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ABSOLUTE ACTIVITY MEASUREMENTS OF MOLYBDENUM 99 AND 4π-γ ION CHAMBER MEASUREMENTS OF TECHNETIUM 99m AND OF MOLYBDENUM 99 WITH INGROWN TECHNETIUM 99m

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ABSTRACT

The activity of molybdenum 99 freshly separated from technetium is absolutely measured to ± 1.8 per cent. by 4πB-γ coincidence counting. Internal conversion effects are allowed for and the completeness of the separation is checked from the growth rate of technetium 99m activity as measured in a 4π gamma ionisation chamber. The chamber has been calibrated for molybdenum 99 with ingrown technetium 99m and for pure technetium 99m and serves for routine activity measurements of solutions of these nuclides to an accuracy of ± 3 per cent.

CONTENTS

1. INTRODUCTION

The radionuclide technetium 99m has found wide use in radiation medicine. Its decay is accompanied by virtually monoenergetic gamma emission; moreover the chemical properties of its oxidised form and its short half-life make it highly suitable for scanning purposes (Smith 1964).

The technetium 99m activities employed for therapeutic purposes have been measured most commonly by gamma counting relative to cobalt 57 where the accuracy of the absolute activity of the latter was ± 2 per cent. at best (Troughton 1965). More recently absolute counting procedures for molybdenum 99, the parent activity of technetium 99m, were reported (Crowther and Eldridge 1965) and also an ingenious absolute measurement of technetium 99m itself (Goodier and Williams 1966). Since users of technetium 99m commonly elute it from an alumina column charged with molybdenum 99 activity (Smith 1964), determinations of technetium 99m via those of molybdenum 99 remain of interest.

This paper reports an absolute method of calibration of molybdenum 99 to ± 1.8 per cent by $4\pi\beta - \gamma$ coincidence counting and allowing for internal conversion in the molybdenum 99 decay scheme. Parts of the standardised solution are used to calibrate a 4π gamma ionisation chamber for pure molybdenum 99, pure technetium 99m, and their secular equilibrium mixture. Solutions containing these activities can then be measured in this ion chamber easily and quickly and with an accuracy of ± 3 per cent. for technetium 99m. Ion chamber measurements beginning with freshly separated molybdenum 99 permit subsequent detection of as little as 1 per cent. technetium 99m carried over accidentally with the separated molybdenum 99 which would affect the molybdenum 99 counting result by about 0.1 per cent. Because separations must be made quickly if absolutely counted molybdenum 99 is to be relatively free of ingrown technetium 99m, accidental carry-over can easily occur. Its detection from counting results alone is rather more difficult than from ion chamber measurements.

2. EQUIPMENT AND MATERIALS

2.1 Radioactivity Measuring Equipment

Equipment very similar to that described by Campion (1959) was used for the coincidence counting. The 4π gamma ion chamber was an air filled instrument of the type described by Mann and Seliger (1958). The conditions in which the ion chamber was used had been carefully standardised to achieve highly reproducible results; for technetium 99m the precision was better than ± 0.2 per cent. for activities above 0.2 mCi, and was ± 0.4 per cent. when the activity had fallen to 0.04 mCi.

2.2 Preparation of Pure Molybdenum 99 and Technetium 99m

Pure molybdenum 99 free of its daughter technetium 99m was prepared by two different solvent extraction procedures.

(1) Technetium 99m was quantitatively extracted from a mixture of molybdenum 99 and technetium 99m by a single step extraction with tetraphenyl arsonium chloride in chloroform (Tribalat and Beydon 1953).

(2) Technetium 99m was separated almost completely from molybdenum 99 by a double extraction into pyridine from 4M sodium hydroxide solution (Goishi and Libby 1952). The molybdenum was recovered in a solution of low solids content by acidification of the alkaline solution and extraction of the molybdenum into ether as the isothiocyanate compound (Alperovich 1954).

2.3 Solutions and Counting Sources

Radioactivity measurements were made using both 0.1 M HCl and neutral solutions. Close to 10 ml of freshly purified molybdenum 99 solution was weighed into press-sealed vials of uniformly drawn glass, of 10 ml capacity and 1 mm wall thickness. The total activity was adjusted to be initially between 200 and 300 μCi. The solutions were examined for radioisotopic impurities but none could be identified with certainty. The effect of residual impurities on the decay times of the radionuclides was estimated as 0.05 per cent. at most.

