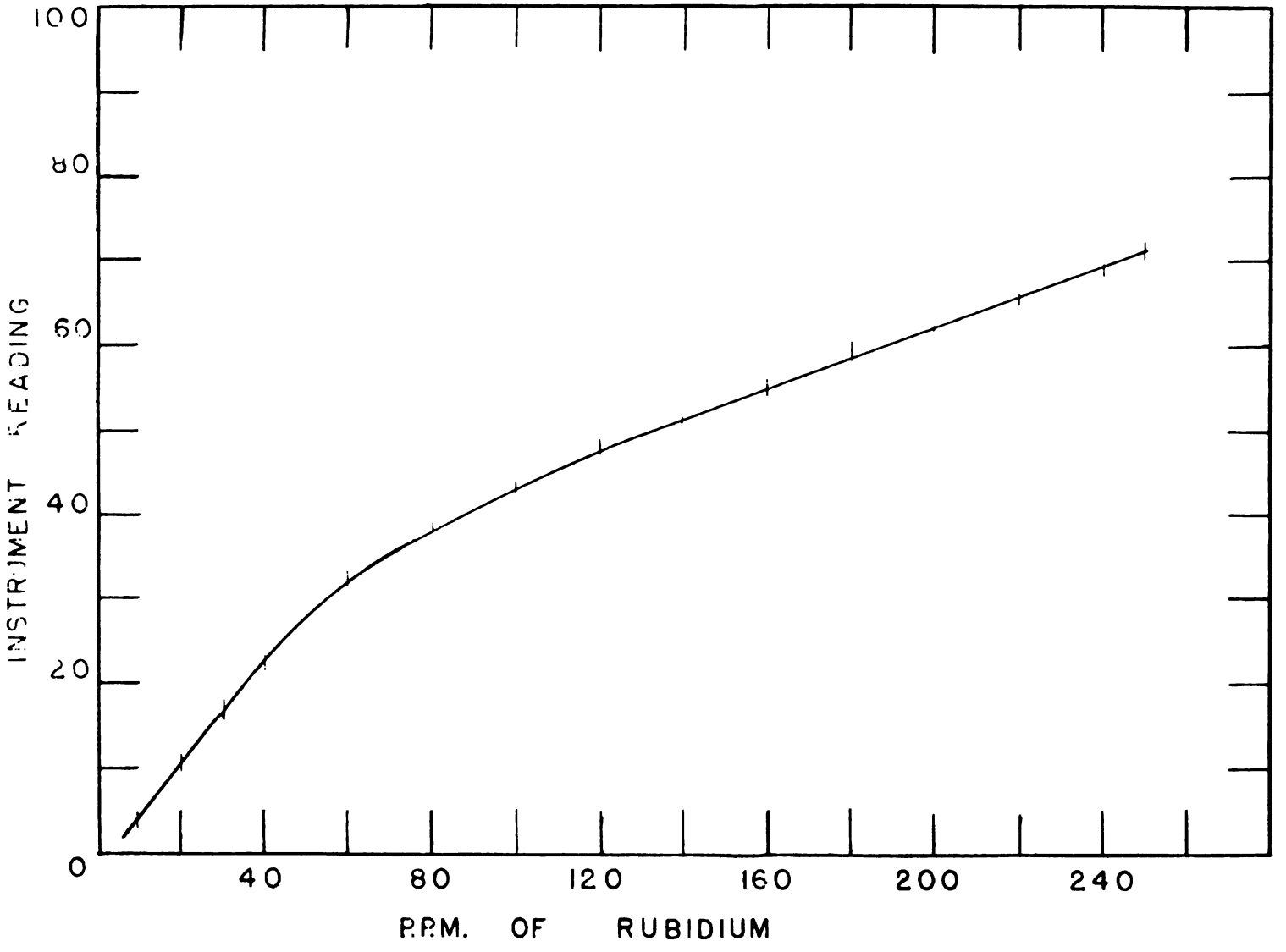

FIGURE 10 CALIBRATION CURVE FOR RUBIDIUM CHLORIDE
0-250 P.P.M. OF RUBIDIUM

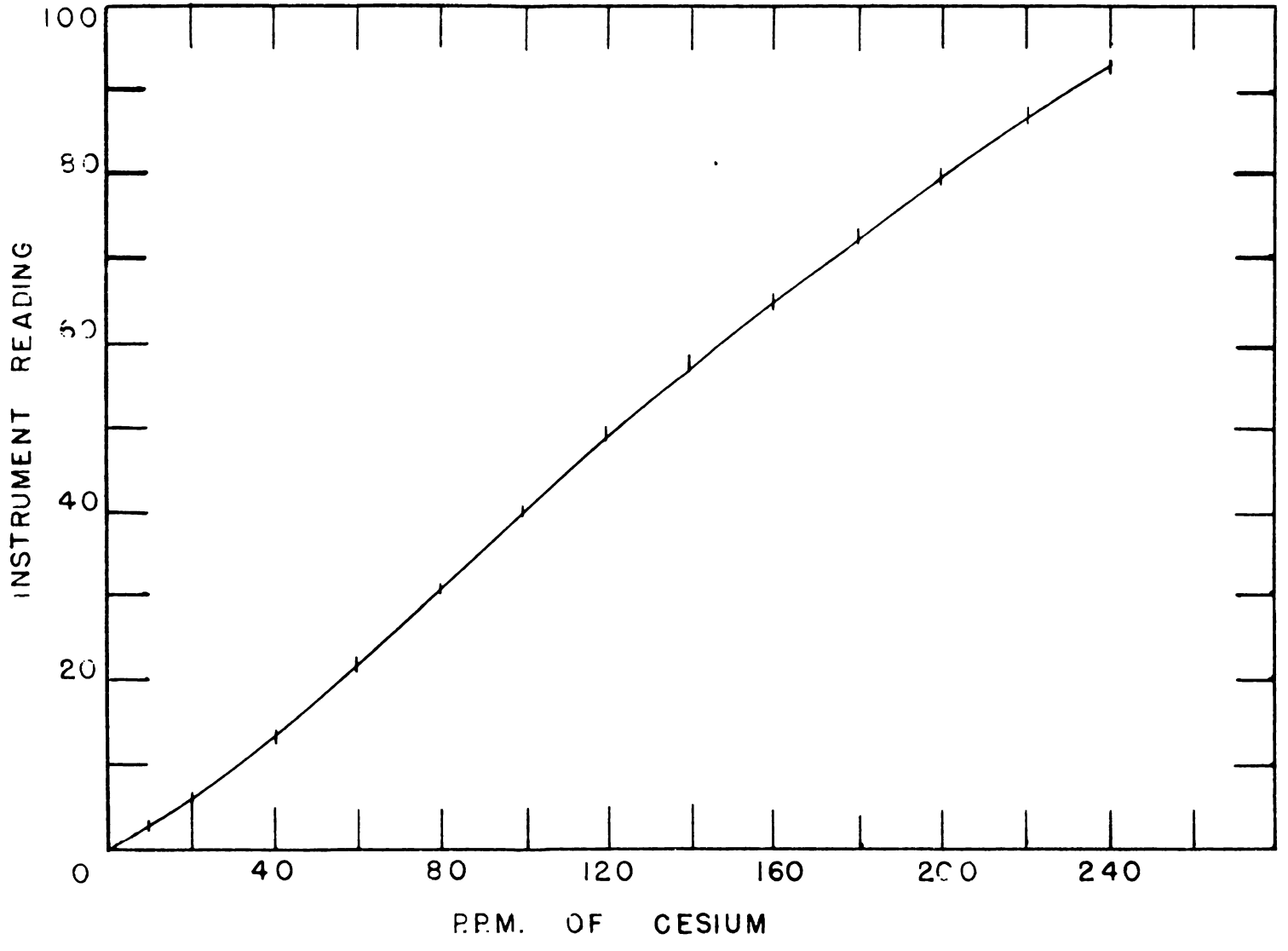

FIGURE 11 CALIBRATION CURVE FOR CESIUM CHLORIDE
0-250 P.P.M. OF CESIUM

detectable, and the effects of a large amount of rubidium upon the other alkali metals at the concentration level expected.

An initial investigation indicated that a large amount of rubidium has an enhancing effect upon small amounts of the other alkali metals and therefore instrument conditions were chosen, in so far as possible, to eliminate this interference.

It has been shown that for a sharp metallic emission line the highest ratio of metallic emission to continuous background is obtained with the narrowest slit width. A slit width of 0.04 mm. was chosen. At this slit width one p.p.m. of cesium, as well as smaller amounts of sodium and potassium, can be detected in the presence of larger amounts of rubidium chloride.

Judging from Table VII and Figures 13, 14 and 15 the concentration of sodium, potassium and cesium appeared to be on the order of 0.1 per cent. Since the limit of detection of the instrument for cesium with the conditions used for analyses is approximately one p.p.m., a solution for analysis needed to contain 1000 p.p.m. of the purified rubidium chloride.

For the purpose of following the purification of the commercial rubidium chloride, solutions of the commercial and purified rubidium chloride containing 1000 p.p.m. were prepared by dissolving 0.0354 g. of the respective chlorides in 25 ml. of distilled water. These solutions were analyzed in the flamephotometer with the flame conditions and wavelengths as given in Table VI. The slit width was 0.04 mm.

