Applied Radiation and Isotopes 69 (2011) 1337–1342

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Production and separation of no-carrier-added thallium isotopes from proton irradiated $^{nat}Hg_2Cl_2$ matrix

Binita Dutta, Moumita Maiti, Susanta Lahiri *

Chemical Sciences Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700064, India

ARTICLE INFO

Article history:
Received 18 December 2010
Received in revised form
4 April 2011
Accepted 11 May 2011
Available online 25 May 2011

Keywords:
Proton irradiation
No-carrier-added
$^{197,198,198m,\ 199,200,201}$Tl
Hg_2Cl_2 target
Trioctylamine
ICP-OES

ABSTRACT

For the first time, $^{nat}Hg_2Cl_2$ target has been used to produce no-carrier-added—NCA ^{197,198,198m,199,200,201}Tl radionuclides using ^{nat}Hg(p,xn) reaction. Liquid–liquid extraction technique was employed in order to separate radiothallium from the bulk mercury matrix using liquid anion exchanger trioctylamine (TOA) dissolved in cyclohexane. In order to verify the presence of stable Hg in Tl fraction, the entire process was repeated with stable salts of Hg and Tl and the extent of separation was examined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). High separation factors were observed both by radiometric and ICP-OES technique when 0.1 M HNO_3 and 0.1 M TOA were used as aqueous and organic phase, respectively. The Hg contamination was less than 0.3 ppm in the aqueous phase containing Tl after three times of extraction at the optimal condition.

1. Introduction

The thallium radionuclide, ^{201}Tl, is considered as one of the key player in nuclear diagnostic studies for its vital contribution in myocardial imaging. Kawana et al. (1970) first proposed ^{201}Tl (72.91 h), a 'potassium analogue', for assessing myocardial perfusion and coronary artery disease. Use of ^{201}Tl and ^{199}Tl (7.42 h) have been reported for the scanning of malignant bone tumours, soft tissue tumours, brain tumours, lung cancer, prostate cancer, breast cancer and even used to differentiate Kaposi's sarcoma in AIDS patient (Santhly and Thakur, 2006).

For the first time Lebowitz et al. (1975) reported production of ^{201}Tl through ^{203}Tl(p,3n)^{201}Pb(EC)^{201}Tl reaction using ^{nat}Tl metal as a target material. Further detailed study was carried out by Lagunas-Solar et al. (1978) and later by Qaim et al. (1979). In 1981, Lagunas-Solar et al. (1981) bombarded ^{nat}Pb target by proton beam for the production of NCA ^{201}Tl through Pb(p,xn)^{201}Bi(EC)^{201}Pb(EC)^{201}Tl reaction. Nagame et al. (1979) studied ^{197}Au(α,2n)^{199}Tl reaction for production of NCA ^{199}Tl. For the first time, Nayak et al. (2002); Nayak and Lahiri (2002) used heavy ion projectiles for the production of NCA Tl radionuclides from Pt/Au targets via ^{197}Au(^{7}Li, xn)$^{198-200}$Pb(EC)$^{198-200}$Tl and ^{nat}Pt(^{7}Li, xn)$^{197-201}$Tl nuclear reactions. They found comparable yield of NCA ^{199}Tl from the gold target with that of light charged particle reaction (after allowing reasonable time to decay its precursor ^{199}Pb) while the same from platinum target was not at all satisfactory.

Several authors reported production and separation of NCA thallium from proton/deuteron irradiated mercury matrix. In 1951, Gile et al. (1951) bombarded liquid mercury with 19 MeV deuterons for production of NCA Tl radionuclides. They reported production and deposition of $^{200-202}$Tl on the walls of glass flask where the liquid mercury target was kept. The NCA $^{200-202}$Tl and traces of mercury adhered to the glass surface was removed by concentrated nitric acid. The solution was taken into 3 M HCl from which 95% Tl was extracted by ethyl ether. Metallic Hg has appreciable solubility in HNO_3 (Lide, 2009; Lahiri et al. 2010), therefore contamination of stable Hg in NCA Tl solution is an important issue. Gile et al. (1951) did not mention about the mercury contamination in the final NCA Tl solution. Comar and Crouzel (1975) bombarded both metallic mercury and mercury oxide targets by proton and deuteron beams for the production of $^{198,198m,199-202}$Tl radionuclides. They extracted NCA thallium radionuclides from 3 M HCl media into ether media. Goetz et al. (1981) separated NCA $^{199-202}$Tl produced in proton irradiated thin metallic Hg target by ethyl ether from HCl medium with radiochemical yield of 70–80%. This paper was also silent about the fate of inactive mercury in thallium fraction. Birattari et al. (1982) used both natural metallic mercury and enriched ^{202}Hg targets for radiothallium production via ^{nat}Hg(p,xn)$^{195-202}$Tl and ^{202}Hg(p,xn)$^{199-202}$Tl reactions. They separated NCA Tl radionuclides from bulk liquid metallic mercury by simple washing of target, in which 40% of radiothallium was adhered, with 3 M HCl.