Drops of between 5 mg and 12 mg of the same solution were weighed on to 7 $\mu g/cm^2$ VYNS foils vacuum coated with 12 - 13 $\mu g/cm^2$ Au - 20 per cent. Pd. The solvent was evaporated by vacuum freeze drying after adding 3-4 times the drop volume of ethanol. The sources were covered with foils equal to the supporting foils and were ready for counting 50-60 minutes after the purification of the molybdenum 99 solution. Each foil had a 4π counting efficiency near 95 per cent.

3. DECAY DATA AND THEIR EFFECT ON THE MEASUREMENTS

3.1 Decay Data and Half-lives

The decay scheme of molybdenum 99 - technetium 99m is reproduced in Figure 1, but some uncertainties exist as regards both relative and absolute transition probabilities (Crowther and Eldridge 1965, Cretzu and Hohmuth 1965).

The decay chain following molybdenum 99 is: Molybdenum 99 (β-γ) - technetium 99m (γ) - technetium 99 (β) - ruthenium 99 (stable). Reported half-lives for these decays are listed in Table 1. The build-up of the technetium 99 beta activity was always negligibly small.

Let the molybdenum 99 activity (A_{Mo}) be separated from technetium 99m at time t_o. The technetium 99m activity at time t measured from t_o is then:

$$(A_{Tc})_t = (A_{Mo})_t \; p \; R_t \; \frac{\lambda_{Tc}}{\lambda_{Tc}-\lambda_{Mo}} + (A_{Tc})_{t_o} \; F_t' \quad , \qquad \ldots\ldots(1)$$

where p is the fraction of molybdenum 99 decays feeding the 142 keV level in technetium 99m, and $R_t = 1 - \exp. t(\lambda_{Mo}-\lambda_{Tc})$ is the growth factor of the technetium 99m activity produced by molybdenum 99 decay where λ_{Tc} and λ_{Mo} are the decay constants of technetium 99m and molybdenum 99 respectively. The term $(A_{Tc})_{t_o}$ accounts for carried over technetium 99m activity where the separation was not 100 per cent. efficient, and F_t' is the technetium 99m decay factor.

The half-lives were measured in the ionisation chamber. The molybdenum 99 half-life was equal to that measured by Crowther and Eldridge (1965) (Table 1). Agreement for the technetium 99m half-life was less satisfactory. The result of Crowther and Eldridge seems to be almost certainly high.

3.2 Transitions to the 142 keV Level and Internal Conversion

Three values of p obtained from recent works are shown in Table 2. Using the mean of these results and our half-life values in Equation 1 and assuming $(A_{Tc})_{t_o} = 0$ then:

$$(A_{Tc})_t = 0.971 \; R_t \; (A_{Mo})_t \qquad \ldots\ldots(2)$$

The uncertainty in the factor 0.971 is estimated as ± 0.9 per cent.

Some of the transitions following the decay of molybdenum 99 and all transitions in the decay of technetium 99m are in part internally converted. Internal conversion rates were taken from several sources and the values adopted for this work are shown in Table 3. Although the uncertainty in these results is large the effect of these uncertainties on the accuracy of the absolute standardisation of molybdenum 99 is considerably reduced by the high beta efficiency of the sources (see Section 4.2 below).

4. THE ABSOLUTE COUNTING OF MOLYBDENUM 99

4.1 The 4π Count Rate

The expression for this count rate is (after correcting for background and dead time):

$$(N_{4\pi})_t = \sum_{i=1}^{4} \left[\left(A_{Mo_i}\right)_t \epsilon_i \, b_i \left(1 + \frac{\alpha_{T_i}}{1+\alpha_{T_i}} \cdot \frac{1-\epsilon_i}{\epsilon_i} \epsilon_{ce}\right) \right] + \left(A_{Tc}\right)_t \epsilon_{Tc} \qquad \ldots\ldots(3)$$

The time t is measured from the separation time t_o and the summation is made over the four beta branches (Figure 1), ϵ_i is the beta efficiency of beta branch i whose relative intensity is b_i, and ϵ_{Tc} stands for the overall response of the 4π counter to the technetium 99m disintegration products; only ingrown technetium 99m is present.

