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Separation of no-carrier-added ^{195,195m,197m}Hg from proton irradiated Au target by TK200 and DGA-N resins

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Abstract
This paper reports the extraction and separation of no-carrier-added (NCA) ^{195,195m,197m}Hg radioisotopes produced in 20 MeV ^{1}H irradiated Au target. The extraction studies were carried out from HNO_3 media by solid–liquid extraction using TK200 and DGA-N resins based on trioctylphosphine oxide (TOPO) and N,N,N,N-tetra-n-octyldiglycolamide (TODGA) respectively. TK200 resin was found to be the superior extractant for separation of NCA Hg radionuclides from 3 M HNO_3 with a separation factor of 3.2×10^5.

Keywords Solid–liquid extraction · TK200 · DGA-N · 195,195m,197mHg · Gamma spectrometry

Introduction

The radioisotope of Hg, ^{197m}Hg ($T_{½} = 23.8$ h, IT = 91%, $E_\gamma = 133.9$ keV) is used in single photon emission computed tomography (SPECT) for lung tumour imaging since 1950s [1]. It is also a potential new therapeutic radionuclide as proposed by Neves et al. [2] along with 19 other suitable radioisotopes due to its auger and conversion emission electrons, thereby, listed as a theranostic radionuclide candidate.

The common production routes of ^{195,195m,197m}Hg radioisotopes are deuteron [3, 4] or proton induced reactions on Au target [1, 5–7]. These studies used stacked foil technique to measure the excitation function and production cross sections of ^{197}Au(d,xn) or ^{197}Au(p,xn) reactions. Tárkányi et al. [3] measured the cross-sections of deuteron induced nuclear reactions on gold target upto 40 MeV projectile energy and later they extended the same measurement upto 50 MeV projectile energy [4]. Alpha or ^{3}He induced reactions on platinum target has been explored for production of mercury radioisotopes [8, 9]. Sudar and Qaim [9] measured the excitation function of ^{nat}Pt(α,xn)^{192,193m,193g,195m,195g,197m,197g,199m}Hg reactions upto 37 MeV projectile energy while Hermanne et al. [8] studied the same reaction in the projectile energy range 17–26 MeV. Heavy ions like ^{7}Li bombardment on Au target [10, 11] or platinum target [11] also produced ^{197m}Hg indirectly by the decay of ^{197}Tl. Available cross section data for production of ^{197m,g}Hg radionuclides and other Hg radionuclides have been tabulated in Table 1. Ghosh et al. [12] mentioned that although several ways of Hg production are possible, use of ^{197}Au(d,x) or ^{197}Au(p,xn) reactions involve the production of least amount of contaminants from the radioisotopes of other elements, which is also evident from Table 1.

There are few reports available on radiochemical studies involving the separation of the no-carrier-added (NCA) Hg radioisotopes either from bulk Au target or from NCA Au radionuclides. Lahiri et al. [13] produced neutron deficient ^{192,193}Hg and ^{192,193}Au radionuclides via heavy ion induced reaction ^{181}Ta(^{16}O,xn)^{192,193}Tl (ϵ)^{192,193}Hg (ϵ)^{192,193}Au. Conventional liquid–liquid extraction (LLX) involving tributyl phosphate (TBP) and trioctyl amine (TOA) was used for the separation of NCA ^{192,193}Hg and NCA ^{192,193}Au radionuclides. Walther et al. [14] separated ^{197m}Hg produced from 18 MeV proton irradiated Au target by solvent extraction using methylisobutyl ketone (MIBK)-HCl system in which Au was extracted by MIBK. A 40% (w/w) Aliquat-336 based TEVA resin (50–100 µm) was used as extractant to separate

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Table 1 Production cross sections of ^{197m,197}Hg radionuclides by various production routes

