

# Application of Ion Exchange, Solvent Extraction, and Ion-Imprinted Methods for Separation of $^{203}\text{Pb}$

M. Yarmohammadi<sup>\*a,b</sup>, M. Mirzaei<sup>a</sup>, and A. Samadi-Maybodi<sup>b</sup>

<sup>a</sup> Radiation Application Research School, Nuclear Science and Technology Research Institute, P.O. Box 14395-836, Tehran, Iran

<sup>b</sup> Analytical Division, Faculty of Chemistry, University of Mazandaran, Babolsar, 47416-95447 Iran

\*e-mail: myarmohammadi78@gmail.com

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**Abstract**—Lead-203 was produced by proton bombardment of natural thallium target. For producing  $^{203}\text{Pb}$ ,  $^{\text{nat}}\text{Tl}$  was electroplated on copper backing as target and was bombarded by energetic proton beam. After bombardment, the target was dissolved in 1 M  $\text{HNO}_3$ . Ion exchange, solvent extraction, and nanomagnetic ion-imprinted polymer methods were used for separating  $^{203}\text{Pb}$  from thallium. The separation efficiency of these methods was studied.  $\gamma$ -Ray spectroscopy was applied for evaluating  $^{203}\text{Pb}$  and others radionuclides. The separation efficiency was determined from the  $\gamma$ -ray spectra. The separation efficiency of the methods using ion exchange, solvent extraction, and nanomagnetic ion-imprinted adsorbent was 98, 99.3, and 96.4%, respectively.

**Keywords:** cyclotron, lead-203, radionuclides, AG-1 $\times$ 8 resin, solvent extraction, ion imprinted method

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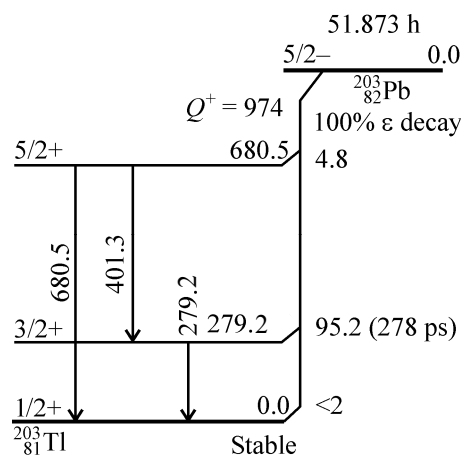
There are at least three criteria in choosing the radioactive isotope for in vivo and in vitro tracer studies. The radiation should be easy detectable; the half-life of the radioisotope should be neither too short nor too long; and the cost of the radioisotope should be moderate [1].

Lead-203 has a very simple decay mode (Fig. 1). It decays by electron capture followed by emission of  $\gamma$ -rays with energies of 279 (81%), 401 (5%), and 680 keV (0.9%).  $^{203}\text{Pb}$  with a half-life of 52 h is potentially useful for clinical scanning. High specific activity and radiochemical purity of  $^{203}\text{Pb}$  are important for radiolabeling. 1–5 mCi of  $^{203}\text{Pb}$  radioisotope contains a trace amount of lead, which is less than 0.1% of the normal daily lead intake [2]. There are a number of methods for the  $^{203}\text{Pb}$  production [2–5].

Lead-203 is produced from either mercury or thallium target. Natural mercury has six stable isotopes. Several radionuclides of lead and thallium can be produced by bombardment of natural mercury with  $^3\text{He}$  or  $^4\text{He}$  particles. Separation of  $^{203}\text{Pb}$  using this method is very difficult. The use of enriched mercury as a target material could partially solve this problem, but the cost of the obtained  $^{203}\text{Pb}$  will be very high. Therefore, the preferred target material for the production of  $^{203}\text{Pb}$  is

natural thallium [1]. Natural thallium contains 29.5%  $^{203}\text{Tl}$  and 70.5%  $^{205}\text{Tl}$ . The possible nuclear reactions and their threshold energies to produce  $^{203}\text{Pb}$  from natural thallium are listed in Table 1.

Horlock et al. reported the use of solvent extraction for separating lead and iron [1]. Garmestani et al. described a simple and rapid method for purification of cyclotron-produced  $^{203}\text{Pb}$  using a commercially available Pb(II)-selective ion-exchange resin [3]. Numerous studies on ion-imprinted polymers and their manipula-



**Fig. 1.**  $^{203}\text{Pb}$  decay scheme (energy in keV).

tion for selective separation of lead ions have been reported [6–14]. In this work, we considered production of  $^{203}\text{Pb}$  by proton bombardment of natural thallium and its purification by conventional ion exchange, solvent extraction, and novel nanomagnetic ion-imprinted polymer methods.

