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THE DETERMINATION OF FISSION PRODUCT LEVELS
IN HIFAR HEAVY WATER

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ABSTRACT

Methods for the determination of Ba-140 and I-131 are described. These methods are suitable for routine monitoring of fission product levels in the HIFAR heavy water circuit. The results obtained over a four-month period are presented and discussed.

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1. INTRODUCTION

With the rise in the activity levels of the D₂O moderator in HIFAR, a method was required for monitoring the fission product concentration on a regular basis. Since catastrophic failure of a HIFAR element or elements would be indicated by the installed instrumentation, it was not essential to devise a method which would respond rapidly to changes in fuel element conditions. The object of periodically assaying the D₂O circuit was to establish long-term trends.

2. CHOICE OF NUCLIDE

Ideally, the nuclide chosen for monitoring a reactor circuit should have the following properties:

(i) A suitable half-life. Short-lived nuclides will respond rapidly to changes in the operating conditions of the reactor.

(ii) Suitable chemical properties. The selected nuclide should exist in well-known valence states and have little tendency to form colloids or be adsorbed around the reactor circuits.

(iii) A suitable decay scheme. The decay scheme should be known accurately and be suitable for the detection of the selected nuclide by gamma spectroscopy.

(iv) Suitable yield. Clearly those nuclides produced in high yield by the fission process are most easily measured.

The nuclides Ba-140 and I-131 satisfy the above criteria and are commonly used for the monitoring of reactor circuits. The nuclide Ba-140 can easily be determined after a few days cooling by gamma spectrometry and the I-131 requires only a short simple chemical separation.

Figures 1 and 2 show the γ spectra of a sample of HIFAR D₂O which had been cooled for a few days. Figure 2 was obtained using a high resolution Ge(Li) detector and it is apparent that the 1.6 MeV peak due to the La-140 daughter of Ba-140 is free from interference from nearby photopeaks. This peak can thus be used for the determination of Ba-140 provided that sufficient time is allowed for the system to reach a state of transient equilibrium. Under these conditions, the disintegration rate of Ba-140 is 0.869 of the disintegration rate of La-140. The derivation of this value is given in Appendix 1. At least six days should be allowed to elapse before counting the La-140.

Kleinberg and Cowan (1960) in their review of the radiochemistry of fluorine, chlorine, bromine and iodine refer to a method for the separation of radioactive iodine from fission products and uranium. The method ensures that all forms of iodine are recovered, by oxidising all the forms of iodine to periodate, reducing to the elemental state, extracting with carbon tetrachloride and reducing to iodide. The iodide is then precipitated as silver iodide. Silver iodide is not the best choice for precipitation since it coagulates readily and is difficult to dry under an infra-red lamp without decomposition. A final separation as cuprous iodide was used in this work.

The iodine sources prepared in this way contain a number of iodine nuclides and about 10 days cooling after sampling was found necessary in order that the I-131 could be counted without

interference. The γ spectra of 17 hour and 10 day cooled sources are shown in Figures 3 and 4 respectively.

3 EXPERIMENTAL

3.1 Spectrometer Calibration

The half lives of both Ba-140/La-140 and I-131 are inconveniently short to permit the use of standard sources of these nuclides for spectrometer calibration. Instead the calibration was effected using the following nuclides Hg-203, Cs-137, Mn-54, Sc-46 and Y-88. The absolute abundances of the γ peaks used are listed in Table 1. Efficiencies for Ba-140/La-140 and I-131 were interpolated from a graph of efficiency versus γ energy.

TABLE 1
 γ ENERGIES AND ABUNDANCES

Nuclide	γ Energy Used (MeV)	Absolute Abundance (%)
Hg-203	0.279	81.5
I-131	0.364	81
Cs-137 (Ba-137m)	0.662	85
Mn-54	0.840	100
Sc-46	1.12	100
La-140	1.60	95.6
Y-88	1.85	99

Since the available high resolution Ge(Li) detector has only a small volume it was decided to count both the Ba-140/La-140 and the I-131 using a 3 in. x 3 in. NaI(Tl) detector with a 256-channel analyser. This combination has adequate resolution and high sensitivity.

