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EXTRACTION OF RUBIDIUM AND CESIUM FROM MINERALS AND ORES

F. M. Perel'man

With detection of the presence of rubidium and cesium in a particular mineral or mineral source, the problem of quantitative determination of these elements arises. The fundamental difficulty was that the properties of both metals are very similar to each other and to those of potassium which constantly accompanies them in natural compounds.

Now, with perfection of spectrophotometric methods, there is no need to use tedious chemical methods of analysis in cases when the concentrations of rubidium and cesium are small. However, the methods which were used by different authors for separating these elements from impurities and from one another are of interest since they were the basis of the technology and the industrial processes.

Without delving on the old investigations, we will cite here only certain works that were carried out in the 1930's, when many of the chemical characteristics of rubidium and cesium were determined with greater accuracy.

To these studies belongs, first of all, the work of Ye. S. Burkser on the determination of rubidium in marine waters, in which negligible concentrations

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of rubidium are found in the presence of an enormous excess of chlorides and sulfates of sodium, potassium, magnesium, and calcium. The method was as follows [164]. Barium hydroxide is added to 1 liter of a solution whose salt content includes between 0.001 and 0.01% RbCl (to separate magnesium); excess barium and calcium are precipitated with sodium carbonate. The filtered solution is subsequently evaporated to incipient crystallization of the potassium and sodium chlorides, and gradually reduced to 20 ml. The crystals are discarded and the solution evaporated to dryness. The dry residue, weighing not more than 0.5 g, is moistened with 1.3 ml of water and 3 ml ethanolic acid mixture is added; after 24 hr the KCl precipitates; the filtrate is again evaporated to dryness and again treated with the ethanolic acid mixture. This operation is repeated until the KCl precipitate no longer forms. Rubidium is then precipatated from solution as chlorostannate. Depending on the concentration, this method makes it possible to separate between 30 to 80% of the initial amount of rubidium.

Fresenius used a slightly different variant for the same purpose [273]. After preliminary evaporation of 25 liters of mineral water to 15 ml, sodium carbonate is added to the solution; the precipitated carbonates are dissolved in HCl, reprecipitated, and discarded, and the combined filtrated evaporated to 200 ml and saturated with gaseous HCl, until separation of sodium chloride occurs. The filtered solution is evaporated to 15 ml; rubidium and cesium with an impurity of potassium are precipitated as cobaltinitrites. The cobaltinitrites are decomposed by heat and from the precipitate obtained the chlorides of the alkali metals, which were first treated with the ethanolic acid mixture to separate KCl, are leached out with water; then antimony chloride is used to precipitate cesium. Rubidium is separated from the final filtrate as chlorostannate.

The determination of cesium in the double salt $3CsCl \cdot 2SbCl_3$ and rubidium in Rb_2SnCl_6 is done by the perchlorate method.

Yu. V. Morachevskiy determined rubidium in native carnalites by a method somewhat similar to the preceding method [272]. The carnalite is dissolved in hot water and the solution evaporated with subsequent addition of ethanol; after separation of the main mass of KCl and NaCl, potassium, rubidium and cesium precipitate together as cobaltinitrites, the precipitate is ignited and leached with water and the residue of cobalt oxide is discarded. Hydrochloric acid is added to the solution and the solution evaporated to dryness. The precipitated chlorides were dissolved in water and chloroplatinates precipitated from the solution; the chloroplatinates were reduced with ammonium formate. The chlorides filtered from metallic platinum were reprecipitated as chloroplatinates; after their reduction rubidium was separated as chlorostannate.

Other authors used similar methods to determine quantitatively rubidium and cesium in minerals and ores, sea water and mineral sources [304, 305].

In all cases of separating rubidium and cesium it was deemed expedient to treat the chlorides of the alkali metals at a definite stage with HCl, ethanol, of an ethanol-acid mixture. This method is indisputably suitable for the most careful separation of rubidium and cesium from the impurities of potassium and sodium. In one of the laboratories of the Institute of General and Inorganic Chemistry, Academy of Sciences, USSR, a pure sample of rubidium sulfate was obtained from commercial rubidium chloride after pretreating with a mixed solvent consisting of equal volumes of ethanol and concentrated HCl. In the samples of Rb_2SO_4 were found

Li . . .	1,10 —5.10^{-5} %
Na . . .	0,04 —0,10%
K . . .	0,01 —0,08%
Cs . . .	0,005 —0,02%

The main form of rubidium and cesium raw material for a long time has been lepidolites which, along with small amounts of rubidium and cesium (about 0.5%), contain up to 4-5% lithium oxide. The lithium salts were the main product while rubidium and cesium were byproducts.

However, in recent years lithium minerals have ceased to be the only raw material source for the extraction of rubidium and cesium.

Cesium is now extracted in considerable amounts from the cesium-rich mineral pollucite, commercial deposits of which were discovered in the USA (Maine, South Dakota), Sweden (Varuträsk), South West Africa, USSR, and other countries.

Rubidium is still obtained mainly from carnalities.

It is completely evident that the sharp difference between these minerals both in the concentration of rubidium and cesium and in chemical reactivity required completely different technological processing methods. In addition, the change-over to a larger, industrial scale forced to a considerably degree the rejection of those refining methods which were developed for quantitative determination of Rb and Cs: new methods, independent of the goals and problems of analytical chemistry, were required.

1. Extraction of Rubidium and Cesium from Lepidolites

Lepidolites, or lithium micas are complex aluminum silicates of lithium and postassium in which a very small part of the alkali metals is preplaced by rubidium and cesium. The total concentration of the Rb and Cs does not exceed 0.5%.

The lepiodolites are subjected to preliminary fusion or sintering under various conditions for removal.

The most widely used method is based on the fusion of pulverized ore with gypsum with subsequent leaching of the melt with hot water. The aluminum alums of rubidium, cesium and potassium crystallize from the solution on cooling. Lithium then separates as carbonate from the mother liquor.

Lepidolites can also be fused with potassium sulfate or with a mixture of barium sulfate and carbonate, or, finally, barium carbonate and ammonium chloride. Sometimes lepidolites are decomposed with H_2SO_4, with addition of fluorite and with heating, or are subjected to prolonged leaching with sulfuric acid. Certain authors suggest to fuse this mineral with a mixture of calcium oxide and chloride or simply roast it without any additions at 1090° with subsequent treatment with sulfuric acid [306]. Thus, in all cases rubidium and cesium are precipitated as alum at a definite stage of the process. Therefore the basic process of Rb and Cs production from leipdolites is the recrystallization of alums to separate them from each other and from the accompanying potassium. The fractional recrystallization of the aluminum alums of rubidium, cesium and postassium is based on their different solubility. This process was used as early as 1882 by Setterberg to separate rubidium and cesium from natural compounds. It is simple in conception, but in view of the isomorphism of potassium, rubidium, and cesium alums it is long and tedious. It was found by a purely empirical method that to free the aluminum alums separated from leipdolites from potassium, six recrystallizations are needed; after seven subsequent recrystallizations it is possible to obtain pure cesium alums; the final separation of rubidium and cesium is effected by another 22 recrystallizations.