The efficiency for counting conversion electrons ϵ_{ce} is taken as unity (Campion 1959). The gammas following the four branches are subject to different α_T values. However, because of the high beta efficiencies attained (see below) the conversion electron correction in Equation 3 is so small that no significant error is made by using for each branch the average total internal conversion coefficient for molybdenum 99, $(\alpha_T)_{av} = 0.24 \pm 25$ per cent., (Table 3).

The correction for the gamma efficiency of the 4π counter to molybdenum 99 has been omitted from Equation 3 since it is here almost certainly much below 0.1 per cent. (Urquhart 1967). Of the approximately 6 per cent. contribution of 2 keV transitions (for pure molybdenum 99) more than 98 per cent. are internally converted (N.R.C. 1962) the products having a maximum energy of about 1.4 keV (M X-rays). The radiations following those few events which are not in coincidence with betas appear to be mostly absorbed in the source and/or cover foils.

The term ϵ_{Tc} is equal to $\epsilon_{ce}\,\alpha_{Tc}/(1+\alpha_{Tc}) + (\epsilon_{\beta\gamma})_{Tc}$, where $\alpha_{Tc} \approx 0.1$ (Table 3) and $\epsilon_{ce} \approx 1$ as before. The contribution of $(\epsilon_{\beta\gamma})_{Tc}$ appears to be a few per cent. at most. Pure technetium 99m sources, made from a solution which had been calibrated in the ion chamber and was chemically very similar to the solution used for the molybdenum 99 sources, and which on microscopic inspection appeared to have much the same distribution of solids, yielded a maximum counting efficiency of 13 per cent. and mostly values ranging from 8 to 12 per cent. It seemed justifiable, therefore, to use $\epsilon_{Tc} = 0.10 \pm 20$ per cent.

4.2 The Beta Efficiency

The coincidence counting of the molybdenum 99 sources was subject to a gamma channel threshold of 300 keV. The results yield the ratio:

$$N_c/N_\gamma = \epsilon'_{Mo} \quad , \qquad \ldots\ldots(4)$$

where N_c and N_γ are the count rates in the coincidence and the gamma channel corrected for dead time and accidental coincidences. The term ϵ'_{Mo} gives a measure of the counting efficiency for the 245 keV, 450 keV, and 880 keV branches (Figure 1). For these measurements ϵ'_{Mo} ranged from 0.90_0 to 0.96_0. Ignoring the very small 245 keV contribution for the moment, the efficiency for the other two branches

should not differ by more than a few per cent. It should be permissible therefore (Campion 1959) to treat ϵ'_{Mo} as the average beta efficiency for the three lower energy branches and to consider these three as a single branch with maximum energy 500 keV, the weighted average of the three maximum energies, and an abundance of 16 per cent. (Figure 1).

Since the spectral shapes are known (Cretzu and Hohmuth 1965) the results for ϵ'_{Mo} (Equation 4) can be used to calculate the beta cut-off energy for each source. This cut-off energy was then used to calculate ϵ_{1230}, the efficiencies for the 1230 keV branch of the spectrum. For $0.90_0 < \epsilon'_{Mo} < 0.96_0$ one obtains $0.97_2 < \epsilon_{1230} < 0.98_9$. With relative abundances of 0.16 and 0.84 respectively, a linear combination of ϵ'_{Mo} and ϵ_{1230} gave the average efficiency range for the entire molybdenum 99 beta spectrum, namely $0.95_8 < \epsilon_{Mo} < 0.98_6$, ϵ_{Mo} being the average efficiency. For these calculations residual instrumental effects on the cut-off threshold were ignored.

In view of the high beta efficiencies realised, a linear combination of efficiencies seemed permissible, the error in the procedure being estimated as between + 0.5 per cent and -1.0 per cent.