3.2 Procedure for Ba-140

Calibrate the spectrometer using standardised sources of Y-88, Sc-46, Mn-54 and Cs-137, having previously adjusted the gain of the spectrometer so that the Y-88 1.85 MeV photopeak occurs near the high energy end of the spectrum.

Place each source in turn centrally on the detector, count for 10 minutes and subtract background.

Sum the counts in the photopeak. (Summing the counts over ten channels each side of the maximum was used by the authors).

Correct the activity of the source for γ abundance (see Table 1) and decay. Half-life values used in this work were

Y-88	107 days
Sc-46	83.8 days
Mn-54	313 days
Cs-137	30.0 years.

Calculate the γ photopeak efficiency for each nuclide and graph it against the γ energy.

Read the γ efficiency for La-140 from the graph and correct for γ abundance (see Table 1) to obtain absolute efficiency.

Count the unknown sample under the same conditions as used for calibration, allowing at least six days cooling before counting. Sufficient counting time should be allowed to produce at least 10,000 counts in the 1.6 MeV La-140 peak.

Subtract the background and find the peak area as before. Correct the peak area for Compton continuum contribution in the usual way.

$$\mu\text{Ci La-140/ml sample} = \frac{\text{corr. peak area} \times 100}{t \times E \times 2.22 \times 10^6 \times V}$$

where t = count duration in minutes,

E = absolute efficiency (3.35% in this work), and

V = sample volume.

Then $\mu\text{Ci Ba-140/ml of sample} = \mu\text{Ci La-140/ml} \times 0.869$.

Correct the Ba-140 figure for decay from sampling to counting time (half-life Ba-140 = 12.8 days).

3.3 Procedure for I-131

Calibrate the spectrometer using standardised sources of Hg-203, Cs-137 and Mn-54, having previously adjusted the gain of the spectrometer so that the 0.84 MeV Mn-54 photopeak occurs near the high energy end of the spectrum.

Place each source in turn centrally on the detector, count and subtract background.

Sum the counts in the photopeak as before.

Correct the activity of the source for γ abundance (see Table 1) and decay. Half-life values used in this work were:

Mn-54	313 days
Cs-137	30.0 years
Hg-203	47 days.

Calculate the γ photopeak efficiency for each nuclide and graph it against the γ energy.

Read the γ efficiency for I-131 from the graph and correct for γ abundance (see Table 1) to obtain absolute efficiency.

Preparation of Sample Source

Pipette 10 ml of a 10-day cooled sample into a 100 ml beaker. Pipette in 2 ml of potassium iodide solution containing 10 mg I⁻/ml.

Add 2 g sodium carbonate and 1 ml of 15% sodium hypochlorite solution.

Heat to boiling and stand 15 minutes.

Neutralise with conc. nitric acid and add 1 ml in excess.

Transfer to a 100 ml separating funnel.

Add approximately 200 mg of hydroxylamine hydrochloride and dissolve.

Extract the iodine formed with 10 ml of carbon tetrachloride and discard the aqueous phase.

Add 10 ml of water and just sufficient sodium bisulphite to de-colourise both layers, shake, allow to separate and discard the carbon tetrachloride phase.

Add approximately 1 ml of 1:1 nitric acid and a few mg of sodium nitrite.

Extract the iodine formed into 10 ml of carbon tetrachloride and discard the aqueous phase.

Add 10 ml of water and sufficient sodium bisulphite to decolourise both layers, shake, allow to separate and discard the carbon tetrachloride phase.

Centrifuge and remove the last of the carbon tetrachloride with a spitzer.

Add 1 g of sodium bisulphite and dissolve.

Add copper sulphate solution dropwise with stirring until present in excess.