A detailed investigation of the solubility of potassium, ammonium, rubidium and cesium alums at different temperatures, which was carried out in recent years by Delepine [142] makes possible to reduce the number of recrystallization, reducing the process of enriching alums with rubidium and cesium to a concentration such that further separation can be done by other methods. In particular, the cesium fraction is reduced to a concentration of 90 or 95% cesium salt, dissolved in hot water and from this solution cesium is precipitated as a double salt with antimony chloride. Refinement of the rubidium fraction is somewhat more difficult because it is contaminated by cesium and potassium. Therefore the obtained precipitate of rubidium chlorostannate is insufficiently pure and requires reprecipitation.

Certain authors recommend to convert rubidium and cesium sulfates to chlorides by dissolving the alums in hot water and adding ethanol and HCl. In this case KCl is precipitated and removed by filtration; stannic chloride is added to the filtrate. Rubidium and cesium are precipitated as chlorostannates.

The double salt of cesium with antimony of, correspondingly, rubidium with tin is subjected to further refining; in particular, antimony (or tin) can be separated with hydrogen sulfide as sulfides [307].

2. Extraction of Cesium from Pollucite

Pollucites have not been known as the main form of cesium raw material very long. A number of methods for processing them are described in the literature. Of these some are used industrially in the USA, Germany, and other countries.

Germany extracts cesium from imported American pollucites by the following method [308].

The pulverized mineral was mixed with water in a cast iron basin to a thick pulp, after which hydrofluoric acid (50-60%) was added with heating. Excess silicon was removed as fluoride. The residue was treated with concentrated sulfuric acid, then heated until excess acid was completely eliminated; the dry product was dissolved in water heated to boiling, the solution obtained was neutralized with aluminum shavings until weakly acid. Then hydrogen sulfide precipitated the heavy metals, and the filtrate was evaporated until crystallization of the aluminum cesium alum.

The alum was dissolved in boiling water and barium hydroxide added to the solution; aluminum precipitated as $Al(OH)_3$ and the sulfate ions as $BaSO_4$. Excess barium was eliminated from the filtrate by addition of ammonium carbonate, the filtrate was boiled to decomposition and removal of excess of $(NH_4)_2CO_3$. The filtrate was evaporated to dryness and cesium obtained as carbonate. The yield of cesium from pollucite by this method reached 93%.

When processing pollucites cesium can also be separated from solutions as a double salt with lead chloride (Cs_2PbCl_6) or antimony chloride ($3CsCl \cdot 2SbCl_3$). To remove antimony the precipitate is boiled with dilute ammonia; as a result of hydrolysis Sb_2O_3 is precipitated and amonium chloride remaining in solution with the cesium is removed by evaporating the solution to dryness and by igniting the dry residue [309]. We can also oxidize this solution with nitric acid, after which it is evaporated to dryness; then cesium nitrate will be in the dry residue and can be easily removed by recrystallization from the rubidium traces. In addition, cesium nitrate is easily converted to carbonate by adding oxalic acid and igniting the obtained cesium oxalate. Finally, if an appropriate amount of iodine dissolved in HCl is added to cesium nitrate and the solution heated to boiling, a very beautiful yellow salt of composition $CsCl_2I$ crystallizes on cooling. Since a similar compound of rubidium is considerably more soluble, this method is suitable for removing cesium from rubidium. When $CsCl_2I$ is ignited it is converted to CsCl.

In the USA the extraction of cesium from pollucite was done by a somewhat different method [310]. The pulverized ore was subjected to treatment with concentrated HCl, with subsequent dilution of the solution to separate the silica, which is later filtered off. Cesium was precipitated from solution as a double salt with antimony chloride.

In place of concentrated HCl we can use 3N HCl in which the $3CsCl \cdot 2SbCl_3$ is least soluble. The aqueous suspension of the double salt was subjected to hydrolysis while boiling, the Sb_2O_3 precipitate was filtered off, and the cesium chloride remaining in solution was converted to a nitrate, then to an oxalate with subsequent ignition to a carbonate.

When cesium is produced on larger scales (with processing of many tons of pollucitic raw materials) the concentrates* were treated with HCl, then leached with water, the filtered solution evaporated and adjusted to 4N HCl, antimony trichloride was added and cesium precipitated as $3CsCl \cdot 2SbCl_3$. As was indicated above, the suspension of the double salt in water was heated to boiling, which led to hydrolysis and separation of Sb_2O_3. Ammonia and ammonium carbonate were added to the filtered solution to precipitate the impurities—aluminum, iron, and the traces of antimony and calcium. The solution, filtered and freed from impurities, was acidified with HCl and the double salt of cesium with antimony was reprecipitated. In this manner the

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* Cs concentrates of the Foot Mineral Company (in %): Cs_2O 28.63; SiO_2 46.0; Al_2O_3 17; Na_2O 2.0; Rb_2O 1.36; K_2O 1.0; Li_2O 0.31; H_2O 2.5.

large excess of ammonium salts, which prevented further progress of the process, was removed. Reprecipitation of the double salt reduced the ammonia excess to a minimum. The final separation of antimony was done with hydrogen sulfide; 99.9% pure CsCl was obtained as the end product.

Pollucite can also be treated with sulfuric acid (50% concentration). For this purpose the mass obtained is diluted with water and filtered hot. The aluminum cesium alum separates from solution (due to the aluminum in the ore); it falls out first, due to their extremely low solubility. It is filtered and the solution evaporated to a small volume, after which aluminum alum enriched with rubidium separates.

A number of other methods of separating cesium from rubidium have been described in the literature. In particular, alkali metals can be converted to bromides [311] and leached with liquid bromine. CsBr goes into solution while the bromides of other alkali metals remain in the precipitate. The filtered solution is evaporated and after removal of bromine cesium bromide crystallizes out.

In the cases when it is necessary to separate cesium only from lithium and sodium (in the absence of potassium and rubidium) one of the best methods is to precipitate it as perchlorate.

Many studies have been devoted in recent years to the technology of extracting cesium from Swedish polluchities.

Investigations showed that the pollucites from Varutrask are difficult to decompose. If 15 g of pollucite is heated with a mixture of 20 g potash and 20 g of sodium carbonate for a half hour at 700-800°, only 4/5 of the selected mineral enters into reaction. Sulfuric acid also does not decompose the mineral completely. Only hydrochloric and hydrofluoric acids produce the desired results. In one of the experiments [312] 0.5 g of finely pulverized pollucite was treated with one liter of 18% HCl on a water bath. A crust of salt formed on the surface that prevented removal of the acid and thus fostered the process. When the reaction ended,the dry residue was leached with one liter of water containing 100 ml of concentrated HCl; the undisolved residue was filtered off and leached twice more under the same conditions. All solutions were combined and evaporated to one liter; silica precipitated. To the clear solution 200 ml of concentrated sulfuric acid was gradually added and the aluminum cesium alum crystallized on cooling (for all practical purposes cesium was absent in the filtrate). A total of 545 g of air-dry alum was obtained. Of this, 250 g was dissolved in 2.5 liters of boiling water, and alum again precipitated from the cooled solution. Thus the aluminum alum was recrystallized several times according to the counter-current principle. Multiple recrystallization produced cesium alum of sufficiently high purity.