Production route	E_p,MeV$^{\Psi}$	$\sigma(^{197m}Hg)$, mb	$\sigma(^{197}Hg)$, mb	Other co-produced radionuclides (σ, mb)$^{+}$	References
^{nat}Pt(^{3}He, xn)	30.2±0.2	37.7±4.3	39.7*	^{195m}Hg (177.9), ^{195}Hg (79.6), ^{196m}Au (6.8), ^{196}Au (118.1)	[9]
^{nat}Pt(α,xn)	26.5±0.2	181±15	121±22		[9]
^{nat}Pt(α,xn)	37.1±0.2	212.9±20.0	195.1*	^{199m}Hg (67.5), ^{195m}Hg (488.0), ^{195}Hg (33.4), ^{193m}Hg (6.9), ^{196m}Au (3.5), ^{196}Au (18.8), ^{198m}Au (1.6), ^{198}Au (6.2), ^{199m}Au (2.7)	[8]
^{197}Au(p,n)	11.2±0.2	42.7±6.9	92.5±14.9		[1]
	13	60	96		[5]
	12	42.5	–		[7]
^{197}Au(d,xn)	15.0±0.6	259±25	445±47		[3]
	15.9±0.9	247±25	651±65		[4]

φ Projectile energy at which maximum production cross section of ^{197m}Hg observed

*Interpolated values from the experimental data

+ only > 1 mb cross sections have been noted

^{197}Hg produced from 15 MeV proton irradiated Au foil by anion exchange mechanism [15]. Both NCA Hg and bulk were strongly extracted at 1 M HNO_3 and beyond 10 M HNO_3 only ^{197}Hg gets eluted while Au remained adsorbed on the resin. This behaviour was explained by the formation of anionic complex by Hg at low acid concentration and neutral complexes at high acid concentrations causing the pH selective adsorption of Hg whereas Au formed strongly anionic species. Walther et al. [16] separated NCA ^{197m}Hg and Au by solid phase extraction using LN resin (HDEHP impregnated onto an inert support) with a separation factor as high as 50,000. Studies exploring greener alternatives for separation of radioactive Hg from Au were also reported. Ghosh et al. explored the potential of room temperature ionic liquids (RTILs) in the separation of NCA ^{195m,g,197m}Hg from bulk Au target either by using water soluble ionic liquid-salt (1-butyl-3-methylimidazolium chloride-K_3PO_4/K_2CO_3) based systems [17] or hydrophobic ionic liquids-mineral acid (1-butyl-3-methylimidazoliumhexafluorophosphate or 1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl) imide-HNO_3/HCl) systems [12]. Lahiri and Roy [10] used aqueous biphasic systems i.e. polyethylene glycol (PEG) with five different sodium salts, to separate bulk Au, ^{197m}Hg from NCA $^{197,199-201}$Pb and $^{197,199-201}$Tl radionuclides produced via ^{197}Au(^{7}Li,xn) reactions. Subsequently, ^{197m}Hg was separated from bulk Au, by shaking the PEG rich phase containing both Au and Hg with 2 M H_2SO_4 and zinc metal to selectively precipitate bulk Au over Hg. Other greener approaches using the biopolymer chitosan and cloud point extraction techniques were studied to establish that chitosan and mixed micelle (Triton-X-114 and cetyltrimethylammonium bromide) are efficient reagents for adsorption of ^{195m,g,197m}Hg [18].

On the other hand, recently, we have used the resins TK200 and DGA-N to separate bulk Bi and Pb from proton irradiated lead bismuth eutectic (LBE) target [19]. Both the resins were effective in extracting Bi selectively from nitric acid medium and separating Pb and Bi. The success of TK200 and DGA-N resin in separation of Pb-Bi pair inspired us to extend the study to Hg/Au systems. In this work, ^{195,195m,197m}Hg radioisotopes were produced by ^{197}Au(p,xn) reaction and attempt has been made to separate the bulk Au from NCA Hg radioisotopes by the use of TK200 and DGA-N. The DGA-N is a resin comprised of inert polymer beads loaded with N,N,N,N-tetra-n-octyldiglycolamide or TODGA whereas TK200 resin is based on trioctylphosphine oxide (TOPO). Structures of these two resins are available in our earlier paper [19]. Sato and Nakamura [20] studied the stability constant of the chloro- complex of Hg(II) along with Zn(II), Cd(II) by LLX with TOPO. This study was further expanded by Sato et al. [21] in which the extraction of stable Hg(II) by the same extractant was studied both from HCl and HNO_3 media. These studies involved the extraction of only Hg by the reagents. To the best of our knowledge, this is the first report on the solid phase extraction using TOPO and TODGA based resins to separate NCA Hg radioisotopes from bulk Au target.