## EXPERIMENTAL

**Materials and equipment.** Thallium(I) sulfate (99.9%) was purchased from UCB (Union Chimique Belge). Lead nitrate was purchased from Fluka. Standard 1000 mg L<sup>-1</sup> solutions of lead and thallium were purchased from Sigma–Aldrich. All the other chemicals were purchased from Merck. Cu backings were produced in our workshop. All chemicals used in this study were analytical grade and were used without further purification. Working solutions of Pb and Tl were prepared by diluting appropriate amounts of the stock solutions.

A Hydro Ultrapure water purification system was used for making deionized water needed to prepare all the required solutions. An HPGe detector system (Canberra<sup>TM</sup>, GC1020-7500SL) in conjugation with a PC-based MCA and A Metrohm 827 pH meter was used.

**Target preparation.** Natural thallium(I) sulfate ( $\text{Tl}_2\text{SO}_4$ ), was chosen as the target material. High-quality thallium targets (70  $\mu\text{m}$ ) were prepared by electrodeposition of 1 g of Tl on 12 cm<sup>2</sup> copper backings. The first plating bath is prepared by dissolving a portion of  $^{\text{nat}}\text{Tl}_2\text{SO}_4$  in an aqueous alkaline solution containing EDTA as a complexing agent, hydrazine hydrate as an anodic depolarizer, and Brij-35 as a wetting agent. Constant-current electrolysis was carried out by applying a bipolar chopped saw-tooth voltage between the Pt anode and copper cathode.

**Target irradiation.** The proton-induced nuclear reaction cross section data are very important for the production of medical radioisotopes using cyclotrons. The excitation functions of  $^{203}\text{Tl}(p,2n)^{202}\text{Pb}$ ,  $^{203}\text{Tl}(p,3n)^{201}\text{Pb}$ ,  $^{203}\text{Tl}(p,4n)^{200}\text{Pb}$ ,  $^{205}\text{Tl}(p,2n)^{204}\text{Pb}$ ,  $^{205}\text{Tl}(p,3n)^{203}\text{Pb}$ , and  $^{205}\text{Tl}(p,4n)^{202}\text{Pb}$  reactions have been reported in the literature [15–19]. The  $^{203}\text{Pb}$  radioisotope is generated by  $^{203}\text{Tl}(p,n)^{203}\text{Pb}$  and  $^{205}\text{Tl}(p,3n)^{203}\text{Pb}$  reactions (Table 2).

The target was irradiated for 30 min with 28.5 MeV protons at a beam current of 150  $\mu\text{A}$ . The back of the

**Table 1.** Nuclear reactions for producing  $^{203}\text{Pb}$  from natural thallium [1]

Reaction	Threshold energy, MeV
$^{203}\text{Tl}(d,2n)^{203}\text{Pb}$	11
$^{205}\text{Tl}(d,4n)^{203}\text{Pb}$	18
$^{203}\text{Tl}(\alpha,4n)^{203}\text{Bi}$	54
$^{205}\text{Tl}(p,3n)^{203}\text{Pb}$	15.8
$^{203}\text{Tl}(p,n)^{203}\text{Pb}$	11.5
$^{203}\text{Tl}(^3\text{He},3n)^{203}\text{Bi}^{\text{a}}$	22

<sup>a</sup>  $^{203}\text{Bi}$  ( $T_{1/2} = 11.8$  h)  $\rightarrow$   $^{203}\text{Pb}$ .

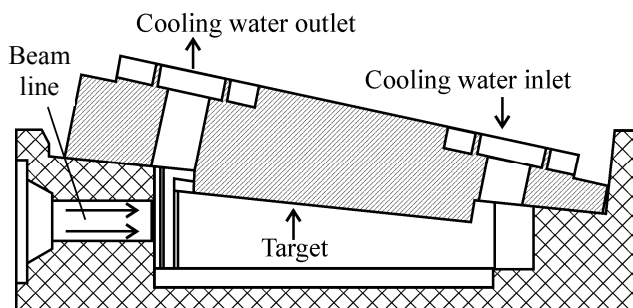
**Table 2.** Threshold energies and optimum energy ranges for  $^{\text{Nat}}\text{Tl}(p,xn)$  reactions [16]