The variable sensitivity knob was in the counterclockwise position and the selector switch at 0.1.

TABLE VII

COMPARISON OF FLAME INTENSITIES OF 1000 P.P.M. SOLUTIONS OF COMMERCIAL AND PURIFIED RUBIDIUM CHLORIDE
(Values are Instrument Readings)

	Sodium	Potassium	Cesium
Commercial	20	100	37
Purified	8	39	3

In attempting to evaluate these observed flame intensities three series of measurements were made. In one a solution containing 1000 p.p.m. of the purified rubidium chloride (page 23) was sprayed into the flame and the intensity determined at various wavelengths. The results are shown in Figure 12.

In another series of measurements two sets of standards were prepared. One set contained 1, 2, 3 and 4 p.p.m. of sodium, potassium and cesium as the chlorides. These were prepared by taking 1, 2, 3 and 4 ml. of stock solutions containing 25 p.p.m. of the respective alkali metals as chlorides and diluting in 25 ml. volumetric flasks. The other set contained the same proportions of sodium, potassium and cesium but in addition one ml. of a stock solution containing 2500 p.p.m. of rubidium as the chloride was added to each 25 ml. volumetric flask giving a final

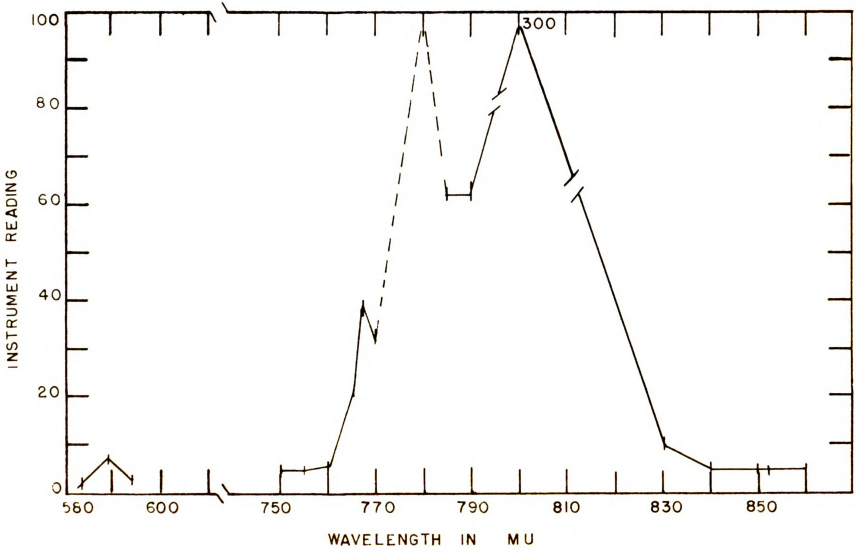

FIGURE 12 FLAME SPECTRUM OF RUBIDIUM CHLORIDE

concentration of 100 p.p.m. of rubidium. The results are shown in Figures 13, 14 and 15.

