

Sequential separation by HDEHP of carrier-free $^{101,105,106}\text{Rh}$, $^{103,104,105,106,110,112}\text{Ag}$ and $^{104,105,107,109,111}\text{Cd}$ produced in alpha-particle activated palladium

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Carrier free $^{101,105,106}\text{Rh}$, $^{103,104,105,106,110,112}\text{Ag}$ and $^{104,105,107,109,111}\text{Cd}$ radioisotopes were produced simultaneously by α -particle irradiation of palladium target material in a variable energy cyclotron. The radioisotopes produced were extracted and separated from the activated target by LLX using HDEHP as liquid cation exchanger. With the help of γ -ray spectrometry the presence of several radioisotopes in the activated target matrix and their purity at each step of the separation was confirmed.

Introduction

Carrier-free radioisotopes are widely used as vital tools either in material research or in biomedical applications. The use of carrier-free radioisotopes in medical research constitutes the most important developments in applied nuclear sciences. An important advantage of carrier free radioisotopes is that they are used in minute quantities in such a way that they do not disturb the physiological process but offer high degree of sensitivity in detection. Due to these advantages they can be used either for *in vitro* assay of trace level hormones, drugs, etc., or for *in vivo* monitoring of biometabolic pathways. The purity requirement of a particular radioisotope is stringently followed in such sophisticated applications especially for *in vivo* systems. Regarding the production of carrier free radionuclides charged particle activation technique is found to be highly favorable to the other nuclear processes since the charged particle activation products are mostly nonisotopic with the target element.

Carrier-free $^{111\text{m}}\text{Cd}$ is an important radionuclide in material science research specially as a "perturbed angular correlation" (PAC) source which causes no serious aftereffects.¹ ^{109}Cd is used in long term metabolic studies because it has suitable long half-life whereas ^{107}Cd can be used in short-time multitracer experiments.² The carrier-free ^{109}Cd isotope is also used as an X-ray source.³ The carrier-free ^{105}Ag and $^{106\text{m}}\text{Ag}$ isotopes have also useful applications in the field of analytical chemistry as tracers.¹

Earlier, the cyclotron production of $^{100,101\text{m}}\text{Rh}$ from natural ruthenium, $^{100,101}\text{Pd}$ from rhodium, $^{105,106\text{m}}\text{Ag}$ from natural palladium and $^{107,109}\text{Cd}$ from natural silver were reported.⁴ NAIR et al.⁵ produced carrier-free radioisotopes of palladium from ruthenium metal target through (α, n) reaction and separated the carrier free palladium from the target matrix by two methods. In the first method palladium was eluted by dilute ammonia from an anion exchange column. In the other method palladium was separated by coprecipitation with tellurium. A method depicting the carrier-free separation of microgram quantity of fission product palladium from irradiated actinides using

dimethylglyoxime (DMG) in chloroform had also been reported.⁶ TARAPCHIK et al.⁷ developed a separation procedure for carrier-free ^{103}Pd from cyclotron irradiated rhodium target by α -furyldioxime into chloroform from acidic solution. Cyclotron production of $^{107,109}\text{Cd}$ by proton irradiation of natural silver followed by radiochemical separation was reported by GOETZ et al.² SMITH-JONES et al.⁸ produced simultaneously ^{109}Cd , ^{57}Co and ^{54}Mn from a composite cyclotron from enriched ^{109}Ag and ^{56}Fe . Simultaneous production of carrier-free $^{111\text{m}}\text{Cd}$ and $^{105,106\text{m}}\text{Ag}$ from a single palladium target by α -particle activation has also been reported.¹ Earlier simultaneous production and separation of multielemental carrier-free radioisotopes from a single target of First Transition Series elements was reported.^{9,10} Simultaneous production and separation of multielemental carrier-free radioisotopes of Second Transition Series from zirconium and molybdenum target has been also reported.^{11,12} The present work deals with the simultaneous production of carrier-free radioisotopes of rhodium, silver and cadmium by α -particle irradiation of the natural palladium target (Table 1) and with the development of a radiochemical separation scheme through liquid-liquid extraction using HDEHP as a cation exchanger.