In another case [179] 50 g of finely pulverized pollucite was boiled under reflux with 100 ml of concentrated HCl for 20 hr, after which the solution was filtered from the precipitate in which, along with the SiO_2, a certain portion of the cesium remained as poorly soluble, orange-red crystals of the double salt $3CsCl \cdot FeCl_3 \cdot H_2O$. Extraction of the cesium was 95-98% complete. The obtained hydrochloric acid solution was evaporated to dryness in a vacuum, and the residue treated with boiling acetic acid, after which antimony trichloride was added.

$AlCl_3 \cdot 6H_2O$ was slightly soluble on acetic acid and therefore precipitated together with $2SbCl_3 \cdot 3CsCl$.

It was found that extraction of cesium in acetic acid by this method is better than in the hydrochloric acid. To purify the double salt containing 3-4% rubidium, it was dissolved in a small amount of 8% HCl and recrystallized. After two recrystallizations the produce contained less than 0.05% rubidium and was free of iron and aluminum.

Further treatment of the double salt ($2SbCl_3 \cdot 3CsCl$) consists of boiling the aqueous-ammoniacal solution, separating the precipitated Sb_2O_3 and precipitating residual antimony with hydrogen sulfide from a weakly acid solution; at pH 4.0-4.5 the traces of iron, which could still remain in the solution after hydrolysis of the double salt, are precipitated.

Vacuum sublimation is also recommended for separating cesium chloride from antimony: $SbCl_3$ is volatilized at 220° while CsCl sublimes at 645°.

Treating the pulverized ore with 30% hydrogen bromide is also proposed for removing cesium from pollucite [313]. The insoluble residue was filtered from solution and the cesium bromides and other alkali metal bromides precipitated with isopropyl alcohol. The filtered and dried bromides were then treated with liquid bromine (1 part Cs_2O, 10 parts Br_2). As noted above, only CsBr went into solution.

In addition to the various hydrometallurgical methods, cesium can be extracted from pollucite by direct vacuum reduction with metallic calcium [32]. The following experiment is described in the literature: 200 g of pollucite is heated for several minutes in air at 900°; the water of crystallization is thus removed from the mineral. The pulverized, dried pollucite is mixed with three parts by weight of metallic calcium (calcium shavings) and slowly heated to 900° under vacuum. At 750° a deposit of metallic cesium forms on the walls of the reaction vessel, and then collects into drops. The yield of cesium by this method is more than 85%, when cesium was contaminated by calcium, rubidium, and potassium. To purify it from these, it was redistalled under vacuum at 350-400^{0}; however, as a result of this operation rubidium could not be separated from the cesium. In spite of its simplicity this method has a number of serious shortcomings.

3. Extraction of Rubidium from Carnallite

As early as 1892 Feit and Kubierschky [314] proved that in spite of the negligible amount of rubidium in carnallite, this mineral could become a practical source for the production of rubidium. The method they developed consisted of precipitating aluminum rubidium alum, isomorphic with analogous alums of potassium (and also cesium) from aqueous solutions of carnallite. However, the demand for rubidium was negligible and the fields of application of this rare metal were so little studied that a serious stimulus to its production in considerable amounts was absent. Only in the 1930's did this question again confront industry. The German salt deposits of Stassfurt were widely represented by carnallites and here the properties of rubidium carnallites and other rubidium-rich salts were studied.

Original investigations were carried out by Jander along with Faber and Busch [315-317], who worked out a method for separating rubidium from solutions in the form of poorly soluble heteropolycompounds with silica and molybdenum oxide. Later D'Ans and Busch [187, 318] studied a number of systems including the chlorides of potassium, magnesium, and rubidium. These authors determined the crystallization conditions for rubidium carnallites from aqueous solutions in which potassium carnallites are present at the same time and developed a method of extracting rubidium salts from natural carnallites. This method based on multiple fractional recrystallization of potassium, magnesium, and rubidium chlorides was used in 1932 on an experimental basis [319]. However, commercial production of rubidium from carnallite was organized in Germany only in 1944, during the Second World War. By this time similar investigations of the solubility in systems formed by the basic components of carnallites and pilot-plant studies on the extraction of rubidium from them were also carried out in the Soviet Union [23].

Thus the problem of the behavior of rubidium (an in part, cesium) during the course of processing of carnallites is now completely understood. At the installation in Toychental, which operated until April 1945, carnallite of the following compositions served as the starting material (see Table 38).

The rubidium content varied between 0.007 and 0.01%; the cesium content was about 0.0002%.

The usual technological process was as follows. The pulverized carnallite was leached at 90°; on cooling, the solution filtered from the potassium chloride precipitate, was evaporated in a vacuum device to a specific volume. As the solution cooled the so-called "artificial" carnallite crystallized, i.e. the recrystallized carnallite which is considerably enriched with rubidium in comparison with the initial carnallite.

The entire recrystallization process, based on the decomposition of potassium carnallite with separation of the KCl and subsequent precipitation of the isomorphous crystal of potassium and rubidium carnallites from the evaporated solutions, was repeated many times. After ten such operations a concentrate was obtained which contained not less than 10% Rb; thus the sediments were enriched a thousandfold.

TABLE 38

Type Analysis of Natural Carnallite

Mineralogic Composition	Chemical composition	Contents, %
Carnallite	KCl	13,17
	$MgCl_2$	16,82
	H_2O	19,10
Kieserite	$MgSO_4$	11,26
	H_2O	1,69
Tachhydrite	$CaCl_2$	0,84
	$MgCl_2$	1,43
	H_2O	1,63
Anhydrite	$CaSO_4$	0,27
Halite	NaCl	33,26
Isoluble residue		0,71
Water		0,82

The enriched concentrate was dissolved in water but without decomposition of the potassium carnallite, by adding magnesium chloride to the solution; after this fractional crystallization of the double salts was carried out, as a result of which the sediment was again enriched with rubidium, in view of the low solubility of the rubidium carnallite. After ten such recrystallizations with return of the filtrates to the preceding stages, a sediment was obtained in which the rubidium concentration reached 34%.

This precipitate was dissolved in water and the rubidium precipitated from it as tetraoxalate $RbH_3(C_2O_4)_2 \cdot 2H_2O$ which was ignited at 600-700° and thus converted to carbonate. The commercial rubidium carbonate obtained by the described method contained 90% Rb_2CO_3, more than 7% K_2CO_3 and up to 2% $CaCO_3$.

To remove the ammonium salts which accumulated in the precipitates during recrystallization of the carnallites, sodium nitrite was added to the solution at one of the intermediate operations.

The yield of rubidium in this process was only 10% of the initial, 90% was lost during recrystallization. Even more cesium was lost because the solubility of cesium carnallite was somewhat greater than that of rubidium carnallite. The tetraoxalate of cesium was also more soluble that the corresponding rubidium salt. Therefore during precipitation of the latter, that portion of the cesium which went into the rubidium concentrate remained mainly in the mother liquors. The following method was suggested to remove cesium from these solutions [320]. By neutralizing the final acid solutions with magnesium oxide, a precipitate of magnesium oxalate is obtained containing admixtures of cesium and rubidium oxalates. This precipitate is boiled with water and from the obtained solution rubidium tetraoxalate is again precipitated. After several separations of rubidium so much cesium accumulated in the mother liquors, that it could be extracted as tetraoxalate, free of rubidium. However, this process was not feasible under factory conditions.