Experimental

Reagents

Au foil (99.95% purity, 0.025 mm thick) was procured from Alfa Aesar and its thickness was reduced to 5 mg/cm^2 by rolling at TIFR target laboratory, Mumbai. Commercially available solid phase extraction resins DGA Normal or DGA-N (100–150 µm) and TK200 (100–150 µm), were procured from TrisKem International. All other reagents were of analytical grade.

Irradiation and data acquisition

The Au foil was irradiated with 20 MeV proton beam for 10.25 h with an integrated charge of 3929 µC at Bhabha Atomic Research Centre-Tata Institute of Fundamental Research (BARC-TIFR), Pelletron facility, Mumbai, India. The maximum production cross sections of ^{195}Hg, ^{195m}Hg and ^{197m}Hg radioisotopes on proton induced reactions on gold target were found at higher energies i.e. 27.5 MeV, 27.1 MeV and 12.3 MeV, respectively [22, 23], but due to limitation of the terminal voltage of the pelletron, we irradiated at the maximum available energy. The energy degradation of the incident projectile energy was calculated by SRIM [24]. The exit energy of the proton beam was 19.94 MeV. Beam current was measured by Faraday cup placed at the rear of the target in combination with a current integrator. Post irradiation, the irradiated target was kept aside for 1 h to avoid instant exposure to high dose. Before dissolution of the sample, series of gamma spectra were taken in a p-type HPGe portable detector of 2.62 keV resolution at 1.33 MeV in combination with a digital spectrum analyzer (DSA 1000, CANBERRA) and Genie 2 K software (CANBERRA). The radionuclides were identified from their corresponding photo peak and decay data. The energy and efficiency calibrations of the detector were performed using ^{152}Eu ($T_{1/2}$ = 13.53 a) source of known strength.

Radiochemical separation

After taking series of spectra, the proton irradiated Au foil was dissolved in 4 mL aqua regia, evaporated to dryness and the residue was dissolved in 2 mL of 1 M HNO_3 to prepare the radioactive stock solution. Solid–Liquid extraction studies were carried out in batch mode using TK200 and DGA-N in which different sets of 0.1 g dry DGA-N and TK200 were separately conditioned in 1.9 mL HNO_3 for 30 min prior to extraction studies. In each set, 0.1 mL of radioactive stock was added to 1.9 mL HNO_3 of different concentration followed by shaking at 40 rpm for 10 min and settling for 10 min. From the supernatant solution, 0.5 mL were taken out carefully by using syringe filters and counted in HPGe detector for 500 s each. The extent of extraction was measured by comparing with standard solution which was prepared in the same way but without shaking with the resins.

Results and discussions

The gamma spectrum revealed the production of ^{195,195m,197m}Hg along with ^{196}Au in the target matrix (Fig. 1). The photopeak of ^{197}Hg at 77.35 keV was also visible. However, this peak is also populated with the X-rays of ^{195}Hg ^{195m}Hg and ^{197m}Hg, therefore was not considered for quantitative analysis. The nuclear characteristics of each of the produced radioisotopes have been mentioned in Table 2. The yields of the produced radionuclides at the end of the bombardment (EOB) have been given in Table 3.

The K_d values $\left(\mathbf{K}_d = \frac{\text{Initial counts} - \text{Counts after adsorption}}{\text{Counts after adsorption}} \times \frac{\text{Volume of solution (mL)}}{\text{Mass of adsorbent (g)}}\right)$ of bulk Au and NCA Hg with TK200 and DGA-N over a range of HNO_3 concentration, i.e. 0.05–3 M have been plotted in Fig. 2a, b. The figures reveal that both the resins extract Au (III) quantitatively over the entire range of HNO_3 concentration. The TK200 resin extracted Hg quantitatively at lower HNO_3 concentration but with increase in HNO_3 concentration, the extraction of Hg decreased and no extraction of NCA Hg radionuclides was observed at 3 M HNO_3