* Corresponding author. Tel.: +913323375345; fax: +913323374637.
E-mail address: susanta.lahiri@saha.ac.in (S. Lahiri).

0969-8043/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.apradiso.2011.05.016

Gallorini et al. (1992) adopted same separation method as above to separate $^{199-202}$Tl from proton irradiated liquid metallic mercury target and achieved more than 97% radiochemical yield of Tl. In the final NCA Tl solution, no other radionuclidic impurities other than Tl isotopes were present, although author did not mention about the stable isotopic impurities (especially impurities from Hg). Fernandes and da Silva (1992) used tributylphosphate (TBP) impregnated Voltalef column (polytrifluorochloroethylene) for the separation of ^{201}Tl from proton irradiated natural mercury target. They passed acidic solution of bulk Hg^{+2} and NCA Tl^{+3} through the column. NCA thallium mostly retained in the column, while Hg was completely eluted by washing with 2 M HCl. Elution of ^{201}Tl was done by reducing Tl^{+3} into Tl^{+} using hydrazine dihydrochloride solution in NaOH. Yin et al. (1993) irradiated 50 g of natural mercury oxide with fast neutron. Bulk mercury target provided proton through Hg(n,p)Au reaction, which in turn produced ^{202}Tl via ^{202}Hg(p,n)^{202}Tl reaction. They used oxidising agents like H_2O_2 and $KMnO_4$ to extract NCA ^{202}Tl in Tl^{+3} form in ether medium.

Thus most productions of NCA Tl via proton/deuteron bombardment involved liquid metallic mercury and in few cases mercury oxide as target material. However, both liquid mercury and mercury oxide are toxic and readily absorbed in respiratory track through inhalation. Moreover, most of the above cited works are silent about the mercury contamination in the aqueous thallium phase. To avoid the obvious complicacy of liquid mercury irradiation, we planned to irradiate solid Hg_2Cl_2 as target material. Hg_2Cl_2 is non-hydroscopic, and less reactive than other salts of mercury. It is also less toxic than liquid metallic mercury or mercury oxide. The salt is insoluble in dilute acid but readily dissolves in aqua regia (CRC Handbook of Chemistry and Physics, 2009).

With these facts in view, we have irradiated $^{nat}Hg_2Cl_2$ with medium energy proton beam and developed subsequent separation technique of NCA Tl radionuclides from bulk target by liquid–liquid extraction (LLX) using trioctylamine (TOA) dissolved in cyclohexane as liquid anion exchanger. To monitor the fate of bulk Hg in the radiometric analysis, we have spiked ^{195,195m,197,197m}Hg produced through ^{197}Au(p,xn) reaction. As any form of stable Hg is not desirable in the Tl fraction, we have simulated the above condition using stable Hg_2Cl_2 and Tl salts. The same extraction conditions were repeated and contamination of stable Hg was checked by ICP-OES in the Tl fraction.

2. Experimental

2.1. Materials used for radiochemical studies

$^{nat}Hg_2Cl_2$, aluminium foil and the liquid anion exchanger, TOA, were procured from E. Merck, Germany. All other chemical reagents also were of analytical grade and used without further purification.

