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Original Scientific Paper

The Precipitation of Rubidium and Caesium with Silicotungstic Acid

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The precipitation of rubidium and caesium with silicotungstic acid has been studied with the aim of investigating such processes as a possible separation method. The influence of hydrochloric acid, ammonium chloride, and the aging of the precipitates was investigated. The results show that there are differences in the precipitation of rubidium and caesium with silicotungstic acid. When accompanying caesium, rubidium was found even in precipitates under such experimental conditions for which it would not precipitate itself. The results also indicate that precipitates formed in the low concentration region of hydrochloric acid are salts either of rubidium or caesium silicotungstate. At higher acid concentrations there is a higher precipitation yield. This is due to the contributions from two processes: precipitation and co-precipitation**. At higher hydrochloric acid concentrations, the precipitation of rubidium or caesium silicotungstate is followed by co-precipitation of rubidium and caesium. It is shown that rubidium can be removed from rubidium-caesium silicotungstates by an exchange reaction.

The quantitative determination of rubidium and caesium is rather difficult because of the chemical similarities of the alkali metals. Procedures for the quantitative determination of rubidium and caesium presented in the literature, therefore, are time-consuming and, in most of them, the interference of some other elements play an important role. It has been suggested that heteropoly acids are specific reagents for the precipitation of rubidium and caesium. A number of authors have demonstrated the application of various heteropoly acids to the separation of rubidium and caesium either by precipitation or by using various salts of heteropoly acids as ion exchangers.

O'Leary and Papish¹ suggested the silicotungstic method for the separation of caesium from rubidium. Glendenin and Nelson² applied this method to caesium separation from the bulk of fission products. Kourim³, then Kourim, Lavrukhina, and Rodin^{4,5} described the coprecipitation of rubidium and caesium with heteropoly acids from strong mineral acid solutions, while Healy⁶⁻⁸ investigated the preparation and properties of some heteropoly acid salts. Since no systematic and detailed studies describing precipitation processes of rubidium and caesium silicotungstate have been presented as yet, the present work was undertaken with the aim of investigating such processes as a possible

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** Term "co-precipitation" is used in this paper for any process in which certain ions are carried down by the precipitate.

separation method. The concentrations of rubidium and cesium used in this work are of interest for conventional analytical determinations of these elements. Since cesium concentrations of about 10^{-1} to 10^{-3} M are probable in reprocessing⁹, the investigated precipitation systems are also of interest in nuclear technology. Conditions for the precipitation of rubidium and cesium silicotungstate following the proposed analytical procedure¹ were investigated in this work using a wide range of concentrations and acidity.

EXPERIMENTAL

All solutions were prepared using analytical grade chemicals (*Merck*) and bidistilled water. Concentrations were tested by standard analytical methods¹⁰. In each case the series of precipitation systems were prepared by mixing either rubidium or cesium chloride solutions with silicotungstic acid solutions. Experiments were performed in the concentration range from 5×10^{-3} M to 5×10^{-2} M of rubidium and cesium. Most of the experiments were made in an excess of silicotungstic acid, and the concentration of hydrochloric acid was varied from 10^{-2} to 10 M. Precipitates were separated from solutions using a laboratory centrifuge and the remaining activity was determined in the liquid phase.

The precipitation yield in each system was determined radiometrically using ^{86}Rb and ^{137}Cs as tracers. Radioactivity measurements were performed using a $1\frac{1}{2} \times 1\frac{1}{2}$ inch well type NaI(Tl) scintillation crystal and an *EKCO-Electronics* scaler. In the case when both rubidium and cesium were present, the activity due to each nuclide was determined using a scintillation spectrometer. The scintillation spectrometer used in this work was a 256-channel pulse height analyser attached to a 3×3 inch thallium activated sodium iodide crystal. In the resultant gamma spectrogram consisting of successive spectra, the heights of the photopeaks due to the 1.08 MeV gamma ray from ^{86}Rb and the 0.662 MeV from ^{137}Cs were measured.