Centrifuge and discard the supernate.

Wash the precipitate twice with 10 to 20 ml of water and once with 10 to 20 ml of ethanol.

Slurry onto a tared watch glass with ethanol. dry under an infra-red lamp and weigh as CuI.

$$1 \text{ mg CuI} = 0.6665 \text{ mg I}$$

Calculate per cent recovery.

Place watch glass and precipitate into a 50 ml 'clearsite' vial, dissolve in dilute ammonia and count under the same conditions of geometry as used for the calibration.

Count the sample source for a time sufficient to give at least 10,000 counts in the 0.364 MeV I-131 peak and subtract background.

Correct peak area for decay from sampling time to counting time (half-life I-131 = 8.05 days).

$$\mu\text{Ci I-131/ml sample} = \frac{\text{corr. peak area} \times 100 \times 100}{t \times E \times R \times 10 \times 2.22 \times 10^6}$$

where t = count duration in minutes,

R = per cent recovery of carrier and

E = absolute efficiency (10.8 per cent in this work).

4. RESULTS

Table 2 gives the results of measurements covering the period 1st June to 3rd October, 1967. In general the changes in the fission product concentrations are consistent with the radiation levels at the 8 in. main in the helium line leading from the reactor aluminium tank.

The levels are very high and the changes in the Ba-140 concentration do not follow the changes in the I-131 concentration. This is most likely due to the fact that barium and iodine isotopes are removed with different efficiencies around the reactor circuits. It is necessary to collect more data before definite conclusions can be drawn.

5. ACKNOWLEDGEMENTS

The authors wish to thank the Radioisotope Standards Group of the Australian Atomic Energy Commission for the supply of the standardised isotopes and information relating to the preferred values for half-life and γ abundance used in this work.

6. REFERENCES

Kleinberg, J. and Cowan, G.A. (1960). - The Radiochemistry of Fluorine, Chlorine, Bromine and Iodine, NAS-NS 3005.

TABLE 2
FISSION PRODUCT CONTENT OF HIFAR D₂O

Date	Time (hours)	Sample Point	Concentration (μCi/ml)	
			Ba-140	I-131
1. 6.67	1100	Weir overflow ^o	2.9 x 10 ⁻³	1.8 x 10 ⁻³
13. 6.67	1600	Weir overflow	2.0	1.6
23. 6.67	1100	Weir overflow	1.4	1.9
5. 7.67	1430	Weir overflow	1.2	1.6
7. 7.67	1100	Weir overflow	1.1	1.6
7. 7.67	1100	Diff. pressure line	9.6 x 10 ⁻⁴	1.7
14. 7.67	1045	Diff. pressure line	1.2 x 10 ⁻³	1.9
14. 7.67	1045	Weir overflow	1.6	2.0
21. 7.67	1000	Weir overflow	1.5	2.2
21. 7.67	1000	Diff. pressure line	1.2	2.0
4. 8.67	1000	Weir overflow	1.2	1.5
4. 8.67	1000	Pump discharge	1.0	1.7
11. 8.67	1200	Weir overflow	1.9	2.0
11. 8.67	1200	Pump discharge	1.8	2.1
18. 8.67	1000	Weir overflow	1.9	2.5
18. 8.67	1000	Pump discharge	1.9	2.6
27. 8.67	1715	Pump discharge	4.1	1.8
4. 9.67	1100	Pump discharge	4.7	1.9
13. 9.67	1000	Pump discharge	3.5	1.9
3.10.67	0200	Pump discharge	2.6 x 10 ⁻²	5.4

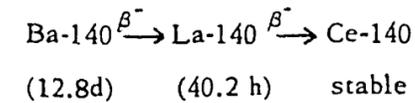
TABLE 3
VALUES OF EQUILIBRIUM RATIO OF La-140 IN Ba-140

Δ	Fraction of Equilibrium Ratio	Time (days)
0.01	0.99	12.8
0.05	0.95	8.35
0.10	0.90	6.4
0.20	0.80	4.5