The average molybdenum 99 beta efficiency ϵ_{Mo} can then be used in Equation 3 as well as the average total internal conversion coefficient (Table 3) and also the results for ϵ_{Tc} and ϵ_{ce}. Equation 3 then becomes:

$$(N_{4\pi})_t = (A_{Mo})_t\ \epsilon_{Mo}\left(1 + 0.194\ \frac{1-\epsilon_{Mo}}{\epsilon_{Mo}}\right) + 0.10\ (A_{Tc})_t \quad . \qquad \ldots\ldots(5)$$

On substituting for A_{Tc} from Equation 2 and solving for the molybdenum 99 activity at the moment of purification t_o one obtains:

$$(A_{Mo})_{t_o} = (N_{4\pi})_t\ F_t \Big/ \left[\epsilon_{Mo}\,(1+f) + 0.0971\ R_t\right] \quad , \qquad \ldots\ldots(6)$$

where F_t is the decay factor for molybdenum 99 at time t and $f = 0.194\ (1-\epsilon_{Mo})/\epsilon_{Mo}$.

4.3 The Overall Error in the Molybdenum 99 Standardisation

Starting with the second term on the r.h.s. of Equation 3, the ± 20 per cent. error in ϵ_{Tc} has only a small effect on the overall error because the counting of the molybdenum 99 sources was always completed within three hours of the separation time. Within this period the product $0.0971\ R_t$ has been on the average about 2 per cent. of the denominator of Equation 6. The total uncertainty in the product is also influenced by the ± 0.9 per cent. error in the factor 0.971 (see Section 3.2) and a ± 1 per cent. error in R_t, the latter being due mainly to the ± 1 minute uncertainty in fixing the time t_o.

The average error contributed by the term 0.0971 R_t discussed above is estimated as ± 0.5 per cent. The other estimated errors are: source preparation ± 0.3 per cent.; overall counting error ± 0.5 per cent.; half-life ± 0.1 per cent.; conversion electron effect ± 0.1 per cent.; and radioisotopic impurities including carried over Tc ± 0.1 per cent. The error in ϵ_{Mo} is taken as ± 0.8 per cent. The four last mentioned errors are of a systematic character, whereas the first three are taken as random errors. The overall error is then ± 1.8 per cent. which is the sum of the systematic errors and the quadrature sum of the random errors.

5. IONISATION CHAMBER MEASUREMENTS

5.1 The Ionisation Current for Pure Molybdenum 99

The ionisation chamber measurements were made on a 10 gram mass of the standardised solution. They can normally be started within 20 minutes of the separation time t_o. Some 10-15 readings were taken before the attainment of secular equilibrium and further readings extending over 3-4 half-lives of molybdenum 99.

A simple graphical extrapolation method could be used to obtain the ion current for pure molybdenum 99 but this method is relatively insensitive to small amounts of technetium 99m activity which may have escaped separation. The ionisation current for pure molybdenum 99, $(I_{Mo})_{t_o}$ is therefore always obtained with the following method which is capable of detecting less than 1 per cent. of non-separated technetium 99m.

Let the ion current due to ingrown technetium 99m be I_{Tc}; then the total ion current at time t (assuming no carry-over of technetium 99m) is:

$$I_t = (I_{Mo})_t + (I_{Tc})_t \qquad .....(7)$$

On substituting for I_{Tc} from Equation 2 and solving for the ionisation current for pure molybdenum 99:

$$(I_{Mo})_{t_o} = I_t F_t \Big/ (1 + 0.971\, q\, R_t) \quad , \qquad .....(8)$$

where the factor q was introduced to allow for the difference in the response of the chamber to equal activities of molybdenum 99 and technetium 99m respectively. The value of q may be calculated from any two measurements of I_t, say at times t and T when:

$$q = \frac{I_T F_T - I_t F_t}{0.971\,(I_t F_t R_T - I_T F_T R_t)} \qquad .....(9)$$

The result obtained from several series of measurements was $q = 0.95_5 \pm 0.01_0$. To achieve such an accuracy it is of course necessary for T - t to be sufficiently large.