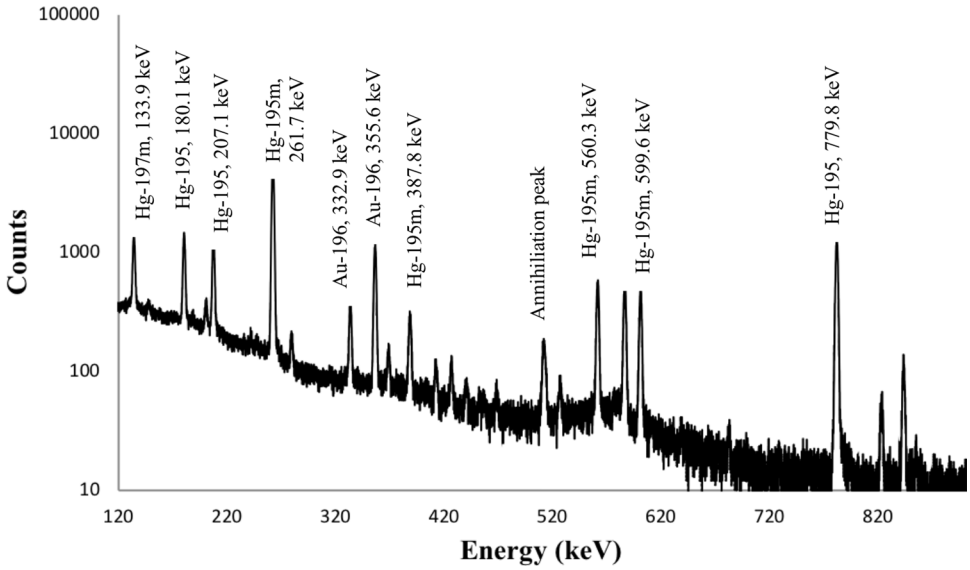

Fig.1 Gamma spectrum of 20 MeV proton irradiated Au foil taken for 1000 s and 2 h after EOB

Table 2 Nuclear characteristics of the radioisotopes produced (https://www.nndc.bnl.gov/nudat2)

Radioisotopes	Half-life	Decay mode	Production route	$E_{threshold}$ (MeV)	Principle γ energy (keV) (% intensity)
^{195m}Hg	41.6 h	ε + β$^+$(45.8) IT (54.2)	^{197}Au(p,3n)	17.1	261.7 (30.9), 560.2 (7)
^{195}Hg	9.9 h	ε + β$^+$ (100)	^{197}Au(p,3n)	17.1	180.1 (2), 779.8 (7)
^{197m}Hg	23.8 h	ε (8.6), IT (91.4)	^{197}Au(p,n)	1.38	133.9 (33)
^{196}Au (tracer)	6.18 days	ε + β$^+$ (92.7) β$^-$(7.2)	^{197}Au(p,pn)	8.1	332.7 (23), 355.8 (87)

Table 3 Yield at EOB (kBq) of the produced radioisotopes

Experimental condition	Radioisotope	Yield at EOB (kBq)
Projectile: ^{1}H (20 MeV) Exit energy: 19.94 MeV Irradiation time: 10.25 h Integrated charge: 3929 μC	^{195m}Hg	221.1 ± 2.3
	^{195}Hg	651.5 ± 6.9
	^{197m}Hg	23.6 ± 0.28
	^{196}Au	22.3 ± 0.47

concentration. The results are in accordance with Sato et al. [21] who revealed that with increase in HNO_3 concentration the distribution coefficient of Hg(II) decreases when using TOPO as extractant. They concluded that the principal species of Hg(II) extracted from higher HNO_3 concentration by TOPO is $H_2Hg(NO_3)_4{\cdot}2TOPO$. The following equilibrium equations may be responsible for extraction of Hg(II) and Au(III) from HNO_3 solution by TOPO:

$$\left[Hg\left(NO_3\right)_4\right]^{2-} + 2H^+ + 2TOPO \rightleftharpoons H_2Hg\left(NO_3\right)_4{\cdot}2TOPO$$

$$\left[Au\left(NO_3\right)_4\right]^{-} + H^+ + 2TOPO \rightleftharpoons HAu\left(NO_3\right)_4{\cdot}2TOPO$$

In the present case, TOPO based resin, TK200, might be selective towards $[Au(NO_3)_4]^-$ ion over $[Hg(NO_3)_4]^{2-}$ in higher acid concentration (i.e., at 3 M HNO_3 concentration), which resulted in very high separation between bulk Au and NCA Hg radionuclides. The TK200 resin contains P=O bond, which makes it an excellent complexing agent.