APPENDIX 1

GROWTH OF La-140 INTO Ba-140

The decay chain may be represented as follows:



Let N_A = atoms of Ba-140 at time t ,
 N_B = atoms of La-140 at time t ,
 N_A^0 = atoms of Ba-140 at $t = 0$,
 N_B^0 = atoms of La-140 at $t = 0$,
 λ_A = decay constant of Ba-140,
 λ_B = decay constant of La-140,

$$\dot{N}_A = -\lambda_A \cdot N_A$$

$$\dot{N}_B = -\lambda_B \cdot N_B + \lambda_A \cdot N_A$$

The solution of these equations is well known (see for example Friedlander and Kennedy. Nuclear and Radiochemistry. John Wiley and Sons, New York, 1955, p.129).

The solutions are:

$$N_A = N_A^0 \exp - \lambda_A \cdot t$$

$$N_B = \frac{\lambda_A}{\lambda_B - \lambda_A} \cdot N_A^0 (\exp - \lambda_A \cdot t - \exp - \lambda_B \cdot t) + N_B^0 \exp - \lambda_B \cdot t$$

Transient equilibrium

Under conditions of transient equilibrium, the ratio of the disintegration rates (A_B/A_A) of parent and daughter is effectively a constant. The time taken to establish transient equilibrium will be longest when $N_B^0 = 0$ i.e. when the daughter has been completely removed from the parent.

For this case,

$$A_A = \lambda_A \cdot N_A = \lambda_A \cdot N_A^0 \exp - \lambda_A \cdot t, \text{ and}$$

$$A_B = \lambda_B \cdot N_B = \frac{\lambda_B \cdot \lambda_A}{\lambda_B - \lambda_A} \cdot N_A^0 (\exp - \lambda_A \cdot t - \exp - \lambda_B \cdot t)$$

Hence,

$$\frac{A_B}{A_A} = \frac{\lambda_B}{\lambda_B - \lambda_A} \cdot \frac{(\exp - \lambda_A \cdot t - \exp - \lambda_B \cdot t)}{\exp - \lambda_A \cdot t}$$

If a sufficiently long time is allowed for 'equilibrium' to become established,

$$\exp - \lambda_B \cdot t \ll \exp - \lambda_A \cdot t$$

APPENDIX I (continued)

Hence

$$\left(\frac{A_B}{A_A}\right)_e = \frac{\lambda_B}{\lambda_B - \lambda_A}$$

where the subscript e refers to the equilibrium condition.

For the Ba-140 - La-140 system,

$$\left(\frac{A_{La-140}}{A_{Ba-140}}\right)_e = 1.15 \quad \text{and} \quad \left(\frac{A_{Ba-140}}{A_{La-140}}\right)_e = 0.869$$

The time taken to reach a specified fraction of the equilibrium ratio is determined by the value of Δ where

$$1 - \Delta = \frac{\exp - \lambda_A \cdot t - \exp - \lambda_B \cdot t}{\exp - \lambda_A \cdot t}$$

Therefore,

$$\Delta = \exp(\lambda_A - \lambda_B) \cdot t$$

$$\text{or } \ln \Delta = (\lambda_A - \lambda_B) \cdot t$$

Values for the time required to reach a given fraction of the equilibrium ratio are shown in Table 3 for the Ba/La pair.

