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THIN-TARGET EXCITATION FUNCTIONS AND OPTIMISED THICK-TARGET YIELDS FOR $^{nat}Mo(p,xn)^{94g,95m,95g,96(m+g)}Tc$ NUCLEAR REACTIONS INDUCED BY PROTONS FROM THRESHOLD UP TO 44 MeV. RADIOCHEMICAL SEPARATION AND QUALITY CONTROL

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Abstract

This work describes the method adopted in our laboratories, to produce ^{94g}Tc, ^{95g}Tc, ^{95m}Tc and ^{96g}Tc radionuclides via proton-cyclotron irradiation on molybdenum targets of natural isotopic composition. Experimental thin-target excitation functions and "effective" cross-sections for direct $^{nat}Mo(p,xn)^{A}Tc$ [with A=94,95,95,96] nuclear reactions, with incident proton energy in the range from threshold up to 44 MeV, are reported. Some definition of the equations used and nuclear data traceability are reported.

Thick-target yield values were calculated and optimised, by numerical fitting and integration of the measured excitation functions. These values allow the optimisation of the production yield of one radionuclide, minimising at the same time the yield of the others.

A novel radiochemical separation on NCA technetium radionuclides from both molybdenum target and niobium, zirconium and yttrium radioactive by-products is reported.

Quality control tests on the radiotracers were developed with several radioanalytical techniques for the applications envisaged in environmental metallo-biochemical toxicology.

Key Words: Excitation Functions / $^{94g,95g,95m,96(g+m)}Tc$ / Thick-target Yields / Radiochemical Separation Tc,Mo,Nb,Zr,Y / No Carrier Added / Quality Controls

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1 INTRODUCTION: TECHNETIUM (OR MASURIUM) SOURCES AND APPLICATIONS

Technetium, Tc (τεχνητο′ς, i.e: *artificial* since Perrier and Segre' [1,2] and Leigh-IUPAC Nomenclature [3]), previously christened masurium, Ma, by Ida Noddack-Tacke, Walter von Noddack and Otto Carl von Berg in 1925 and 1927 [4,5,6], is a *natural* element present in any uranium and thorium containing ore [4,5,7-11]. Medium-lived artificial γ-emitting radiotracers are used to optimise radioanalytical methods for the determination of this element in environmental matrices [12-15] and for the study of metabolic patterns and the kinetics of uptake and release in living organisms and even humans [12,16-19].

Tc presents several different chemical forms concerned with environmental metallo-biochemical studies, such as the very soluble and stable pertechnetate (tetraoxorhenate IUPAC [3]) anion TcO_4^- [20,21] and the poorly soluble technetium(IV) dioxide di-idrate $TcO_2 \bullet 2H_2O$ and chlorocomplexes [22]. Slightly volatile technetium oxides, sulfides, halogenides and oxahalogenides are present in the environment also.

The $Tc(VI)O_4^{2-}$ species precipitates isomorphously, with slightly soluble molydbates (ex: Ag and Pb) and it is almost stable in alkaline solution; as well as the $Tc(IV)O_3^{2-}$ species that is relatively stable in alkaline medium also [23]. Moreover, both Tc(VI) and Tc(V) oxa-anions tend to disproportionate to Tc(VII) and Tc(IV).

Finally, in principle, both neutral (i.e: lipophylic), cationic and anionic coordination compounds of all technetium oxidation states (-I, 0, I, II, III, IV, V, VI, VII) are known and can be synthesised in laboratory, even if most of them are stable in presence of strong *ligands* only, as reported extensively elsewhere [11,23-28]. Thus, technetium (or masurium) *is not an artificial radioactive element*, but is *naturally produced* in measurable amounts via the spontaneous fission of ^{238}U, as shown by Petrzhak e Flerov in 1940, as well as either the spontaneous or induced fission of any fissionable radionuclide, by either thermal or fast neutrons, as well as fast charged particle beams [29-36].

Other than ^{99g}Tc, even the *shielded* long-lived radionuclides ^{98}Tc and ^{97g}Tc are produced by *direct* fission, with not negligible yield (Choppin pp. 378-380 [33]). The direct fission yield of different Tc radionuclides, calculated by the "corrected" Unchanged Charge Distribution model (UCD), are reported in Table 1, in accordance with the theory summarized by Friedlander pp. 162-164 [11,37].

Nevertheless, currently, there are more important sources of production and potential release of this element in the environment, such as former atomic bomb explosions and nuclear energy production (radioactive waste disposal, uranium enrichment industry and nuclear fuel reprocessing) [20,21,38-49]. During the fission process, radionuclides with mass number 99 are largely produced, ^{99g}Tc being the last radioactive nuclide of the isobaric chain of mass 99. The specific activity of ^{99g}Tc is low (0.634 kBq/μg), the maximum energy of its β^- decay is not very high (293.7 keV End-Point) and it does not emit γ-rays [50]. Thus, it is relevant to establish the potential radiological impact of this radionuclide on living organisms as a consequence of a Low Level and Long Term Exposure (LLE) because of the long ^{99g}Tc half-life ($t_{1/2} = 2.111 \cdot 10^5$ a), the non negligible amount produced yearly and the *wide geomobility* of the TcO_4^- anion.

TAB. 1: Calculated gaussian probabilities **P(Z)** for the "direct fission" production of different nuclides of isobars 96, 97, 98, 99 and 100, by thermal fission of ^{235}U, under the “corrected” UCD assumption [11,33,37].
The direct fission yield of Tc radionuclides is not negligible and varies from 10^{-7} to 10^{-14} .

A		***NAME***	***Kr***	***Rb***	***Sr***	***Y***	***Zr***	***Nb***	***Mo***	**Tc**	***Ru***	Σ
	Z_{ucd}	**Z**	**36**	**37**	**38**	**39**	**40**	**41**	**42**	**43**	**44**	Σ%
96	37.583	**P(Z)**	2.61E-3	1.44E-1	6.29E-1	2.19E-1	6.06E-3	1.33E-5	2.33E-9	**3.25E-14**	3.6E-20	1
		%	0.261	**14.4**	**62.9**	**21.9**	0.0606					100
97	37.974	**P(Z)**	2.73E-4	4.05E-2	4.77E-1	4.47E-1	3.34E-2	1.98E-4	9.32E-8	**3.50E-12**	1.0E-17	1
		%	0.0273	**4.05**	**47.7**	**44.7**	**3.34**	0.0198				100
98	38.366	**P(Z)**	1.94E-5	7.74E-3	2.46E-1	6.20E-1	1.25E-1	1.99E-3	2.53E-6	**2.55E-10**	2.1E-15	1
		%	0.00194	0.774	**24.6**	**62.0**	**12.5**	0.199				100
99	38.757	**P(Z)**	9.32E-7	1.00E-3	8.58E-2	5.84E-1	3.16E-1	1.36E-2	4.65E-5	**1.27E-8**	2.7E-13	1
		%		0.100	**8.58**	**58.4**	**31.6**	**1.36**	0.00465			100
100	39.149	**P(Z)**	3.04E-8	8.81E-5	2.03E-2	3.72E-1	5.43E-1	6.30E-2	5.81E-4	**4.26E-7**	2.5E-11	1
		%		0.00881	**2.03**	**37.2**	**54.3**	**6.30**	0.0581			100

In the last few decades, many experiments have been carried out, which seek to help understand the phenomena that regulate the technetium distribution in different echo-systems and to evaluate the role of the food chains in its shift from the environment to humans [19,21,43-45,48,49].

Even if the available information does not give a complete evaluation of the effects of Tc on living systems as a result of a continuous release of small doses of this element in the environment, the first question to ask is whether a radiological protection standard is desired (ICRP 1990 [51]). To answer this question, it is necessary to calculate the radiological risk, to identify the critical organs and to study the biochemical mechanisms responsible for an eventual accumulation. With regard to the metabolic patterns, it is particularly important to evaluate the Tc gastrointestinal absorption factor, the fractions of the element that reach the critical organs and its biological half-life in the different tissues (ICRP 1977, ICRP 1978, ICRP 1990, UNSCEAR 2000 [51-54]).

In practice, ^{99g}Tc, together with ^{237}Np, ^{129}I and some Pu radionuclides [33,42,46,55,56] is one of the most critical isotopes which contributes to the risk associated with the long-term storage of high activity radioactive waste as many countries store nuclear waste in geological sites, such as argillaceous or rocky areas and sea sediments after *vitrification* ([12], Choppin pp. 639-670 and refs. therein [33]).

For this reason, it is very important to establish the safety levels of these geological barriers in the case of an accidental release, since Tc could come in contact with ground water resulting in a potential pollution of surface water and the biosphere [41].

Conversely, the contribution of Tc environmental pollution from Nuclear Medicine applications (in practice the long-living ^{99g}Tc from the decay of ^{99m}Tc) can be considered as negligible with respect to the previous sources [20,21]. Unfortunately, both ^{99g}Tc and ^{99m}Tc ($t_{1/2}$ = 6.01 h) are not good radionuclides for medium-term (months) experiments because of the long and short half-life respectively. Other technetium γ-emitting radiotracers, with half-lives suitable for this purpose, are needed.

Tc is an odd element and the *shell model* suggests that no stable nuclides of this element do exist ([57,58], Friedlander pp. 379-406 [37], Krane pp. 116-158 [31], Choppin pp. 54-56 [33]), nevertheless nowadays, up to 42 Tc radioisotopes and radioisomers are known [36,50,59], 21 of which are "neutron poor" (β^+ or EC decay), while the others 21 present a dominant β^- decay. In the first group, 15 radionuclides (A= 86-94m, 96m) have half-lives shorter than 3 h and only one (the odd-even ^{97g}Tc) longer than 10^6 a. The other five (^{94g}Tc, ^{95g}Tc, ^{95m}Tc, ^{96g}Tc and ^{97m}Tc) have half-lives between 4.883 h and 90.5 d. Amongst the "neutron-rich" radionuclides, 15 (A=100-113) have half-lives shorter than 1 h and two, the odd-odd ^{98}Tc, that is at the *bottom of beta stability valley* (its odd-odd configuration does explain while no Tc nuclides are stable) and the odd-even ^{99g}Tc, longer than 10^6 and 10^5 a respectively; finally the only one with a half-life of the order of hours is the odd-even radioisomer ^{99m}Tc ($t_{1/2}$ = 6.01 h).

On the basis of half-life considerations, we directed our attention at the five “neutron-poor” radionuclides, whose half-life ($t_{1/2}$), Carrier Free Specific Activity, SA(CF) and main γ-emissions are summarised in Table 2 [60]. As can be seen from Table 2, ^{97m}Tc is not a

suitable radiotracer for our purpose because it presents one low energy and intensity γ-emission at 96.5 keV (0.3 %) only, as well as a low specific activity; while ^{94g}Tc presents a half-life and γ-emissions suitable for very short-term experiments on cell cultures only.

TAB. 2: Half-life, calculated atomic mass and Carrier Free Specific Activity (1 u = 931.501626 MeV, Avogadro's constant = 6.022045(31)·10^{23} g/mol), and principal γ-emissions for neutron poor Tc radionuclides, with a half-life suitable for medium term (day, months) biological and environmental experiments (from Browne 1986) [60].

radionuclide	$t_{1/2}$	atomic mass (g/mol or u)	CFSA (GBq/μg)	γ-emissions, keV (intensity %)
^{94g}Tc	4.883 h	93.909654	252.853	871.097 (99.9) 702.639 (99.6) 849.70 (95.8)
^{95m}Tc IT 4 %	61 d	94.907698	0.83449011	204.114 (66.2) 582.062 (31.4) 835.126 (27.9)
^{95g}Tc	20.0 h	94.907657	61.08470	765.789 (94.0) 1073.713 (3.7)
^{96g}Tc	4.28 d	95.907870	11.769404	778.196 (99.78) 849.89 (98) 812.54 (82)
^{97m}Tc# IT 100 %	90.5 d	96.906467	0.55087255	96.5 (0.31)

excluded from further studies because both its E_γ and intensity are too week.

2 PRODUCTION AND USES OF "ARTIFICIAL" Tc RADIONUCLIDES

Many Tc radioisotopes have been artificially synthesised and sometimes chemically separated from irradiated targets. Some Tc isotopes can be used as general-purpose radiotracers to study the physical-chemical properties of the element.

Amongst them, ^{99m}Tc is at present, without any doubt, the most extensively used radiotracer in Nuclear Medicine imaging. In fact, the short-lived ^{99m}Tc, which is commercially available from the decay of its parent generator ^{99}Mo ($t_{1/2}$ = 2.7477 d), is widely used to label a wide range of organic complexes and coordination compounds for diagnostic purposes since 1956, when the generator was developed at Brookhaven National Laboratory ([25,26,61-63], Ehmann pp. 332-337 [32]). In more recent years, Nuclear Medicine has shown a growing interest in the cyclotron-produced short-lived positron-emitter ^{94m}Tc, as a flow agent and suitable radiotracer for labeling radiopharmaceuticals bridging Single Photon Emission Computerised Tomography (SPECT, SPET) and Positron Emission Tomography (PET) imaging [64-71].