Repeated recrystallizations of potassium, rubidium, and cesium tetraoxalates can produce a very pure rubidium salt, since potassium and cesium in this case are collected in the mother liquors. According to the data of the Japanese authors, after 31 recrystallizations the precipitate salt $RbH_3(C_2O_4)_2 \cdot 2H_2O$ contained [129] Li $< 0.001\%$, Na $< 0.01\%$, K 0.05-0.1%, Cs $\sim 0.001\%$.

The precipitation of rubidium from enriched rubidium concentrates can be done by other methods as well, as some kind of slightly soluble [321] salt (chlorostannates, silicomolybdate, permanganates, etc.). To separate rubidium and cesium from large amounts of potassium (and also from sodium) we can use a mixture of ethanol and HCl. A solvent composed on 1 volume concentrated hydrochloric acid and 5 volumes of ethanol is especially suitable [104]. By this method we can separate with negligible losses one part RbCl in 1000 parts NaCl, and one part of CsCl in 5000 parts NaCl. This method yields somewhat poorer results in separating both rare alkali metals from a large excess of KCl; in this case the loss of cesium is not very great, but for rubidium the losses are up to 30%.

In recent years new studies have been devoted to the problem of the separation of rubidium and cesium. Certain of these methods are associated directly with the technological process of extracting both metals from ores. In particular, the precipitation of cesium as a double chloride with antimony was studied by various authors. This reaction was used for freeing rubidium from a large amount of potassium (15%) and cesium (15%) [129]. After their precipitation in hydrochloric acid,the rubidium remaining in solution is converted to the tetraoxalate. Since rubidium tetraoxalate is less soluble than the corresponding cesium salt, it is possible to enrich the precipitated with rubidium by recrystallation. However, complete elimination of cesium and potassium by this method required 31 recrystallizations; 3.3% of the initial rubidium was lost each time. The end product, pure rubidium tetraoxalate, contained not more than

0.1% potassium and traces ($< 0.001\%$) of cesium.

An original method for separating the salts of rubidium and cesium was proposed by Treadwell and Werner [284]. It consists of sublimation of the cesium chloride has a considerably higher volatility than rubidium and potassium chlorides; for example, in one of the experiments with a mixture, in which $CsCl : RbCl : KCl = 1 : 2 : 5$ after 6 hr sublimation, 1 mg KCl, 2.5 mg RbCl, and 84 mg CsCl were found in the sublimate. If during the process the temperature is raised above 445°, CsCl changes into another modification isomorphic with the chlorides of other alkali metals, which leads to a less complete separation of the cesium salts. Cesium cannot be separated by this method when KCl is absent and with a large excess of rubidium.

Finally, it was found that very small amounts of cesium can be extracted from solutions by certain ion-exchange resins [322]. Sulfonated resins are especially suitable in this case.

Experiments have been carried out with radioactive cesium (Cs^{137}). The maximum adsorption of cesium by a sulfonated resin was attained at pH 4.4; adsorption dropped in a more acidic or alkaline medium. The maximum adsorption for phenolic sulfonated resin occurs both at pH 4.0 and at pH 6.0. In dynamic experiments the cesium was absorbed quantitatively from solution with a cesium concentration of $4 \cdot 10^{-5}\%$.

We must add however that not more than 112 volumes of solution were used per volume of resin.

Greater attention in recent years has been devoted to the problem of extracting rubidium and cesium from solutions using ion-exchange resins.

Various authors have carried out a number of experiments on the investigation of factors influencing the ion-exchange equilibrium between resins of different composition and cations of alkali metals [323, 324], and also on the kinetics of the process [325, 326].

It was found that the equilibrium constants of ion exchange between Rb or Cs and H in Dowex-50 is in some relation to the content of divinylbenzene, but are very close for both metals under all conditions (Table 39).

During subsequent elution, rubidium and cesium are eluted simultaneously from the various ion-exchange resins.

The use of hydrochloric acid with a concentration between 2.6 and 12.2 M as an eluant did not yield any substantial differences in the behavior of the salts of both metals. Thus, if the extraction of rubidium and cesium is possible even from very diluted solutions by using certain types of ion-exchange resins, the attempts to separate them by this method have still been without success.

TABLE 39

Equilibrium Constants of Ion Exchange

$Rb^{\cdot}$—$H^{\cdot}$ и $Cs^{\cdot}$—$H^{\cdot}$

Divinylbenzene content, %	Exchange reaction	Equilibrium constant
4	$Rb^{\cdot}$—$H^{\cdot}$	1,71
4	$Cs^{\cdot}$—$H^{\cdot}$	1,82
8	$Rb^{\cdot}$—$H^{\cdot}$	2,29
8	$Cs^{\cdot}$—$H^{\cdot}$	2,31
16	$Rb^{\cdot}$—$H^{\cdot}$	2,89
16	$Cs^{\cdot}$—$H^{\cdot}$	2,86

4. Processing Other Types of Raw Materials

Methods based on the direct reduction of cesium to metal have been used in certain cases for extracting it from rich ores (pollucites).

A similar method of direct extraction has been proposed for the poorer ores, the silicates or phosphates (in which cesium and rubidium are in small concentrations). It consists of roasting the ore with lime at 1050-1150° under a high vacuum (0.01-0.001 mm Hg). Rubidium and cesium are thus converted to oxides [327]. If an excess of aluminum, silicon, or ferrosilicate is added to the charge, rubidium and cesium silicates are reduced to metals. Even in the case when rubidium and cesium are found in silicates in negligible amounts they can be extracted without preconcentration of the ore. For this purpose it is recommended to mix pulverized ore with fluorite, water, and acid to a pasty consistency, after which it is first heated at a low, then at a higher temperature. As a result of this operation rubidium and cesium are converted to fluorides [328]. The roasted product is then leached with water.

Certain authors propose to reduce a mixture of silicate ores with hydrogen not under vacuum but, conversely, under a pressure of 3.5 atm [329]. If the reduction is carried out in the presence of sodium chloride, cesium and rubidium are also converted to chlorides.

Finally, in connection with the development of atomic engineering a serious problem has arisen concerning the processing of waste products which are accumulated in considerable amounts in atomic boilers.

In order to imagine the scope of the work in this field it suffices to say that according to the plans throughout the world for using atomic energy for peaceful purposes, the consumption of nuclear fuel in the near future will consist of hundreds of tons per year. Cs^{137} and Sr^{90}, which belong to the number of very active and long-lived products, predominate in the waste products. Therefore their separation makes the wastes of atomic power stations safer.

The process of separating rubidium and cesium from other decay products is as follows. The irradiated specimens are dissolved in concentrated nitric acid after which the solutions are treated further.

At first the solution with an addition of HCl is distilled to eliminate the elements of the fourth and in part the fifth group of the periodic system; Mo, I, and Br are extracted. Most of the remaining elements are precipitated in the presence of carriers in a definite sequence; in this case Rb and Cs separate last, after elimination of chemical elements forming slightly soluble sulfides, hydroxides, and carbonates. The solutions thus purified are adjusted to 6 N with respect to HCl and cesium precipitates as the salt of silicotungstic heteoropoly acid and rubidium remaining in solution is precipitated by the chloroplatinate method [330].