Experimental

A sample of pure palladium metal mounted on an aluminium disc was placed on an aluminium target holder flange for irradiation. The irradiation was carried out in a variable energy cyclotron, at VECC, Calcutta with 40 MeV α -particle beam of 2 μA current with a total dose of $\sim 10\,000\ \mu\text{C}$. During the irradiation electron suppression was done by using a cylindrical aluminium tube attached to the flange and the sample was kept cooled by circulating low conductivity chilled water. After irradiation the sample was allowed to cool for reasonable periods before the actual chemical processing. Formation of several radioisotopes of rhodium, palladium, silver and cadmium, namely, $^{101,105,106}\text{Rh}$, $^{100,101,109}\text{Pd}$, $^{103,104,105,106,110,112}\text{Ag}$ and $^{104,105,107,109,111}\text{Cd}$ has been verified by non-destructive

Table 1. Nuclear characteristics of the various radioisotopes formed by α -particle activation of palladium target

Target nuclei (%, abundance)	Nuclear reaction	Product nuclei	E_{th} MeV	Half-life	Principal γ -energies, (intensity, %) keV
^{102}Pd (1.0)	(α, n)	^{105}Cd	9.57	55.5 m	346.8(4.2), 433.2(2.8), 607.2(3.7), 961.8(4.7)
	$(\alpha, 2n)$	^{104}Cd	18.33	57.7 m	83.6(47), 709.4(19.5)
	(α, p)	^{105}Ag	5.91	41.29 d	280.5(31.0), 344.6(42), 443.4(10.8), 644.6(10.1)
	(α, pn)	^{104}Ag	16.33	1.15 h	555.8(92.8), 767.8(65.9), 858.0(10.3), 926.0(12.5), 941.7(25.2)
	$(\alpha, p2n)$	^{103}Ag	25.06	1.09 h	118.6(31.2), 148.1(28.3), 266.8(13.3)
	$(\alpha, \alpha n)$	^{101}Pd	10.95	8.4 h	296.2(19.2), 590.5(12.1),
	$(\alpha, \alpha 2n)$	^{100}Pd	19.55	3.6 d	74.7(98), 84(100), 126.0(11)
	$(\alpha, \alpha p)$	^{101}Rh	8.08	4.34 d	306.8(86), 545.0(4)
	^{104}Pd (11.1)	(α, n)	^{107}Cd	8.36	6.5 h
(α, pn)		^{106}Ag	15.97	8.46 d	406.2(13.2), 429.7(13.1), 451.0(27.6), 616.2(21.7), 717.4(29.0), 748.4(20.4), 804.3(12.5), 824.8(15.3), 1045.8(29.9), 1128.0(11.7), 1199.4(11.9),
^{106}Pd (27.3)	(α, n)	^{109}Cd	7.28	1.26 y	88.03(3.6)
	$(\alpha, \alpha p)$	^{105}Rh	9.69	1.47 d	306.3(5.1), 319.2(19.0)
^{108}Pd (26.5)	(α, n)	^{111}Cd	6.13	48.6 m	150.8(29.1), 245.4(94)
	(α, pn)	^{110}Ag	15.55	249.8 d	446.8(3.8), 657.8(94.6), 706.7(16.4), 763.9(22.3), 884.7(72.7), 937.5(34.4)
	$(\alpha, 2pn)$	^{109}Pd	22.96	13.7 h	88.0(3.6)
	$(\alpha, \alpha pn)$	^{106}Rh	19.19	2.17 h	406.2(12.0), 429.7(13.5), 451.0(24.9), 511.8(87), 616.2(20.6), 717.4(29.4), 748.4(19.8), 804.3(13.2), 824.8(13.9), 1045.8(30.8), 1128.0(11.1), 1199.4(10.8), 1222.9(8.0), 1527.9(17.4)
^{110}Pd (11.72)	(α, pn)	^{112}Ag	15.18	3.1 h	606.7(3.1), 617.4(43), 694.8(3), 1387.7(5.4)

γ -ray spectroscopy of the activated palladium metal (Fig. 1).

A stock solution was prepared by dissolving the activated palladium metal in 4N HNO_3 in order to separate the produced carrier-free radioisotopes formed during irradiation. The solution was made ammoniacal followed by addition of H_2O_2 . The solution was then shaken with an equal volume of 0.1% HDEHP octanol solution. After disengagement, the radioisotopes of cadmium were found to be extracted by the organic phase leaving the radioisotopes of rhodium and silver along with palladium in the aqueous phase. The aqueous phase was treated with equal volume of 0.1M citric acid and 10% HDEHP and it was found that the carrier-free radioisotopes of silver along with bulk palladium were

completely extracted by the cationic extractant HDEHP. The radioisotopes of carrier free silver, i.e., $^{103,104,105,106,110,112}\text{Ag}$ then can easily be stripped into an aqueous 6N HNO_3 solution. The chemical procedure developed for separation of the carrier free radioisotopes of rhodium, silver and cadmium produced by α -activation has been summarized in Fig. 2.