A third series of measurements was made on solutions containing one p.p.m. of sodium, potassium and cesium in which rubidium was added in varying amounts from 100 p.p.m. to 1000 p.p.m. These solutions were prepared in 25 ml. volumetric flasks by adding one ml. of 25 p.p.m. solutions of sodium, potassium and cesium. The varying rubidium content was introduced by adding 1, 2, 4, 6, 8 and 10 ml. of a 2500 p.p.m. solution of rubidium. Figure 16 shows the effect of increasing amounts of the purified rubidium chloride on these one p.p.m. amounts.

The recommended procedure for compensation of interference that cannot be removed is to prepare a series of standards that are identical to the sample but contain varying amounts of the element in question (17,27). Then, by a direct comparison of flame intensities the unknown concentration can be determined with the contribution of the interference taken into account. Since spectrographically pure rubidium chloride was not available this recommended procedure could not be followed.

It has been shown that when a brillant flame, such as obtained from appreciable concentrations of sodium, is produced the line often is not resolved and there is an increased emission at other wavelengths (3,4,17). Figure 12 represents this phenomenon with respect to rubidium.

In Figure 12 the peaks at 780 mu and 800 mu are rubidium lines, while the one at 767 mu indicates the presence of potassium since rubidium has only a weak line at 767 mu, which probably is not excited by an