PREPARATION OF VARIOUS COMPOUNDS OF RUBIDIUM AND CESIUM

Rubidium and cesium are generally precipitated as alums, chlorides, nitrates, or carbonates. However, other salts of these metals, their hydroxides or some other more complex compounds are frequently required in practice.

Rubidium and cesium carbonates are most easily produced. These are easily converted to bromides, chlorides, iodides, nitrates, chromates, and also to oxides. Most pure cesium compounds available on the world market are produced in this way.

If the final products of the industrial process are pure aluminum cesium (or rubidium) alums, they are processed in the following manner.

To separate aluminum and convert it to the sulfate, barium, hydroxide is added to the boiling solution of alum; at pH 7.6 (bromothymol blue indicator) aluminum precipitates completely. The filtrate, which in this case does not show a positive reaction for aluminum or to barium, is evaporated to dryness and thus pure Cs_2SO_4 (or correspondingly Rb_2SO_4) is produced.

To convert the sulfate into hyroxide, an equivalent amount of a boiling solution of $Ba(OH)_2$ is added to the Cs_2SO_4 solution in boiling water; the $BaSO_4$ precipitates and the CsOH remains. After removing the precipitate by filtration and evaporating the solution to dryness, pure hydroxide is obtained or, by passing a stream of CO_2 through the solution, it is converted to cesium carbonate.

It is somewhat more difficult to obtain other salts from cesium chloride; for instance, cesium sulfate is more difficult to obtain from it because during the reaction with sulfuric acid and acid salt $CsHSO_4$ is formed, hence it is recommended to add appropriate amounts of CsOH so that the acid salt is converted to the normal sulfate.

Cesium chloride is comparatively easy to convert to the nitrate by evaporation with nitric acid, and to chromate by the metathetical reaction with Ag_2CrO_4.

From cesium chloride we can obtain many cesium salts by electrolysis with a mercury cathode* [331]. The monohydrate $CsOH \cdot H_2O$ is thus formed which, of course, is easily converted to chromate, dichromate, etc.

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* This process is described in greater detail below.

$CsOH \cdot H_2O$ melts at 180° and gives off water of crystallization only at 400°, when CsOH already has considerable volatility.

The organic compounds of cesium can be obtained by the reaction of the metal with organic reagents. Thus, for example, to prepare cesium ethoxide an ampule with metal vacuum distilled is placed in a container with liquid air, then ethanol is gradually introduced into the ampule [171]. This reaction does not take place at very low temperatures. On heating the reactions takes place according to the equation

$$2C_2H_5OH + 2Cs \rightarrow C_2H_5OCs + H_2$$

To eliminate the hydrogen liberated, the entire container is connected with a large evacuated cylinder. The cesium ethoxide formed dissolved the excess ethanol.

It was found that cesium alcoxides are more stable than the corresponding potassium compounds. Among the alcoxides the most stable is cesium propoxide $C_3H_7OCs \cdot C_3H_7OH$ which eliminates the alcohol only at 100° while the ethoxide $C_2H_5OCs \cdot C_2H_5OH$ decomposes at 50°, and the methoxide $CH_3OCs \cdot CH_3OH$ is unstable even at room temperature.

1. Production of Metallic Rubidium and Cesium

Metallic rubidium and cesium were first obtained by electrolysis of their fused salts. But in view of the considerable activity of these metals, electrolysis required special handling and considerable losses were involved. Therefore other methods were more suitable in practice; these were based on the reduction of rubidium and cesium salts in an atmosphere of inert gas or under vacuum.

As early as 1888 N. N. Beketov [332] reported that he succeeded in preparing metallic rubidium by reduction of rubidium hydroxide with metallic aluminum at the temperature of bright red heat. The reaction can be expressed by the following equation:

$$4RbOH + Al_2 \rightarrow Rb_2O + Al_2O_3 + 2Rb + 2H_2.$$

The hydrogen liberated in this process fills the entire apparatus and prevents oxidation of the rubidium being distilled into the glass receiver. Theoretically one-half the rubidium present is extracted and the other half remains as an oxide. In practice there are considerable losses, therefore extraction of rubidium in the first experiments was only 28-33% of the initial amount.

Subsequently Hackspill showed that this reaction occurs in two stages. First (at 600°) the aluminate of the metal and free metal are formed

$$Al + 2KOH \rightarrow KAlO_2 + K + H_2;$$

with a rise in temperature to 1350° the second stage occurs

$$3KAlO_2 + 4Al \rightarrow 2Al_2O_3 + 3K.$$

Bunsen obtained metallic rubidium by heating its tartrate with carbon, the yeild was only 18%.

Later all alkali metals including rubidium and cesium were produced by the reduction of their oxides with metallic magnesium [333, 334]. Cesium and rubidium carbonates can be used in place of the oxides. In the 1890's Beketov replaced cesium carbonate with cesium aluminate [335]. On reduction with magnesium in a stream of hydrogen the yield of metal is close to the theoretical.

N. S. Kurnakov and co-workers produced both metals, rubidium and cesium, by reduction of carbonates with magnesium in a hydrogen stream [94, 98]. The reaction was carried out in an iron tube under hydrogen. Simultaneously, Hackspill continued experiments on the reduction of various cesium salts under vacuum. The essence of the Hackspill method, which subsequently was widely used, is as follows [36, 336].

Rubidium (or cesium) chloride is carefully mixed with pulverized (as powder or shavings) calcium, 3-4 times the theoretical. The mixture is placed in an iron tube 15-20 cm long which is inxerted in a tube of high-melting glass (Fig. 15). The glass tube a 30-35 cm long with a diameter of 2.5-3 cm is sealed at one end; to its center is attached, slightly on a slant, a narrower tube b, 15-20 cm long, constricted in the center and also closed at one end. The iron tube c protects the glass from the corroding effect of the rubidium and cesium vapors. The entire instrument is placed at a slope in an electric furnace d so that the projection b is vertical. The open end of the glass tube was connected with a vacuum.

After the mixture was loaded into the iron tube, the vacuum was switched on and the apparatus was heated gradually, bringing the furnace temperature after 3-4 hours from the start of the experiment to 700-800°, without overheating, in order to avoid contamination of the alkali metal with calcium. The residual pressure was 1-5 mm Hg.

The distilled rubidium (or cesium) was cooled on the cold walls of the glass tube and flowed off as shining heavy drops into the projection b. When the reaction was ended, tube b was sealed and removed. Thus, metallic rubidium or cesium obtained during the process was stored in the sealed ampule under vacuum. To obtain a purer product the sample is redistilled under vacuum at 300°. It is possible to obtain in this apparatus up to 25 g of metallic rubidium or, correspondingly, cesium in a yield close to the theoretical.

