

## Isolation of $^{109}\text{Cd}$ from Irradiated $^{107}\text{Ag}$

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**Abstract**—A procedure based on precipitation methods for separation and purification of the desired radionuclide was developed for isolating  $^{109}\text{Cd}$  from irradiated  $^{107}\text{Ag}$ .

**Keywords:** cadmium-109, silver-110m, silver-107, precipitation methods

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Cadmium-109 is used for fabricating reference ionizing radiation sources. It can be produced by neutron irradiation of silver.

In irradiation of the starting material with >98% enrichment for 6 months in the SM reactor with thermal neutrons at a flux density of  $1 \times 10^{15} \text{ n cm}^{-2} \text{ s}^{-1}$ , the total yield of all the Cd isotopes is about 50% relative to the initial silver weight; the specific activity of  $^{109}\text{Cd}$  is 4–4.2 Ci g<sup>-1</sup>. The production of the desired radionuclide is accompanied by the production of a significant amount of  $^{110m}\text{Ag}$ . The subsequent radiochemical processing of the irradiated sample is performed to remove  $^{110m}\text{Ag}$  from  $^{109}\text{Cd}$ , obtain the required chemical form of the product, and regenerate expensive  $^{107}\text{Ag}$  for the repeated irradiation. The  $^{110m}\text{Ag}/^{109}\text{Cd}$  activity ratio in the final product should not exceed  $3 \times 10^{-4}\%$ .

Extensive experimental data are available on the separation of Ag and Cd by ion exchange, extraction, and selective precipitation of Ag [1, 2]. The overwhelming majority of methods are methods of analytical chemistry, unsuitable for operation with gram amounts of Ag and Cd in hot cells under the conditions of remote control. Only the precipitation methods based on precipitation of poorly soluble silver halides or of Ag metal after the silver reduction are an exception. We believe that the precipitation of Ag metal, which is a compact readily settling powder that can be readily washed, is the easiest in implementation. This method was used for isolation and purification of  $^{109}\text{Cd}$  [3]; silver was precipitated from 0.1–2 M HNO<sub>3</sub> in the presence of NaNO<sub>3</sub> on SKN carbon sorbent. At equal

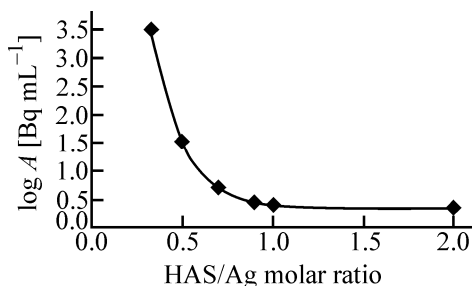
initial activity of  $^{109}\text{Cd}$  and  $^{110m}\text{Ag}$ , the Cd/Ag separation factor was approximately 500–800. Final purification of Cd to remove Ag was performed by isotope dilution of Ag, followed by the AgCl precipitation.

In contrast to [3], in numerous procedures for recovering Ag from wastes the reduction, as a rule, is performed in weakly alkaline or ammonia solutions, because specifically in these media it is most complete [4]. This study was aimed at developing a procedure for Cd purification to remove Ag in one process cycle by reduction and precipitation of Ag from ammonia solutions, followed by the Cd concentration in the form convenient for the subsequent preparation of the  $^{109}\text{Cd}$  product (hydrochloric acid solution with preset HCl concentration).

We chose as reductant hydroxylamine sulfate (HAS), which does not react with Cd. The precipitated Ag metal is the ready starting product for fabricating targets. Then, Cd is precipitated from the mother liquor in the form of basic cadmium carbonate, which is then readily dissolved in hydrochloric acid. In this study, we determined the conditions for the most complete reduction of Ag and precipitation of basic cadmium carbonate from ammonia solutions.