RESULTS

Figures 1. and 2. illustrate a typical reaction of rubidium chloride with silicotungstic acid as a function of hydrochloric acid concentration. The precipitation yields for 2.5×10^{-2} M RbCl with various concentrations of silicotungs-

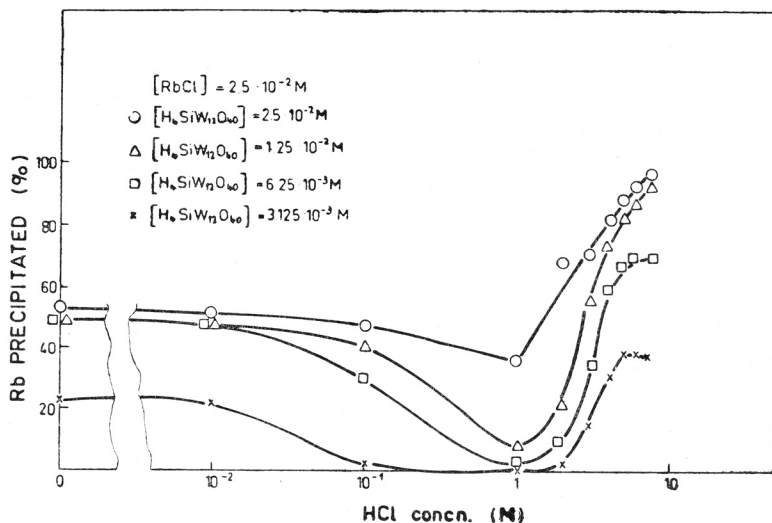


Fig. 1. The influence of hydrochloric acid concentration on the precipitation of rubidium from 2.5×10^{-2} M solution.

tic acid between $3.125 \times 10^{-3} M$ and $2.5 \times 10^{-2} M$ are shown in Fig. 1. Rubidium was found to be present in the precipitates in concentrated hydrochloric acid solutions for all rubidium concentrations investigated. Moreover, rubidium did not precipitate in diluted HCl solutions when its concentration was $5 \times 10^{-3} M$, as seen from Fig. 2.

The yields of cesium found in the precipitates are shown in Fig. 3 and 4. The concentrations of cesium and silicotungstic acid used in these series of

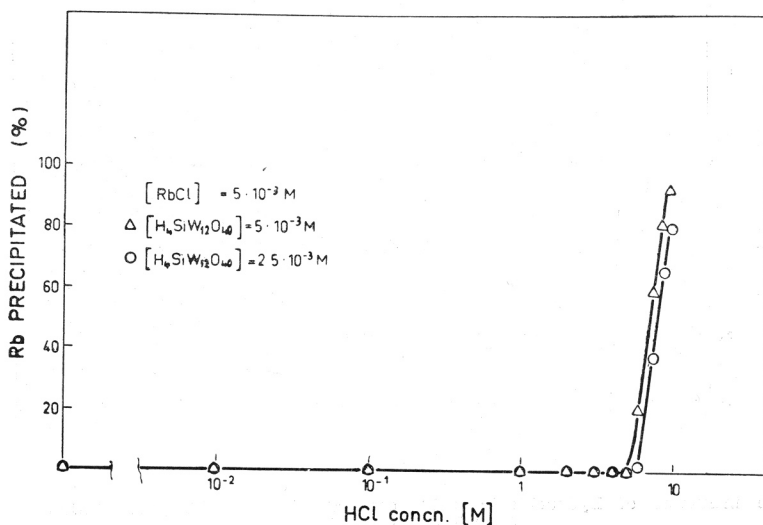


Fig. 2. The influence of hydrochloric acid concentration on the precipitation of rubidium from $5 \times 10^{-3} M$ solution.