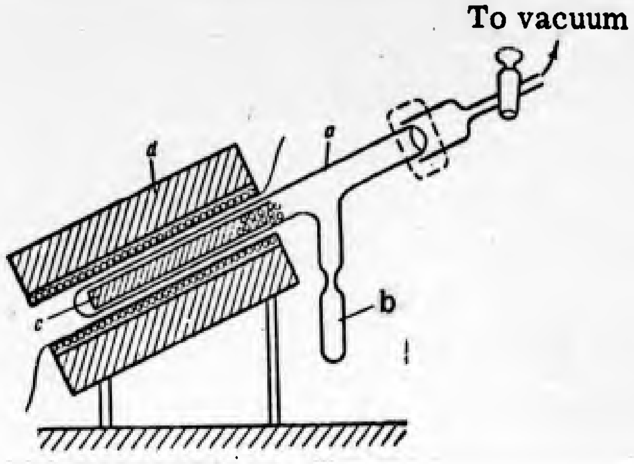

Fig. 15. Apparatus for obtaining rubidium and cesium by reduction under vacuum.

Hackspill and others [337] carried out many similar experiments, substituting other salts of rubidium and cesium for chlorides and other metals (also calcium carbide) for calcium.

It was found that with iron and nickel the reduction takes place with greater difficulty than with calcium. In this case to realize an irreversible course of the process a higher vacuum and in part a higher temperature are required as a rule.

If we start with rubidium or cesium hydroxide and use iron as the reducing agent, the reaction takes place at temperatures not below 700° and at a pressure of 0.001 mm Hg. The necessary temperature at the same pressure is slightly lower for nickel. Rubidium and cesium cyanides can be used by reducing them with iron or with nickel oxide (metallic nickel is not suitable here). The reaction occurs according to the following equations:

$$2\,y(\mathrm{MeCN}) + x\,\mathrm{Fe} \rightarrow 2\,y\,\mathrm{Me} + y\,\mathrm{N_2} + \mathrm{Fe}_x\mathrm{C}_{2y};$$
$$\mathrm{MeCN} + \mathrm{NiO} \rightarrow \mathrm{Me} + {}^1/_2\mathrm{N_2} + \mathrm{CO} + \mathrm{Ni}$$

Since ferrocyanides of alkali metals when heated to 700° under vacuum decompose with formation of metallic iron and cyanides of alkali metals, we can assume that (with the addition of excess iron) this method is suitable for reducing pure and mixed rubidium and cesium ferrocyanides to metal.

Thiocyanates behave similarly to cyanides. They react with iron (and nickel) when heated under vacuum to 600° according to the equation

$$\mathrm{Fe} + \mathrm{MeCNS} \rightarrow \mathrm{FeS} + \mathrm{MeCN}.$$

The cyanide of the alkali metal being formed is reduced under vacuum by metallic iron or nickel oxide.

The reaction of metallic iron or nickel with the sulfides of alkali metals is also very convenient. For sodium this reaction takes place at 1000° and under a high vacuum according to the equations

$$\mathrm{Na_2S} + \mathrm{Fe} \rightarrow \mathrm{FeS} + 2\,\mathrm{Na} + 68\ \mathrm{Cal.}$$
$$\mathrm{Na_2S} + \mathrm{Ni} \rightarrow \mathrm{NiS} + 2\,\mathrm{Na} + 72\ \mathrm{Cal.}$$

Here no gaseous products are formed, and the iron and nickel sulfides are quite stable, which is an important advantage of this method. We can assume that the rubidium and cesium sulfides will react in a similar manner since their heat of formation is lower than that of sodium sulfide and the metals themselves are more volatile than sodium.

Sulfates of alkali metals decompose at high temperatures, forming the oxide of the alkali metal, sulfur dioxide, and oxygen. K_2SO_4 starts to decompose in the same manner at 1000^{o}; Rb_2SO_4 at 850^{o}, and Cs_2SO_4 at 800^{o}. In the presence of a reducing agent such as iron which is able to absorb the gases being liberated, the decomposition should take place at lower temperatures; under a vacuum the excess of iron reduces the oxide being formed to metal. However, the oxygen given off during the decomposition of the sulfates retards the reduction process. Therefore for Rb_2SO_4 the reaction occurs only at 1000^{o} and in 80% yield, and for Cs_2SO_4 the metal is obtzined contaminated with the products of oxidation.

Analogously, starting with rubidium and cesium carbonates it is also impossible to obtain pure metals since the gases being liberated partially oxidize them and, as a result, the yield of the process does not exceed 50% at temperatures below 1000^{o}-1360^{o} (depending on whether iron or nickel is taken as the reducing agent).

The nitrates of the alkali metals are reduced at lower temperatures. For potassium the reaction takes place as low as 600^{o}, according to the equation

$$MeNO_3 + 2Fe \rightarrow Fe_2O_3 + Me + 1/2N_2.$$

However, for rubidium and especially for cesium, the yield is small, apparently because during the course of decomposition nitrogen oxides are formed that partially oxidize the reduced metal. Nickel is a less vigorous reducing agent than iron.

In all these examples reduction occurs only after careful mixing and begins close to the melting point of one of the components (usually the salt of the alkali metal). If the substances used do not have a definite melting point and are capable of forming glasslike products, the reduction reaction is hampered and occurs at higher temperatures. Thus borax, orthophosphates, and arsenides of alkali metlas are reduced by iron under vacuum only partially and at temperatures of the order of 1300-1400°.

The problems connected with the study of the electron emission of rubidium and especially of cesium demanded completely pure metal devoid of even the faintest traces of occluded gases, particularly hydrogen. The reduction methods described above were unacceptable for these purposes.

It was convenient to use some type of decomposition or exchange reaction. Positive results were originally obtained with the azides of alkali metals [86,87].

The azides RbN_3 and CsN_3 were decomposed in a high-melting glass vessel at 500° under high vacuum, so that the pressure did not exceed 0.1 mm Hg during heating. The experiment lasted several days. The decomposition temperature of RbN_3 was 395° and CsN_3, 390°.

The yield of suitable products was considerably less for rubidium than for cesium (60 and 90% respectively). This is explained by the fact that rubidium forms a nitride Rb_3N, thus resulting in considerable losses. Certain authors recommend the use of a mixture of cesium chloride with barium azide ($Ba(N_3)_2$):

$BaN_6 + 2CsCl = BaCl_2 + 3N_2 + 2Cs$.

Barium azide is considerably less stable than cesium azide and decomposes at 200°, after which an intimate mixture of cesium chloride with metallic barium is left in the reaction vessel and this reacts under vacuum at 350° with the formation of cesium. This proposal, however, was not widely accepted since the mixture of cesium chloride and barium azide was unsuitable for storate in the air. The same is true for a mixture of cesium chloride and metallic calcium—the calcium is oxidized in the air. If the calcium if replaced by a metal more stable in air, e.g., magnesium, reduction of cesium occurs poorly and a higher temperature is required; but at 500° magnesium itself is distilled along with cesium.

All this led to a number of experiments to search for some kind of other methods to produce metallic cesium from its compounds.

