CYCLOTRON PRODUCTION OF PT, PD AND RH RADIOTRACERS TO STUDY THE ENVIRONMENTAL IMPACT OF THE CATALYTIC CONVERTER EMISSIONS

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Pt, Pd and Rh radioisotopes were produced by irradiation, using both α and proton beams of the SCANDITRONIX MC40 cyclotron of the JRC-Ispra of the EU, on iridium, osmium, palladium and rhodium targets. In this work the preliminary experimental yields of 189-Pt, 188-Pt, 191-Pt, 103-Pd, 100-Rh and 101m-Rh isotopes, employed for biological applications, are presented.

1 Introduction

The increasing interest on the use of catalytic converters to reduce the concentration of carbon monoxide and hydrocarbons in the exhaust streams, makes it necessary to carry out toxicological studies on the possible effects of the emission of some trace metals, such as platinum, palladium and rhodium, on biological matrices. The extremely low environmental concentration of these metals requires a very sensitive analytical technique, such as the use of High Specific Activity Radiotracers, to investigate the metabolic behaviour at low doses[1]. To this purpose the Pt, Pd and Rh radioisotopes were produced by cyclotron irradiation, using both α and proton beams on osmium, iridium, rhodium and palladium targets. The lack of data in the literature concerning the thin-target excitation functions for the production by charged particles of these isotopes on the targets cited makes the optimization of the irradiation parameters (target thickness, beam energy, beam current intensity and irradiation time) impossible[2,3,4,5]. They can only be estimated by theoretical considerations (Th E, ICB). Moreover, some preliminary irradiations were necessary in order to select the most suitable energy and target thickness to keep the production of radionuclidic interferences down.

Our interest was focused on those radioisotopes whose characteristics are a good compromise among a $T_{1/2}$ suitable for medium term biochemical studies, reasonable γ-emission abundances, good γ-energies and few spectral interferences[1].

1.1 Pt isotopes

Two methods were investigated for the production of the Pt radiotracers selected (^{191}Pt, ^{189}Pt and ^{188}Pt): ^{nat}Ir(p,xn)*Pt and ^{nat}Os(α,xn)*Pt, as reported in Table 1.

1.2 Rh isotopes

Rh radioisotopes production can be carried out through cyclotron irradiation via two main different methods: ^{nat}Ru(p,xn)*Rh and ^{nat}Pd(p,xn)*Ag→*Pd→*Rh, as reported in Table 1. The choice of the second method is based on the practical possibility to use thin metallic foil targets, while Ru is commercially available only as metallic powder. Anyway several problems are connected also with the selected method: the analysis of the irradiated targets requires high sensitivity and accuracy since more spectral interferences are present and lower yield values are achievable.

Among the Rh isotope produced, the ^{100}Rh and ^{101m}Rh were selected. Long-term radiobiological studies could be carried out also with ^{99g}Rh, but the production of this nuclide is based on a (p,4n) reaction on ^{102}Pd, that has a low natural abundance (1.02 %), resulting in a low yield value.

1.3 Pd Isotopes

The direct method for the cyclotron production of Pd radioisotopes consists on ^{nat}Rh(p,xn)*Pd reactions. This method leads to higher yield values and less problems in the subsequent radiochemical separation if compared to the other possible.

Table 1 reports the characteristics of the two isotopes examined: ^{100}Pd and ^{103}Pd. The first one is hardly usable in radiobiological experiments since it is in equilibrium with the daughter ^{100}Rh; for this reason, the second one is the best choice even if its γ - emissions are extremely weak.

2 Experimental

The irradiations were carried out with the SCANDITRONIX MC40 cyclotron of the JRC-Ispra of the EU, whose maximum energy is 38 MeV for both proton and α beams.

Small aliquots of the chemically dissolved irradiated targets were analysed by γ-spectrometry with HPGe detectors (EG&G Ortec - USA) accurately calibrated in both energy and efficiency using ^{226}Ra and ^{152}Eu certified γ-sources (Amersham, CEA). The radioisotope decays were followed from 24 hours to at least 2 months

Table 1 - Radioisotopes produced via (p,xn) and (α,xn) nuclear reactions on ^{nat}Ir (^{191}Ir 37%, ^{193}Ir 63%), ^{nat}Os (^{184}Os 0.02%, ^{186}Os 1.58%, ^{187}Os 1.6%, ^{188}Os 13.3%, ^{189}Os 16.1%, ^{190}Os 26.4%, ^{192}Os 41.0%), ^{nat}Pd (^{102}Pd 1.02%, ^{104}Pd 11.14%, ^{105}Pd 22.33%, ^{106}Pd 27.33%, ^{108}Pd 26.46%, ^{110}Pd 11.72%) and ^{nat}Rh (^{103}Rh 100%).