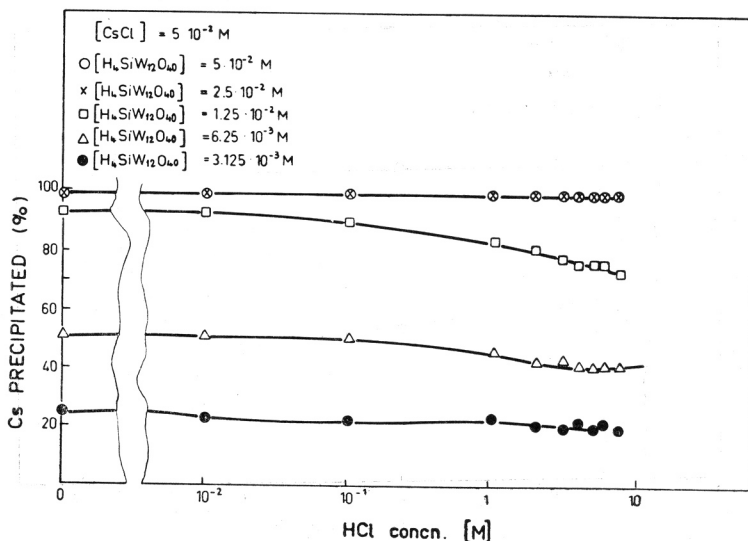


Fig. 3. The influence of hydrochloric acid concentration on the precipitation of cesium from $5 \times 10^{-2} M$ solution.

experiments were the same as described above in the rubidium precipitation experiments. Experimental data indicate that at higher concentrations of cesium, e. g. 5×10^{-2} M, the process of precipitation is almost quantitative if an excess of silicotungstic acid is used.

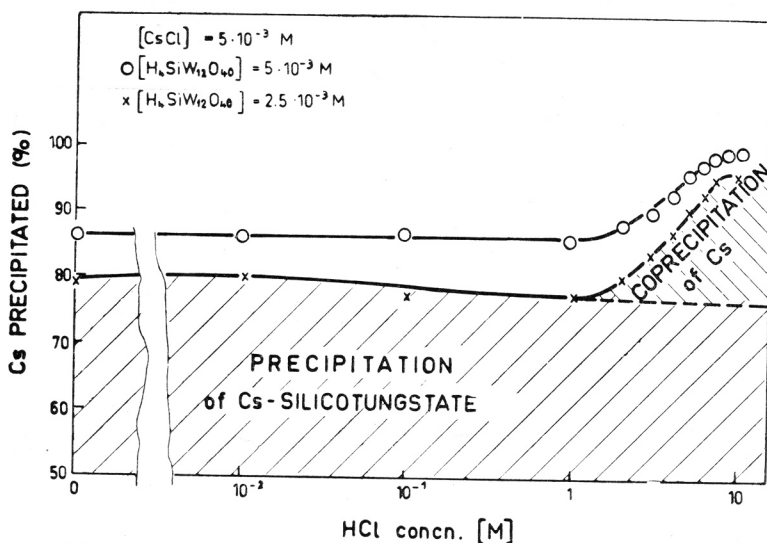


Fig. 4. The influence of hydrochloric acid concentration on the precipitation of cesium from 5×10^{-3} M solution.

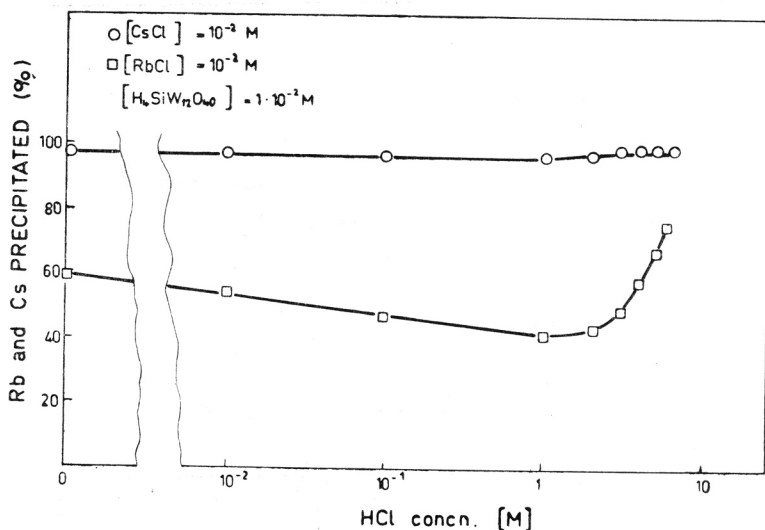


Fig. 5. Precipitation yields of rubidium and cesium when precipitated from 10^{-2} M solution as a function of hydrochloric acid concentration.

Results concerning the precipitation of the rubidium-caesium mixture are presented in Fig. 5 and 6. From both diagrams it can be seen that the precipitation yield of caesium in all cases is over 90%, and in concentrated acid solutions even close to 100%. On the other hand, the precipitation yield curves for rubidium are not of the same shape in comparison with the case when no caesium is present. Moreover, when accompanying caesium, rubidium was found even in precipitates formed under such experimental conditions for which it would not precipitate itself.