While ^{99m}Tc is usually produced in nuclear reactor by both thermal neutron irradiation of ^{nat,98}Mo(n,γ)^{99}Mo → and thermal fission ^{235}U(n,fiss)^{99}Mo → processes [63], whose cross-section and yield can be taken from Pfenning [36], ^{94m}Tc is more commonly produced by accelerators via irradiation by protons, deuterons, helium-3 and alpha beams of either ^{93}Nb or Mo enriched targets [69,70,72-74]. Up to now, less effort in this area was devoted to production of other very short-lived Tc radionuclides, such as ^{92}Tc and ^{93g}Tc, even if their application in the Nuclear Medicine imaging field by PET, seems promising [68,75].

In the literature, several but non-systematic data are available, which describe either the nuclear cross-sections or the thin-target yields of Tc in targets of natural isotopic composition, in a sufficiently wide energy range [68,76-81]. The studies were mostly carried out with proton [69,70,81-88], deuteron [18,73], alpha [71,72,74,89,90], ^{3}He [68,91] and even ^{12}C beam[76] irradiation on either ^{93}Nb or enriched Mo targets, with the aim of investigating the nuclear properties of Tc radioisotopes and radioisomers and not for production purposes. In particular, alpha and helium-3 irradiations on ^{93}Nb are justified - from basic nuclear physics point of view - by the mono-isotopic composition of natural niobium.

Some papers were published on photonuclear reactions on ^{99g}Tc [92,93] and other reports deal with irradiation of ^{99g}Tc to produce Ru radionuclides, reporting data concerning also the production of ^{95,96,99m}Tc via side reactions [94]. Some authors investigated the (p,xn) reactions induced on metallic foils of Mo to study the nuclear level density through outgoing neutron spectra [95]. Comparetto and Qaim [96] irradiated natural Mo targets by helions in order to produce useful Ru radionuclides.

For production purposes, proton beams are normally preferred [97,98], due to the lower *stopping-power* and larger *range* than deuterons and helions, as calculated by either Tables [99,100] or Monte Carlo codes [101]. In any case the stopping-power and range values are calculated by the former Bethe-Bloch theory, after introduction of several corrections, as discussed by Friedlander pp. 211-221 [37], Krane pp. 193-196 [31], Knoll pp. 31-44 [102] and Ziegler [101,103]. The TRIM 95-01 code[101], in particular, allows the calculation of both longitudinal and lateral range and energy straggling of any energetic ion in different materials. As described in previous papers [14,15,97,98,104-107], the use of variable energy proton-cyclotron beams presents remarkable advantages to induce (p,xn) reactions on either natural or isotopically enriched targets with the aim of determining excitation functions and cross-sections. For this reason, we engaged in the experimental determination of the thin-target yields for the nuclear reactions ^{nat}Mo(p,xn)^{A}Tc [with A = 94, 95 and 96], where the ^{nat}Mo has the following “average” composition [36,60]: ^{92}Mo (14.84 %), ^{94}Mo (9.25 %), ^{95}Mo (15.92 %), ^{96}Mo (16.68 %), ^{97}Mo (9.55 %), ^{98}Mo (24.13 %) and ^{100}Mo (9.63 %). Production via irradiation of Mo is very advantageous due to the low cost of natural metallic molybdenum, its good thermal and electrical conductivity and its very high melting point (2623 °C) [59]. Some literature works comparable with the present one do exist, but were carried out with different aims: they report only some thick-target yield values at specific energies for wear studies [108], or consist of systematic studies, but in a lower energy range [69]. Besides the direct (p,xn) reactions, other side reactions that produce some Mo, Nb and Zr radionuclides occur in the ^{nat}Mo target, such as (p,pxn), (p,αxn) and (p,αdxn) depending on

the beam energy. The reactions that occur in ^{nat}Mo for the nuclides of interest are reported in Table 3, with their calculated Q values and energy thresholds (E_{th}).

TAB. 3: Principal direct nuclear reactions and charging, leading to the main radionuclides we are interested in, that occur in proton irradiated ^{nat}Mo and their calculated Q values and energy thresholds, E_{th} (mass defects from Browne 1986 [60]). ICB and OCB values are reported in the text. All the radionuclides cited are identified in the γ-spectra of this experiment, either at EOB or some time later (see Table 4).

radionuclide produced	main nuclear reactions and charging	**Q value** (MeV)	E_{th} (MeV)
^{93g}Tc 2.75 h	^{97}Mo(p,5n) ^{96}Mo(p,4n) ^{95}Mo(p,3n) ^{94}Mo(p,2n) ^{93m}Tc $\xrightarrow{\text{I.T.}}$	- 37.004 - 30.183 - 21.028 - 12.056	37.39 30.50 21.25 12.19
^{94g}Tc 4.883 h	^{98}Mo(p,5n) ^{97}Mo(p,4n) ^{96}Mo(p,3n) ^{95}Mo(p,2n) ^{94}Mo(p,n) ^{94m}Tc $\xrightarrow{\text{I.T.}}$	- 37.024 - 28.382 - 21.560 - 12.406 - 3.433 negligible (< 0.1 %)	37.41 28.68 21.79 12.54 3.47
^{95g}Tc 20.0 h	^{100}Mo(p,6n) ^{98}Mo(p,4n) ^{97}Mo(p,3n) ^{96}Mo(p,2n) ^{95}Mo(p,n) ^{95m}Tc $\xrightarrow{\text{I.T.}}$	- 41.307 - 27.092 - 18.449 - 11.627 - 2.474	41.72 27.37 18.64 11.75 2.50
^{95m}Tc 61 d IT 4 %	Mo(p,xn)	same values of ^{95g}Tc plus 0.0390 MeV	same values plus 0.0390 MeV
^{96g}Tc 4.28 d	^{100}Mo(p,5n) ^{98}Mo(p,3n) ^{97}Mo(p,2n) ^{96}Mo(p,n) ^{96m}Tc $\xrightarrow{\text{I.T.}}$	- 33.435 - 19.219 - 10.577 - 3.755	33.77 19.42 10.69 3.79
^{93m}Mo 6.85 h	^{98}Mo(p,p5n) ; (p,d4n) ^{97}Mo(p,p4n) ; (p,d3n) ^{96}Mo(p,p3n) ; (p,d2n) ^{95}Mo(p,p2n) ; (p,dn) ^{94}Mo(p,pn) ; (p,d)	- 44.864 ; -42.639* - 35.449 ; -33.224* - 28.627 ; -26.403* - 19.473 ; -17.248* -10.500 ; -8.276*	45.33 ; 43.08* 35.82 ; 33.57* 28.93 ; 26.68* 19.68 ; 17.43* 10.61 ; 8.36*

^{99}Mo 2.7477 d	^{100}Mo(p,pn) ; (p,d)	- 8.290 ; - 6.511*	8.37 ; 6.58*
^{90}Nb 14.60 h	^{95}Mo(p,2p4n) ; (p,α2n) ^{94}Mo(p,2p3n) ; (p,αn) ^{92}Mo(p,2pn) ; (p,dp) ^{90m}Nb $\xrightarrow{\text{I.T.}}$ ^{90}Mo $\xrightarrow{\text{E.C., }\beta^+}$	- 44.625 ; - 16.329* - 35.652 ; -7.482* - 19.509 ; -17.284*	45.10 ; 16.50* 37.66 ; 7.56* 19.72 ; -17.47*
^{91m}Nb 62 d IT 95 %	^{96}Mo(p,2p4n) ; (p,α2n) ^{95}Mo(p,2p3n) ; (p,αn) ^{94}Mo(p,2p2n) ; (p,α)	- 41.833 ; - 13.537* - 32.678 ; -4.382* - 23.706 ; + 4.59*	42.27 ; 13.68* 33.03 ; 4.43* 23.96 ; 0*#
^{95g}Nb 34.97 d	^{100}Mo(p,2p4n) ; (p,α2n) ^{98}Mo(p,2p2n) ; (p,α) ^{97}Mo(p,2pn) ; (p,dp) ^{95m}Nb $\xrightarrow{\text{I.T.}}$ ^{95}Zr $\xrightarrow{\beta^-}$	- 38.741 ; - 10.382* - 4.525 ; + 3.771* - 15.883 ; -13.658*	39.13 ; 10.55* 24.78. ; 0*# 16.05 ; 13.80*
^{95m}Nb 3.61 d IT 97.5 %	^{100}Mo(p,2p4n) ; (p,α2n) ^{98}Mo(p,2p2n) ; (p,α) ^{97}Mo(p,2pn) ; (p,dp)	same values of ^{95g}Tc plus 0.2361 MeV	same values plus 0.2361 MeV
^{96}Nb 23.35 h	^{100}Mo(p,2p3n) ; (p,αn) ^{98}Mo(p,2pn) ; (p,dp)	- 32.084 ; - 3.788* - 17.869 ; - 15.644*	32.41 ; 3.83* 18.05 ; 15.81*
^{88}Zr 83.4 d	^{92}Mo(p,3p2n) ; (p,αp)	- 33.903 ; - 6.019*	34.27 ; 6.09*
^{89g}Zr 3.268 d	^{94}Mo(p,3p3n) ; (p,αd) ^{92}Mo(p,3pn) ^{89m}Zr $\xrightarrow{\text{I.T.}}$ ^{89}Nb $\longrightarrow$	- 40.731; - 10.211* - 24.588	41.168 ; 10.32* 24.86*
^{87g}Y 3.346 d	^{92}Mo(p,4p2n) ; (p,α2p)	- 41.804; - 13.508*	42.23; 13.66*
^{87m}Y 12.9 h IT 98.4 %	^{92}Mo(p,4p2n) ; (p,α2p) ^{87m}Zr $\xrightarrow{\text{I.T.}}$ ^{87}Zr $\longrightarrow$	same values of ^{87g}Y plus 0.3820 MeV	42.65; 14.04*
^{88}Y 106.61 d	^{92}Mo(p,4pn) ^{88}Zr $\longrightarrow$	- 32.452	32.81*

* in case of cluster emission, like: α, d , ^{3}He and ^{3}T, instead of single nucleons, the corresponding binding energy must be substracted by calculated Q values (see text).
# exoergic nuclear reactions (see text).

The energy thresholds for protons **p** on a target **T** and Incoming particle Coulomb Barrier (ICB) are calculated with kinematics in the laboratory system (Lieser pp. 130-131[35)], Friedlander pp. 112-114 [37)] and Ehmann pp. 87-90 [32)]), by the mass defects from Browne [60)]

and the eqs. (1 and 2), in which the charges Z are adimensional, nuclear radii are approximated as $\approx 1.4\ A^{1/3}\ 10^{-15}$ m and $e^2 = 1.44\ 10^{-15}$ m MeV (let us remember that 1 fm = 10^{-15} m and 1 barn = 10^{-28} m^2):

$$E_{th} = |Q|\ (M_p + M_T) / M_T \qquad [MeV] \qquad (1)$$

$$ICB \approx (1.44/1.4)[(M_p + M_T) / M_T]\ Z_p\ Z_T / (A_p^{1/3} + A_T^{1/3}) \qquad [MeV] \qquad (2)$$

In case of (p,xn) reactions, the ICB values varies in the range 7.92 MeV (^{92}Mo) to 7.73 (^{100}Mo) MeV, thus their value are larger than some (p,n) reaction thresholds (Table 3), nevertheless - as happens in most similar cases - our experimental data show that “under barrier” (p,n) reaction cross-sections are not negligible, by tunnelling phenomena (see next sections and results on experimental thin-target excitation functions). In case of production of metastable nuclides, the energy of metastable level must be added to calculated *Q* value.

Moreover, the calculated *Q* values of some (p,xpyn) nuclear reactions are reported also, even if in practice only (p,αxn), (p,dxn) and (p,αdxn) reactions are expected, whose thresholds values are lower of a factor equal to the binding energy of the emitted cluster (i.e: mainly, α, d, ^{3}He and ^{3}T).

Direct nuclear reaction cross-sections with emission of more than 3 protons, leading to direct yttrium radionuclides production, must be considered as negligible in this energy range, even if they are allowed from energetic point of view. Finally, in case of cluster emission, the Coulomb Barrier of the Outgoing particle (OCB) must be added to the calculated E_{th} values. The OCB is calculated by an equation similar to eq. (2), in which both masses, charges and mass numbers of reaction products must be used, even if for energies larger than the threshold value the nuclear reaction is allowed by Coulomb Barrier tunnelling [37,109,110]. In case of (p,αxn) reactions the OCB values ranges between 14.24 MeV (^{96}Nb) to 14.52 MeV (^{90}Nb).

In order to minimise spectral interferences for a particular isotope from the wide number of radionuclides produced, it is important to choose the most useful γ-emissions and optimum waiting times from the End Of Bombardment (EOB), before making the high resolution HPGe γ-spectrometry measurement. Another important factor to evaluate is the elapsed time between the EOB and the End Of the radioChemical Processing (EOCP), since the natural decay could either avoid some separation steps or require additional purification step, depending upon the particular circumstances (see next section on radiochemistry).