A positive result in solving the stated problem was obtained with metallic zirconium. When $4CsCl + Zr$ reacts, $4Cs + ZrCl_4$ is formed, whereby under vacuum both products are distilled at 350°, which favors the course of the reaction towards the obtainment of metallic cesium. True, on the cold parts of the instrument where the vapors of $ZrCl_4$ and Cs are condensed, the potentiality of a reverse reaction is created and the reduced metallic cesium is partially reconverted to the chloride. The most favorable results were obtained when cesium chloride was preplaced by the chromate with a fourfold excess of zirconium as compared to the theoretical* [338]. The mixture of $2Cs_2CrO_4 + 2.5Zr$ is nonexplosive (in contrast to the bichromate) and is not hygroscopic. The reaction occurs at 725° and is usually carried out at 1000° with a yield of 90-96%. The reduction of metallic rubidium occurs similarly during the reaction of $2Rb_2CrO_4 + 2.5Zr$; in this case the reaction occurs at 700° and the yield is 100%.

An increase of the relative content of zirconium to tenfold against the theoretical fosters a drop in the reaction temperature to 370°, but in this case

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* The reaction takes place according to the equation $2Cs_2CrO_4 + 2.5Zr = Cr_2O_3 + 2.5ZrO_2 + 4Cs$.

the yield of rubidium does not exceed 80-90%.

As a result of all the investigations of obtaining metallic cesium or rubidium of high purity, the method developed by Hackspill is the one used, i. e., reduction under vacuum of the chloride of the appropriate metal and the metal obtained was redistilled under vacuum at 300°.

If it is necessary to obtain "superpure" metallic cesium (or rubidium) for the manufacture of photocells, the reaction used is based on the reduction of cesium chromate (or rubidium chromate) with metallic zirconium under the conditions described above.

2. Electrochemistry of Rubidium and Cesium

The electrochemical properties of rubidium and cesium and their compounds have been studied inadequately. In recent years we more frequently find studies on the application of electrochemical methods to the analysis of rubidium and cesium and to the production of the pure salts of these metals.

Information on the electric potentials of Rb and Cs in aqueous and nonaqueous solutions, as well as in salt fusions, are rather scarce and in part contradictory. However, by comparing various other properties of alkali elements we can assume that the very difficult problem of separating potassium, rubidium, and cesium can be solved successfully by the electrochemical method if, of course, all necessary precautions resultant of the enormous reactivity of these elements are taken.

One of the most promising electrochemical methods which could be used for determining rubidium and cesium or for their division and separation in pure form is the method of electrolysis with a mercury cathode that was postulated by

Goldbaum and Smith (Fig. 16). The principle on which this method is based is that as a consequence of the potential differences of rubidium and cesium, the removal of one of them from solution entails a potential jump [339-342].

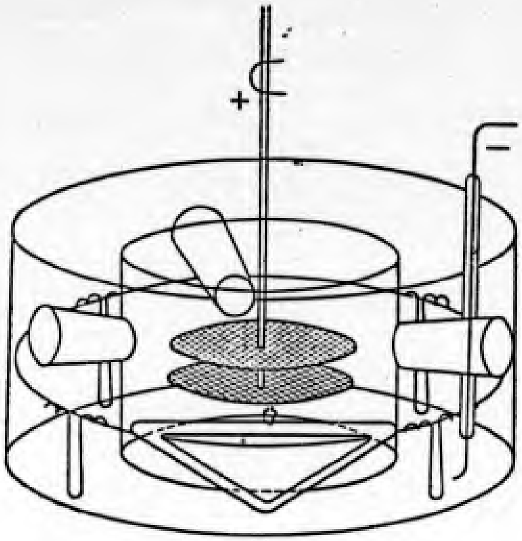

Fig. 16. Apparatus for determining rubidium and cesium by electrolysis of aqueous solutions.

When an electrical current passes through an aqueous solution of any two salts, for example, potassium and rubidium chlorides, the first metal to be deposited on the cathode at a given current voltage is the metal whose potential is less electropositive (in our case potassium). When all the potassium is deposited and rubidium begins to precipitate, the potential jump occurs. If at this moment the experiment is terminated and the liquid at the cathode analyzed (to determine the concentration of hydroxyl ions) we can calculate accurately the potassium content in the investigated sample.

Mercury was used as the cathode to tie up the alkali metal; in this case an amalgam is produced which is then gradually decomposed by water, resulting in the formation of an alkali. A silver plate was used as the anode to tie up chlorine being liberated. Silver chloride, the amount of which can also be determined accurately by weighing is formed on the silver plate.

The anode and cathode spaces were separated from one another by a bottomless glass cylinder suspended around the centrally placed anode. A thin layer of mercury was poured on the bottom of the reaction vessel (also made of glass). The anode was constantly rotating at a speed of 750 rpm and was not more than 1 cm from the cathode. Due to this the liquid was vigorously mixed and the amalgam being formed was decomposed only in the outer space removed from the anode. The cathode surface in the original experiments was 20 cm and the total volume of the liquid 50 ml.

To determine the amount of alkali obtained as a result of the experiment, the entire contents of the vessel along with the mercury were poured into a beaker as soon as electrolysis ceased; after this the mercury was washed with pure water which was added to the total mass of liuqid and titrated with it.

Goldbaum and Smith determined the conditions of the decomposition of each salt separately and found: for RbCl the voltage is 3 v, the current density $(A_{ND_{20}})$ is 0.040-0.015; for CsCl the voltage is 3 and the current density 0.051-0.02.

To determine best the potential jump during the transition from one metal to another it is convenient to use graphs, laying off the current density on the abscissa and the voltage on the ordinate. The abrupt bend of the curve obtained (the "inflection point") will correspond exactly to the magnitude required to decompose the given salt. We must, however, remember that the numbers obtained are not absolute. They have a relative value and depend on the following conditions: 1) the distance between electrodes; 2) the rotational speed of the anode; 3) the concentration of the electrolyte; 4) the condition of the cathode surface. Therefore these values must be determined each time before the experiment. The results on the obtained quantitative determination of rubidium and cesium in the presence of other alkali metals are given in Table 40.

TABLE 40

Determination of Rb and Cs by Electrolysis

Salt content of solution, g					Voltage, v	Current ma	Duration of experiment, min.	Salt determined
NaCl	KCl	RbCl	CsCl	LiCl				
0,05	—	—	0,07	—	2,30—2,33	0,030	90	NaCl
0,06	—	0,08	—	—	2,30	0,025	85	NaCl
—	0,08	0,08	—	—	2,30	0,020	90	KCl
—	0,083	—	0,085	—	2,33	0,019	110	KCl
—	—	0,056	—	0,023	2,45	0,015	75	LiCl
—	—	—	0,05	0,04	2,30	0,013	90	LiCl
—	—	0,05	0,07	—	2,20	0,010	120	RbCl

The "inflection points" of all alkali metals are extremely close; for example, for NaCl and KCl they differ in all only by 4/30 v. Therefore the apparatus needed (voltmeter, rheostat) must be sufficiently sensitive. The voltage found for a given salt must then, when analyzing the salt mixture, be carefully maintained throughout the experiment, especially towards the end.

The accuracy of the analysis does not exceed 1-2% of the theoretical value even in the most favorable cases. Mercury, which is used in the experiments should be carefully purified.

In recent years the old works have received very interesting use for obtaining pure salts of cesium from its chloride [179].