### EXPERIMENTAL

We used for the experiments solutions of silver and cadmium nitrates labeled with  $^{110m}\text{Ag}$  and  $^{109}\text{Cd}$ , respectively. For the experiments on the Ag reduction, the mixture of the solutions was evaporated to wet salts and dissolved in an ammonia buffer solution of



**Fig. 1.** Logarithm of the mother liquor activity as a function of the HAS/Ag molar ratio at pH 10,  $\log A_{in} = 5.35$ .

the preset composition. The mass concentration of Ag and Cd was 4–10 mg mL<sup>-1</sup>. A preset amount of HAS was added to the solution, and the solution was mixed and allowed to stand for 24 h. The mother liquor was separated from the Ag precipitate on a green ribbon paper filter, the precipitate was washed with distilled water, and the wash waters were combined with the mother liquor. The precipitate was dissolved in 4 M HNO<sub>3</sub>. The content of Cd and Ag in the combined mother liquor and in the solution obtained after dissolving the Ag precipitate was determined using radioactive tracers.

To precipitate basic cadmium carbonate, moist cadmium nitrate spiked with <sup>109</sup>Cd was dissolved in an ammonia buffer solution of the preset composition. The mass concentration of Cd was 4–10 mg mL<sup>-1</sup>. To this solution, we added a K<sub>2</sub>CO<sub>3</sub> solution to a concentration of 0.3 N, mixed, and allowed to stand for 4–6 h. The mother liquor was separated from the precipitate on a green ribbon filter, the precipitate was washed with distilled water, and the wash waters were combined with the mother liquor. The Cd content in the combined mother liquor and in the solution obtained after dissolving the precipitate of basic cadmium carbonate was determined with the radioactive tracer.

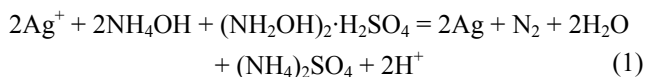
The activity of <sup>109</sup>Cd and concomitant  $\gamma$ -emitting impurities (<sup>110m</sup>Ag, <sup>108m</sup>Ag) was determined according to [5] on a  $\gamma$ -ray spectrometric installation with a DGDK-150V semiconductor germanium–lithium detector [6]. The activity of these radionuclides was determined from the results of measuring the counting rate (intensity) in the main peaks of total photon absorption in the detector at the following energies, keV: <sup>109</sup>Cd 88; <sup>110m</sup>Ag 657, 884, 937; <sup>108m</sup>Ag 434, 723. The relative uncertainty of the activity determination ranged from  $\pm 7$  to  $\pm 20\%$  depending on the peak intensity in accordance with [5]. In the case of no peaks

(the nuclide was not detected), we estimated the detection limit corresponding to the minimum detectable activity.

## RESULTS AND DISCUSSION

### *Influence of the HAS/Ag Molar Ratio on the Completeness of the Ag Reduction*

The Ag ions are reduced with HAS in an ammonia solution, presumably, in accordance with the following equation



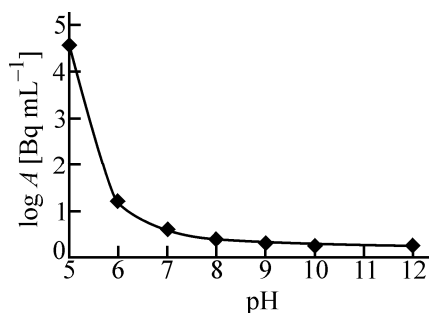
As seen from Eq. (1), the Ag and HAS ions react in the 2 : 1 molar ratio. For the successful removal of Ag from Cd, it is important to know at what excess of HAS the residual concentration of Ag in the mother liquor will be the lowest. Figure 1 shows the results of experiments on the influence of the HAS/Ag molar ratio on the degree of reduction (precipitation) of Ag in an ammonia buffer solution at pH 10.

As seen from Fig. 1, at HAS/Ag = 0.5, i.e., at a stoichiometric amount of HAS, 0.014% of Ag remains in the mother liquor, which corresponds to a decrease in the Ag concentration by a factor of  $7.1 \times 10^3$ . At HAS/Ag  $\geq 1$ , the Ag concentration decreases by a factor of  $1 \times 10^5$ .