All chemicals used were of analytical grade and the extractant HDEHP was procured from ICN pharmaceuticals. The extractant solution of desired concentration was prepared by dissolving calculated amounts of HDEHP in required amount of cyclohexane. A well type HPGe detector with 2.53 keV resolution at 1.33 MeV, in conjunction with a PC based MCA was used for γ -ray spectrometric studies.

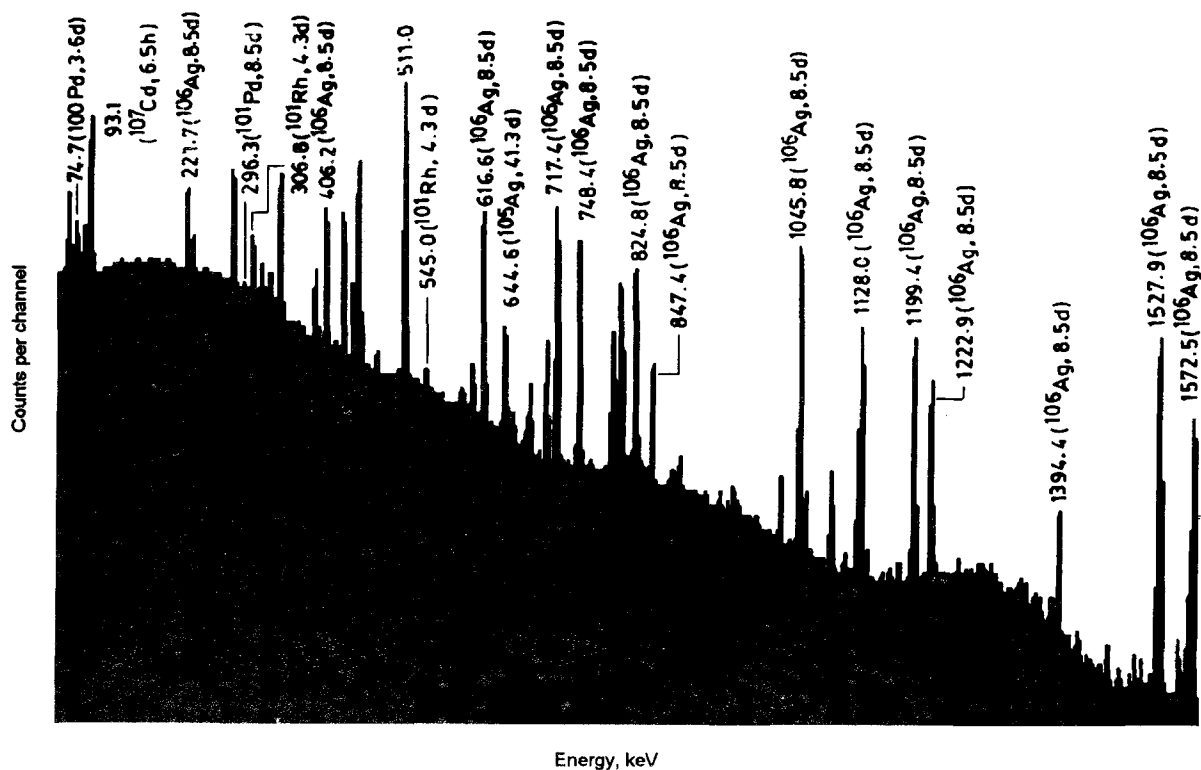


Fig. 1. A non-destructive γ -spectrum of α -particle activated palladium taken after two days of irradiation