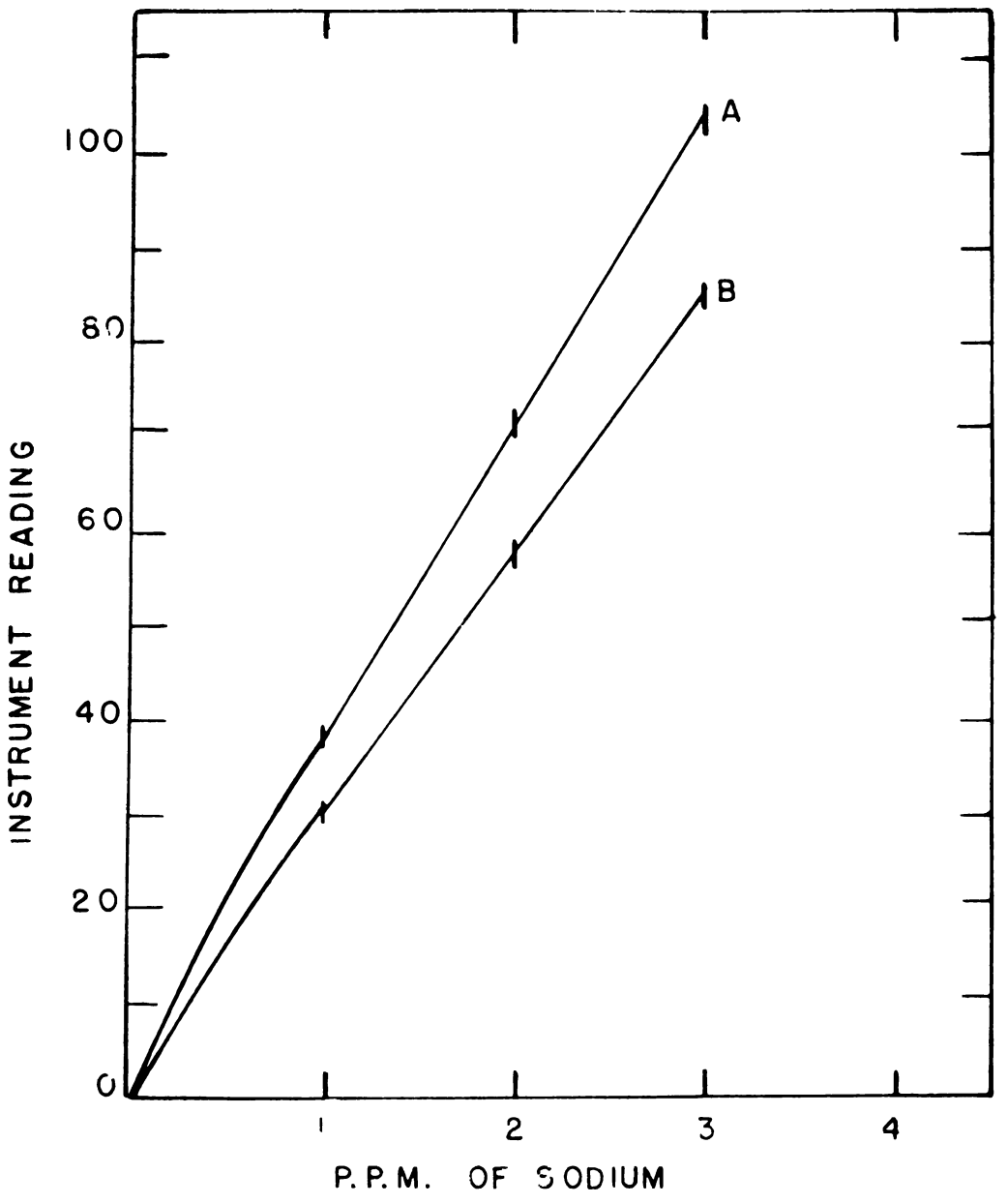

FIGURE 13 EFFECT OF 100 P.P.M. OF RUBIDIUM ON THE FLAME INTENSITY OF SODIUM

CURVE A SODIUM CHLORIDE + 100 P.P.M. RUBIDIUM

CURVE B SODIUM CHLORIDE

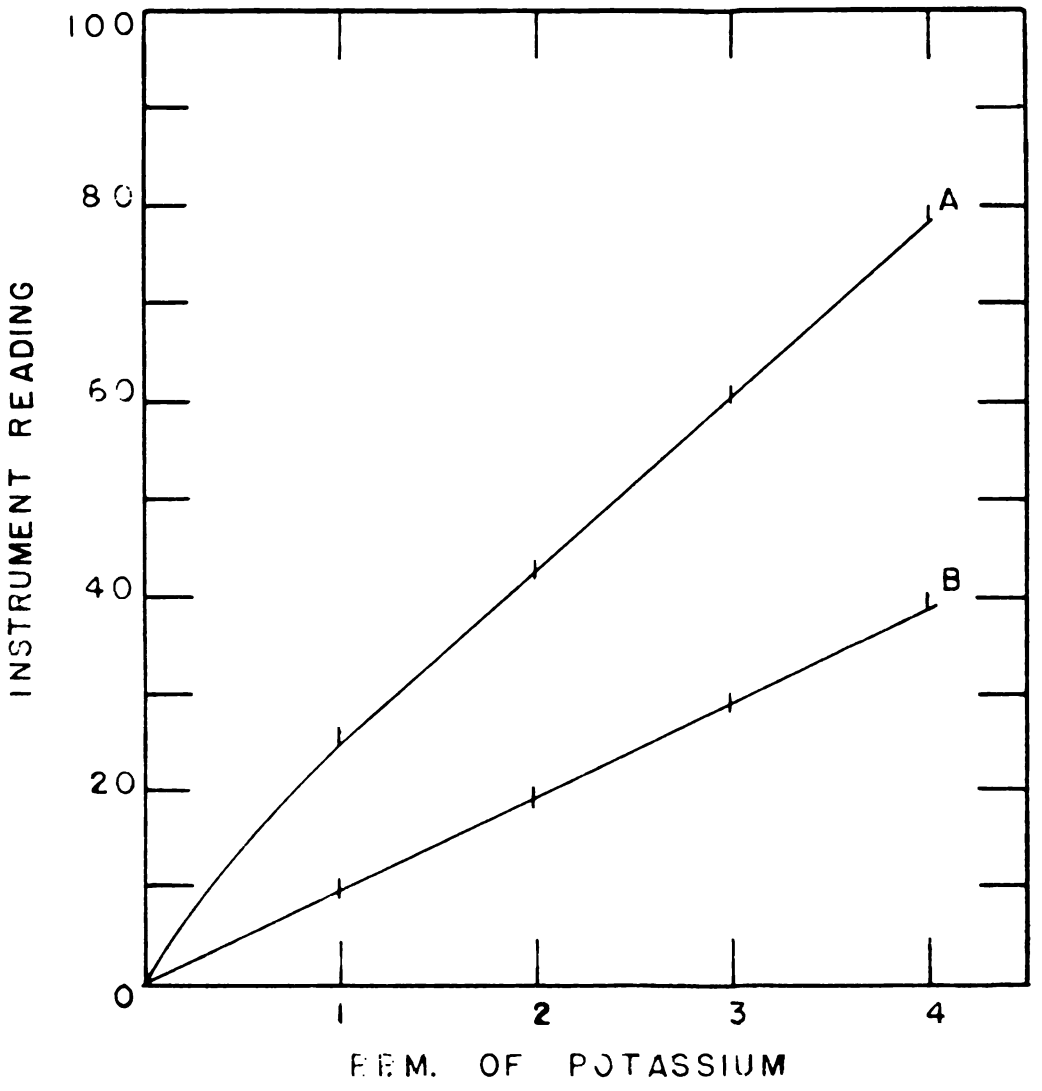

FIGURE 14 EFFECT OF 100 P.P.M. OF RUBIDIUM ON THE FLAME INTENSITY OF POTASSIUM

CURVE A POTASSIUM CHLORIDE + 100 P.P.M. RUBIDIUM

CURVE B POTASSIUM CHLORIDE

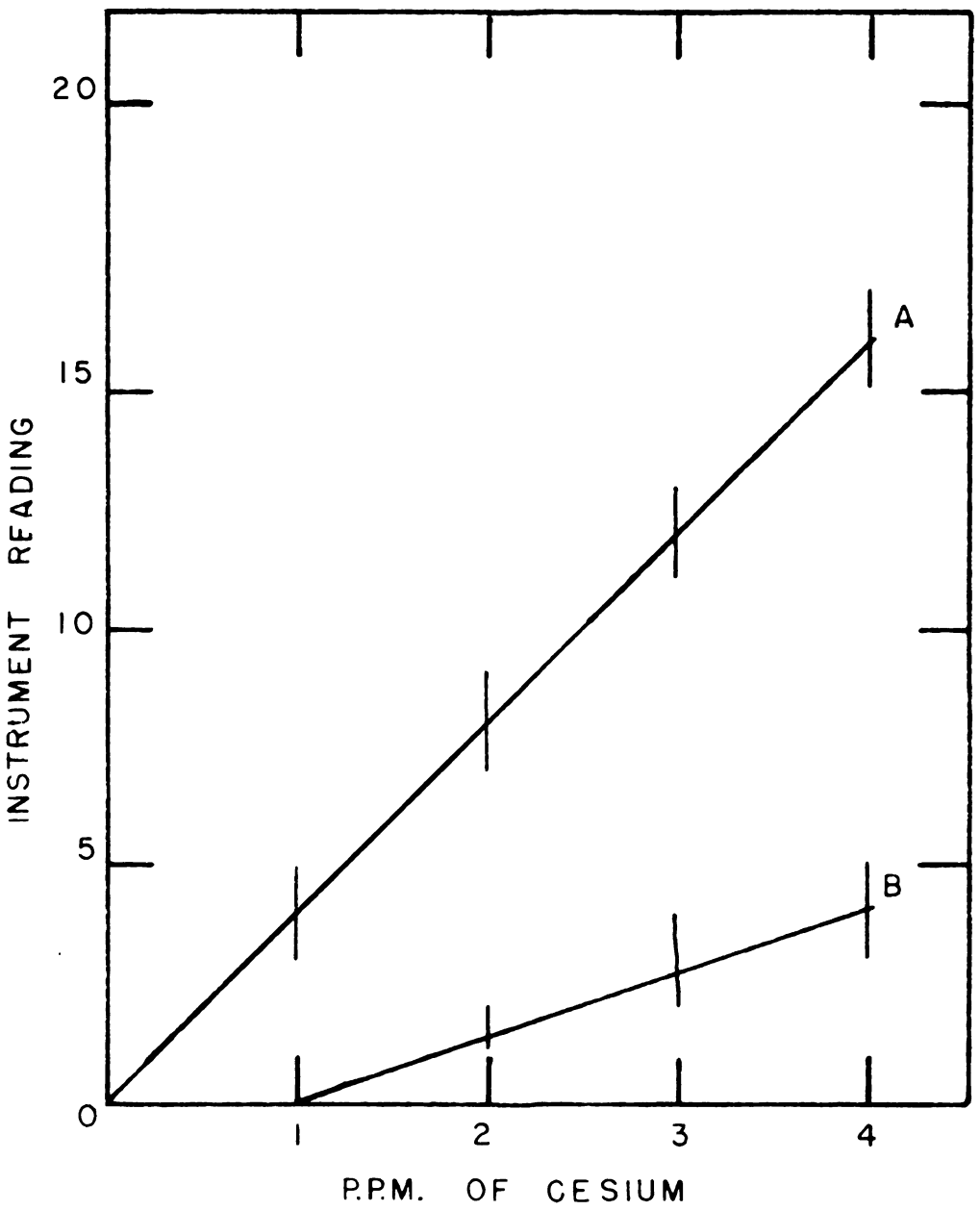

FIGURE 15 EFFECT OF 100 P.P.M. OF RUBIDIUM ON THE FLAME INTENSITY OF CESIUM

CURVE A CESIUM CHLORIDE + 100 P.P.M RUBIDIUM

CURVE B CESIUM CHLORIDE

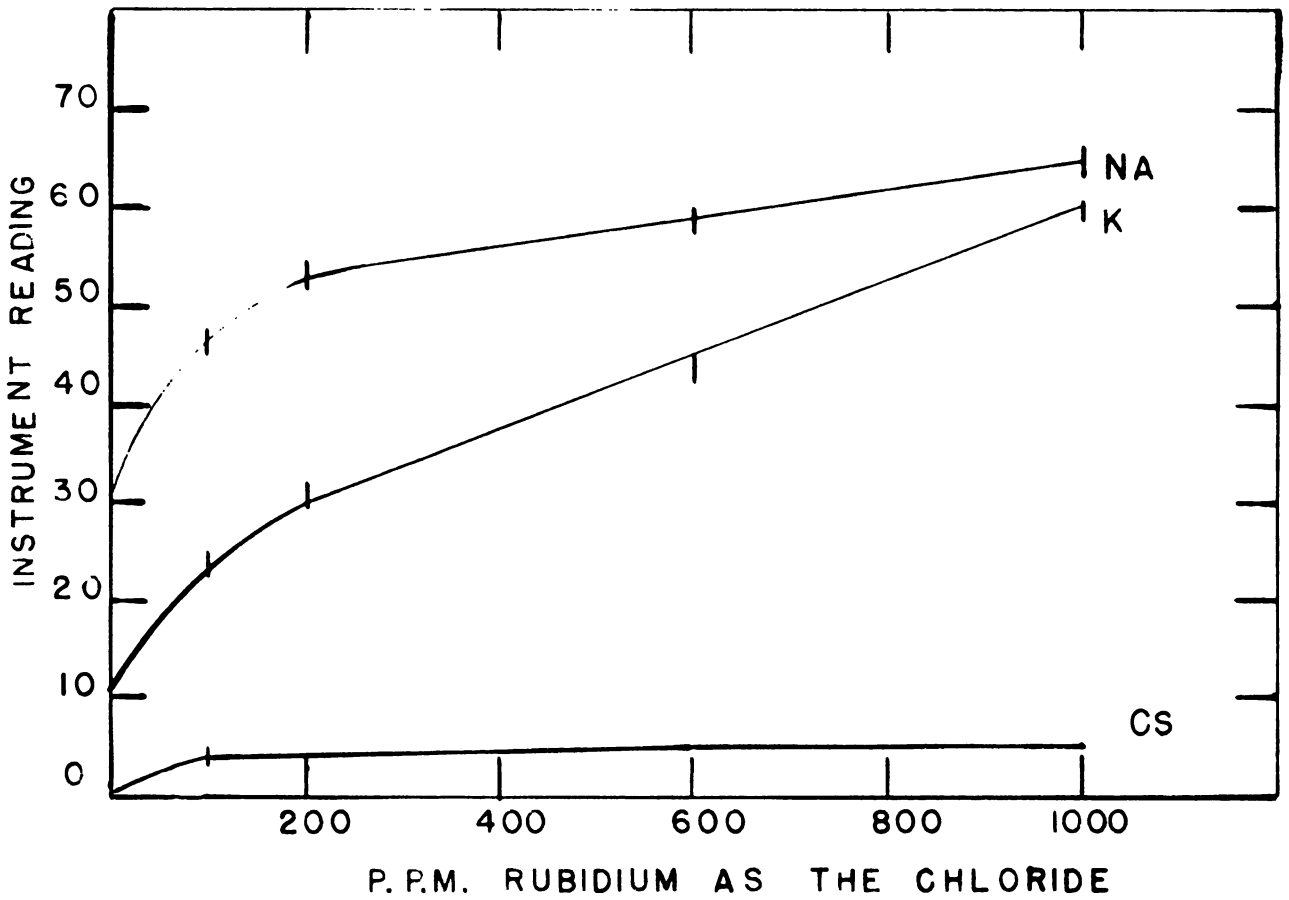

FIGURE 16 EFFECT OF RUBIDIUM ON THE FLAME INTENSITIES OF 1 P.P.M. OF SODIUM, POTASSIUM, AND CESIUM AS THE CHLORIDES

oxygen-gas flame, and sodium, as well as cesium, does not emit at this wavelength. The peak at 589 mu is evidence of sodium being present. Since there isn't any peak at 852 mu above the background intensity, cesium is assumed absent to the extent of less than one p.p.m. (4,14).

The enhancement effect of rubidium upon small amounts of sodium, potassium and cesium is illustrated by the two series of curves in Figures 13, 14 and 15. A concentration of 100 p.p.m. of rubidium as the chloride was chosen to show this enhancement effect, since at this dilution the concentration of the other alkalies would be below the detection limits of the instrument as is shown by the 0 p.p.m. points on the various curves.

In Figures 13, 14 and 15 solutions A and B contain the same amount of sodium, potassium and cesium but solution A contains 100 p.p.m. of rubidium as the chloride. It is seen that the greatest enhancement occurs with potassium and the least with cesium.

Figure 16 shows the effect of increasing amounts of the purified rubidium chloride upon one p.p.m. of sodium, potassium and cesium. The effect is not entirely due to enhancement since beyond some concentration of rubidium chloride between 100 and 1000 p.p.m. the concentrations of the impurities also contribute to the flame intensity.

From these curves and Table VII three estimates of the amounts of sodium, potassium and cesium can be made.