2.2. Irradiation details

We have estimated the excitation function for the ^{nat}Hg (p,xn) reaction theoretically using Alice 91 (Blann and Vonach, 1983) statistical model code (Fig. 1a) considering weighted average of the abundances of natural Hg isotopes—^{196}Hg (0.15%), ^{198}Hg (9.97%), ^{199}Hg (16.87%), ^{200}Hg (23.1%), ^{201}Hg (13.18%), ^{202}Hg (29.86%) and ^{204}Hg (6.87%). To have an idea about the production routes of different isotopes, we have also shown theoretical excitation functions of Hg (p,xn) reactions for each individual stable isotopes of Hg, except ^{196}Hg, which has very low (0.15%) natural abundance. These excitation functions have been plotted in Fig. 1(b)–(g). For radiochemical studies maximum amount of radioisotopes is preferable so that one can develop the method with good statistics. Below 22 MeV projectile energy (maximum proton energy available in BARC-TIFR Pelletron) excitation functions of only two radionuclides ^{199}Tl and ^{201}Tl pass through maxima. Amongst these two radionuclides, ^{99}Tl has shorter half life than the ^{201}Tl. Therefore yield of ^{199}Tl will be higher. In previous studies, Goetz et al. (1981) found maximum experimental yield of ^{199}Tl from ^{nat}Hg (p,xn) reaction in the range of 20–23 MeV proton energy, which corroborates with Alice 91 data. Therefore we have chosen projectile energy ~21 MeV to get maximum amount of ^{199}Tl.

For the present study $^{nat}Hg_2Cl_2$ target of thickness 6 mg/cm^2 was prepared by centrifugation of Hg_2Cl_2 powder on the support of thin Al foil of thickness 1.5 mg/cm^2. The target was irradiated with 20.8 MeV proton beam for 9 h with ~140 nA beam current at the BARC-TIFR Pelletron Accelerator Facility, Mumbai, India. The exit energy of the projectile was 20.7 MeV as calculated from the software code 'Stopping and Range of Ions in Matter (SRIM)' (Ziegler et al., 1985).

To investigate the behaviour of bulk mercury radiometrically, some radioisotopes of Hg need to be spiked. According to the threshold energy calculation of Hg(p,pxn) reaction, production of ^{197,197m}Hg is feasible from ^{198}Hg(9.97%) isotope at 20–21 MeV proton energy or as a decay product of ^{197}Tl, and production of ^{203}Hg is feasible from ^{204}Hg(6.68%). Therefore overall weighted average cross-section for production of ^{197,197m,203}Hg from natural Hg target is poor and need high current beam to get considerable radioactivity so that these radionuclides can be used as a precursor of stable Hg in radiochemical process. As we have used low beam current, in this experiment we have to spike Hg radionuclide externally to monitor the fate of bulk Hg.

Therefore a gold foil of thickness ~7.4 mg/cm^2 was bombarded with 20.9 MeV proton beam of ~140 nA current for 9 h aiming the production of ^{195,195m,197,197m}Hg through ^{197}Au (p,xn) reaction. The projectile energy for ^{197}Au+p reaction was chosen according to the cross-section data using Alice 91 nuclear model code estimated by Mandal and Nayak (2010).

After bombardment, the targets were assayed for the γ-ray activity measurements of the product radionuclides before dissolving the targets for radiochemical separation studies. The product yields of ^{197,198,198m,199,200,201}Tl in the Hg_2Cl_2 target at the end of bombardment—EOB were measured from the background subtracted peak area counts of the γ-energies 152.22 keV (^{197}Tl), 675.884 keV (^{198}Tl), 587.13 keV (^{198m}Tl), 455.46 keV (^{199}Tl), 367.943 keV (^{200}Tl) and 167.43 keV (^{201}Tl) (http://nucleardata.nuclear.lu.se/nucleardata/toi/).

An n-type High Purity Germanium detector (CANBERRA) of 2.13 keV resolution at 1.33 MeV in conjunction with a PC based MCA, PCA2 (OXFORD), was used for the γ-spectroscopic studies. The efficiency calibration of the detector was done with a standard ^{152}Eu (13.5 yr) (http://nucleardata.nuclear.lu.se/nucleardata/toi/) source of 401 kBq on May 01, 1983.

2.3. Radiochemical studies

The gold foil was dissolved in a minimum amount of aqua regia and evaporated to dryness thrice and was finally taken into 1 M HNO_3 media. NCA ^{195,195m,197,197m}Hg radionuclides were separated from proton activated bulk gold using LLX as reported by Nayak et al. (2002). The irradiated Hg_2Cl_2 target was collected from the aluminium foil by careful scratching with spatula followed by mild ultra-centrifugation in 2 mL triple distilled water in the same glass container. Minimum amount of aqua regia was added to dissolve the Hg_2Cl_2 powder. The solution was spiked with NCA ^{195,195m,197,197m}Hg radioactivity and was evaporated to dryness twice, followed by redissolution in 0.001 M HNO_3 to obtain same chemical form of ^{195,195m,197,197m}Hg and bulk Hg.