When non-separated technetium 99m is present, q is no longer constant because the activity of this technetium 99m is independent of $(I_{Mo})_{t_o}$. If the current due to non-separated technetium 99m is initially about 3 per cent. of $(I_{Mo})_{t_o}$ the value of q as calculated within four hours of t_o falls to about 0.90, that is, by nearly 6 per cent. The technetium 99m activity which has not been separated can therefore be clearly detected provided it is not much less than 1 per cent. of $(I_{Mo})_{t_o}$.

5.2 Results and Error Estimates

Values of $(I_{Mo})_{t_o}$ were calculated from Equation 8. Since the radioactive concentration of the solution was known (Section 4), and also its mass, the current per millicurie or specific ionisation current for molybdenum 99, under standard conditions, $(I_{sp})_{Mo}$, could be calculated.

The systematic errors affecting these results are the counting error ± 1.8 per cent., ± 0.2 per cent. for geometry and self absorption effects and ± 0.2 per cent. for decay. The random error estimate was based on the reproductibility of the measurements of $(I_{sp})_{Mo}$. This was ± 0.6 per cent. which was the result for the standard deviation from four independent series of measurements. The overall error is again given by the sum of these terms, that is ± 2.8 per cent.

The specific ionisation current of molybdenum 99 - technetium 99m secular equilibrium mixtures, $(I_{sp})_{SE}$, was calculated from measurements made more than 2.8 days after t_o when secular equilibrium had been attained to within 0.1 per cent. The overall error for $(I_{sp})_{SE}$ was taken as equal to that in $(I_{sp})_{Mo}$.

With $(I_{sp})_{Mo}$ and $(I_{sp})_{SE}$ known, the specific ionisation current due to technetium 99m alone, $(I_{sp})_{Tc}$, could be calculated using the fact that at secular equilibrium the ratio of the activities of technetium 99m and molybdenum 99 is 0.971 (Equation 2). The standard deviation of the mean of four results for $(I_{sp})_{Tc}$ was also ± 0.6 per cent. But allowing for the uncertainty in the branching ratio, the overall error in the technetium 99m result was estimated as ± 3 per cent.

6. CONCLUSION

The activity of technetium 99m can be measured in a 4π gamma ionisation chamber with an accuracy of ± 3 per cent. The ionisation chamber was calibrated with solutions which had been standardised by the absolute counting of the molybdenum

± 1.8 per cent. The quoted errors include uncertainties due to incomplete knowledge of the decay schemes but these uncertainties are shown to account for much less than half of the total errors. The dominant uncertainties are those in the molybdenum 99 beta efficiency and those due to the consequences of the rapid build-up of technetium 99m.

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TABLE 1

HALF-LIVES OF Mo^{99}, Tc^{99m}, AND Tc^{99}

Nuclide	N.R.C. (1962)	Crowther and Eldridge (1965)	Goodier and Williams (1966)	This work
Mo^{99}	67 h	66.7 h ± 0.15%	-	66.7 h ± 0.2%
Tc^{99m}	6.0 h	6.13 h ± 0.8%	6.006 h ± 0.03%	6.017 h ± 0.13% *
Tc^{99}	2.1×10^5 y	-	-	-

* from measurements on two independently prepared samples over about four half-lives. Mo^{99} content < 0.01 per cent.

TABLE 2

TRANSITIONS FEEDING THE 142 keV LEVEL IN TECHNETIUM PER 100 DECAYS OF Mo^{99}

Reference	1230 keV (beta)	780 keV (gamma)	273 keV (gamma)	Total (p)
Ravier et al. (1961)	83	2	3	88
Crowther and Eldridge (1965)	82	4.4	1.3	87.7
Cretzu and Hohmuth (1965)	84	3.4	1.7	89.1
			Average:	88.3 ± 0.7

TABLE 3

AVERAGE TOTAL CONVERSION COEFFICIENTS $(\alpha_T)_{av}$

Radionuclide	Transitions per 100 decays of principal nuclide		$(\alpha_T)_{av} = e/\gamma$
	γ	e	
Mo^{99}	26	6.2	0.24 ± 25%
Mo^{99} - Tc^{99m}	108	14.2	0.13 ± 15%
Tc^{99m}	91	9.1	0.10 ± 10%

Note: The transition rates are taken from Crowther and Eldridge (1965), Cretzu and Hohmuth (1965), Ravier et al. (1961) and N.R.C. (1962). The indicated error limits have been estimated from the range of published results.