3 THEORY: THIN-TARGET YIELD AND “EFFECTIVE” CROSS-SECTIONS

Thin-target yield calculations were carried out definition of eq.(3), giving the *thin-target yield, y(E,0)* as a function of projectile energy E, at the End Of an Instantaneous Bombardment (EOIB), $y(E)_{EOIB}$, that is the *slope at the origin of the growing curve* of the activity per unit current (A/I) of a radionuclide vs. irradiation time, for a target in which the energy loss is negligible in respect to the projectile energy [97,98,107]. In practice, *y(E)* is

defined from eq. (3), as the second derivative of (A/I) in respect to particle energy and irradiation time, calculated when the irradiation time τ tends to zero (i.e: EOIB):

$$y(E) = y(E)_{EIOB} = y(E,0) = \left(\frac{\partial(\partial[A/I]}{\partial E \partial \tau} \right) \quad \text{with } \tau \to 0 \qquad (3)$$

Experimentally, the function $y(E)_{EOIB}$ is calculated by the eq. (4), that holds for a radionuclide produced by direct nuclear reaction only, without any decay charging and for very low dead counting times (i.e: $LT \cong RT$, $DT \to 0$):

$$y(E)_{EIOB} = \frac{C_\gamma}{(\varepsilon_\gamma \alpha_\gamma LT)\ Q\ \Delta E}\ D(RT)\ G(\tau)\ e^{\lambda\ WT} \qquad \text{[Bq/C MeV]} \qquad (4)$$

where: A = N λ = radionuclide activity (Bq), N = number of radioactive atoms, I = beam current (A), Q = integrated proton charge (C) (obtained either from Faraday cup read-out or beam monitor reactions), C_γ = net photo-peak counts at energy E_γ above background continuum, α_γ = γ-emission absolute intensity, ε_γ = experimental efficiency at the γ-energy considered, $\lambda = \ln 2/T_{1/2}$ = decay constant (s^{-1}), *LT* = Live counting Time (s), *DT* = Dead counting Time (s), *RT* = Real counting Time (s) = LT + DT, *WT* = Waiting Time from the EOB (s), τ = Irradiation Time (s), ΔE = beam energy loss in the target (MeV) and the non dimensional quantities *D(RT)* = decay factor to correct decay during counting time and *G(τ)* = growing factor to correct decay during irradiation, are defined as:

$$D(RT) = \frac{\lambda\, RT}{1 - e^{-\lambda\, RT}} \qquad (5) \qquad\qquad G(\tau) = \frac{\lambda\, \tau}{1 - e^{-\lambda\, \tau}} \qquad (6)$$

Eq. (4) can be deduced from the eq. (7), that defines the thin-target yield *y(E)* at the energy E:

$$y(E) = \frac{\sigma^*(E)\ N_A\ \lambda}{a.m.\ Ze \left(\frac{dE}{dS(E)} \right)} \qquad \text{[Bq/MeV]} \qquad (7)$$

where: a.m. = target atomic mass (g/mol), N_A = Avogadro's Number = $6.022045(31)\cdot 10^{23}$ (atms/mol), E = <E> = “average” proton beam energy in the “thin” target (MeV), σ*(E) = "effective", or "weighed" (as explained below) reaction cross-section (cm^2/part), dE/dS = massic stopping-power (MeV/g/cm^2), e^- = electron charge = $1.6022\cdot 10^{-19}$ C, Z = atomic number of the projectile, S = massic thin-target thickness (g/ cm^2).

In practice, the approximation ΔE ≈ S (dE/dS) was considered too crude for an accurate energy loss evaluation to be used in eq. (4), thus ΔE was calculated by the difference of ranges of incoming and outgoing particle in the target from fitted proton range tables from Williamson [99].

The “effective” cross-section $\sigma^*(E)$ as a function of projectile energy is defined by eq. (7 and 8) even if, as stated in other papers [97,107], the physical meaning of this parameter is poor, being only a raw summation of the several cross-sections $\sigma_i(E)$ of the *reaction channels* concerned, weighted on target isotopic composition (w_i and $\Sigma w_i = 1$), as obtained by the definition (8):

$$\sigma^*(E) = \sum_i w_i \, \sigma_i(E) \qquad (8)$$

4 EXPERIMENTAL: THIN-TARGET YIELDS AND CROSS-SECTIONS FOR $^{94g,95g,95m,96(m+g)}$Tc RADIONUCLIDE PRODUCTION

Thus, in order to study the experimental behavior of the excitation functions for Tc radionuclides already cited, it was necessary to irradiate "thin" molybdenum targets of uniform thickness, in which the proton energy loss was of the order of about 100 keV (data calculated by Williamson [99]). By several tens measurements with a μ-meter made in different points of a high purity metallic Mo foils (Goodfellow Metals, UK), the thickness uniformity determined was of 30.1 μm ± 1.4%, thus a 30.9 mg/cm^2 ± 1.4 % massic thickness - measured by accurate weighting – was used for energy loss calculation. Each target was irradiated with the external proton beam of the former AVF (Azimutally Variable Field) Cyclotron of the University of Milano, using the “single target” activation technique at different proton energies [104]. The AVF cyclotron we used, was a negative ions (H^-) machine, with a thin Al stripping foil extraction system. The targets were all set in the same geometric configuration, with a beam current of about 100 nA and an integrated charge varying from 200 to 400 μC, measured with an error smaller than 1-2 % by a long shaped Faraday cup, connected to a charge integrator (EG&G, Ortec, USA). The beam intensity was checked by the $^{12}C(p,n)^{11}C$ monitor reaction also [104,111], obtaining similar results within the 3 %. The maximum extracted beam energy was 45 MeV ± 0.2 MeV; with an *intrinsic energy spread* of ± 0.05 MeV. A 25 μm thick tantalum window was used to separate the beam line from irradiation chamber, that was irradiated under pump vacuum The beam energy was set from 44 to 5 MeV, at about 2.5 MeV intervals. Calibrated (by weighting) aluminum absorbers were used to set the energy [99], where the desired value was lower than 18 MeV (that was the minimum extracted beam energy by the stripping foil probe). The beam energy was calibrated from 18 to 45 MeV with a ± 0.2 MeV accuracy, by a 4 m long analysing magnet and a calibrated internal beam probe, while the *energy straggling* due to the Al absorbers, for energies lower than 18 MeV, was evaluated by the TRIM-95-01 code [101] and was of the order of 1.5 MeV at the lower energies. The gamma-ray emissions were measured by 50 cm^3 coaxial Ge(Li) and HPGe detectors (EG&G, Ortec, USA) connected to a MCA (Canberra, Series 80, USA); the system was calibrated for both energy and efficiency with a ^{226}Ra (at secular equilibrium) gamma source (Amersham, UK) of 0.148 MBq ± 1.5% certified at feb/04/1969, whose emission intensities are taken from Reus and Westmeier [112]. The specific γ-emissions and intensities [60] and the optimum waiting times after the EOB used to

determine the activity of each radionuclide are reported in Table 4. The decay of the different radionuclides was followed for *not less than three half-lives* (one year for the longer half-living radionuclides) and the times of measurement were chosen for each radionuclide so that the statistical error on the photo-peak area was always of the order of less than 0.1-1%. Cases requiring radioactive decay equilibrium considerations (A= 95 and 96), were corrected using the equations of the radioactive chains (Friedlander pp. 191-199 [37], Krane pp. 169-173 [31]).

TAB. 4: Half-life, γ-emissions [60] and optimal waiting times after the EOB for determination of the radionuclides produced in the proton irradiated ^{nat}Mo target.

radionuclide	$T_{1/2}$	γ-line used (keV) and intensity (%)	waiting time after the EOB
^{96g}Tc	4.28 d	849.89 (98)	3 d
^{95m}Tc	61 d	582.062 (31.4)	40 - 60 d
^{95g}Tc	20.0 h	1073.713 (3.7)	1 d
^{94g}Tc	4.883 h	702.630 (99.6)	< 2 h
^{99}Mo	2.7477 d	739.508 (12.14)	6 d
^{95g}Nb	34.97 d	765.789 (99.8)	60 d
^{92m}Nb	10.15 d	934.53 (99.0)	2 d
^{88}Zr	83.4 d	392.9 (97.30)	60 d
^{88}Y$_D$	106.61 d	898.06 (92.7) 1836.077 (99.35)	60 d
^{87g}Y$_D$	3.346 d	484.90 (92.2)	2 d
^{87m}Y$_D$	12.9 h	381.4 (78.05)	

[D] yttrium radionuclides are not produce by direct nuclear reactions, but only via zirconium radionuclides decay after the EOB (see Table 3).

Regarding the radioisomers ^{94g}Tc and ^{94m}Tc, the Isomeric Transition between the metastable and ground state levels is considered either negligible [36,60,112,113] or less than 0.1% [50,59], thus no decay equilibrium correction was required for ^{94g}Tc curve, while ^{94m}Tc yield was not measured. However, for the identification of ^{94g}Tc, it was necessary to follow the decay of the γ-emission at 702.630, since the gamma ray at 871.097 keV is shared with the metastable state. The experimental and bibliography half-lives [50,60,59] agreed within 0.1-0.9 % for all the radionuclides, except that of ^{95g}Tc (the disagreement was less than 1.5 %), as shown in Table 5. In practice, our experimental half-lives were used for the weighted regression fitting of the data.

TAB. 5: Δ% between our experimental and bibliography half-life for Tc radionuclides concerned. The best agreement amongst experimental data and database half-lives is with Reus, Browne and Firestone.

Radio-nuclide	Experimental half-life and σ	Reus [113]	Browne [60]	Pfenning [36]	Firestone [59]
^{96g}Tc	4.24 ± 0.08 d	4.28 d (-0.935)	4.28 d (-0.935)	4.3 d (-1.415)	4.28 d (-0.935)
^{95m}Tc	61.3 ± 0.5 d	61 d (0.491)	61.0 d (0.491)	60 d (2.121)	61 d (0.491)
^{95g}Tc	19.7 ± 0.7 h	20.0 h (-1.500)	20.0 h (-1.500)	20 h (-1.500)	20.0 h (-1.500)
^{94g}Tc	4.89 ± 0.05 h	4.88 h (0.205)	4.883 h (0.143)	4.9 h (-0.205)	293 min (0.136)

The cumulative statistical errors on each thin-target yield data due to errors on photo-peak areas, decay constants, target thickness, integrated charge and detector efficiency, were smaller than a few percent and are summarised in Table 6 and then reported in Tables 7 and 8. Systematic errors related to both stopping-power calculations [99] and absolute γ-emission intensities [60] were not considered. We carried out the high-resolution gamma-spectrometry measurements in geometrical conditions (not less than 20-25 cm distance from the detector), suitable to minimise any counting loss due to both counting dead time and random pile-up corrections (Debertin [114], Knoll, pp. 387-443 [102] and Gilmore [115]). In the case of ^{94g}Tc, the dead time (*DT*) was of the order of 5%, which is acceptable for an accurate correction, by commercial electronics (EG&G, mod. 572 spectroscopy amplifier), without use of constant frequency pulse generator correction method.

The experimental thin-target yields are reported in Table 7; while Fig. 1 shows the thin-target excitation functions for $^{94g,95g,95m,96(g+m)}$Tc radionuclides vs. the “average” proton energy in the thin-target, together with the weighed fitting function used for the following calculations. In case of ^{96}Tc the cumulative yield of both metastable and ground levels is reported. Table 8 gives the "effective" cross-sections σ*, defined by eq. (8). The thin-target yield data of Table 7, were numerically fitted using a commercial PC computer code (Table Curve for Windows, Jandel Sci., FRG), taking into account the overall statistical errors (1 standard deviation) as weights. All nuclear reactions considered are endoenergetic, with negative *Q* values, thus the calculated energy threshold for the different reactions (Table 3) were also taken into account, imposing a *yield value equal to zero* in the fitting equation. The fitting parameters are summarised in Table 9. The *isomeric ratio* of the fitted polynomials of the excitation functions of ^{95m}Tc and ^{95g}Tc are plotted in Fig. 2 as a function of proton energy.

