

## Radiochemical separation of $^{109}\text{Cd}$ from a silver target

K. Aardaneh,\* C. Naidoo, G. F. Steyn

*iThemba LABS, P.O. Box 722, Somerset West 7129, South Africa*

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A radiochemical separation method was developed for the separation of  $^{109}\text{Cd}$  from a  $^{\text{nat.}}\text{Ag}$  target (6.6 g, pressed into a 19 mm disc). The method comprised of two stages. In the first stage, after dissolution of the target in nitric acid, silver was separated from Cd by precipitation into the metallic form using 20 g of Cu turnings for the reduction of  $\text{Ag}^+$  ions. In the second stage,  $^{109}\text{Cd}$  in the filtrate, that contained trace amount of silver and substantial quantity of Cu(I), was purified by use of a Bio-Rad AG1-X10 anion-exchange resin. The ion-exchange chromatography employed a column with (1.6 cm i.d. and 4 cm length) with a flow rate of 2 ml/min throughout the separation.  $^{109}\text{Cd}$  was quantitatively recovered from the first stage and the recovery yield from the ion-exchange chromatography was greater than 96%. 2M HCl containing  $\text{H}_2\text{O}_2$  was used for the adsorption of  $^{109}\text{Cd}$  and elution of Cu.  $^{109}\text{Cd}$  was eluted by 50 ml 1M  $\text{HNO}_3$ . The concentrations of stable isotopes of Ag and Cu in the final solution (5 ml 0.05M HCl) were measured by an ICP-OES method and found to be  $<1$  ppm.

### Introduction

$^{109}\text{Cd}$  with a half-life of 462.6 days decays by electron capture to  $^{109\text{m}}\text{Ag}$  ( $T_{1/2} = 39.6$  s) which decays to stable  $^{109}\text{Ag}$  by emission of 88 keV  $\gamma$ -ray.  $^{109}\text{Cd}$  is used as a calibration source of X-ray and  $\gamma$ -ray detectors, as a radioactive tracer for environmental study of Cd pollutant<sup>1,2</sup> and can be employed in nuclear medicine when used in a  $^{109}\text{Cd}/^{109\text{m}}\text{Ag}$  generator system.<sup>3,4</sup> However, the major world-wide produced  $^{109}\text{Cd}$  is employed as a source in X-ray fluorescence (XRF) instruments, which is used in a great variety of applications.<sup>5–7</sup>

Cyclotron-produced  $^{109}\text{Cd}$  can be obtained from Ag or In targets via nuclear reactions of  $^{\text{nat.}}\text{In}(\text{p},\text{xn})^{109}\text{Cd}$ , which requires a high energy proton beam (50–200 MeV) for a good yield,<sup>3</sup>  $^{109}\text{Ag}(\text{d},2\text{n})^{109}\text{Cd}$ <sup>8,9</sup> and  $^{\text{nat.}}\text{Ag}(\text{p},\text{n})^{109}\text{Cd}$ .<sup>1,2,10</sup> The last nuclear reaction was used for the production of  $^{109}\text{Cd}$  at the Radionuclide Production Group of iThemba LABS.

Several radiochemical methods for separation of cadmium radionuclides from Ag targets have been reported. GOETZ et al.<sup>2</sup> employed a solvent extraction system for the separation of Cd radionuclides ( $^{107}\text{Cd}+^{109}\text{Cd}$ ) from major part of Ag target (0.4 g). For further purification of Cd from trace amounts of Ag, they used an ion-exchange chromatography method using anion-exchange resin Dowex 1-X8, 10M HCl for adsorption and 1M  $\text{HNO}_3$  for the elution of Cd radionuclides. SMITH-JONES et al.<sup>9</sup> used hydrazine hydrate as well as Cu metal to reduce  $\text{Ag}^+$  ions (0.8 g in 0.2M  $\text{HNO}_3$ ) to metallic silver prior to final purification of  $^{109}\text{Cd}$  from trace amount of Ag and Cu (used for reduction and the target preparation) using an ion-exchange chromatography method. The method consisted of two ion-exchange columns in tandem; an AG50-X4 cation-exchange resin (16 $\times$ 10 mm<sup>2</sup>) and an

AG1-X8 anion-exchange resin (10 $\times$ 65 mm<sup>2</sup>) using 3M  $\text{HNO}_3$  for elution of  $^{109}\text{Cd}$ . Precipitation of Ag (~1.9 g) as AgCl using 6M HCl prior to ion-exchange chromatography using Dowex 1-X10 anion-exchange resin was employed by PALEODIOPOULOS et al.<sup>10</sup> for the separation of  $^{109}\text{Cd}$  from Ag and Cu. They used 2M HCl for the adsorption and 1M  $\text{HNO}_3$  for the elution of  $^{109}\text{Cd}$  with a total yield of 90%. LANDINI et al.<sup>1</sup> used metal Cu to reduce the  $\text{Ag}^+$  ions to precipitate metallic silver followed by ion-exchange chromatography using Dowex 1-X8 anion-exchange resin.