In order to study the influence of the electrolyte on the precipitation of rubidium and caesium with silicotungstic acid, the precipitation yields were measured in the presence of various concentrations of ammonium chloride.

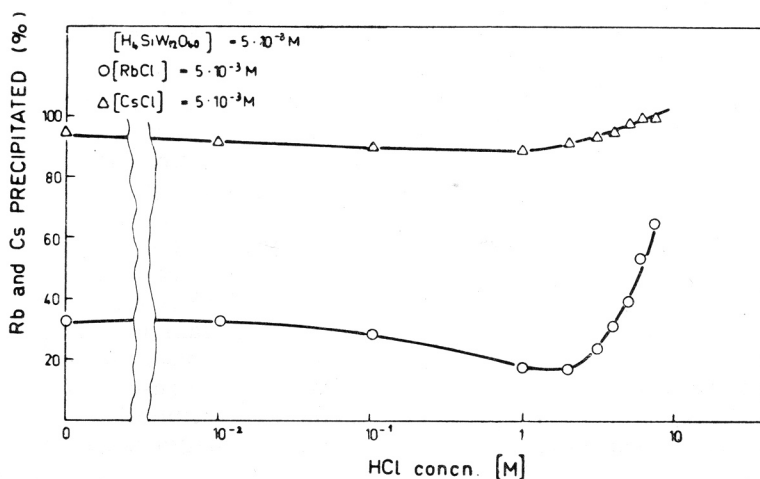


Fig. 6. Precipitation yields of rubidium and caesium when precipitated from 5 × 10⁻³ M solution as a function of hydrochloric acid concentration.

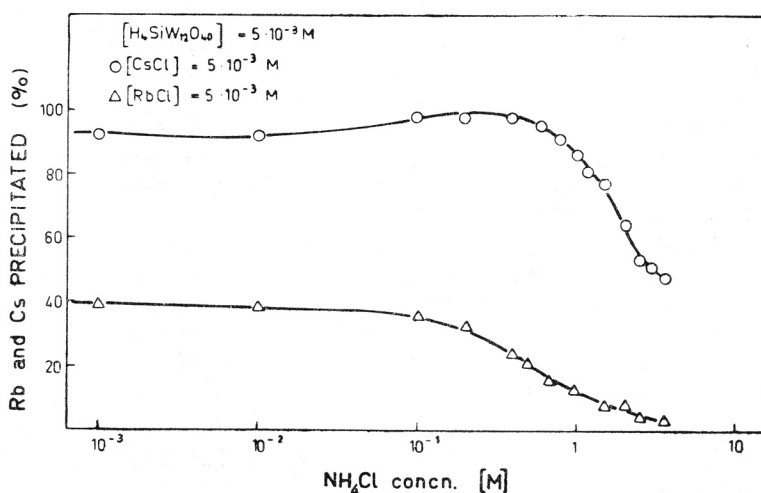


Fig. 7. The influence of NH₄Cl concentration on the precipitation yield of rubidium and caesium.

Typical results are presented in Fig. 7. The results indicated that at high ammonium chloride concentrations, rubidium and cesium precipitation yields decrease, and over a certain concentration of ammonium chloride there is no more rubidium in the precipitate.

DISCUSSION

As can be seen from the results presented above, there are some differences in the precipitation of rubidium and cesium with silicotungstic acid. In the low concentration region, *e.g.* $5 \times 10^{-3} M$, rubidium does not precipitate, whereas cesium precipitates with a reasonable yield. At higher concentrations they were both found in the precipitates, but the cesium yield was higher. That is due to the fact that the solubility of alkali element salts decreases with mass number, and salts formed by silicotungstic acid are among the most soluble heteropoly acid salts¹².

Since the experimental results indicate that at HCl concentrations up to about 1 N the precipitation yield is practically constant, but above 1 N it increases rapidly, it may be supposed that various processes take place. Precipitates formed in the low concentration region of hydrochloric acid are salts either of rubidium or cesium silicotungstates. On the other hand, at higher acid concentrations a better precipitation yield is due to the sum of two processes present: precipitation either of rubidium or cesium silicotungstate and a complex process in which the silicotungstic acid precipitation is followed by a coprecipitation of rubidium or cesium. The explanation might be found in the well-known fact that heteropoly acids can be precipitated from concentrated mineral acid solutions. Thus, according to the results of Lavrukhina *et al.*⁵, in such systems both a precipitation and a coprecipitation process occur. Contributions of each process can be seen from the diagrams shown in Fig. 4.