TAB. 6: Typical Statistical Error Range (1 standard deviation) considered in excitation function calculation. The systematic errors on decay intensities (α) and stopping power values are not valuable and thus are not included.

counting statistics $C \pm \sigma$ %	target thickness $S \pm \sigma$ %	efficiency calibration $\varepsilon \pm \sigma$ %	integrated charge $Q \pm \sigma$ %	half-Life $t_{1/2} \pm \sigma$ %	OVERALL ERROR $X \pm \sigma$ %
0.1-1 %	± 1.5 %	± 1.5 %	± 1-2 %	See Table 5	Tables 7, 8

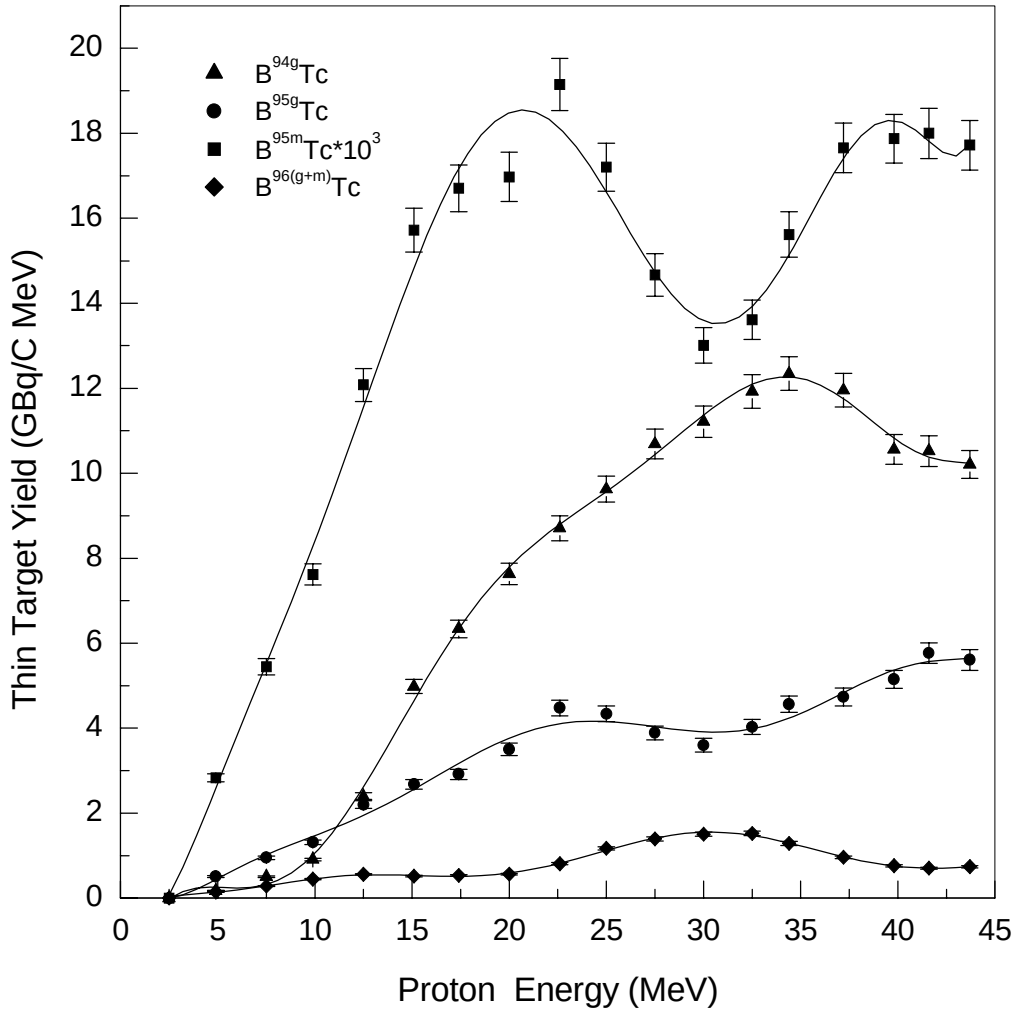

FIG. 1:.Thin-target excitation functions for the ^{nat}Mo(p,xn)^{94g}Tc, ^{95g}Tc, ^{95m}Tc and $^{96(m+g)}$Tc nuclear reactions. The yield of ^{95m}Tc is multiplied by a factor 1000.

TAB 7: Thin-target yields for ^{94g}Tc, ^{95g}Tc, ^{95m}Tc and $^{96(g+m)}$Tc production via (p,xn) reactions on Mo targets of natural isotopic composition. The energy straggling for energies lower than 18 MeV is calculated by the TRIM 95-01 code [101] .

"average" proton energy (MeV) a)	thin-target yield (MBq/C MeV) for ^{94g}Tc	thin-target yield (MBq/C MeV) for ^{95m}Tc	thin-target yield (MBq/C MeV) for ^{95g}Tc	thin-target yield (MBq/C MeV) for $^{96(g+m)}$Tc b)
4.9 ± 1.5	174.9 ± 6.3	2.84 ± 0.09	506.8 ± 21.3	146.4 ± 5.0
7.5 ± 1.1	504.8 ± 18.7	5.44 ± 0.19	951.8 ± 39.0	283.5 ± 9.6
9.9 ± 0.8	908.7 ± 30.9	7.62 ± 0.25	1312.2 ± 55.1	449.5 ± 15.3
12.5 ± 0.5	2399.0 ± 79.2	12.08 ± 0.39	2200.1 ± 90.2	559.4.8 ± 19.0
15.1 ± 0.3	4982.7 ± 164.4	15.72 ± 0.52	2678.7 ± 109.8	517.4 ± 17.6
17.4 ± 0.2	6338.2 ± 209.2	16.71 ± 0.55	2913.8 ± 119.5	534.0 ± 18.1
20.0 ± 0.2	7632.9 ± 251.9	16.97 ± 0.58	3501.7 ± 147.1	563.8 ± 19.2
22.6 ± 0.2	8707.1 ± 296.0	19.15 ± 0.61	4478.1 ± 183.6	813.4 ± 26.8
25.0 ± 0.2	627.5 ± 308.1	17.20 ± 0.57	4340.8 ± 186.6	1170.0 ± 38.6
27.5 ± 0.2	10687.7 ± 352.7	14.67 ± 0.50	3888.6 ± 159.4	1395.9 ± 47.5
30.0 ± 0.2	11217.0 ± 370.2	13.01 ± 0.42	3601.2 ± 162.0	1505.8 ± 48.2
32.5 ± 0.2	11926.5 ± 393.6	13.61 ± 0.46	4030.7 ± 173.3	1523.8 ± 50.3
34.4 ± 0.2	12344.9 ± 395.0	15.62 ± 0.53	4564.4 ± 196.3	1289.8 ± 46.4
37.2 ± 0.2	11955.2 ± 394.5	17.66 ± 0.58	4735.6 ± 213.1	960.2 ± 31.7
39.8 ± 0.2	10560.1 ± 348.5	17.88 ± 0.57	5149.5 ± 211.1	761.7 ± 25.9
41.6 ± 0.2	10521.3 ± 357.7	18.00 ± 0.59	5767.1 ± 242.2	705.5 ± 23.3
43.7 ± 0.2	10208.7 ± 326.7	17.72 ± 0.58	5607.0 ± 246.7	738.1 ± 25.1

a) Mean value between the incident beam energy and the outgoing beam energy (calculated using range and stopping-power tables by Williamson [99] that differ because of the small beam energy loss in the target.

b) These values include the contribution due to the ^{96m}Tc charging.

TAB 8: "Effective" reaction cross-sections for ^{94g}Tc, ^{95m}Tc, ^{95g}Tc and $^{96(g+m)}$Tc production via (p,xn) reactions on Mo targets of natural isotopic composition.

proton energy MeV a) (see text)	cross-section x 10^{-27} cm^2 for ^{94g}Tc	cross-section x 10^{-27} cm^2 for ^{95m}Tc	cross-section x 10^{-27} cm^2 for ^{95g}Tc	cross-section x 10^{-27} cm^2 for $^{96(g+m)}$Tc b)
4.9 ± 1.5	4.2 ± 0.15	20.6 ± 0.7	50.3 ± 2.1	74.6 ± 2.5
7.5 ± 1.1	9.2 ± 0.4	29.7 ± 1.0	70.9 ± 2.9	108.4 ± 3.7
9.9 ± 0.8	13.6 ± 0.5	34.3 ± 1.1	80.8 ± 3.4	142.1 ± 4.8
12.5 ± 0.5	31.5 ± 1.0	47.5 ± 1.5	118.2 ± 4.8	154.4 ± 5.2
15.1 ± 0.3	57.8 ± 1.9	54.7 ± 1.8	127.3 ± 5.2	126.3 ± 4.3
17.4 ± 0.2	66.7 ± 2.2	52.7 ± 1.7	125.6 ± 5.1	118.2 ± 4.0
20.0 ± 0.2	72.8 ± 2.4	48.6 ± 1.6	136.9 ± 5.7	113.2 ± 3.8
22.6 ± 0.2	76.0 ± 2.6	50.2 ± 1.6	160.3 ± 6.6	149.5 ± 4.9
25.0 ± 0.2	78.1 ± 2.5	41.9 ± 1.4	144.3 ± 6.2	199.8 ± 6.6
27.5 ± 0.2	80.8 ± 2.7	33.3 ± 1.1	120.5 ± 4.9	222.2 ± 7.6
30.0 ± 0.2	79.5 ± 2.6	27.7 ± 0.9	104.6 ± 4.7	224.7 ± 7.2
32.5 ± 0.2	79.6 ± 2.6	27.3 ± 0.9	110.3 ± 4.7	214.1 ± 7.1
34.4 ± 0.2	79.0 ± 2.5	30.0 ± 1.0	119.7 ± 5.1	173.8 ± 6.3
37.2 ± 0.2	72.1 ± 2.4	32.0 ± 1.1	117.1 ± 5.3	122.0. ± 4.0
39.8 ± 0.2	60.6 ± 2.0	30.8 ± 1.0	121.1 ± 5.0	92.0 ± 3.1
41.6 ± 0.2	58.4 ± 2.0	30.0 ± 1.0	131.2 ± 5.5	82.4 ± 2.7
43.7 ± 0.2	54.6 ± 1.7	28.4 ±0.9	122.9 ± 5.4	83.1 ± 2.8

a) Mean value between the incident beam energy and the outgoing beam energy (calculated using range and stopping-power tables by Williamson [99], which differ because of the small beam energy loss in the target.

b) These values include the contribution due to the ^{96m}Tc charging.

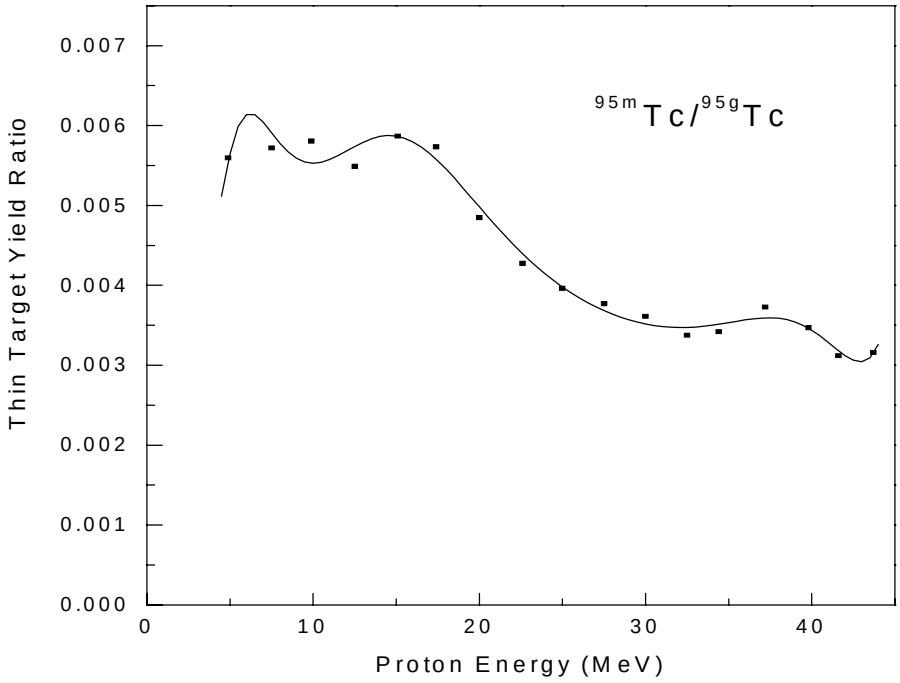

FIG. 2: Calculated ratio (arbitrary units x 1000) between the metastable and ground levels of ^{95}Tc, obtained by direct (p,xn) reactions. The fitted values of thin-target yields have been used for plotting the graph.

5 THICK-TARGET YIELD CALCULATION

The Thick-Target Yield *Y(E,ΔE)* is defined, as a two parameter function of *incident particle energy* E(MeV) on the target and *energy loss* in the target itself ΔE (MeV), by the eq. (9), that holds in the approximation of a *monochromatic beam* of energy E, *not affected by either intrinsic energy spread or straggling* :

$$Y(E,\Delta E) = \int_{E-\Delta E}^{E} y(x)\,dx \qquad (9)$$

in which, the integrand *y(x)* represents the thin-target excitation functions of eq. (4 and 7). In case of total particle energy absorption in the target (i.e: energy loss ΔE = E), the function *Y(E,ΔE)* reaches a value *Y(E,E-E_{th})*, for ΔE = E-E_{th}, that represents mathematically the *envelope* of the *Y(E,ΔE) family of curves*. This *envelope* is a *monotonically increasing* curve, never reaching either a maximum or a saturation value, even if its slope becomes negligible

for high particle energies and energy losses. Eq. (9) states obviously that the production yield of a thick-target does not increase further, if the residual energy in the target is lower then the nuclear reaction energy threshold, E_{th}. In practice, the use of a target thickness larger than the "effective" value, is unsuitable from technological point of view, due to the larger power density P(watt/g) deposited by the beam in target material itself, instead of target cooling system [97,98,105-107,110,116-118].

TAB. 9: Optimized parameters of polynomials fittings and correlation factors for thin-target yields for the main technetium radionuclides.

	^{94g}Tc r^2=0.9988135779	^{95m}Tc r^2=0.9968617879	^{95g}Tc r^2=0.9941659025	$^{96(m+g)}Tc$ r^2=0.9988637258
a	-19123.6647	-4.52364506	-5613.03707	-5069.03959
b	10081.13158	2.066527070	5146.931967	3638.748163
c	-1937.14487	-0.069688875	-1836.74779	-1064.33089
d	164.9297820	-0.028320565	355.1544671	169.5378948
e	-4.65280532	0.0054969108	-40.5201804	-16.0118466
f	-0.18469382	-0.00038657082	2.892130861	0.941849928
g	0.017727184	$1.289531\ 10^{-5}$	-0.13214531	-0.035365775
h	-0.00054037336	$-2.0650195\ 10^{-7}$	0.0038514106	0.00084898582
i	$7.608057\ 10^{-6}$	$1.2803635\ 10^{-9}$	$-6.9125869\ 10^{-5}$	$-1.2643224\ 10^{-5}$
j	$-4.1738903\ 10^{-8}$		$6.9556974\ 10^{-7}$	$1.0678048\ 10^{-7}$
k			$-3.0014655\ 10^{-9}$	$-3.9245479\ 10^{-10}$

The analytical expressions of the yields from Table 9 were analytically and numerically integrated at 0.25 MeV intervals obtaining the families of curves reported in Figs. 3, 4, 5 and 6. In the same pictures, the first and second calculated loci of the maxima of thick-target yield are represented (the second maximum is present only in some cases). These maxima correspond to couples of optimised values (E,ΔE), having different values for each different radionuclides, as presented in previous papers [15,97,107,109,110,116,117].