The first estimate, based on curve B in Figures 13, 14 and 15, neglects any enhancement effect. Evaluation of the instrument readings

for a 1000 p.p.m. solution of the purified rubidium chloride reported in Table VII by use of the B curves gives the concentration of sodium as less than one p.p.m. (approximately 0.5 p.p.m.), potassium less than 4 p.p.m. and cesium less than 2 p.p.m. or a percentage purity, based on alkali metal content, of 99.3%.

A second estimate, taking into account that an enhancement effect exists and that the true enhancement caused by 1000 p.p.m. of rubidium (shown in Figure 16) would be greater than that produced by a 100 p.p.m. of rubidium, shows the sodium content to be less than one p.p.m. (approximately 0.3 p.p.m.) or 0.1 per cent, potassium less than 2 p.p.m. (approximately 1.6 p.p.m.) or 0.2 per cent and cesium less than one p.p.m. or 0.1 per cent. These values, taken from curve A, Figures 13, 14 and 15. give a percentage purity for rubidium chloride, based on alkali metal content, between 99.6 and 99.7 per cent.

From Table VII and Figure 16 the effect of adding one p.p.m. each of sodium, potassium and cesium to 1000 p.p.m. of the purified rubidium chloride can be seen. For sodium the instrument reading increases from 8 to 65, for potassium from 38 to 60 and cesium from 3 to 5. If it is assumed that these increases in flame intensity are strictly proportional then the concentration of sodium is 0.2 p.p.m. or 0.02 per cent and potassium 1.3 p.p.m. or 0.13 per cent. The increase in flame intensity for cesium is within the measurement error so no calculation was attempted other than to consider its concentration less than one p.p.m. As some justification for these calculations the same analysis was applied to Figure 14. In Figure 14 the increments of increase in flame intensity

from 1, 2, 3, 4 p.p.m. of potassium in the presence of 100 p.p.m. of rubidium are directly proportional if 9 is subtracted from each total value. This amount, 9, apparently due to the initial enhancement, can be evaluated by extrapolating to zero the line obtained by plotting the difference between curves A and B versus the concentration in p.p.m. The percentage purity of rubidium chloride based on these calculations is more than 99.7.

From these measurements the rubidium chloride content appears to be more than 99.7 per cent. In each set of measurements the true enhancement effect is probably greater than that calculated and for a closer estimate more measurements are necessary.

THE QUANTITATIVE DETERMINATION OF RUBIDIUM AND CESIUM

A simple, accurate method for the determination of sodium and potassium employing an ion exchange technique has been proposed (7). The method consists of separating the sodium and potassium by elution through a cation exchanger, evaporation of the separate fractions of eluate and titration of the alkali chloride residues. An extension of this technique to rubidium and cesium appeared very promising.

It was found that a 0.2 gram sample of rubidium and cesium chlorides could be separated by elution with 0.7 normal hydrochloric acid at a flow rate of approximately 2.7 ml. per min. from a column containing a resin bed 87 cm. high and 2.2 cm. in diameter of minus 400 mesh Dowex 50. Rubidium appeared from approximately 4650 ml. to 5770 ml., while cesium was found in the fractions from 6150 ml. to 7450 ml.

After elution the fractions containing the respective alkalies were transferred to 400 ml. Vycor beakers, each beaker from the fraction collector rinsed twice with distilled water, and then evaporation of the fractions and washings carried out as in the preparative procedure.

An attempt was made to determine the alkali metal content of the evaporated residues by the combination of a base titration for the residual hydrogen chloride and a Mohr titration of the total chloride.

A mixture containing 50.2 mg. of purified rubidium chloride and 49.9 mg. of purified cesium chloride was separated by elution from the column and the respective fractions combined. After evaporation the residues were transferred to 300 ml. Erlenmeyer flasks. Upon the

addition of distilled water a brown solution was formed due to the resin that had been carried over from the column.

After 10 ml. of potassium chromate indicator was added the solution turned yellow brown. When the stoichiometric amount of silver nitrate was added no sharp change in color occurred which would serve as an endpoint. The resin also caused the particles of silver chloride to remain dispersed.

Another sample of rubidium and cesium chlorides was carried through the separation procedure and a silver nitrate titration of the chloride residues made using dichlorofluorescein as an indicator. No detectable endpoint was observed.

A potentiometric method, using a silver indicator electrode and a mercurous sulfate reference electrode, was investigated. After observing the gradual slope of the potentiometric curves and the erratic nature of blank values obtained from titrating residues of evaporated effluent the potentiometric method was abandoned.

The alkali metal content of the residues was finally determined by weighing both as the chlorides and as the sulfates. For weighing, the evaporated residues were transferred to platinum dishes, dried at 120°C for one hour and, after cooling for an hour in a desiccator, were weighed to the nearest tenth of a milligram. To convert the chlorides to sulfates a few drops of concentrated sulfuric acid were added and the dishes rotated until the entire residue was wetted. The platinum dishes were then placed in a cold muffle furnace which was fitted with an aspirator to remove the evolved fumes. The temperature was gradually raised to

300°C where it was held until the evolution of fumes ceased and then increased to 550°C. This ignition temperature was chosen after a preliminary study of the effect of heating upon rubidium and cesium sulfates (Table VIII). After the samples had been heated to 550°C for one-half hour they were removed, ammonium carbonate added and the heating continued for another one-half hour. Following removal from the furnace the dishes were placed in a desiccator, cooled for one hour and then weighed to the nearest tenth of a milligram. The ammonium carbonate treatment, heating to 550°C, cooling in a desiccator and weighing were repeated until constant weight was obtained.

TABLE VIII

EFFECT OF HEATING UPON RUBIDIUM AND CESIUM SULFATES

Time and Temperature of Heating	Rubidium Sulfate Weight in Mg.	Cesium Sulfate Weight in Mg.
1 Hr. at 500°C.	108.3	108.9
2 Hr. at 500°C.	108.0	108.5
3 Hr. at 500°C.	108.0	108.5
2 Hr. at 600°C.	108.0	108.7
2 Hr. at 700°C.	106.6	106.2
2 Hr. at 800°C.	100.9	92.0

Upon evaporating portions of 0.7 normal hydrochloric acid effluent it was observed that a certain amount of residue remained. Thus a

determination based on a direct weighing of the combined fractions must take this into account. In order to determine the magnitude of the correction necessary for the residue contributed by the action of the eluant on the resin, volumes of effluent were collected, evaporated, and the residues treated in the same manner as the samples. Table IX shows the results of weighing both as the chloride and the sulfates. The blanks, 1 through 11, were determined from effluent taken while the column was under continuous operation, that is a constant flow of 0.7 normal hydrochloric acid was maintained except during sample and eluant addition. The blanks, 12 through 15, were determined after the column had stood for nearly two weeks with 0.7 normal hydrochloric acid.