The formation of either rubidium or cesium silicotungstates in the low concentration region of HCl is in agreement with Healy's results relating cesium and rubidium silicotungstate formation in nitric acid media⁷. Precipitates in this region may have various hydrogen to alkali metal ratios. Since Matijević and Kerker¹¹ demonstrated the tetravalent nature of silicotungstic acid, the substitution of the four hydrogen ions by alkali metal is possible. For this purpose we measured radiometrically the Rb⁺ or Cs⁺ to SiW₁₂O₄₀⁴⁻ ratio in precipitates formed from systems where concentration of each ion was $5 \times 10^{-2} M$, and ⁸⁶RbCl, ¹³⁷CsCl, and H₄Si¹⁸⁵W₁₂O₄₀ solutions were used. The results are presented in Fig. 8. It can be seen that with increasing acidity the content of the alkali metals in the precipitate decreases.

The results also indicated that there is no region where either rubidium or cesium can be precipitated separately. Because of the similarity in the ionic radii of rubidium and cesium and their similar chemical behaviours, isomorphism should also be taken into account. Rubidium can be removed from cesium-rubidium silicotungstate by an exchange reaction. Fig. 9 illustrates the rubidium removal from such precipitates using 1 M HCl.

The proposed procedure¹ recommends aging the precipitate for about ten hours. Investigations of the influence of aging on the Rb/Cs ratio in the precipitates were therefore carried out. Fig. 10 illustrates the changes in the rubidium to cesium ratios as a function of time when the rubidium-cesium

silicotungstate precipitate was allowed to stay in the mother liquor. It can be assumed that a recrystallization process takes place, so that rubidium ions from the mother liquor exchange with those of hydrogen. The aging of the precipitate is therefore not preferable in the separation process.

Experiments concerning the precipitation of rubidium and caesium silicotungstates in the presence of a large amount of ammonium chloride indicate that the rubidium and caesium yields in the solid phase decrease with increasing

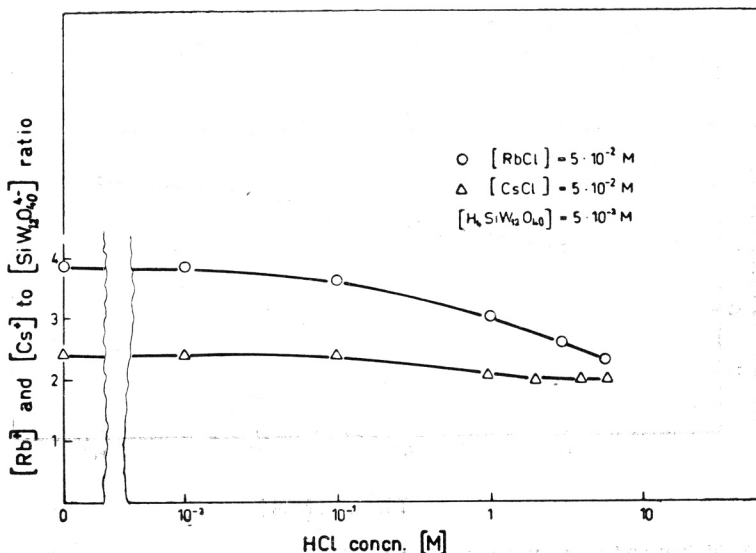


Fig. 8. The influence of hydrochloric acid concentration on the Rb or Cs to $\text{SiW}_{12}\text{O}_{40}^{4-}$ ratio.