In Table 10 are reported the fitting parameters of the loci of the maxima of the thick-target yields. This set of thick-target yields allows calculating the optimum irradiation conditions to have radiotracers with higher radionuclidic purity as possible.

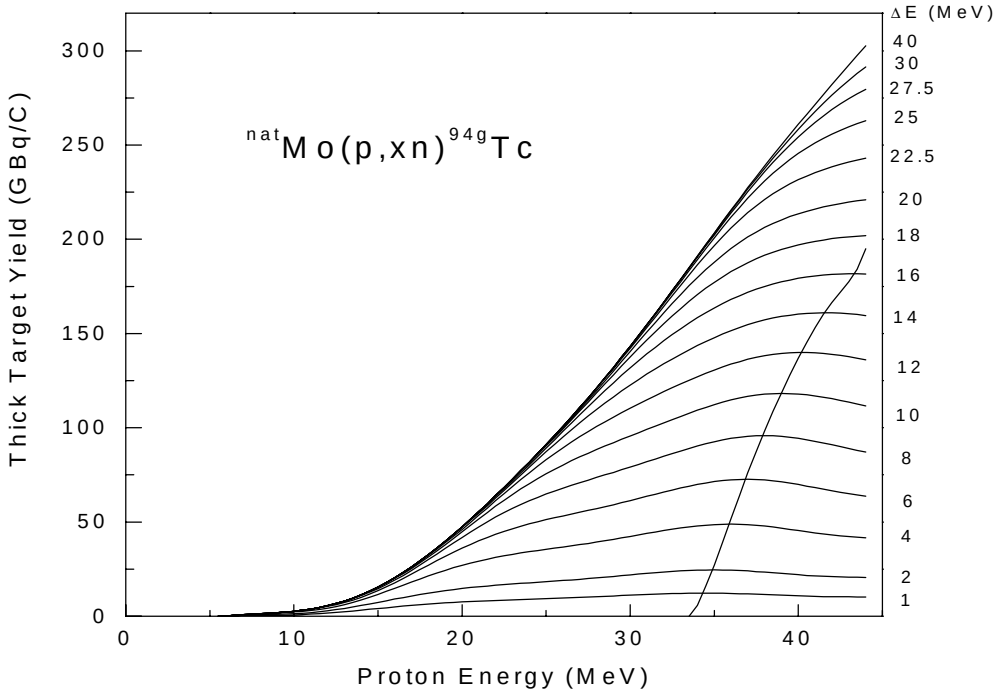

FIG. 3: Calculated TTY as a function of target thickness (in MeV) for ^{94g}Tc production.

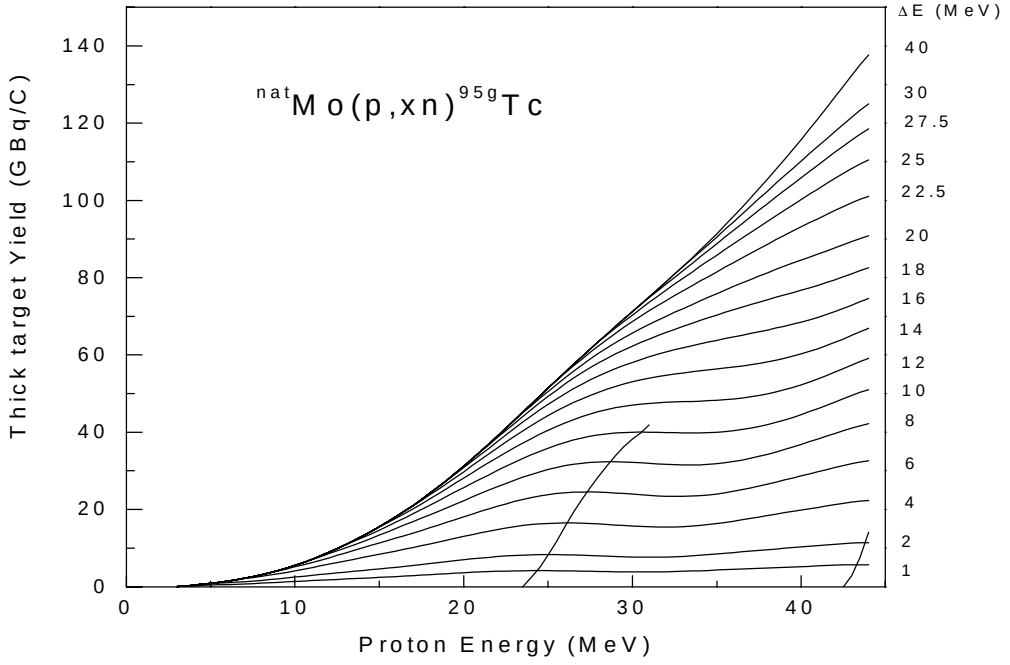

FIG. 4: Calculated TTY as a function of target thickness (in MeV) for ^{95g}Tc production.

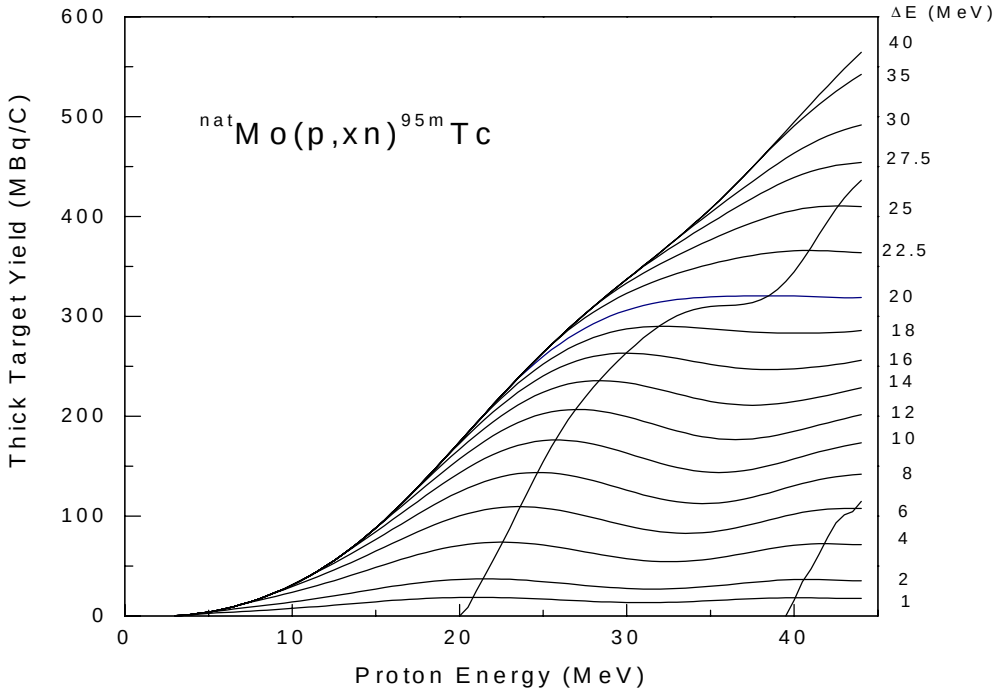

FIG. 5: Calculated TTY as a function of target thickness (in MeV) for ^{95m}Tc production.

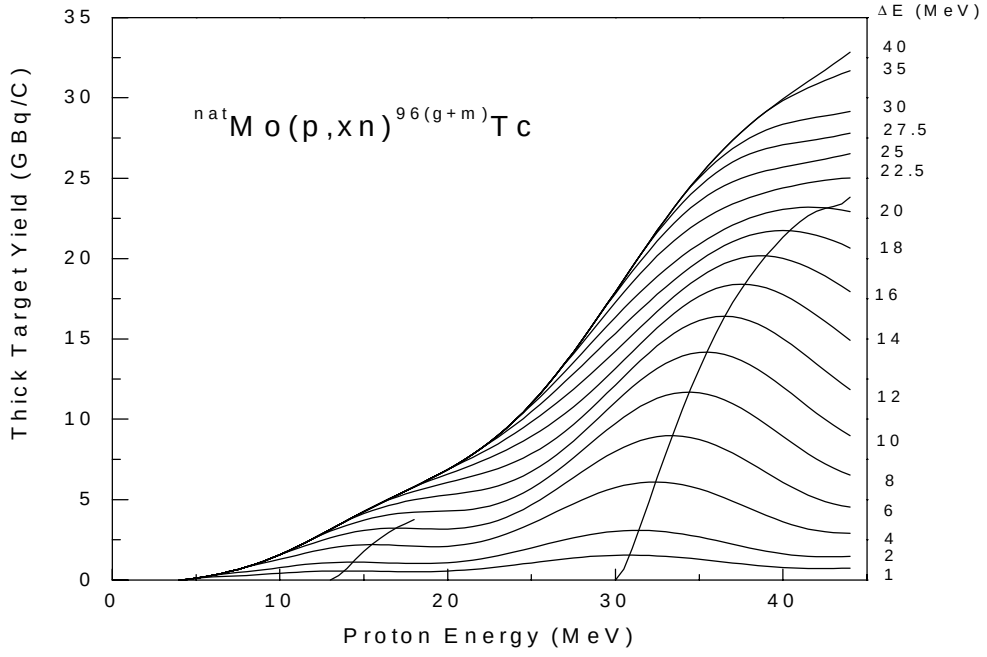

FIG. 6: Calculated TTY as a function of target thickness (in MeV) for $^{96(m+g)}$Tc production.

TAB 10: Optimized parameters of polynomial fittings and correlation factor for the “loci of the maxima” of TTY for the Tc radionuclides.

	^{94g}Tc		^{95m}Tc		^{95g}Tc		$^{96(m+g)}$Tc	
	1-st maximum r^2=0.997895704	2-nd maximum	1-st maximum r^2=0.998867011	2-nd maximum r^2=0.985990881	2-nd maximum r^2=0.996281404	1-st maximum r^2=0.765752393	1-st maximum r^2=0.998501225	2-nd maximum r^2=0.992568523
a	-4069551.9		-2897638.8	-28018834	-2376499.7	123814.6862	1317981.1	-363346.792
b	544329.7080		878938.2182	2081297.5	451063.4418	-2087.46149	-239990.266	157043.5836
c	-24805.1257		-117259.282	-35148.7522	-30769.2469	-74.7704155	17500.30365	-28247.4915
d	257.1175369		9029.307136	-637.843553	750.5718200	0.631898270	-607.812323	2678.437478
e	12.18325025		-442.259596	20.95883968	2.646638929	0.015784636	7.290826575	-135.783471
f	-0.28533154		14.29029956	-0.21387086	0.157870215		0.138854756	2.780832654
g	-0.0020671595		-0.30464016	0.0053232062	-0.038180858		-0.0041097231	0.048465120
h	$5.033506\ 10^{-5}$		0.004132055	$1.8425639*10^{-5}$	0.00091732913		$-3.9437016\ 10^{-5}$	-0.0034551726
i	$2.3500894\ 10^{-6}$		$-3.236184\ 10^{-5}$	$-4.5905191\ 10^{-6}$	$8.9968307\ 10^{-6}$		$2.6539685\ 10^{-6}$	$4.8499134\ 10^{-5}$
j	$-5.9760918\ 10^{-8}$		$1.115201\ 10^{-7}$	$6.8848369\ 10^{-8}$	$-5.6096474\ 10^{-7}$		$-3.6759004\ 10^{-8}$	
k	$3.8553406\ 10^{-10}$			$-2.588065\ 10^{-10}$	$5.4226147\ 10^{-9}$		$1.7507568\ 10^{-10}$	

7 RADIOCHEMISTRY FOR Tc/Mo/Nb/Zr/Y AND QUALITY CONTROLS

Several classical methods for technetium radiochemical processing are available from the literature (ex: Cotton and Wilkinson [24], Nesmeyanov, pp. 296-310 [23]). Most of them are based on the high volatility of technetium eptaoxide, Tc_2O_7, in both dry and wet chemistry.

We preferred to develop and use a different one, due to the very high specific activity of Tc radiotracers concerned and the necessity to have a radiochemical separation as fast as possible. The separation was carried out rigorously, without addition either of isotopic, isomorphous or iso-dimorphous carrier (i.e: in order of effectiveness - perrhenate > phosphate > perchlorate > periodate > tetrafluoborate and even molybdate itself anions) [77].