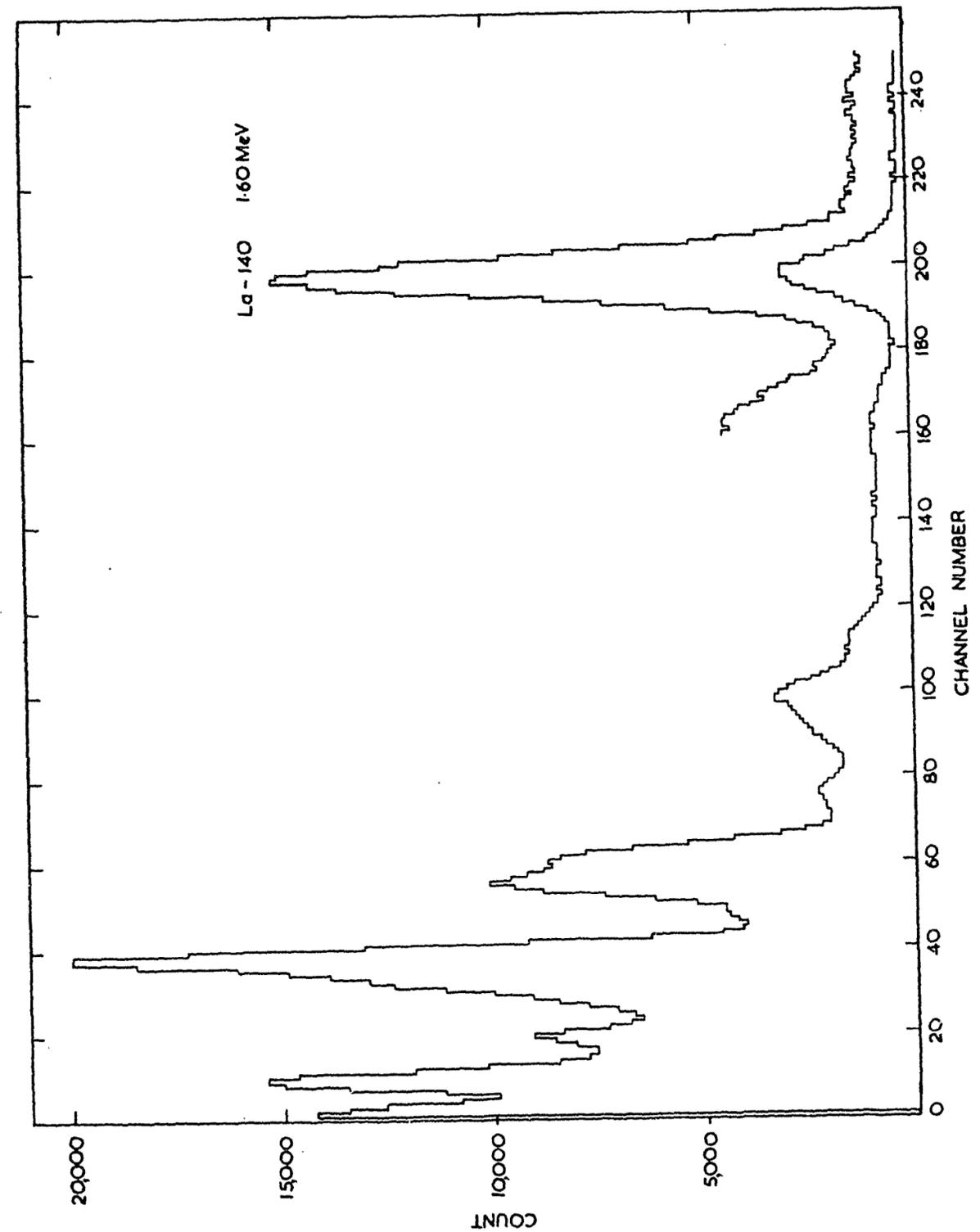


FIGURE 1. γ SPECTRUM OF D_2O COOLED 7 DAYS (NaI (TI) DETECTOR)