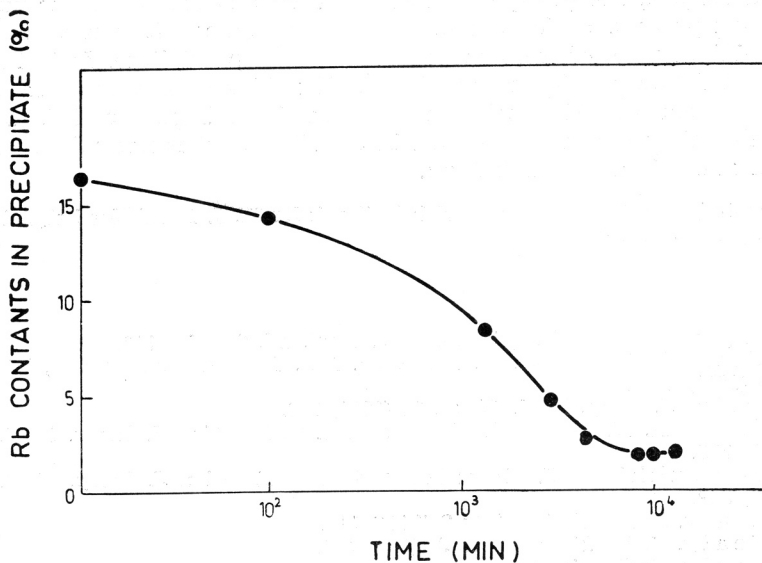


Fig. 9. Rubidium removal from rubidium-caesium silicotungstates using 1 M HCl.

electrolyte concentration. This phenomenon is due to the effect of the NH_4^+ concentration and the solubilities of the certain silicotungstates in concentrated electrolyte solution. It is possible to have such conditions that the precipitates does not contain rubidium. Moreover, under such conditions the cesium yield in the precipitate is much lower.

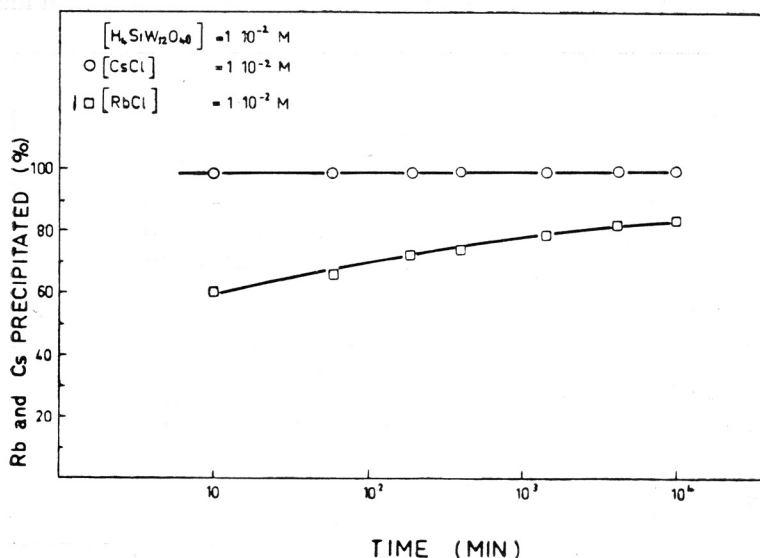


Fig 10. Rubidium and cesium content in precipitates vs. contact time in mother liquor.

In this respect, the precipitation of rubidium and cesium silicotungstates is a complex process. Under the investigated conditions it is not possible to obtain rubidium free of cesium silicotungstate precipitate. It is therefore evident that following this mechanism both rubidium and cesium will be precipitated from 6 M HCl solution, as seen from Figs. 5 and 6. This also indicates that the procedure proposed in the literature¹ is not suitable for the separation of cesium from rubidium.

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IZVOD

Taloženje rubidijuma i cezijuma silikovolframatom kiselinom

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Ispitivano je taloženje rubidijuma i cezijuma s aspekata njihove separacije. Rezultati ukazuju na razlike u taloženju rubidijuma i cezijuma. Kada je u smjesi s ceziumom, rubidium taloži i kod eksperimentalnih uslova, gdje sam ne bi taložio. Rezultati također ukazuju da su talozi nastali u nižim koncentracijama solne kiseline soli rubidium ili cezium silikovolframata. Kod viših koncentracija solne kiseline, međutim, prinos taloženja mnogo je veći što pripisujemo sumi dvaju procesa: taloženju i sutaloženju. Prikazani su eksperimentalni uslovi kod kojih se može dobiti talog, koji sadrži samo cezijum. Ispitivan je uticaj solne kiseline, amonijum klorida i starenja taloga na separaciju cezijuma.

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