The last two aforementioned works were chosen for further investigation for routine production of  $^{109}\text{Cd}$  from a silver target (6.6 g) at the Radionuclide Production Group of iThemba LABS.

### Experimental

#### Reagents and equipment

The AG1-X8 and AG1-X10 anion-exchange resins (100–200 mesh, in  $\text{Cl}^-$  form) were supplied by Bio-Rad Laboratories (USA). Cu turnings for reduction of  $\text{Ag}^+$  ions was supplied by BDH (B.D.H. Laboratory Chemicals Group, England). All other chemicals were of analytical grade and used without further purification. The solutions were prepared using deionized water (18  $\text{M}\Omega\cdot\text{cm}^{-1}$ ) from a Milli-Q water purification system supplied by Microsep (Pty) Ltd. (South Africa). An HPGe detector coupled with a multi-channel analyzer was used for the measurement of the radionuclides involved in the radiochemical separation.

#### Precipitation of $\text{Ag}^+$ as metallic silver by Cu

The irradiated target (6.6 g) was dissolved in 50 ml concentrated nitric acid and the solution was evaporated to dryness. The residue was then dissolved in 30 ml of

\* E-mail: aardaneh@yahoo.com

$\text{H}_2\text{O}$  and evaporated. This process was repeated twice. Finally, the residue was reconstituted in 50 ml of  $\text{H}_2\text{O}$  obtaining a pH between 2 and 7. Approximately 20 g of Cu turnings were then added to the solution and the solution was stirred for 30 minutes. The reduced Ag deposited on the Cu turnings and excess Cu was filtered by decanting the solution into a 50-ml syringe that contained glass fibre at the bottom. The precipitate was washed twice with 25 ml of  $\text{H}_2\text{O}$  and the washings were decanted into the syringe. To the collected filtrates (~100 ml) 10 ml of 30% hydrogen peroxide solution ( $\text{H}_2\text{O}_2$ ) was added and evaporated to dryness. The residue was re-dissolved in 100 ml of 2M HCl containing 5 ml of  $\text{H}_2\text{O}_2$ .

#### *Ion-exchange chromatography*

The column (4 cm $\times$ 1.6 cm $^2$ ) was packed with the AG1-X10 anion exchange resin and conditioned with 50 ml 2M HCl at a flow rate of 2 ml/min using a peristaltic pump. The solution obtained from the precipitation step, containing  $^{109}\text{Cd}$ , trace amount of Ag radionuclides and substantial amounts of  $\text{Cu}^{2+}$  (and possibly  $\text{Cu}^+$ ) ions was loaded onto the column, followed by washing the column with 200 ml of 2M HCl containing 5 ml  $\text{H}_2\text{O}_2$ . For the elution of  $^{109}\text{Cd}$ , 50 ml 1M  $\text{HNO}_3$  was used. The eluate was evaporated to dryness and the residue was reconstituted in 5 ml 0.05M HCl.

### Results

Preliminary experiments for the separation of  $^{109}\text{Cd}$  from Ag target were performed with 10 g  $\text{AgNO}_3$ , which approximately corresponds to the 6.6 g Ag target, using  $^{109}\text{Cd}$  and  $^{105}\text{Ag}$  as tracers. In these experiments, the efficiency of the two precipitation techniques for the recovery of  $^{109}\text{Cd}$  were investigated, that is, (1) precipitation of  $\text{Ag}^+$  ions as  $\text{AgCl}$  using 6M HCl<sup>10</sup> and (2) as metallic Ag using Cu for the reduction.<sup>1</sup> The recovery of  $^{109}\text{Cd}$  in the first technique was very poor. In contrast,  $^{109}\text{Cd}$  was quantitatively recovered by use of Cu as the reducing agent. Furthermore, the filtration of the second technique was much easier; in fact, the supernatant was decanted into a syringe equipped with a fibre glass at the bottom. The results of the first stage of  $^{109}\text{Cd}$  separation are summarized in Table 1.