Results and discussion

Non destructive γ -ray spectroscopic studies of the activated palladium target material irradiated by 40 MeV α -particle indicated the formation of several radioisotopes of rhodium, palladium, silver and cadmium, $^{101,105,106}\text{Rh}$, $^{100,101,109}\text{Pd}$, $^{103,104,105,106,110,112}\text{Ag}$ and $^{104,105,107,109,111}\text{Cd}$. The production of the above radioisotopes from the natural palladium target involve many nuclear reactions such as $\text{Pd}(\alpha, \alpha p n)^{101,105,106}\text{Rh}$, $\text{Pd}(\alpha, \alpha x n)^{100,101,109}\text{Pd}$, $\text{Pd}(\alpha, p x n)^{103,104,105,106,110,112}\text{Ag}$, $\text{Pd}(\alpha, x n)^{104,105,107,109,111}\text{Cd}$, etc., having threshold values less than 40 MeV. The activation products had been identified by their corresponding γ -peaks and decay studies. The activity of the different isotopes produced were calculated by the (GAMMA VISION software (EG & G ORTEC) and it was found that the different isotopes produced had their activities between 10 to 500 μCi , the lowest being ^{100}Pd and the highest being ^{107}Cd .

Studies on the extraction behavior of bulk palladium along with its activation products indicated that in ammoniacal medium only the radioisotopes of cadmium, i.e., $^{104,105,107,109,111}\text{Cd}$ are quantitatively extracted into the organic phase by 0.1% HDEHP and octanol in the presence of H_2O_2 . The quantitative extraction of cadmium by HDEHP in ammoniacal medium may be due to the formation of cationic species of cadmium like

$[\text{Cd}(\text{OH})(\text{H}_2\text{O})_x]^+$, $[\text{Cd}_2(\text{OH})(\text{H}_2\text{O})_x]^{3+}$, etc.¹³ When the aqueous phase containing the radioisotopes of palladium, rhodium and silver is extracted by 10% HDEHP in 0.1(M) citric acid (pH = 8) the radioisotopes of palladium and silver is stripped into the organic phase leaving those of rhodium in the aqueous phase. Under such experimental conditions the radioisotopes of palladium and silver form cationic hydrated species like $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Ag}(\text{H}_2\text{O})_2]^+$ which are thereby taken up by the cationic exchanger HDEHP. The organic phase was then treated with 6N HNO_3 to strip the radioisotopes of silver into the aqueous phase. This may be attributed to the higher stability of the cationic complex of palladium in comparison to that of silver.

The purity and the extent of separation of the carrier free activation products in different phases had been verified through γ -ray spectroscopy. The developed radiochemical charged particle activation procedure for the production and separation of carrier free radioisotopes can be successfully and potentially applied for biomedical, technological or other fields. Moreover, the simultaneous production of different carrier free radioisotopes in a single run will reduce the costly beam time in comparison with the single production.

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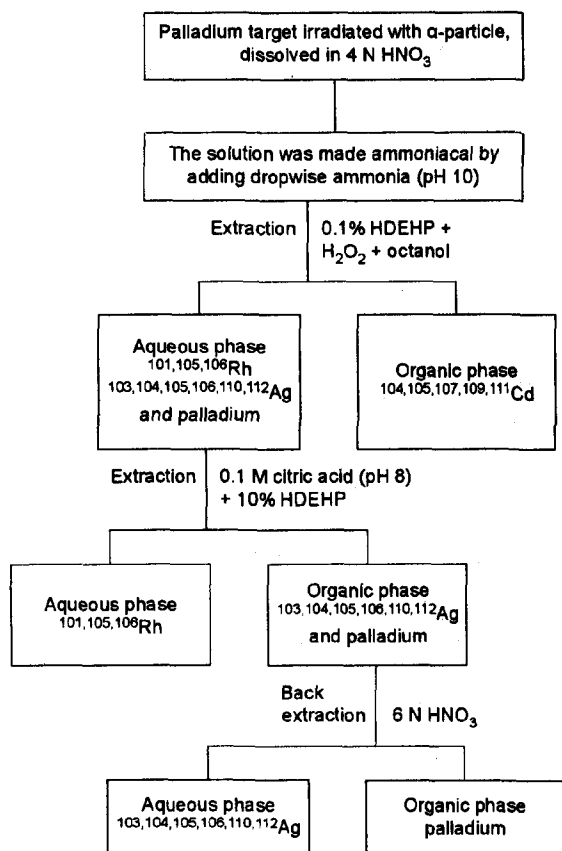


Fig. 2. Flow sheet for the separation of carrier-free $^{101,105,106}\text{Rh}$, $^{103,104,105,106,110,112}\text{Ag}$ and $^{104,105,107,109,111}\text{Cd}$ from the α -particle activated palladium target by HDEHP