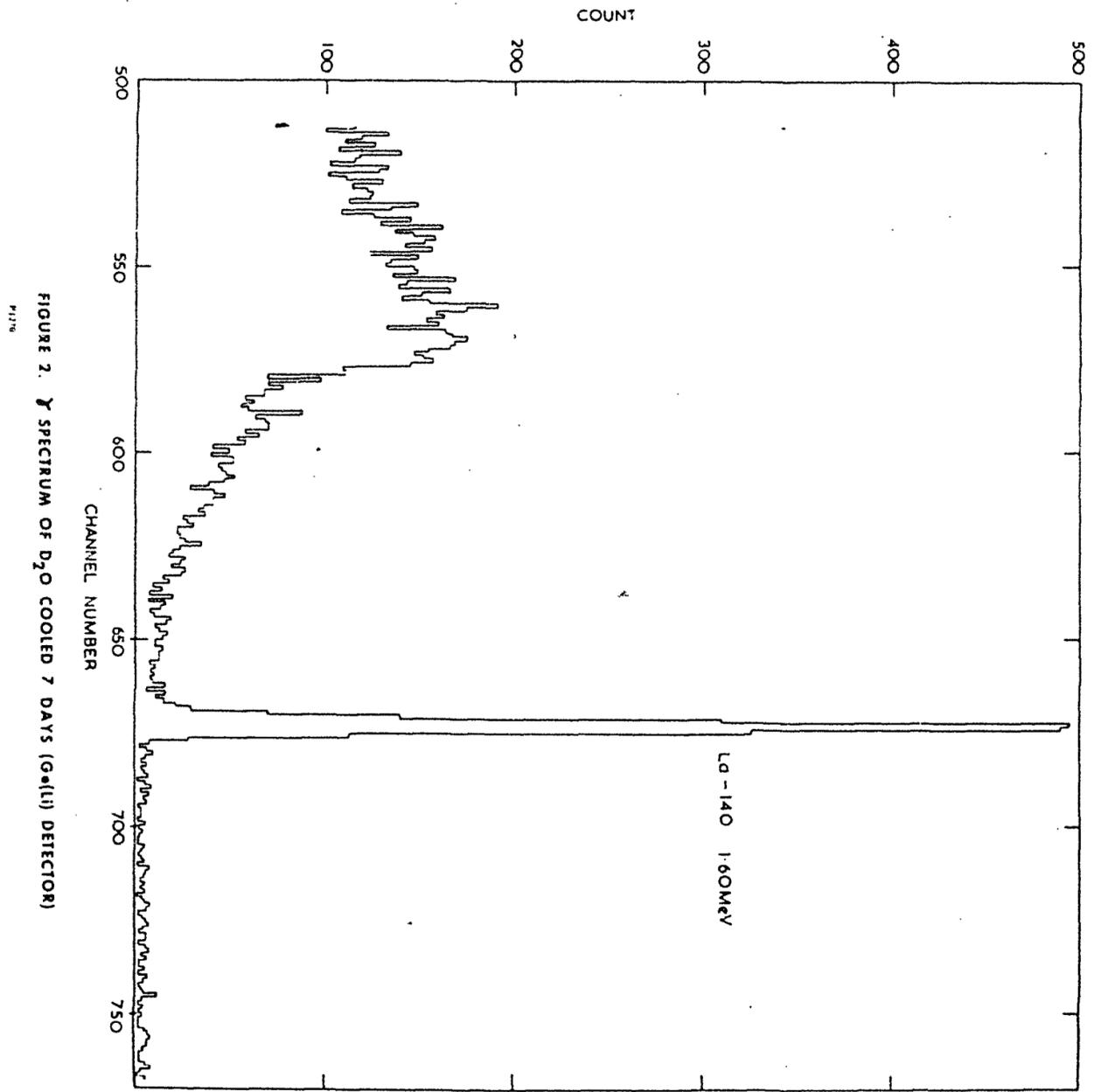


FIGURE 2. γ SPECTRUM OF D_2O COOLED 7 DAYS (Ga(Li) DETECTOR)