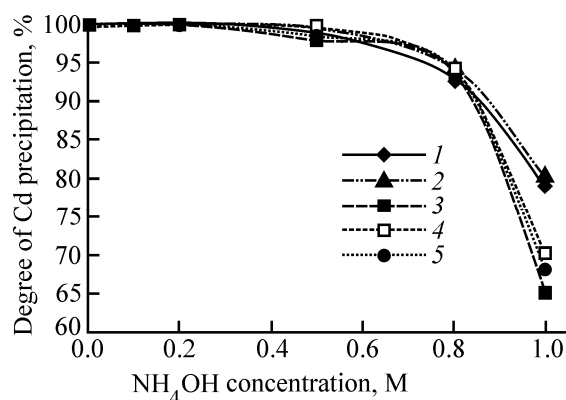
### *Influence of pH on the Completeness of the Ag Reduction*

Because the Ag reduction is performed in an ammonia solution, Ag and Cd occur in the form of ammine complexes. Therefore, it is hardly probable that an increase in the ammonia concentration and hence in pH will influence the completeness of the Ag reduction. On the other hand, determination of the lower pH limit is very important for performing the process efficiently.

HAS contains 1 mol of sulfuric acid per mole of the salt. According to Eq. (1), the Ag reduction is accompanied by the formation of 2 mol of hydrogen ions from 1 mol of HAS. Apparently, the buffer capacity of the initial ammonia solution should exceed the sum of the concentrations of hydrogen ions released in the reaction of silver with HAS and introduced with HAS.



**Fig. 2.** Logarithm of the mother liquor activity as a function of pH of the Ag reduction (precipitation) at HAS/Ag = 2.



**Fig. 3.** Degree of precipitation of cadmium carbonate as a function of the  $\text{NH}_4\text{OH}$  concentration at different  $\text{NH}_4\text{NO}_3$  concentrations.  $[\text{NH}_4\text{NO}_3]$ , M: (1) 0, (2) 0.3, (3) 0.4, (4) 0.5, and (5) 0.6.

Figure 2 shows how pH of the solution influences the degree of reduction (precipitation) of Ag in an ammonia buffer solution at the molar ratio HAS/Ag = 2. As seen from the above data, the best results are obtained when the HAS/Ag molar ratio is higher than unity and pH is higher than 6. Under these conditions, the weight fraction of Ag in the mother liquor does not exceed 0.014%.

#### *Precipitation of Basic Cadmium Carbonate*

Cadmium and silver form poorly soluble carbonates and soluble ammonia complexes [4]. The solubility products of cadmium and silver carbonates are of the same order, about  $5 \times 10^{-12}$  and  $8 \times 10^{-12}$ , respectively. The Ag ammine complexes are more stable than those of Cd by almost an order of magnitude. Apparently, the distribution of Ag and Cd between the carbonate

precipitate and solution depends on the concentration ratio of metal, ammonium, and carbonate ions and molecular ammonia as a complexing agent. For the efficient separation of Ag and Cd, it is necessary to find conditions at which Cd would completely occur in the carbonate precipitate and Ag would occur in the solution in the form of the ammine complex. Apparently, the minimal concentration of ammonia should be sufficient for dissolving Ag and Cd nitrates with the formation of the corresponding soluble ammine complexes of Ag and Cd. The maximal concentration of ammonia should be so as to allow no less than 95% precipitation of cadmium carbonate.

The ammonia concentration in the  $\text{NH}_4\text{OH}$ – $\text{NH}_4\text{NO}_3$ – $\text{K}_2\text{CO}_3$  system can be maintained not only by introducing the preset amount of  $\text{NH}_4\text{OH}$ , but also by introducing the preset amount of  $\text{NH}_4\text{NO}_3$ . In this case,  $\text{NH}_4\text{OH}$  is formed by the reaction



Figure 3 shows the dependence of the degree of the  $\text{CdCO}_3$  precipitation on the  $\text{NH}_4\text{OH}$  concentration at different  $\text{NH}_4\text{NO}_3$  concentrations. The concentrations of potassium and cadmium carbonates in all the experiments were constant and equal to 0.3 and 0.1 M, respectively. As can be seen, at an  $\text{NH}_4\text{NO}_3$  concentration of 0–0.6 M the ammonia concentration should not exceed 0.8 M to ensure no less than 95% precipitation of Cd.

Thus, the procedure described in this study allows efficient separation of  $^{109}\text{Cd}$  from  $^{110m}\text{Ag}$  in one process cycle with quantitative isolation of purified  $^{109}\text{Cd}$ .

#### CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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