Reaction	Threshold energy, MeV	Optimum energy range, MeV
$^{203}\text{Tl}(p,n)^{203}\text{Pb}$	1.766	15–20
$^{205}\text{Tl}(p,3n)^{203}\text{Pb}$	16.037	25–35
$^{203}\text{Tl}(p,2n)^{202}\text{Pb}$	8.724	15–25
$^{205}\text{Tl}(p,4n)^{202}\text{Pb}$	22.996	35–45
$^{203}\text{Tl}(p,3n)^{201}\text{Pb}$	17.515	25–35
$^{205}\text{Tl}(p,5n)^{201}\text{Pb}$	31.786	40–60
$^{203}\text{Tl}(p,4n)^{200}\text{Pb}$	24.636	40–50
$^{205}\text{Tl}(p,6n)^{200}\text{Pb}$	38.907	55–65

backing was cooled with circulating cooled water. The setup is shown in Fig. 2.

$^{203}\text{Pb}$  was detected by 279.2 and 401.3 keV lines in the  $\gamma$ -ray spectra of the samples. Only the more intense 279.2 keV line was used for the quantitative evaluation.

**Target dissolution.** To separate  $^{203}\text{Pb}$ , the target (after irradiation) should be dissolved in an appropriate solvent. The target was eluted with 1 M  $\text{HNO}_3$ , and  $^{\text{nat}}\text{Tl}$  and  $^{203}\text{Pb}$  were collected in a beaker. This solution was stored and tagged with A.



**Fig. 2.** Target holder, beam current, and cooling water system (inlet and outlet).

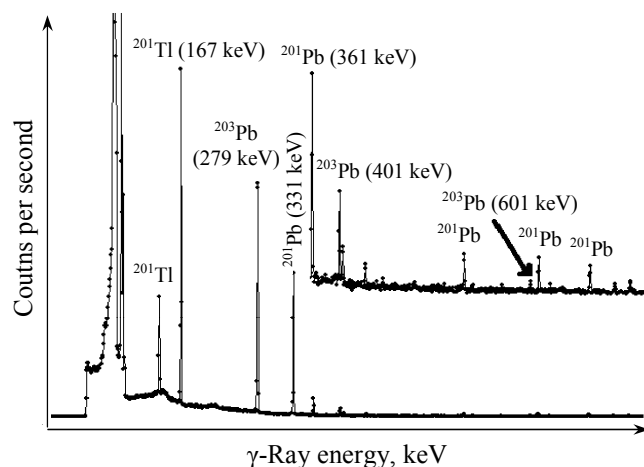


Fig. 3.  $\gamma$ -Ray spectrum of the dissolved target (EOB, before separation).

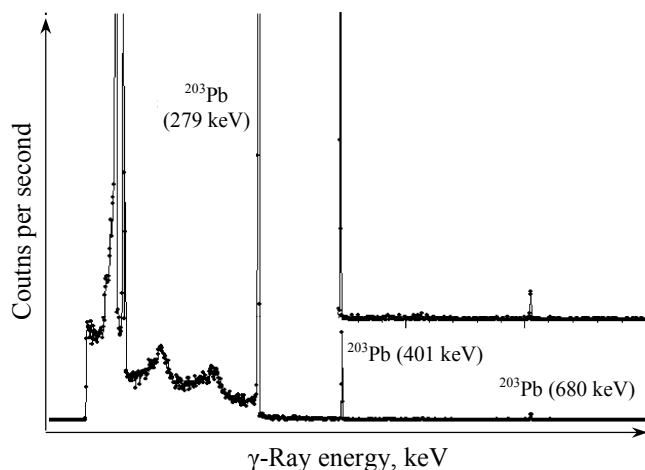


Fig. 4.  $\gamma$ -Ray spectrum of  $^{203}\text{Pb}$  (after separation).

After at least 37 h to ensure the decay of most of  $^{201}\text{Pb}$  ( $T_{1/2} = 9.33$  h) to  $^{201}\text{Tl}$ , about 5 mg of  $\text{FeCl}_3$  was added to a part of the nitrate solution (solution A) for precipitating  $^{203}\text{Pb}$ . Then, the solution was alkalized to pH 12 with ammonium hydroxide.  $^{203}\text{Pb}$  is coprecipitated with ferric hydroxide. To separate trace amounts of thallium that can be adsorbed, the precipitate was dissolved in dilute nitric acid, reprecipitated in the same way, and washed with aqueous ammonia. Finally, excess ammonia was removed by heating. The residue was stored with tag B.