Ion-exchange chromatography was then used for the purification of  $^{109}\text{Cd}$  from trace amount of Ag and substantial amount of Cu, obtained in the filtrate. Two anion exchange resins AG1-X8 and AG1-X10 using 8M HCl and 2M HCl, respectively, were investigated for the purification. Although  $^{109}\text{Cd}$  was quantitatively retained by both resins and the recovery yield of the elution using 50 ml 1M  $\text{HNO}_3$  was greater than 96%, the results with AG1-X10/2M HCl system was better in terms of chemical impurity of Cu (Table 2). The experiments were, therefore, repeated with the latter system. For routine production and primary separation of  $^{109}\text{Cd}$ , a simple radiochemical separation system was installed in the hot cell for the precipitation of Ag. This system to date has been successfully used for the processing of two irradiated targets. For the purification of  $^{109}\text{Cd}$  in the filtrate, the ion-exchange chromatography was achieved in a fume hood using a lead castle.

Investigations on the production yields of the radionuclides produced in the  $^{\text{nat}}\text{Ag}(p,n)$  nuclear reactions, i.e.,  $^{109}\text{Cd}$ ,  $^{107}\text{Cd}$  ( $T_{1/2}=6.5$  h) and  $^{106\text{m}}\text{Ag}$  ( $T_{1/2}=8.46$  d), LANDINI et al.<sup>1</sup> suggest that the optimum energy range for the production of  $^{109}\text{Cd}$  is 14–9 MeV. It has also been mentioned that in this energy range the contamination of  $^{106\text{m}}\text{Ag}$  is minimized. So far two Ag targets (6.6 g) were irradiated with a proton beam at a current of up to 90  $\mu\text{A}$  and the incident energy of the beam on the target was 36 MeV. This energy is usually available for the second target (in this case, Ag target) when a 66 MeV proton beam is degraded by passing through the first target (Mg target for  $^{22}\text{Na}$  production) in a tandem arrangement. The separations were performed 10 days after EOB and a production yield of  $^{109}\text{Cd}$  was on average 70 kBq/ $\mu\text{Ah}$ . This production yield is very close to the one reported by LANDINI et al. (71.4 $\pm$ 5.5 kBq/ $\mu\text{Ah}$ ).<sup>1</sup>

The presence of a large amount of  $^{105\text{g}}\text{Ag}$  in the original solution, obtained from target dissolution, was exploited for determination of stable Ag by  $\gamma$ -spectrometry. The concentration of stable Ag in the final product (5 ml 0.0M HCl) was estimated to be <0.5 ppm which was similar to the data obtained from ICP-OES measurements (Table 2).

The radionuclide impurities measured by  $\gamma$ -spectrometry are listed in Table 3.

Table 1. Primary separation of  $^{109}\text{Cd}$  from Ag target by two precipitation techniques

Nuclide	Half-life, days	Recovery in the filtrate, %	
		Precipitation by HCl	Precipitation by Cu
$^{109}\text{Cd}$	462	20	100
$^{105\text{g}}\text{Ag}$	41.3	<1 $\cdot$ 10 $^{-4}$	7 $\cdot$ 10 $^{-4}$
$^{101\text{m}}\text{Rh}$	4.3	0	2.7

Table 2. Purification of  $^{109}\text{Cd}$  from Cu and Ag using anion-exchange resins with varied HCl concentrations<sup>a</sup>

Element	AG1-X8/8M HCl	AG1-X8/2M HCl <sup>b</sup>	AG1-X10/2M HCl <sup>b</sup>
Cu	120 ppm	3.2 ppm	0.95 ppm
Ag	0.35 ppm	0.25 ppm	0.30 ppm

<sup>a</sup> The elements were measured in the final solution (5 ml 0.05M HCl) by ICP-OES.

<sup>b</sup> The HCl solution contained  $\text{H}_2\text{O}_2$  for oxidation of Cu(I) to Cu(II).

Table 3. Radionuclide impurities of  $^{109}\text{Cd}$  final solution using AG1-X10/2M HCl system

Nuclide	Half-life	Energy, keV	Activity	
			Original	Final
$^{109}\text{Cd}$	462 d	88 (3.6%)	$1.0 \cdot 10^3$ MBq	962 MBq
$^{105}\text{gAg}$	41.3 d	344.5 (41.6%)	$1.4 \cdot 10^4$ MBq	ND
$^{106\text{m}}\text{Ag}$	8.5 d	451 (28.4%)	51.4 MBq	ND
$^{101\text{m}}\text{Rh}$	4.3 d	307 (87%)	669.7 MBq	27.7 kBq
$^{101\text{g}}\text{Rh}$	3.2 y	127 (70%)	29.6 kBq	ND

ND: Not detected.