TABLE IX

BLANK CORRECTIONS FOR ACTION OF 0.7 N HYDROCHLORIC ACID ON DOWEX 50

Blank Number	Volume in Ml. Evaporated	Weight per 1000 ml. in Mg. of Chloride Residue dried at 120°C	Weight per 1000 ml. in Mg. of Sulfate Residue ignited at 55°C
1	1500	2.1	1.0
2	1500	2.2	1.1
3	1500	2.3	1.1
4	1500	1.9	0.9
5	2000	4.8	1.2
6	1000	2.2	1.4
7	1000	2.5	1.3
8	1000	3.4	1.5
9	1000	3.5	1.6
10	475	2.5	1.4
11	1000	3.1	1.3
12	880	10.3	2.1
13	1000	3.9	2.3
14	1000	2.6	1.9
15	1000	3.9	2.4

These blank corrections were applied to the individual determinations. The amount of correction depended upon the volume of effluent combined for the respective fractions and the weight of residue per 1000 ml. for that run.

The results, using the procedure given for elution, evaporation, ignition and weighing, from a series of runs in which samples of sodium, potassium, rubidium and cesium were eluted from the analytical column are shown in Tables X and XI. Table X shows the results calculated from weighing the sulfates, Table XI from weighing the chlorides. The elution in runs 1 through 5 was uninterrupted until the samples were completely removed. In runs 6 and 7 elution was halted after the elution of rubidium and then later continued until the last of the cesium was removed.

In carrying out these determinations samples of the alkali chloride solutions were pipetted into weighed platinum dishes, evaporated to dryness, the sample weights determined, and after the samples were placed on the column elution begun. In general the volumes of effluent collected for the blank determinations were taken immediately before and after the samples were eluted, however in some runs volumes for blank determinations were collected only at the beginning or the end of a run. The blank values used for the calculations of a specific run in Tables X and XI were values obtained by evaporating volumes of effluent from that run. The volumes of effluent combined for rubidium and cesium were determined from the preliminary run described at the beginning of this section. In each run one or more samples were analyzed in the regions of separation

TABLE X

DETERMINATION OF ALKALI METALS BASED ON ION EXCHANGE
ALKALI METALS WEIGHED AS CHLORIDES

Run No.	Sodium Chloride				Potassium Chloride				Rubidium Chloride				Cesium Chloride			
	Blank mg.	Taken mg.	Found mg.	Error mg.	Blank mg.	Taken mg.	Found mg.	Error mg.	Blank mg.	Taken mg.	Found mg.	Error mg.	Blank mg.	Taken mg.	Found mg.	Error mg.
1									2.9	100.5	101.1	+0.4	4.0	99.9	101.5	+0.6
2									5.9	100.8	99.9	-0.9	6.2	100.2	99.3	-0.9
3										50.2	--	--		49.9	--	--
4	4.4	53.3	53.2	-0.1	3.5	51.7	53.6	+1.9	2.9	50.4	52.4	+2.0	4.2	50.2	52.0	+1.8
5	12.4	52.4	44.2	-8.2	17.5	51.8	40.7	-11.1	12.4	50.3	42.1	-8.2	19.6	49.3	37.3	-12.0
6									4.0	10.3	9.1	-1.2	6.8	99.4	115.4	+16.0
7									4.1	100.0	100.8	+0.8	5.5	9.9	13.8	+3.9

TABLE XI

DETERMINATION OF ALKALI METALS BASED ON ION EXCHANGE
ALKALI METALS WEIGHED AS SULFATES

Run No.	Sodium Chloride				Potassium Chloride				Rubidium Chloride				Cesium Chloride			
	Blank mg.	Taken mg.	Found mg.	Error mg.	Blank mg.	Taken mg.	Found mg.	Error mg.	Blank mg.	Taken mg.	Found mg.	Error mg.	Blank mg.	Taken mg.	Found mg.	Error mg.
1									1.4	100.5	99.7	-0.8	1.8	99.9	99.8	-0.1
2									2.5	100.8	99.9	-0.9	2.6	100.2	101.3	+1.1
3									1.7	50.2	50.1	-0.1	1.5	49.9	49.8	-0.1
4	2.8	52.7	53.2	+0.5	2.3	51.7	52.3	+0.6	1.9	50.4	50.5	+0.1	2.7	50.2	51.2	+1.0
5	2.5	52.4	51.5	-0.9	3.4	51.8	50.8	-1.0	2.5	50.3	49.6	-0.7	4.0	49.3	49.2	-0.1
6									2.5	10.3	9.2	-1.1	4.4	99.4	110.0	+10.6
7									2.8	100.0	100.4	+0.4	2.7	9.9	13.2	+3.3

and with the conditions of analysis used the separations are complete to the extent of 0.05 mg. In every case the separation interval fell within the values determined from the preliminary run, that is from 5770 to 6150 ml. No effort was made to keep the volumes of effluent combined for a particular alkali metal to a minimum and the average volume combined for ribidium was 1650 ml. (4400-6050 ml.) and for cesium 1950 ml. (6050-8000 ml.).

As a specific example of the procedure, in run number 4, Tables X and XI, a sample containing 52.7 mg. of sodium chloride, 51.7 mg. of potassium chloride, 50.4 mg. of rubidium chloride and 50.2 mg. of cesium chloride was placed on the column (87 cm. high and 2.2 cm. in diameter of minus 400 mesh Dowex 50) and eluted with 0.7 normal hydrochloric acid at a flow rate of 2.7 ml. per minute. The volume of effluent combined for sodium was 2070 (0-2070) ml., for potassium 1569 (3154-4723) ml., for rubidium 1260 (4723-5985) ml. and for cesium 1880 (6278-8158) ml. Two, one liter volumes of eluate were collected after the cesium fractions were eluted and evaporated for blank determinations. The two blank values were 2.2 and 2.5 mg. per 1000 ml. when weighed as the chlorides and 1.4 and 1.3 mg. per 1000 ml. when weighed as the sulfates. The averages of these values were then multiplied by the volume of eluate in liters to obtain the blank correction for the respective alkali metals. These values were then subtracted from the residue weights and the amount of the respective alkali chlorides calculated. Final results are shown in Tables X and XI.