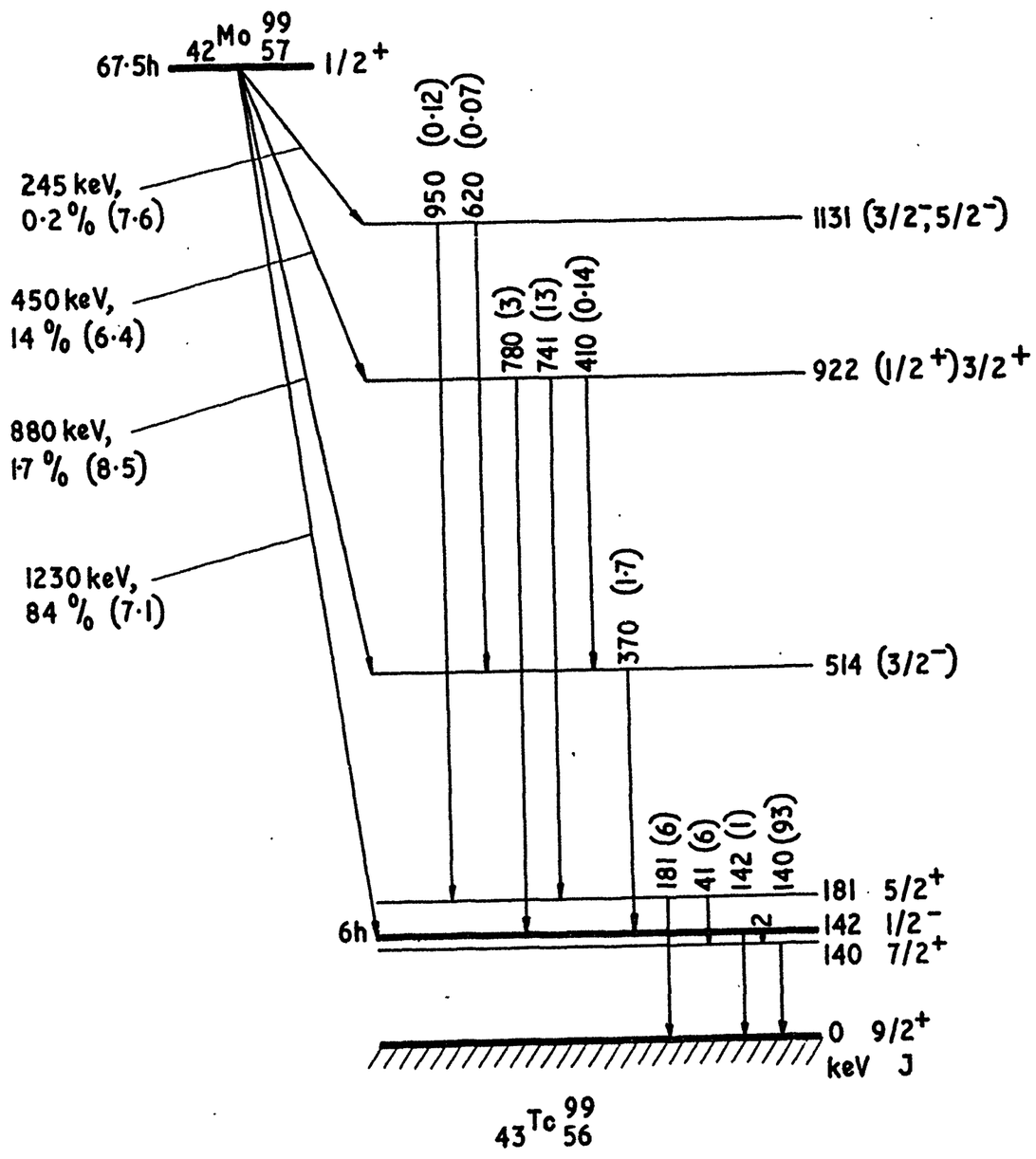

FIGURE 1. DECAY SCHEME OF Mo99 — Tc99m (After Cretzu and Hohmuth 1965)