Production reactions	Th E (*,**) MeV	Isotope	$T_{1/2}$	γ-emission keV(%)	Interferences
^{191}Ir(p,4n)	24.0 (-)	**^{188}Pt**	10.2 d	**155.0** (35.9) D	
^{186}Os(α,2n)	19.3 (*21.3)			187.6 (19.4)	^{190}Ir (186.7 keV, 48.2%)
^{187}Os(α,3n)	25.7 (-)			195.1 (18.6)	^{190}Ir (196.9 keV, 2.5%)
^{188}Os(α,4n)	33.9 (-)			478.0 (17.8) D	^{188}Pt (478.2 keV, 1.8%)
				381.4 (7.5)	^{190}Ir (380.0 keV, 2.0%)
				423.3 (4.4)	^{190}Ir (420.6 keV, 1.6%)
				140.3 (2.3)	^{189}Pt (141.1 keV, 2.6%)
^{191}Ir(p,3n)	17.2 (-)	**^{189}Pt**	10.9 h	**721.4** (5.8)	
^{193}Ir(p,5n)	31.2 (-)			607.6 (5.1)	^{190}Ir (605.1 keV, 38.5%)
^{186}Os(α,n)	12.4 (*21.3)			568.8 (4.4)	^{190}Ir (569.3 keV, 27.5%)
^{188}Os(α,3n)	27.0 (-)			243.5 (4.4)	^{185}Pt (243.0 keV, 6.0%)
				544.9 (3.6)	
				141.1 (2.6)	^{188}Pt (140.3 keV, 2.3%)
^{191}Ir(p,n)	1.8 (*11.4)	**^{191}Pt**	2.9 d	**538.9** (13.7)	
^{193}Ir(p,3n)	15.8 (-)			409.4 (8.0)	^{190}Ir (407.2 keV, 27.5%)
^{188}Os(α,n)	11.3 (*21.2)			359.9 (6.0)	^{190}Ir (361.1 keV, 12.6%)
^{189}Os(α,2n)	17.4 (*21.2)			172.2 (3.5)	
^{190}Os(α,3n)	25.3 (-)			**456.5 (3.4)**	
				351.2 (3.4)	
				129.4 (3.2)	
^{100}Ru(p,n)	4.5 (*7.9)	**^{100}Rh**	20.8 h	**539.6** (78.4)	^{100}Pd (539.6 keV, 103.0%) D
^{101}Ru(p,2n)	11.3 (-)			2376.1 (35.0)	^{100}Pd (2376.1 keV, 45.9%) D
^{102}Ru(p,3n)	20.5 (-)			822.5 (20.1)	^{106m}Ag (824.7 keV, 15.4%)
^{102}Pd(p,3n)^{100g,m}Ag→	27.0 (-)			1553.4 (20.5)	^{102g}Ag (1555.8 keV, 2.6%)
^{104}Pd(p,αn)	7.01 (**21.7)				
^{105}Pd(p,α2n)	14.2 (**28.8)				
^{101}Ru(p,n)	1.5 (*7.9)	**^{101m}Rh**	4.34 d	**306.9** (86.3)	^{105g}Ag (306.3 keV, 0.8%)
^{102}Ru(p,2n)	10.8 (-)			545.1 (4.0)	^{101g}Ag (543.3 keV, 2.3%)
^{104}Ru(p,4n)	35.9 (-)				
^{102}Pd(p,2n)^{101}Ag→	15.7 (-)				
^{104}Pd(p,4n)^{101}Ag→	33.5 (-)				
^{104}Pd(p,α)	0 (**14.5)				
^{105}Pd(p,αn)	2.2 (**16.8)				
^{103}Rh(p,4n)	28.1 (-)	**^{100}Pd**	3.63 d	**539.6** (103.0) D	^{100}Rh (539.6 keV, 78.4%)
^{103}Rh(p,n)	1.4 (*7.9)	**^{103}Pd**	16.96 d	**357.5** (0.022)	

*: Incident Coulomb Barrier. **: Th E+Outgoing Coulomb Barrier.
-:ICB under Th E value. D: Dauther γ emission.