The ion exchange studies described here were not intended to be a systematic evaluation of the various factors involved in the ion exchange process, but rather were intended to develop a set of working conditions that would yield a separation which could be adapted to the preparation of limited amounts of high purity rubidium chloride and to the quantitative determination of sodium, potassium, rubidium and cesium. These conditions are not necessarily the optimum ones but they do give satisfactory and reproducible separations. In determining conditions for future ion exchange separations these will serve as a guide.

No two columns of identical dimensions necessarily give the same separation under identical conditions of elution. This difference probably is due to the resin, as shown by Riemam (39), and the difference in column packing. Due to these differences a preliminary run must be made to establish the characteristics of a particular column. In this run various fractions must be analyzed. These analyses, if done flamephotometrically, need only be qualitative and require little time. Once the characteristics are established they should remain constant and in subsequent runs it is only necessary to note the volume of effluent for location of the various alkali metals.

The preparative procedure, while consuming nearly a week for the purification of a one gram sample, actually requires very little of the operator's time. Once the conditions for separation are established the time required is less than one-fourth of this. In the procedure,

as described here, only an occasional check is needed until the first 15 liters of eluant have passed through the column. After 15 liters of effluent have been obtained the fraction collector is started and further attention is not required for another 12 hours. When elution is complete the proper volumes, as determined by a preliminary run, are simply combined, evaporated and the purified rubidium chloride recovered.

Perhaps the most serious disadvantage is the method of recovery of the rubidium chloride. In this recovery nearly 6 liters of effluent are evaporated. This evaporation concentrates the impurities present as well as the rubidium chloride, however the purity is still high.

In the analytical procedure conditions were chosen to give a separation that would allow ample margin for sample recovery and yet not involve prohibitive volumes of eluant. As in the preparative procedure, these conditions may not be the optimum ones but the separation intervals are large enough to allow considerable variation in experimental conditions during elution and yet yield reliable results. In each analytical run at least one sample, and in most cases two or three, in the critical regions were analyzed. In every case the separation intervals fell within those of the preliminary run. The time for elution requires two days but during this time attention is required only at the end of each twelve hour period to combine the various fractions from the collector. No change in operating conditions during this time is necessary and at least two fractions of ninety ml. are

found between each alkali metal. In combining the various fractions only the volume need be noted.

By comparing the results based on weighing the alkali metals as chlorides and sulfates, Tables X and XI, it can be seen that in general the sulfate values are more accurate, although for some samples the two methods are comparable.

In runs 1 through 5, where 50 and 100 mg. samples were taken, the maximum error for the calculations based on weighing as the sulfates is 2 per cent; for the chlorides over 20 per cent. For runs 6 and 7, Tables X and XI, in which the rubidium-cesium ratio was varied the absolute error for the rubidium samples is comparable to that found in the other runs. However, the error for both cesium samples is much greater. In runs 6 and 7 the elution was interrupted after the rubidium had been removed from the column and presumably an additional amount of resin was added to the effluent that was not corrected for by the blank value.

The blank corrections, shown in Table IX, are the most serious source of error in this proposed method. The values in Table IX are arranged in the chronological order in which the samples were taken from the column. The blank values for any particular run had a maximum variation of 0.5 mg. and in most cases, under 0.3 mg. Apparently the amount of blank contributed by 1 liter of 0.7 normal hydrochloric acid eluant increases with the amount of exposure of the resin to the eluant while under continuous elution as seen by blanks 1 through 11. The

blanks from 12 through 15 were taken after the column had stood for two weeks with 0.7 normal hydrochloric acid. The higher value of these is presumed due to this period of standing.

If the conditions of the analytical procedure are followed the maximum error for 100 and 200 mg. samples of the mixed chlorides, in which the rubidium-cesium ratio is one to one, is 2 per cent. While the total time consumed for a complete analysis of sodium, potassium, rubidium and cesium is somewhat larger than the present methods the number of actual man hours required is considerably less. The ion exchange procedure is much simpler and no previous experience is necessary as in certain of the precipitation methods.

SUMMARY

SUMMARY

The ion exchange separation of rubidium and cesium has been accomplished and two procedures, based on ion exchange, are proposed. One procedure is for the preparation of gram quantities of high purity rubidium chloride and the other is for the quantitative determination of rubidium and cesium.

The preparative procedure consists essentially of eluting one gram quantities of commercial rubidium chloride from a column containing a resin bed 81 cm. high and 3.8 cm. in diameter of 200-400 mesh Dowex 50 resin with 0.7 normal hydrochloric acid at a flow rate of 4.4 ml. per minute. The rubidium chloride is recovered from the proper volume of effluent by evaporation and precipitation with hydrogen chloride. Flamephotometric analysis of the purified product shows the rubidium chloride content to be approximately 99.7 per cent.

The procedure for the quantitative determination of rubidium and cesium involves separating samples of the mixed chlorides by elution from a column containing a resin bed of Dowex 50 resin, minus 400 mesh, 87 cm. high and 2.2 cm. in diameter with 0.7 normal hydrochloric acid at a flow rate of 2.7 ml. per minute and then determining the alkali metal content of the appropriate fractions by weighing the ignited rubidium and cesium sulfates. An accuracy of two per cent is obtained for 100-200 mg. samples of the chlorides when rubidium and cesium are present in a one to one ratio.

A method for the preparation of high purity cesium chloride from pollucite is described in which the mineral is treated with a mixture of hydrofluoric and sulfuric acids. This treatment eliminates the silica filtration of the other methods (43) and gives directly cesium alum which can be obtained in a fairly pure state by recrystallization from water (8).

A procedure for the flamephotometric determination of rubidium and cesium is given in which the flame intensity at 780 and 852 mu were measured for the estimation of rubidium and cesium respectively. The enhancement effect of large amounts of rubidium on small amounts of the other alkalies is demonstrated and methods described for their approximation in the purified rubidium chloride.

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