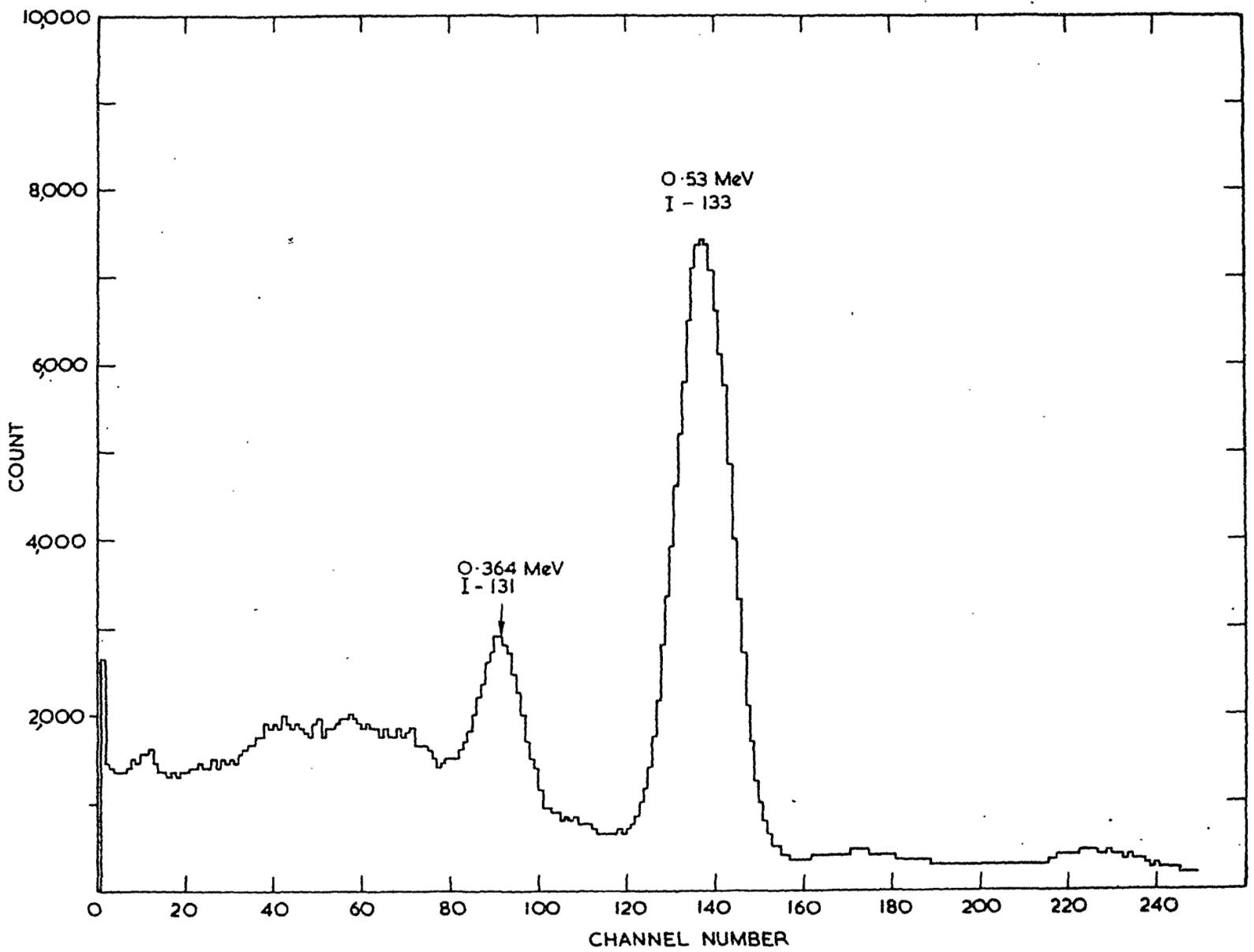


FIGURE 3. γ SPECTRUM OF IODINE ACTIVITIES SEPARATED FROM D_2O 17 HOURS AFTER SAMPLING