Elemental impurities, introduced by reagents during the separation procedures, were limited by use of ultra-high purity chemicals and teflon-PFA equipment, instead of glassware (Nalgene, Nalge Company, Rochester, Kent, UK), whereas the radioactive impurities, resulting from side reactions on chemical elements present in the metallic molybdenum target (Nb, W, etc.), were minimised by use of both extra-pure target materials (Goodfellow Metals, UK) and a highly efficient and selective radiochemical separation. Nevertheless, besides the Tc radionuclides, the irradiation of the Mo target with protons induces the direct and indirect (by charging) production of Mo, Nb and Zr radionuclides.

On the contrary, there was **no** experimental evidence of direct production of Y radionuclides, which could be identified in the γ-spectra, after only some time from the EOB, due to the $^{87}Zr \rightarrow {}^{87m}Y \rightarrow {}^{87g}Y$, $^{88}Zr \rightarrow {}^{88}Y$ and $^{89}Zr \rightarrow {}^{89m}Y$ chains [50,59,60]. Obviously, the very short-lived ^{89m}Y ($T_{1/2}$ = 16.06 s), was identified in the γ-spectra, but was present at secular equilibrium with its precursor only.

The irradiated thick metallic Mo target (about 500-1000 mg) was dissolved in the minimum volume of 7 M HNO_3. The bulk of poorly soluble precipitated molybdic acid (MoO_3•x hydrate) was filtered off and the residue Mo(VI) present in the solution was extracted several times with 0.25 M HDEHP (diethylhexylphosphoric acid) in mesitylene. In this step, Nb(V) and Zr(IV) radionuclides were co-extracted quantitatively in the organic phase, without any addition of carriers, as determined by HPGe γ-spectrometry.

The Y(III) radionuclides extraction, on the contrary, was not quantitative and non reproducible. The aqueous solution was then washed with isopropyl-ether to remove the HDEHP traces, evaporated to almost dry and the residue re-dissolved in physiological saline in order to obtain an appropriate pH (5-8) and a suitable radioactive concentration.

The present separation should be carried out immediately after the EOB and after a short irradiation only, in order to avoid the charging of Y radionuclides, otherwise, it is necessary to introduce after the EOCP a further purification step from Y, based on cationic ion exchange chromatography (Bio-Rad AG50Wx8, 100-200 mesh; Bio-Rad disposable plastic column, 7 x 20 mm) in diluted nitric medium. In the previous conditions Y(III) is retained, while TcO_4^- is eluted almost quantitatively.

The overall Tc radiochemical yield of this method is greater than 90 %, with the loss of Tc activity mainly due to the filtration step of molybdic acid. We suppose that technetium(VII,VI) oxidation states are co-precipitated isomorphously or iso-dimorphously as either TcO_4^- or TcO_4^{2-} anions, with molybdic acid itself; anyway any attempt to improve the

recovery of Tc activity by washing of precipitate led to a non tolerable elution of molybdenum. Activity concentrations of GBq/ml were obtained for both ^{95m,g}Tc and ^{96g}Tc.

Further quality control tests are needed just before the radiotracer biological application, because physico-chemical changes could happen after the radiochemical separation [13-15,109,120,121]. The ultra-low concentration of Tc radionuclides, that are in a Nearly Carrier Free condition, can be greatly influenced by the presence of impurities that could induce Tc oxidation state changes, such as pH, ionizing radiation fields and other purity parameters that tend to spoil with time [18,30,120,122].

Quality control tests of the radiotracer were carried out, in order to verify its chemical, radiochemical and radionuclides purities [14,15,109,120,122]. The overall decontamination factor from the Mo target was of the order of 10^6, as determined by INAA via both ^{93m}Mo (and ^{99}Mo), GF-AAS and ICP-OES.

The Tc was eluted quantitatively as pertechnetate anion by a cation exchange column (Bio-Rad AG50Wx8, 100-200 mesh) and its radiochemical purity, that was furtherly tested by ascending paper and TL radiochromatography (Berthold radi-scanner, with flowing Ar/methane Geiger-Mueller detector, Switzerland) with acetone as eluent in NaCl medium (developing length 10-15 cm), was greater than 99% at the EOCP. Further tests were carried out, by cutting the chromatographic paper in slices 0.5 cm wide.

No other radionuclides were identified in the various radiochromatographic slices other than those of Tc, either by γ-spectrometry, or liquid scintillation counting (Beckman, USA, mod. LS500TD). After a proper cooling time, the radionuclidic purity of $^{95m+96g}$Tc was close to 100%, apart the ^{97m}Tc and other long-lived radionuclides of Tc (^{97g}Tc, ^{98}Tc and ^{99g}Tc), whose content was not quantified.

Obviously, the NCA $^{95m+96g}$Tc radiotracers are not in a real Carrier Free condition, due to the long-lived Tc radio-nuclides ^{97g,97m,98,99g}Tc, that are produced by other (p,xn) reactions, with similar cross-sections. We guess, from the calculation of the “average” cross-sections for Mo(p,xn) reactions, that a dilution factor not larger than 10-100 was obtained. The quality assurance results are summarized in Table 11.

8 CONCLUSIONS

The possibility of producing medium-lived and high-purity Tc (Ma) radionuclides, such as $^{94g,95(m+g),96g}$Tc, by irradiation of natural molybdenum with proton beams, has been investigated in this paper. The Tc radiotracer was obtained in NCA form, without addition either of isotopic, isomorphous or iso-dimorphous carrier, with a specific activity that is close to the theoretical CF one, with an IDF of 10-100. With regard to ^{95m}Tc, the experimental thin-target yield curve and “effective” cross-sections for ^{nat}Mo(p,xn)^{95m}Tc reactions shows a dependence on the proton energy in the range 10-45 MeV. Nevertheless, a typical irradiation of a 20 MeV thick molybdenum target (i.e: either 40 → 20 MeV or 35 → 15 MeV) led to a thick-target yield of about 310 MBq/C (i.e: 30 μCi/μAh), that means to obtain 333 MBq (i.e: 9 mCi) of ^{95m}Tc at the End Of a 10 hour bombardment, with a 30 μA proton beam. In the case of $^{96(m+g)}$Tc, on the contrary, the thin-target excitation function presents a well-shaped

maximum of 1.54 GBq/C MeV (i.e: 0.15 mCi/μAh MeV) at 32.5 MeV. Large activities of this radionuclide could be produced, even using a low beam intensity, in the 35 → 25 MeV energy range (i.e: 14.3 GBq/C or 1.4 mCi/μAh thick-target yield).

TAB. 11: Quality control test made on the NCA $^{95m+96g}$Tc radiotracers for environmental metallo-biochemical experiments.

Purity parameter	Radioanalytical Technique	Results
Chemical purity	INAA , ICP-AES, and GF-AAS HPGe γ-spectrometry	Decontamination factor: from Mo > 10^6 from Nb, Zr , Y > 99.9%
Specific Activity Isotopic Dilution Factor	calculation	not determined 10-100
Radiochemical purity	Paper and TLC radiochromatography	TcO_4^- > 99% (in NaCl) eluent acetone
Radionuclidic purity	HPGe γ-spectrometry	^{95m}Tc + ^{96g}Tc > 99% (after the proper waiting time)
Biological Purity	medium pH meter autoclaving not verified	NaCl 0.9 % pH = 5-8 steryle pyrogens ???
Activity Concentration		37-370 MBq/ml

The radiochemical separation adopted to decontaminate the radiotracer from Mo, Nb and Zr (and Y) radionuclides proved highly selective and efficient, so that the $^{95m+96g}$Tc radiotracer obtained could be used for metallo-biochemical studies on either rats or cell cultures. At the JRC-Ispra of the European Community, some preliminary experiments were carried out on nine male Sprague-Dawley rats in order to determine the Tc distribution in the organs at low doses and to study its elimination by excretion.

After 4 hours from administration, the radioisotope was mainly present in the stomach, the kidney, the liver and the lung. Moreover the concentration of dose was higher if the animals had not been fed before being sacrificed. From the third group the biological half-life was deduced, and proved to be very short in animals (1-2 days). A fast elimination of the Tc during the first 2 days after the administration was observed, reaching about 60 % in the faeces and 45 % in the urine after 15 days [12)] and Table 12.

TAB. 12: Percentage dose per gram of organ (% dose/g) in the three groups of rats.
In bold are the organs with the largest uptake.

Compartment	First group	Second group	Third group
Brain tissue	0.031 ± 0.017	0.017 ± 0.012	0.0008 ± 0.0005
Lung	0.235 ± 0.012	0.099 ± 0.016	0.0017 ± 0.0009
Thymus	0.094 ± 0.010	0.046 ± 0.009	0.0003 ± 0.0001
Heart	0.102 ± 0.033	0.069 ± 0.018	0.0007 ± 0.0004
Liver	0.446 ± 0.020	0.264 ± 0.112	0.0046 ± 0.0020
Spleen	0.144 ± 0.007	0.077 ± 0.025	0.0027 ± 0.0011
Kidney	1.322 ± 0.085	0.720 ± 0.149	0.1183 ± 0.0326
Pancreas	0.144 ± 0.016	0.053 ± 0.008	0.0003 ± 0.0002
Stomach	3.419 ± 0.356	2.016 ± 0.882	0.0037 ± 0.0017
Small intestine	0.367 ± 0.119	0.408 ± 0.159	0.0014 ± 0.0005
Large intestine	0.167 ± 0.076	0.101 ± 0.025	0.0014 ± 0.0008
Testes	0.124 ± 0.009	0.068 ± 0.015	0.0037 ± 0.0017
Epididymis	0.115 ± 0.021	0.064 ± 0.020	0.0033 ± 0.0011
Skin	0.679 ± 0.326	0.049 ± 0.245	0.1985 ± 0.1443
Fat	0.535 ± 0.460	0.057 ± 0.030	0.0038 ± 0.0019
Muscle	0.050 ± 0.007	0.025 ± 0.011	0.0010 ± 0.0004
Femur	0.142 ± 0.046	0.087 ± 0.026	0.0015 ± 0.0004
Carcass	0.199 ± 0.005	0.081 ± 0.012	0.0073 ± 0.0011
Blood	0.485 ± 0.029	0.266 ± 0.051	0.0012 ± 0.0008
Plasma*	66.49 ± 6.90	57.95 ± 3.67	9.16 ± 6.47
RBC*	33.51 ± 6.90	42.04 ± 3.67	80.84 ± 6.47

* Percentage of total blood.

8.1 Nuclear Data Traceability

The excitation functions measurements have been carried out in accordance with the IAEA recommendations [123,124]. All nuclear data adopted in this paper (i.e: half-lives, gamma energies and intensities, decay schemes, mass defects) are taken from Browne [60]. Gamma emission intensities of the ^{226}Ra calibration source have been taken from Reus [113]. Stopping-power and range calculations are based on Williamson Tables [99]. Different nuclear data bases [50,59,113] and stopping-power values [100,101,103], lead obviously to different results about cross-section and thin-target yield values. The statistical analysis of the nuclear data was carried out in agreement with the more updated literature [125,126].

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10 REFERENCES

(1) Perrier C., Segre' E., 1937. Some chemical properties of element 43. J. Chem. Phys. **5**, 712-716.

(2) Perrier C., Segre' E., 1939. Some chemical properties of element 43. II. J. Chem. Phys. **7**, 155-156.

(3) Leigh G.J., ed., 1991. International Union of Pure and Applied Chemistry, IUPAC, Commission of the Nomenclature of Inorganic Chemistry. Nomenclature of Inorganic Chemistry. Blackwell Sci. Publ., Oxford, UK. ISBN: 0-632-02319-8.

(4) Noddack W., Tacke I., Berg von O., 1925a. Die ekamangane. Die Naturwissenschaften. **13** (1925) 567-574.

(5) Noddack W., Tacke I., Berg O., 1925b. Zwei neue Elemente der Mangangruppe. Chemischer Teil und Roentgenspektroskopischer Teil. Sitzung der Physikalisch-mathematischen Klasse. **11** (1925) 400-409.

(6) Noddack von W., Noddack I., 1927. Uber den Nachweis der Ekamangane. Zeits. f. Angewandte Chemie 40, 250-254.

(7) Berg von O., 1925. Roengtenspektroskopie und Nachweis der Ekamangane. Zeits. f. Technische Physik **6**, 599-603.

(8) Berg von O., 1927. Ueber den roengenspektroskopischen Nachweis der Ekamangane. Zeits. f. angewandte Chemie. **40** (1927) 254-256.

(9) Van Assche P. H. M., 1988a. The ignored discovery of the element Z=43. Nucl. Phys. **A480**, 205-214.

(10) Van Assche P. H. M., 1988b. Ignored priorities: first fission fragment (1925) and first mention of fission (1934). Nuclear Europe J. Eur. Nucl. Soc. **6/7**, 24-25.

(11) Bonardi M., Groppi F., 2001. Masurio-99m, masurio-99g, renio-186g e renio-188g: radioelementi chimici isomorfi, ma con attivita' specifica e proprieta' chimico-fisiche differenti. Storia e produzione di radiotraccianti. Metodiche di produzione e controllo di qualita'. Report **INFN/TC-01/04**, SIS-Pubblicazioni, Frascati, Roma, Italy.

(12) Birattari C., Bonardi M., Castiglioni M., Edel J., Gattinoni M., Mousty F., Sabbioni E., 1984. International Conference on Nuclear and Radiochemistry, Lindau, FRG, 1984. Gamma-emitting Tc radiotracers production for waste disposal studies at Milan AVF Cyclotron. Report **INFN/TC-84/24**, Frascati, Roma. Italy.