from the End Of Bombardment (EOB) in order to detect the medium and long $T_{1/2}$ isotopes. For each γ-emission that seemed to be not contaminated, the corresponding radionuclide activity at the beginning of the γ-spectrum measurement $A(t_{BOM})$ versus time from the EOB was reported, where the expression

$$A(t_{BOM}) = \frac{C_\gamma}{\alpha_\gamma \varepsilon_\gamma \Delta t}\left(\frac{\lambda \Delta t}{1 - e^{-\lambda \Delta t}}\right) = \frac{C_\gamma}{\alpha_\gamma \varepsilon_\gamma \Delta t} D(\Delta t)$$

was adopted for a simple decay, and the relation:

$$A(t_{BOM}) = \frac{\lambda \frac{C_\gamma}{\alpha_\gamma \varepsilon_\gamma} + \frac{\lambda}{\lambda - \lambda_F} A_F^{EOB}\left[\left(1 - e^{-\lambda \Delta t}\right) - \frac{\lambda}{\lambda_F}\left(1 - e^{-\lambda_F \Delta t}\right)\right]}{1 - e^{-\lambda \Delta t}}$$

was employed in the case of presence of a father radioisotope (F). In these relations λ = radionuclide decay constant, α_γ = γ-emission abundance, ε_γ = equipment detection efficiency for the selected γ-emission, C_γ = net experimental counts, Δt = real counting time, D(Δt) = decay factor during measurement, λ_F = father decay constant and A_F^{EOB} = father activity at the EOB[6]. In both

constant and A_F^{EOB} = father activity at the EOB[6]. In both cases, $A(t_{BOM})$ was calculated considering the radioisotopes decay during the data acquisition.

2.1 Pt radiotracers experimental production

Two different experiments were carried out for Pt radiotracers production. In the first, iridium metallic foils (Ir > 99.9%, Goodfellow Metals - UK) and some osmium powdered targets (Os LAB purity, Merck - FRG), pressed at 100 kg/cm^2 between two aluminium foils 16 μm thick, were used (see Table 2). In the second one, preliminary values of thick-target yields were deduced from the irradiation of ten Os pressed powdered targets whose characteristics are summarised in Table 3.

2.2 Rh radiotracers experimental production

All the irradiations were carried out on palladium metallic foils (Pd > 99.9%, BDH Chemicals, Poole UK) of square shape with 12 mm side and 0.025mm certified thickness; however, the true massive thickness reported in Table 4 were deduced from weight measurements.

Some of the side reactions connected to the proton irradiation on Pd targets lead to ^{103}Pd production; this radionuclide, here considered as an interference, was studied in comparison with the direct production method described in par. 2.3.

2.3 Pd radiotracers experimental production

Thin metallic Rh targets (930 μg/cm^2), available only with polyester backing 0.150 mm thick, were used for the direct Pd isotopes production.

3. Results and discussion

As far as ^{188}Pt is concerned, all the γ-emissions present a theoretical interference; however, since the interference ^{189}Pt has a short half-life with respect to ^{188}Pt, the 140.3 keV γ-emission can be used for the yield calculation. The thick-target yield values reported in Figure 1 refer to the 155.0 keV γ-emission that has a highest abundance value. Since this is a daughter emission, the yield values obtained were corrected for the theoretical factor of the transient equilibrium. The values obtained are comparable with the correspondent experimental values from the 140.3 keV emission.

Concerning ^{191}Pt, we found that the 456 keV γ-emission was the best choice for the production from Ir targets: this emission was used for thin and thick-target yield calculations. In the case of ^{nat}Os(α,xn) reactions, the emission of highest abundance (538.9 keV) can also be used, for several days after the preparation of the tracer. This emission was used to plot Figure 2.

^{189}Pt presents a simpler situation since the most abundance emission (721.4 keV) does not show interferences. For this reason thick-target yield calculations and the data of Figure 3 are obtained from this emission.

Table 2 - Irradiation parameters applied for the Pt isotopes production (first experiment).

Target	Iridium metallic foil	Os pressed powder (TAR. 1)	Os pressed powder (TAR. 2)
Geometric properties	108 mg/cm^2 7.5x7.5mm^2	220 mg/cm^2 ∅ 12 mm	158 mg/cm^2 ∅ 10 mm
Beam particles	p	α	α
Real beam energy	35 MeV	22 MeV	33 MeV
(ΔE)*	1 MeV	22 MeV	15.2 MeV
Time of irradiation	1 h	7 h	8 h **
Integrated charge	374 μC	7.7 10^4 μC	8.7 10^4 μC

*: Beam mean energy loss into the target, calculated with the TRIM code (J.F.Ziegler and J.P.Biersack).
**: Irradiation carried out in two steps, at 15 h 33 m one from the other.