**Ion-exchange separation of  $^{203}\text{Pb}$ .** An appropriate amount of B was dissolved in 25 mL of HCl (30% w/v). A column (1 cm i.d.) was packed with AG-1 $\times$ 8 resin. The resin was pretreated by washing

with 25 mL of 30% HCl. The solution containing  $^{203}\text{Pb}$  was transferred onto the column. In the course of elution,  $^{203}\text{Pb}$  is washed out from the column, and the other nuclides remain adsorbed. The collected solution was heated to remove HCl, and the residue was dissolved in normal saline solution.

**Solvent extraction.** Another part of B was dissolved in 8 M HCl. Iron was extracted with diisopropyl ether (DIPE), the aqueous phase was heated to evaporate the HCl, and the residue was dissolved in normal saline (0.9% w/v NaCl).

**Solid phase extraction with nanomagnetic ion-imprinted polymer.** The magnetic nanoparticles were prepared according to [20]. Briefly, to 20 mL of a 2 M  $\text{FeCl}_3$  solution in an Erlenmeyer flask, 13.3 mL of 1 M sodium sulfite was added dropwise under sonication over the course of 1 min. This solution was transferred to 250 mL of 0.85 M aqueous ammonia with vigorous stirring. The solution color turned from orange to black immediately. Then, 500 mL of deionized water was added to the mixture, and the mixture was heated at 90°C for 2 h with stirring in an air flow.

To prepare Pb-imprinted amino-functionalized sorbent based on magnetic nanoparticles (MNPs), 1.5 g of  $\text{Pb}(\text{NO}_3)_2$  was dissolved in 10 mL of ethanol with stirring and heating, and 5 mL of 3-aminopropyltriethoxysilane (APS) was added to the mixture. The solution was stirred and refluxed for 2 h. After that, 10 mL of glycerol and 30 mL of deionized water were added. Then, a portion of the suspension of MNPs in water was added. After stirring for 24 h and at 90°C, the sorbent was collected with a power magnet. Amino-functionalized MNPs were washed four times, each time with 25 mL of ethanol and 25 mL of 0.02 M NaCl. Finally, the particles were dried under a vacuum at 70–80°C for 12 h.

## RESULTS AND DISCUSSION

The  $\gamma$ -ray spectrum of the dissolved target is shown in Fig. 3. Radioisotopes of Tl and Pb are manifested in the spectrum. The  $\gamma$ -ray spectrum of the  $^{203}\text{Pb}$  solution is shown in Fig. 4. The 279.2 keV peak (fundamental  $\gamma$ -photon energy of  $^{203}\text{Pb}$ ) is in the middle of the optimum range for detection with high efficiency. Samples for analysis of radionuclidic impurities were taken with a coring needle and analyzed by  $\gamma$ -ray spectroscopy. The radionuclidic purity of  $^{203}\text{Pb}$  exceeded 99.5%.

The total amount of  $^{203}\text{Pb}$  before and after separation was determined in all cases by the region of interest (ROI) values. The separation yield was evaluated by dividing the amount of  $^{203}\text{Pb}$  after the separation by that before the separation. The yields of the ion exchange and solvent extraction methods were 98.2 and 99.3%, respectively. No detectable radioactive impurities were observed in the  $\gamma$ -ray spectrum.

The characteristics of MNPs and magnetic ion-imprinted polymers (MIIPs) and the effect exerted by the type, concentration, volume, and pH were considered. The lead ions were removed from MIIPs with 1 M  $\text{HNO}_3$ , and the solution containing  $^{203}\text{Pb}$  (solution A) was loaded onto the sorbent at pH 6. Lead-203 was eluted from the sorbent with quantitative recovery (96.3%) in 2.5 mL of the eluent. Thus, the suggested method ensures high sensitivity of Pb determination.

Thus, the cyclotron production of  $^{203}\text{Pb}$  from thallium provides a convenient source of this isotope for both tracer applications and SPECT imaging. The  $^{203}\text{Tl}(p,n)^{203}\text{Pb}$  reaction is an efficient route to this isotope. The loss of  $^{203}\text{Pb}$  is less than 2% in both solvent extraction and ion exchange methods. The irradiation yield is  $2.2 \text{ mCi } \mu\text{A}^{-1} \text{ h}^{-1}$ .

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#### CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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