(13) Gallorini M., Birattari C., Bonardi M., Magon L., Sabbioni E., 1992. Preparation of high specific activity radiotracers for radioanalytical studies. J. Radioanal. Nucl. Chem. **160**, 493-503.

(14) Bonardi M., Gallorini M., Groppi F., Magon L., Marchi A., Saponaro S., Ulrici L., 1995a. Irradiation methods for production of high specific activity radionuclides in No Carrier Added form. J. Radioanal. Nucl. Chem. **195**, 227-236.

(15) Bonardi M., Gallorini M., Groppi F., Saponaro S., 1995b. Preparation and purification of high specific activity radio-nuclides for environmental studies. Microchem. J. **51**, 278-286.

(16) Philippon B., Christofidis D., Munsch R. C., Galy G., Berger M., 1977. Dosimetrie des Tc 95 m et Tc 96 sous forme de pertechnetate et comme marquer d'ematies. Possibilite' d'utilization humaine. Int. J. Appl. Rad. Isot. **28**, 529-531.

(17) Guillemart A., Besnard J. C., Le Pape A., Galy G., Fetissoff F., 1978. Skeletal uptake of pyrophosphate labelled with technetium-95m and technetium-96, as evaluated by autoradiography. J. Nucl. Med. **19**, 895-899.

(18) Galy G., Philippon B., Bardy A., Munsch R. C., 1981. Preparation et controle de qualite' des technetium-95m et technetium-96. Int. J. Appl. Rad. Isot. **32**, 277-281.

(19) Blaylock B. G., Frank M. L., De Angelis D. L., 1982. Bioaccumulation of ^{95m}Tc in fish and snails. Health Phys. **42**, 257-266.

(20) Lieser K. H., 1993. Technetium in the nuclear fuel cycle, in medicine and in the environment. Radiochim. Acta **63**, 5-8.

(21) Trautmann N., 1993. Ultratrace analysis of technetium. Radiochim. Acta **63**, 37-43.

(22) Ben Said K., Fattahi M., Musikas Cl., Revel R., Abbe' J. Ch., 1983. The speciation of Tc(IV) in chloride solutions. Radiochim. Acta **32**, 567-572.

(23) Nesmeyanov An. N., 1974. Radiochemistry. MIR Publishers. English translation, Moskow, USSR.

(24) Cotton F. A., Wilkinson G., 1968. Chapter 30-D Tecnezio e Renio, In : Chimica Inorganica, traduzione italiana di: Advanced Inorganic Chemistry, 1967, a cura di Bombi G. G., Bresadola S., Cattalini L., Peloso A. Casa Editrice Ambrosiana, Milano, Italy, pp. 968-987.

(25) ISRC, 1976-2001. International Symposia on Radiopharmaceutical Chemistry, Series from I to XIV: Upton (New York, BNL) (I, USA, 1976), Oxford (II, UK, 1978), St. Louis (III, USA, 1980), Juelich (IV, FRG, 1982), Tokyo (V, Japan, 1984), Boston (VI, USA, 1986), Groeningen (VII, The Netherland, 1988), Princeton (VIII, USA, 1990), Paris (IX, France, 1992), Kyoto (X, Japan, 1993), Vancouver (XI, Canada, 1995), Uppsala (XII, Sweden, 1997), St. Louis (XIII, USA, 1999), Interlaken (XIV, Switzerland, 2001). Proc. Published on J. Labelled Cpd. Radiopharm.

(26) Eckelman W. C., Coursey B. M., eds., 1982. Tecnetium-99m-Generators, Chemistry and Preparation of Radio-Pharmaceuticals. In: Special Issue of Int. J. Appl. Radiat. Isot. **33**, 793-950.
(27) Marchi A., Magon L., Bonardi M., Gallorini M., Groppi F., Saponaro S., 1995. Technetium complexes with ligands of pharmacological interest. J. Radioanal. Nucl. Chem. **195**, 237-242.
(28) Nicolini M., Bandoli G., Mazzi U., eds., 1995. Technetium and Rhenium in Chemistry and Nuclear Medicine. SGE Editoriali, Padova, Italy.
(29) Katcoff S., 1958. Fission-product yields from U, Th and Pu. Nucleonics Data Sheets **24**,78-86.
(30) Vertes A., Kiss I., 1987. Nuclear Chemistry. Topics in Inorganic and General Chemistry, Clark R. J. H. ed., Elsevier, Amsterdam, The Netherland.
(31) Krane K. S., 1988. Introductory Nuclear Physics. John Wiley & Sons, New York, USA.
(32) Ehmann D. W., Vance D. E., 1991. Radiochemistry and Nuclear Methods of Analysis. A series of Monographs on Analytical Chemistry and its Applications, Vol. **116**. John Wiley & sons, New York, USA. ISBN: 0-471-60076-8.
(33) Choppin G., Liljenzin J. O., Rydberg J., 1995. Radiochemistry and Nuclear Chemistry. Butterworths-Heinemann, Oxford, UK. ISBN 0-7506-2300-4.
(34) Hoffman D. C., Lane M. R., 1995. Spontaneous fission. Radiochim. Acta **70/71**, 135-145.
(35) Lieser K. H., 1997. Nuclear and Radiochemistry: Fundamentals and Applications. John Wiley & Sons, New York, USA. ISBN: 3-527-29453-8.
(36) Pfenning G., Klewe-Nebenius H., Seelmann-Eggebert W., 1998. Karlsruher Nuklidkarte, 6. Auflage 1995, korrigierter Nachdruck 1998, KFK, Karksruhe, Druckhaus Haberbeck GmbH, D-32791 Lage, Lippe, Germany. ISBN: 3-92-1879-18-3.
(37) Friedlander G., Kennedy J. W., Macias E. S., Miller J. M., 1981. Nuclear and Radiochemistry, 3rd Ed, John Wiley & Sons, New York, USA.
(38) Burkholder H. C., Cloninger M. O., Baker D. A., Jansen G., 1975. Report **USERDA BNWL-1927**, Note Tech. Inf. Serv., Springfield, Virginia, USA.
(39) Wildung R. E., Fadden K. M., Garland T. R., 1979. Technetium sources and behaviour in environment. J. Environ. Qual. **8**, 156-161.
(40) Bittel, R., 1980. Le technetium et l'environment. Radioprotection **15**, 141-146.
(41) Skytte J. B., 1980. Report Risø, **R-430**. Roskilde, Denmark.
(42) Beasley, T. M., 1981a. Report **DOE-EV/10251**, Newport, USA.
(43) Fowler S. W., Benayoun G., Parsi P., et al., 1981. Impacts of radionuclidese releases into the marine environment, IAEA, Vienna, p.319.
(44) Masson M., Aprosi G., Laniece A., et al., 1981. Impacts of radionuclidese releases into the marine environment. IAEA, Vienna, p.341.
(45) Schulte, E.H., Scoppa, P., Secondini, A., 1982. Boll. Soc. Ital. Biol. Sperim. **58**, 1361.
(46) Mobbs S. F., Harvey M. P., Martin J. S., Mayall A., Jones M. E., 1991. Comparison of the waste management aspects of spent fuel disposal and reprocessing; post disposal radiological impact. NRPB Report EUR-13561, EN, UK.
(47) Kubota M., 1993. Recovery of technetium from high-level liquid waste generated in nuclear fuel reprocessing. Radiochim. Acta **63**, 91-96.
(48) Holm, E., 1993. Radioanalytical studies of Tc in the environment: progress and problems. Radiochim. Acta **63**, 57-62.

(49) Nevissi A. E., Silverston M., Strebin R. S., Kaye J. H., 1994. Radiochemical determination of technetium-99. J. Radioanal. Nucl. Chem. **177**, 91-99.
(50) Firestone R. B., Baglin C. M., Chu F. S. Y., Zipkin J., 1996. Table of Isotopes, 8th Ed., Vols I and II: John Wiley & Sons, New York. ISBN: 0-471-29090-4.
(51) ICRP Publication 60, 1990. 1990 Recommendations of the International Commission on Radiological Protection. Annals of the ICRP. 21, Pergamon Press, Oxford, UK.
(52) ICRP Publication 26, 1977. Recommendations of the International Commission on Radiological Protection. Pergamon Press, Oxford, UK.
(53) ICRP Publication 29, 1978. Radionuclide release into the environment: Assessment of Doses to Man. In: Recommendations of the ICRP. Annals of the ICRP, 2. Pergamon Press, Oxford, UK.
(54) UNSCEAR 2000, 2000. Sources and Effects of Ionizing Radiation, Vols. I and II. United Nations Publication, New York, USA. ISBN: 92-1-142238-8; ISBN: 92-1-142239-6.
(55) Beasley T. M., Ball L. A., Andrews III J. E., Halverson J. E., 1981b. Hanford-derived plutonium in Columbia river sediments. Science **214**, 913-915.
(56) Radiochimica Acta, 1983. Special issue on the Chemistry of Actinide and other Radioelements. A. Chemistry of Actinides and Fission Products in Natural Aquatic Systems. A.1. Solubilities and Dissolution Reactions. **32**, 507-546. A.2. Complexation with Inorganic and Organic Ligands. **32**, 547-608. A.3. Redox Reactions. **32**, 609-618, A.4. Colloid Formation. **32**, 619-632. A.5. Experimental Methods. **32**, 633-650. B. Geochemical Interactions and Transport Phenomena. B.1. Diffusion and Migration in Geological Media. **32**, 651-674. B.2. Sorption/Desorption Phenomena. **32**, 675-738. B.3. Natural Analogue Studies. **32**, 739-768. B.4. Effects of Biological Activities and Organic Material: **32**, 769-788. B.6. Radionuclides in Soil. **32**, 789-814. C. Data Base Development and Modeling. **32**, 815-830.
(57) Mayer M. G., Jensen J. H. D., 1955. Elementary Theory of Nuclear Shell Structure. John Wiley & Sons, New York, USA.
(58) Myers W. D., 1977. Droplet Model of Atomic Nuclei. IFI Plenum data Co., Plenum Publ. Corp., New York, USA.
(59) Firestone R. B., Baglin C. M., Chu F. S. Y., 1998. Table of Isotopes, 8-th Ed., Update on CD-ROM, John Wiley & Sons, New York. ISBN: 0-471-24699-9.
(60) Browne E., Firestone R. B., 1986. Table of Radioactive Nuclides, 1st ed., John Wiley & Sons, New York, USA. ISBN: 0-471-84909-X.
(61) Tucker D., Greene M. W., Weiss A. J., Murrenhoff A., 1958. Methods of preparation of some carrier-free radioisotopes involving sorption on alumina. Report BNL-3746, BNL, Upton, New York, USA.
(62) Powell R., Steigman J., 1975. Technetium. In: Subramanian G., Rhodes B. A., Cooper J. F., Sodd V. J., Eds. Radiopharmaceuticals. The Society of Nuclear Medicine Inc., USA. pp. 21-70. ISBN: 0-88416-041-6.
(63) Boyd R. E., 1983. The special position of 99ΣTc in Nuclear Medicine. In: Helus F., ed. Radio-nuclides Production, Vol II, CRC Press, Inc. Boca Raton, Florida, USA, pp. 125-152. ISBN: 0-8493-6004-8.
(64) Nickles R. J., Christian B. T., Martin C. C., Nunn A. D., Stone C. K., 1991a. Tc-94m radio-nuclidesic purity requirements for pharmacokinetic studies with PET. J. Nucl. Med. **32**, 850.

(65) Nickles R. J., Nunn A. D., Stone C. K., Perlman S. B., Levine R. L., 1991b. Tc-94m flow agents: brindging PET and SPECT. J. Nucl. Med. **32**, 925.

(66) Nickles J. R., Christman B. T., Nunn A. D., Stone C. K., 1992. Cyclotron production of high-purity Tc-94m by *in situ* sublimation. Proc. 9th ISRC, Paris, France, pp. 447-448.

(67) Sajjad M., Lambrecht R. M., 1993. Cyclotron production of medical radionuclides. Nucl. Inst. Meth. **B79**, 911-915.

(68) Faβbender M., Novgorodov A. F., Roesch F., Qaim S. M., 1994. Excitation functions of ^{93}Nb(^{3}He,xn)^{93m,g,94m,g,95m,g}Tc-processes from threshold up to 35 MeV: possibility of production of ^{94m}Tc in high radiochemical purity using a thermochromatographic separation technique. Radiochim. Acta **65**, 215-221.

(69) Roesch F., Qaim S. M., 1993. Nuclear data relevant to the production of the positron emitting technetium isotope ^{94m}Tc via the ^{94}Mo(p,n)-reaction. Radiochim. Acta **62**, 115-121.

(70) Roesch F., Novgorodov A. F., Qaim S. M., 1994. Thermochromatographic separation of ^{94m}Tc from enriched molybdenum targets and its large scale production for nuclear medical application. Radiochim. Acta **64**, 113-120.

(71) Denzler F.-O., Roesch F., Qaim S. M., 1995. Excitation functions of α-particle induced nuclear reactions on highly enriched ^{92}Mo: comparative evaluation of production routes for ^{94m}Tc. Radiochim. Acta **68**, 13-20.

(72) Graf H. P., Muenzel H., 1974. Excitation functions for α-particle reactions with molybdenum isotopes. J. Inorg. Nucl. Chem. **36**, 3647-3657.