Table 3: Irradiation parameters applied for Pt radioisotope production (second experiment)

Target N.	Massive thickness (mg /cm^2)	Incident Energy (MeV)	Current intensity (nA)	Irradiat. time (h.m)
1		37.38		
2		34.84	50	1
3	382	31.72		
4		29.55		
5		27.25	30	1
6		27.22		
7		24.75	50	1
8	255	22.07		
9		19.53		

Table 4: Irradiation parameters applied for Pd and Rh production

Target	Pd-TAR 1	Pd-TAR2 (for applications)
Massive thickness (mg/cm2)	36	36
Beam energy (MeV)	36	36
Al thickness window (mm)	0.29	0.3
Energy (MeV)	35	35
Time of irradiation (h)	1	5
Integrated charge (C)	3.6 10^{-4}	1.8 10^{-2}

The yield value for ^{103}Pd was obtained from the Pd irradiation used to product Rh isotopes because the

presence of many interferences and the weakness of the ^{103}Pd emission made the detection of this isotope in the direct production method impossible.

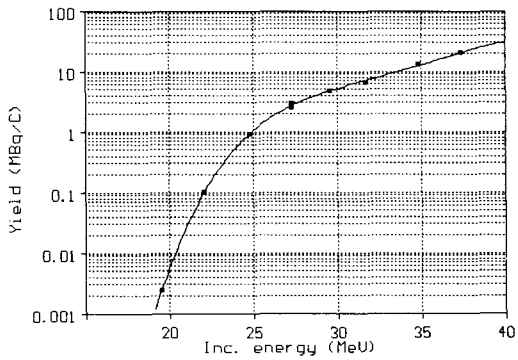

Figure 1: Thick-target yield for ^{188}Pt (155.0 keV γ-emission).

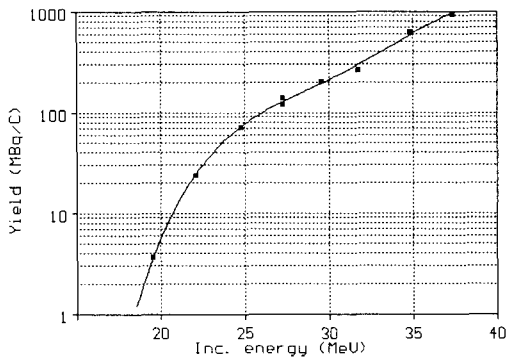

Figure 2: Thick-target yield for ^{191}Pt (538.9keV γ-emission)

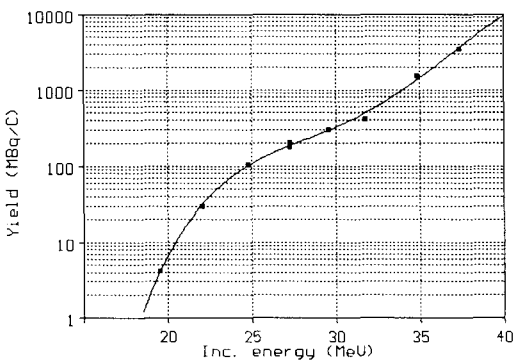

Figure 3: Thick-target yield for ^{189}Pt (721.4 keV γ-emission)

Table 5 reports, for each target, the experimental thick-target yield for the radiotracers of interest.

For ^{100}Rh production the second expression reported was used to fit the $A(t_{BOM})$ versus time from the EOB, because of the equilibrium situation between this isotope and its father.

Table 5 - Experimental production thin-target or thick-target yields for the Pt, Rh and Pd radiotracers of interest (calculated by the underlined γ-emissions of Table 1)

ISOTOPE	PRODUCTION METHOD	YIELD ± σ (MBq/C MeV) *(MBq/C)
^{188}Pt	^{nat}Ir(p,xn) ^{nat}Os(α,xn) TAR1 ^{nat}Os(α,xn) TAR2	340±2 *0.40±0.01 *16±1
^{189}Pt	^{nat}Ir(p,xn) ^{nat}Os(α,xn) TAR1 ^{nat}Os(α,xn) TAR2	 *1.5
^{191}Pt	^{nat}Ir(p,xn) ^{nat}Os(α,xn) TAR1 ^{nat}Os(α,xn) TAR2	730±12 *17±1 *240±3
^{100}Rh	^{nat}Pd(p,xn)-TAR1	14.68 ± 0.02
^{101m}Rh	^{nat}Pd(p,xn)-TAR1	34.4 ± 0.2
^{103}Pd	^{nat}Pd(p,xn)-TAR1	106.7 ± 41.4

4. Conclusions

In this report it was described the production methods adopted in our laboratory in order to produce Nearly Carrier Free (NCF) radiotracers of the three elements considered.

Preliminary in-vitro and in-vivo toxicological studies showed that Pt and Rh have a linear growing cellular intake vs. the dose. Furthermore inorganic Pt salts result more toxic with respect to Pd and Rh ones.

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