On the other hand, the DGA-N resin also extracted Au quantitatively over the entire range of HNO_3 concentration studied. However, for Hg, the extent of extraction was ~ 95% till 1 M HNO_3 concentration and sharply decreased to 40% at 3 M HNO_3 concentration. The oxygen donor hard bases present in diglycolamides (DGA-N) bind the cations in high oxidation state by Hard-Soft-Acid–Base (HSAB) principle. Complex formation takes place between Au (III) and DGA-N through the three oxygen donor groups. Under the experimental conditions, separation between bulk Au and NCA Hg radionuclides could not be achieved with DGA-N. The distribution coefficients of Hg and Au have been presented at the best separation condition in Table 4.

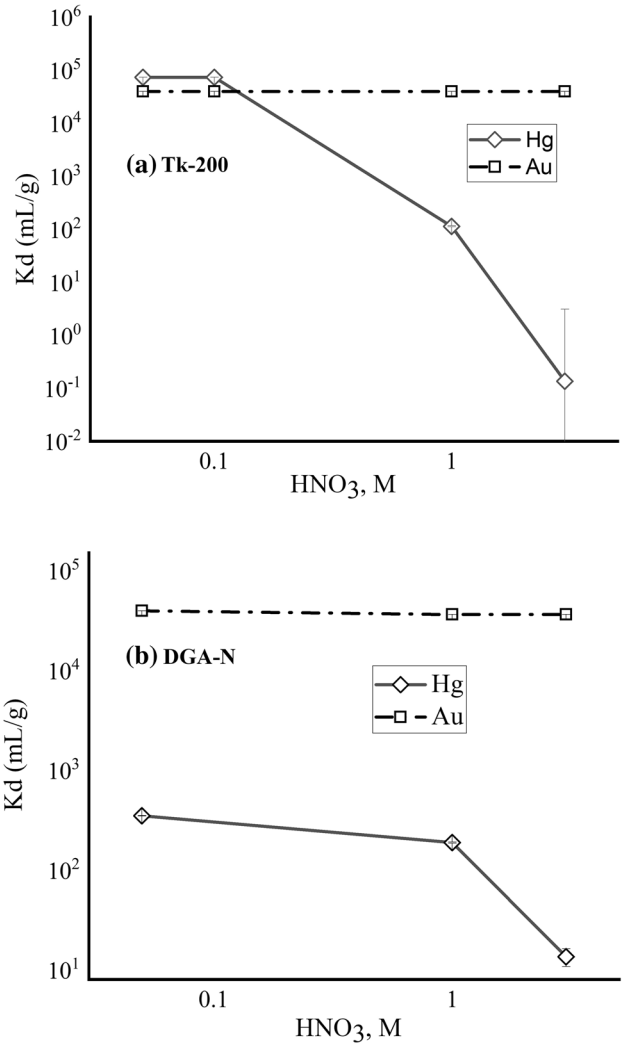

Fig.2 Extraction profile of NCA Hg and bulk Au by **a** TK200 and **b** DGA-N resins at varying concentrations of HNO_3

Conclusion

This is the first report on the extraction and separation of NCA Hg radioisotopes from bulk Au by the two solid phase extractants TK200 and DGA-N from nitric acid

Table 4 Distribution coefficients (D) and separation factor (S) of NCA Hg and bulk Au

Experimental conditions	Radionuclide	D*	$S_{Au/Hg}$
0.1 g DGA-N + 3 M HNO_3	Hg	0.67 ± 0.02	2705
	Au	1813 ± 77	
0.1 g TK200 + 3 M HNO_3	Hg	0.006 ± 0.0001	3.2×10^5
	Au	1975 ± 84	

*D = counts in resin phase/counts in aqueous phase

S = Separation factor

solutions. Comparative analysis of the extraction efficiency of the two resins revealed that both are suitable for carrying out extractions of either Hg or Au but TK200 resin serves as an excellent separating agent for NCA Hg radionuclides from bulk Au target. This method offers the advantage of availability of NCA Hg radioisotopes in the aqueous phase after radiochemical separation, thereby reducing secondary steps such as back extraction. The process reported in this paper does not involve any organic solvent, therefore can be considered as a clean process. The radiochemical method developed for separation of NCA Hg radionuclide is also fast and single step.

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