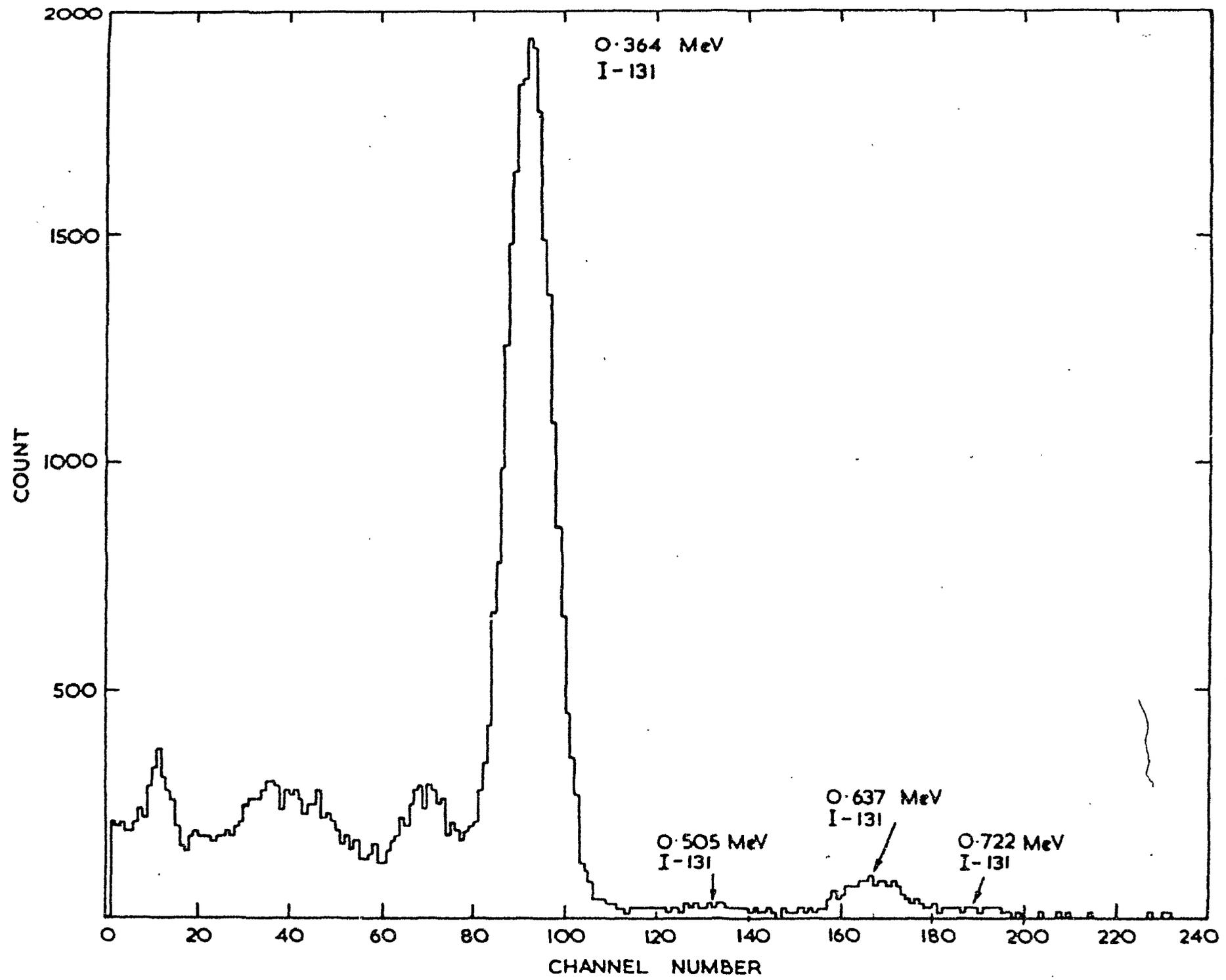


FIGURE 4. γ SPECTRUM OF IODINE ACTIVITIES SEPARATED FROM D_2O 10 DAYS AFTER SAMPLING