Besause the cesium amalgam formed during electrolysis is slowly decomposed by water, cesium hydroxide in an aqueous solution is obtained at the cathode. In this case hydrogen is given off at the cathode and chlorine at the anode. A graphite rod is the anode; the chlorine is removed from the electrolyzer. The mercury at the cathode can tie up to 3% of the metallic cesium.

Electrolysis is carried out at a potential difference of 5-6 v, a current of 4-4.5 amp, and a current density of 35 amp/dm^2. In the solution obtained at the cathode the concentration of cesium hydroxide can reach 50%; by evaporating this solution to dryness the monohydrate $CsOH \cdot H_2O$ is obtained which is easily converted to the chromate needed to obtain metallic cesium.

The quantitative determination of rubidium and cesium by the electrolytic method with a mercury cathode is a lengthy process. Therefore there is a tendency to use it in microanalysis since the duration of electrolysis will not be great when working with microquantities. In this case the usual methods of qualitative determination of the decomposition products will become unsuitable. Schleicher and Laurs [343] suggested combining the electrolysis method with the spectrographic method of analyzing the amalgam obtained. Here it is necessary to observe the following precaustions. First, the silver anode can be made as a cover which is easily purified mechanically from AgCl. Second, the chlorides of the alkali metals can be replaced by their hydroxides. The authors, however, indicate that this method will yield more accurate results only with individual salts of potassium, rubidium, and cesium, but not with mixtures of the salts of these elements.

Analogous results were obtained when applying the so-called method of paper chromatography, described above in greater detail, to the rare alkali metals.

Deserving our attention are the works on the electrolysis of halides of rubidium and cesium in anhydrous solvents, e. g., 99.5% acetic acid.* In this case acetates are formed, hydrogen is liberated at the cathode, and the free halogen at the anode. A silver plate is used as the anode to remove and bind the haologen [344]. The results of the experiments are given in Table 41.

TABLE 41

Conditions for the Electrolysis of Rb and Cs Halides in an Acetic Acid Solution

Compound	Duration of Expt, Min.	Voltage, v	Current, ma	Increase in anode wt, %	Yield with respect to current, %
CsCl	30	3.0	308	100.21	100.2
	60	1.5	112	99.68	99.7
RbBr	30	2.0	100	–	99.7
	60	1.0	50	–	99.5

In addition to the electrolysis of solutions, numerous attempts to electrolyze the fused salts of rubidium and cesium are known. Metallic cesium

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* Glacial acetic acid is obtained by heating 96% acetic acid in the presence of acetic anhydride with subsequent rectification with addition of anhydrous boron triacetate.

was first obtained by this method.

Setterberg [345] describes this experiment in the following manner.

The electrolysis of cesium chloride does not occur smoothly since the lower chloride is formed along with the metal. Therefore, it was decided to use CsCN, which fuses at a lower temperature, as the starting product. During the decomposition of cesium cyanide the experiment at first went very nicely, but then the electric current became uneven and after 15 min from the start of the experiment ceased completely. An attempt was made to use a mixture of 4 moles CsCN and 1 mole $Ba(CN)_2$. Electrolysis was carried out in porcelain cell 20 mm wide and 45 mm high. Metallic aluminum was used as the cathode. (All other metals used, as well as the graphite, were quickly dissolved in the fused cesium salt or were destroyed under its effect). The temperature was held at the melting point of the salt mixture, so that the crust from the unfused salt was retained on the surface; only under these conditions was it possible to avoid instantaneous combustion of the metallic cesium separated. At the end of the experiment the porcelain cell, filled with metallic cesium, was opened under kerosene. The mass contained particles of incompletely decomposed salt. Therefore the contents of the cell were slightly heated under kerosene and the metallic cesium collected as droplets on the surface.

Metallic rubidium was first obtained by electrolysis of fused salt by Hevesy [346] considerably later than cesium.

For this purpose, 100 g of rubidium hydroxide was fused in a nickel container, after which two magnesite cylinders were placed in it, as shown in Fig. 17. The magnesite cylinder, serving as the cathode diaphragm, was covered on the top. A 3-mm wide opening was made in the center of it, through which an iron wire, the cathode, 2-mm thick was passed. This wire was slightly expanded at the bottom, so as to support the magnesite cylinder. The small opening remaining in its lid was needed since the melt liberates a large amount of hydrogen during the first minutes after the current is switched on. If there were no opening the hydrogen would violently pass through the melt, destroying the arrangement of the parts in the instrument and changing the subsequent course of the process. Several minutes after the experiment started liberation of hydrogen ceased, after which the top opening in the magnesite crucible at the cathode must be closed with magnesite powder.

The surface of the iron cylinder which was only slightly submerged in the melt was the anode diaphragm. The anode should permit easy and rapid removal of the liberated oxygen. The magnesite crucible at the anode was 3 cm high and 1.5 cm in diameter.

When electrolysis ended, the nickel container was placed in a desiccator, then cooled to room temperature, then below 0, to avoid burning of the metallic rubidium.

Electrolysis lasted 45 min at a current of 5 amp and a current density at the cathode of 0.5 amp per 1 mm^2. The yield relative to the current was 28.6-32.7%. Possibly better results can be obtained when working on a large scale.

The current losses were due to various causes. Metallic rubidium is first partially dissolved in the melt and reacts with it with liberation of hydrogen according to the equation

$$RbOH + Rb \leftrightarrows Rb_2O + 1/2\, H_2.$$

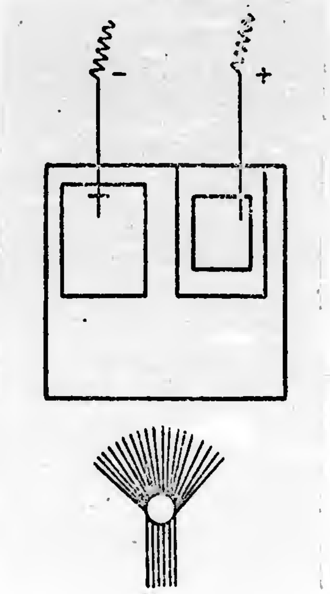

Fig. 17. Apparatus for obtaining rubidium and cesium by the electrolysis of fused salt.

But the transfer of oxygen by the melt is the main and deciding factor here as in the case of electrolysis of fused KOH. The oxygen liberated is partially transported to the cathode where it reacts with metallic rubidium, forming a metal oxide.

Hevesy later, however, considered the method based on the reduction of rubidium and cesium slats by metals as more advantageous for obtaining metallic rubidium and cesium. The reaction occurred most easily when metallic sodium of potassium reacted with the fused and dehydrated hydroxides of rubidium and cesium. Here alloys of the alkali metals enriched with rubidium or cesium were obtained. In these cases metallic sodium or potassium were added to the fused RbOH under nitrogen. It is also possible to alloy RbOH and Na or K in a hermetically sealed nickel tube or in a brass shell casing. Here alloys containing up to 80% Rb are obtained. Similar results were obtained with cesium hydroxide. Because metallic rubidium (or cesium) instantaneously ignites in air, all apparatus must be strongly cooled at the end of the experiment and only after this the alloy which was formed removed from it.

This reaction also occurs with rubidium and cesium chlorides but in this case it is less convenient to experiment since the chlorides are higher melting than the hydroxides of both metals.

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