## Discussion

Distribution coefficients ( $K_d$ 's) are the most valuable data for an ion exchange chromatography separation method. The distribution coefficients of Cu(II) on strongly basic anion-exchange resins in HCl solutions increase as the concentration of HCl increases and reaches to a maximum  $\sim 12$  at 8M HCl.<sup>11</sup> The  $K_d$  values for Ag(I) and Cu(I), which is produced in the process of reduction of  $\text{Ag}^+$  ions (see the Experimental section), decrease as the concentration of HCl increases. The distribution coefficients of Cd(II) on strongly basic anion-exchange resin reaches its maximum of  $\sim 1000$  at 2M HCl. In 8M HCl, the  $K_d$ 's of Ag(I), Cu(I) and Cd(II) are  $\sim 1$  and  $\sim 10$  and  $\sim 100$ , respectively.<sup>11</sup> These data suggest that although 8M HCl is a good medium for separation of  $^{109}\text{Cd}$  from Ag, it could result in tailing phenomenon when eluting either Cu(I) or Cu(II). Indeed, the Cu concentration in the final product was very high (Table 2) when we employed the AG1-X8/8M HCl system, used by LANDINI et al.<sup>1</sup> for the separation using 200 ml HCl for the elution of Cu. For the elution of  $^{109}\text{Cd}$  from Dowex1-X8 resin, LANDINI et al. have used 60 ml of 0.1M HCl and obtained a 80% separation yield. The distribution coefficient of Cd in this concentration of HCl is  $\sim 500$ <sup>11</sup> indicating a strong retention. Nevertheless, we used 200 ml of 0.1M HCl for the elution of  $^{109}\text{Cd}$  from a column containing the AG1-X8 anion-exchange resin and the recovery yield was only 2.3%.

The above mentioned distribution coefficients data on strongly basic anion-exchange resins also indicate that in 2M HCl system Cu(I), Ag(I) and Cd(II) are strongly retained but Cu(II) is not adsorbed. A successful separation of  $^{109}\text{Cd}$  from the appreciable quantities of Cu (as  $\text{Cu}^+$  obtained in the filtrate) could be achieved if copper is present as Cu(II). A Dowex 1-X10 anion-exchange resin/2M HCl system for the

purification of  $^{109}\text{Cd}$  from Ag and Cu has been reported by PALEODIPOULOS et al.<sup>10</sup> Using reducing agents (e.g., ascorbic acid) and oxidizing agents (e.g.,  $\text{H}_2\text{O}_2$ ) is quite common for some selective separations. In this work,  $\text{H}_2\text{O}_2$  was used to oxidize strongly adsorbed Cu(I) to non-adsorbable Cu(II). As a result the concentrations of Cu in the final solutions (5 ml 0.05M HCl), using both AG1-X10 and AG1-X8 resins, were  $< 4$  ppm (Table 2). From Table 3 it can be seen that the Ag content in the final solution is very low despite that Ag was quantitatively adsorbed by the resins. This indicates that on the elution of  $^{109}\text{Cd}$  with 50 ml 1M  $\text{HNO}_3$ , Ag is still retained by the resins. Table 3 also shows that an unexpected large amount of  $^{101\text{m}}\text{Rh}$  has been produced on the irradiation of Ag target.  $^{101\text{m}}\text{Rh}$  can be obtained by decay of  $^{101}\text{Pd}$  ( $T_{1/2} = 8.47$  h) and according to the experimental cross sections data reported by FASSBENDER et al.,<sup>12</sup>  $^{101}\text{Pd}$  can be produced at proton beam  $\geq 36$  MeV. The results, however, in Table 1 shows that more than 97% of original  $^{101\text{m}}\text{Rh}$  was left in the precipitate obtained by the reduction process. Moreover during the purification process, it was observed that more than 98% of  $^{101\text{m}}\text{Rh}$ , present in the filtrate, passed through the column.

## Conclusions

$^{109}\text{Cd}$  can be separated efficiently from a silver target with a recovery of greater than 96% using a two-stage procedure. The major portion of the Ag target can be removed by a reduction of  $\text{Ag}^+$  ions to the metallic Ag using copper metal. This primary removal of Ag, facilitated an ion exchange chromatography procedure for the purification of  $^{109}\text{Cd}$  from trace amount of Ag and significant amounts of Cu. A good separation was achieved using anion exchange resin AG1-X10 and 2M HCl system containing  $\text{H}_2\text{O}_2$ .

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