(73) Randa Z., Svoboda K., 1976. Excitation functions and yields of (d,n) and (d,2n) reactions on natural molybdenum. J. Inorg. Nucl. Chem. **38**, 2289-2295.

(74) Vishnevskil I. N., Zheltonozhskil V. A., Lashko T. N., 1985. Measurement of the isomeric ratios for the isotopes ^{93,94}Tc in reactions induced by protons and α particles. Sov. J. Phys. **41**, 910-912. English translation from Yad. Fiz. **41** (1985) 1435-1439.

(75) Lambrecht R. M., Montner S. M., 1982. Production and radiochemical separation of ^{92}Tc and ^{93}Tc for PET. J. Labelled Cpd. Radiopharm. **19**, 1434-1435.

(76) Misaelides P., 1981. Excitation functions for ^{12}C-induced reactions on ^{93}Nb. Radiochim. Acta **28**, 1-5.

(77) Omori, T., Omori, K., Ochi, C., Yoshihara, K., Yagi, M., 1984. Simultaneous production of ^{96}Tc and ^{111}In by α-particle irradiation of stacked Nb and Ag foils, and their carrier-free separations. J. Radioanal. Chem. **82**, 61-69.

(78) Finn R., Boothe T., Sinnreich J., Tavano E., Gilson A., Wolf A. P., 1985. Ancillary cyclotron production of technetium-95m for clinical and chemical research. In: Radiopharmaceuticals and Labelled Compounds 1984, IAEA-CN-45/22, IAEA, Vienna, Austria, pp. 47-54.

(79) Bond, P., Jha, S., 1970. Nuclear-structure and hyperfine-field studies with Mo^{95}. Phys. Rev. **C2**, 1887-1897.

(80) Das M. K., Sarkar B. R., Ramamoorthy N., Mani R. S., 1989. Yields of some radioisotopes formed in α-particle induced reactions on natural molybdenum. Radiochim. Acta **47**, 29-32.

(81) Lagunas-Solar M. C., Haff R. P., 1993. Theoretical and experimental excitation functions for proton induced nuclear reactions on Z=10 to Z=82 target nuclides. Radiochim. Acta **60**, 57-67.

(82) Hogan J. J., 1972. ^{96}Mo(p,xn) reaction from 10 to 80 MeV. Phys. Rev. **C6**, 810-816.

(83) Hogan J. J., 1973. Isomer ratios of Tc isotopes produced in 10-65 MeV bombardments of ^{96}Mo. J. Inorg. Nucl. Chem. **35**, 705-712.

(84) Hogan J. J., 1973. The ^{96}Mo(p,n) ^{96}Tc^{m,g} reaction from 10 to 65 MeV. J. Inorg. Nucl. Chem. **35**, 1429-1433.

(85) Hogan J. J., 1973. Comparison of the ^{94}Mo(p,n)^{94}Tc^{m,g} and ^{96}Mo(p,n)^{96}Tc^{m,g} reactions. J. Inorg. Nucl. Chem. **35**, 2123-2125.

(86) Poppe C. H., Grimes S. M., Anderson J. D., Davis J. C., Dunlop W. H., Wong C., 1974. Anomalous behavior of the (p,n) analog reaction on the molybdenum isotopes. Phys. Rev. Letters **33**, 856-859.

(87) Shakun E. A., Batii V. S., Rakivnenko Yu. N., Rastrepin O. A., 1987. Excitation functions and isomeric ratios for the interaction of protons of less than 9 MeV with Zr and Mo isotopes. Sov. J. Nucl. Phys. **46**, 17-24. English translation from Yad. Fiz. **46** (1987) 28-39.

(88) Izumo M., Matsuoka H., Sorita, T., Nagame Y., Sekine, T., Hata K., Baba S., 1991. Production of ^{95m}Tc with proton bombardment of ^{95}Mo. Appl. Radiat. Isot. **42**, 297-301.

(89) Branquinho, C. L., Hoffmann, S. M., Newton, G. W. A., Robinson, V. J., Wang H.-Y., Grant I. S. Goodall, J. A. B., 1979. Excitation functions and isomer ratios in the reactions ^{93}Nb(α,xn) (x=1-4). J. Inorg. Nucl. Chem. **41**, 617-623.

(90) Ramamoorthy, N. R., Das, M. K., Sarkar, B. R., Mani, R. S., 1986. Production of ^{96}Tc and ^{95m}Tc via the ^{93}Nb(α,xn) reactions. J. Radioanal. Nucl. Chem. **98**, 121-126.

(91) Auler L. T., Da Silva A. G., Newton G. W. A., 1981. Excitation functions and isomer ratios in ^{93}Nb(^{3}He,xn) reactions with X=2 and 3. J. Inorg. Nucl. Chem. **43**, 2611-2615.

(92) Lakosi L., Safar J., Ver(t)es A., Sekine T., Yoshihara K., 1993. Photonuclear reactions of ^{99}Tc, isomer excitation functions and deexcitation, implications in nucleosynthesis. Radiochim. Acta **63**, 23-28.

(93) Sekine T., Yoshihara K., Safar J., Lakosi L., Ver(t)es A., 1994. ^{95}Tc and ^{96}Tc production by (γ,xn) reactions. J. Radioanal Nucl. Chem. **186**, 165-174.

(94) Zaitseva N. G., Rurarz E., Vobecky M., Hwan Kim Hyn, Novak K., Tethal T., Khalkin V. A., Popinenkova L. M., 1992. Excitation function and yield for ^{97}Ru production in ^{99}Tc(p,3n)^{97}Ru reaction in 20-100 MeV proton energy range. Radiochim. Acta **56**, 59-68.

(95) Trufanov A. M., Lovchikova G. N., Sal'nikov O. A., Simanov S. P., 1982. Combined study of the mechanism of the reactions ^{95,98}Mo(p,n)^{95,98}Tc and the nuclear level density. Sov. J. Nucl. Phys. **36**, 174--178. English translation from Yad. Fiz. **36** (1982) 299-307.

(96) Comparetto G., Qaim S. M., 1980. A comparative study of the production of short-lived neutron deficient isotopes ^{94,95,97}Ru in α- and ^{3}He-particle induced nuclear reactions on natural molybdenum. Radiochim. Acta **27**, 177-180.

(97) Bonardi M., Silari M., 1988b. Fundamental parameters for the optimisation of yield and radionuclides purity of accelerator produced radioisotopes. Part I: thin-target excitation functions. Phys. Med. **1**, 23-46.

(98) Bonardi M., Silari M., 1988c. Fundamental parameters for the optimisation of yield and radionuclides purity of accelerator produced radioisotopes. Part II: beam control and monitoring. Phys. Med. **2**, 83-101.

(99) Williamson C. F., Boujout, J. P., Picard J., 1966. Tables of range and stopping-power of chemical elements for charged particles of energy 0.5 to 500 MeV. Rapport **CEA R-3042**, Saclay, France.
(100) Janni J. F., 1982. Protons range energy tables. ADNDT **27**, 148-527.
(101) Ziegler J. F., 1995. TRIM 95.4 code. IBM-Research, Yorktown, New York, USA.
(102) Knoll G. F., 1989. Radiation Detection and Measurement, 2nd ed. John Wiley & Sons, New York, USA.
(103) Ziegler J. F., Bierzack J. P., 1985. The stopping and range of ions in solids, Vol. I, Vols. II-VI 1977. Pergamon Press, New York, USA.
(104) Birattari C., Gadioli E., Grassi Strini A. M., Strini G., Tagliaferri G., Zetta L., 1971. (p,xn) reactions induced in ^{169}Tm, ^{181}Ta and ^{209}Bi with 20 to 45 MeV protons. Nucl. Phys. **A166**, 605-623.
(105) Birattari C., Bonardi M., 1980a. Ottimizzazione delle condizioni di irraggiamento per la produzione del radioisotopo ^{67}Ga con il Ciclotrone di Milano. Report **INFN/TC-80/9**, Frascati, Roma, Italy.
(106) Birattari C., Bonardi M., 1980b. Funzioni di eccitazione per le reazioni nucleari (p,xn) e (p,pxn) su targhette d'oro e studio del "generatore" del radioisotopo a vita ultra-breve ^{195m}Au. Report **INFN/TC-80/17**, Frascati, Roma, Italy.
(107) Bonardi M., 1988a. The contribution to nuclear data for biomedical radioisotope production from the Milan Cyclotron Laboratory. In: IAEA Consultant's Meeting On Nuclear Data Requirements for Medical Radioisotope Production, Tokyo, april 1987, **INDC(NDS)-195/GZ**, IAEA, Vienna, Austria, pp. 98-112.
(108) Ouellet J. M. L., Oxorn K., Hamel L. A., Lessard L., Matte C., 1993. Cross-sections and activation profiles for wear monitoring. Nucl. Instr. Meth. Phys. Res. **B79**, 579-581.
(109) Bonardi M., Birattari C., Gallorini M., Groppi F., Arginelli D., Gini L., 1998. Cyclotron production, radiochemical separation and quality control of platinum radiotracers for toxicological studies. J. Radioanal. Nucl. Chem. **236**, 159-164.
(110) Groppi F., Bonardi M., Birattari C., Gallorini M., Gini L., 2001. Thin-target excitation functions for (α,xn) reactions on osmium targets for platinum radiotracer. J. Radioanal. Nucl. Chem. **234**
(111) Cumming J. B., 1964. Nucl. Phys. **49**, 417.
(112) Reus U., Westmeier W., 1983b. Catalog of gamma rays from radioactive decay, Part II. ADNDT **29**, 193-406.
(113) Reus U., Westmeier W., 1983a. Catalog of gamma rays from radioactive decay, Part I. ADNDT **29**, 1-192.
(114) Debertin K., Helmer R. G., 1988. Gamma- and X-ray Spectrometry with Semiconductor Detectors, North-Holland, Amsterdam, The Netherland.
(115) Gilmore G., Hemingway J. D., 1995. Practical Gamma-Ray Spectrometry. John Wiley & Sons, New York, USA.
(116) Basile D., Birattari C., Bonardi M., Goetz L., Sabbioni E., Salomone A., 1981. Excitation functions and production of arsenic radioisotopes for environmental toxicology and biomedical purposes. Int. J. Appl. Rad. Isot. **32**, 403-410.
(117) Bonardi M., Birattari C., 1983. Optimization of irradiation parameters for ^{67}Ga production from ^{nat}Zn(p,xn) nuclear reactions. J. Radioanal. Chem. **76**, 311-318.
(118) Groppi F., Alberti G., Birattari C., Bonardi M., Silari M., 1992. Multiple scattering and thermal dissipation of charged particle beams in multiple thin metallic targets. Proc. "IV

Workshop on Targetry and Target Chemistry", PSI, Villigen, Switzerland, sept 1991, PSI Ed., pp. 89-95.

(119) Bonardi M., Groppi F., Birattari C., Alberti G., 1989. MSCT and HEAT: computer codes for simulation of multi-scattering and thermal dissipation of charged particle beams in multiple thin metallic targets. J. Labelled Cpd. Radiopharm. **26**,185-187.

(120) Sabbioni E., Goetz L., Birattari C., Bonardi M., 1981. Environmental biochemistry of current environmental levels of heavy metals: preparation of radiotracers with very high specific activity for metallobiochemical studies on laboratory animals. The Sci. Total Env. **17**, 257-276.

(121) Gallorini M., Bonardi M., Groppi F., Saponaro S., 1995. Analytical and radioanalytical quality control in high specific activity radiotracers preparation. J. Radioanal. Nucl. Chem., **193**, 39-47.

(122) Sabbioni E., Bonardi M., Gallorini M., Pietra R., Fontaner S., Tartaglia G. P., Groppi F., 1992. Application of very high specific activity radiotracers to metallotoxicological studies. J. Radioanal. Nucl. Chem. **160**, 549-561.

(123) IAEA 1988. IAEA Consultant's Meeting On Nuclear Data Requirements for Medical Radioisotope Production, Tokyo, april 1987, **INDC(NDS)-195/GZ**, IAEA, Vienna, Austria.

(124) IAEA, 2001. TECDOC-1211. Charged-particle Cross-Section Database for Medical Radioisotope Production. IAEA Co-ordinated Research Project (1995-1999), IAEA, Vienna, Austria, May 2001. Available online at: http://www-nds.iaea.org/medical/

(125) Kleinbaum D. G., Kupper L. L., 1986. Applied Regression Analysis and Other Multivariable Methods. Duxbury Press, Boston, Massachusetts, USA. ISBN: 0-87150-355-7.

(126) Smith D. L., 1991. Probability, Statistics, and Data Uncertainties in Nuclear Science and Technology. OECD/NEA, ANS, Illinois, USA. ISBN: 0-89448-036-7.

(127) Hippe D., Heits B., Schuh H.-W., Zell K. O., Friederichs H.-G., Brentano von P., 1975. High spin states in ^{95}Tc populated in the ^{93}Nb(α,2nγ) reaction. Z. Physik **A 273**, 349-357.

(128) Kim H. J., Robinson R. L., Johnson C. H., Raman S., 1970. Energy levels of ^{91}Nb, ^{93}Nb, ^{95}Tc and ^{97}Tc via (p,n) reactions and the reaction *Q*-values. Nucl. Phys. **A142**, 35-48.

(129) Thomas K. E., 1984. Isotope production from molybdenum targets. Radiochim. Acta **37**, 137-141.