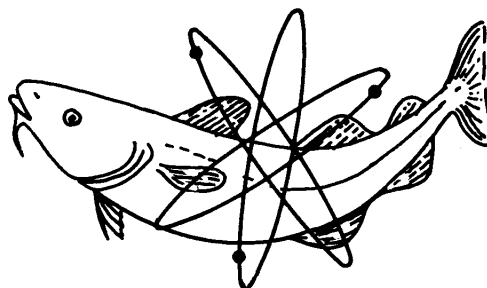


MINISTRY OF AGRICULTURE, FISHERIES AND FOOD

FISHERIES RADIOBIOLOGICAL LABORATORY



GAMMA-SPECTROMETRIC ANALYSIS OF ENVIRONMENTAL MATERIALS

BY

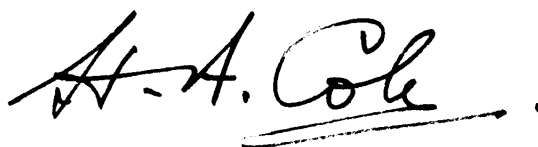
J. W. R. DUTTON

TECHNICAL REPORT FRL 4

HAMILTON DOCK
LOWESTOFT, SUFFOLK

NOVEMBER
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In continuation of our policy of describing the methods used at the Ministry's Fisheries Radiobiological Laboratory to monitor radioactive waste discharge, John Dutton describes in this leaflet the methods employed in the gamma-spectrometric analysis of materials from the aquatic environment. He also describes the method of computing the results and gives some examples.

A handwritten signature in black ink, reading "H. A. Cole". The signature is written in a cursive style with a horizontal line underneath the name.

H. A. Cole

Director of Fishery Research

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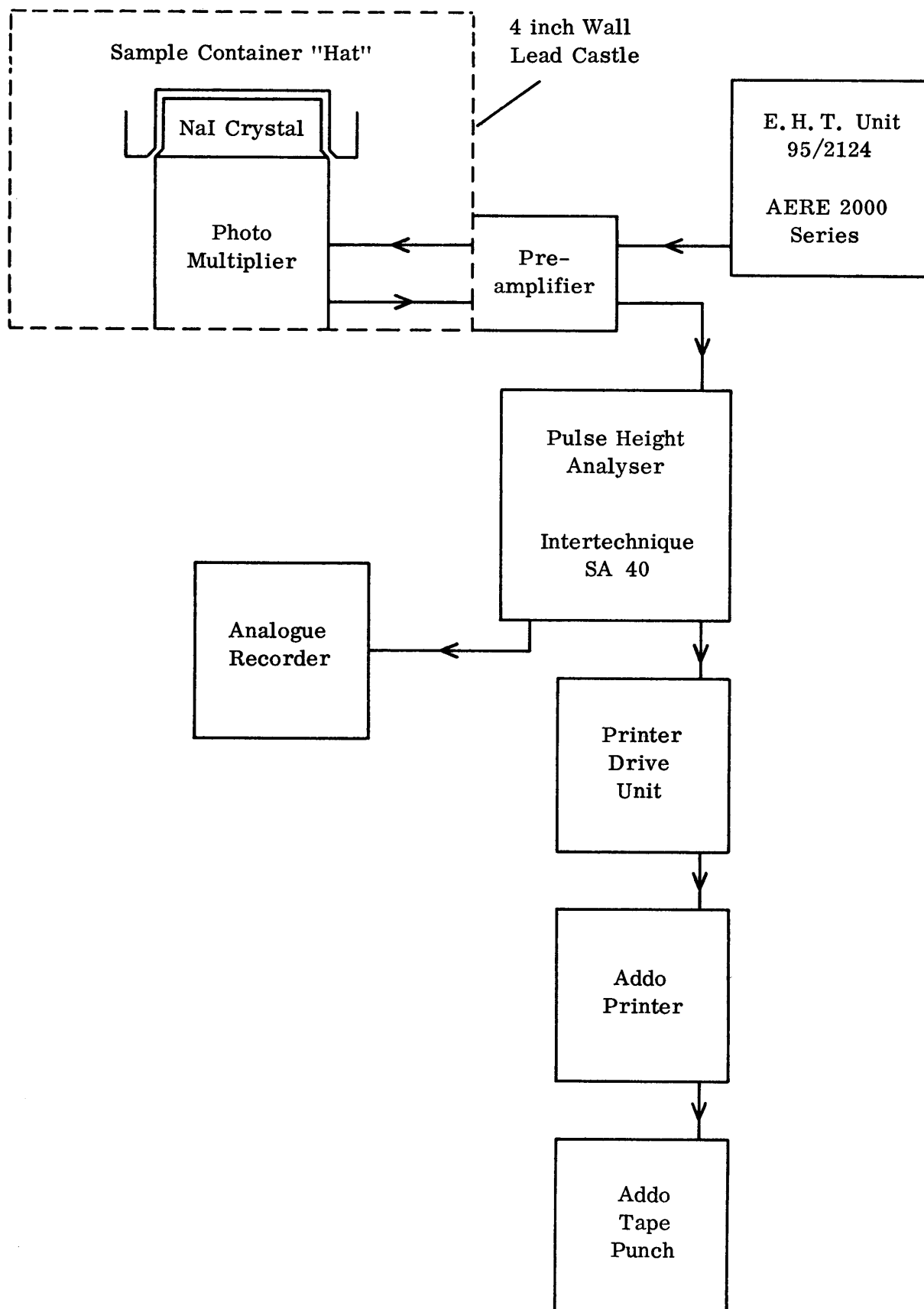


Figure 1 Diagrammatic gamma-spectrometric assembly.

GAMMA-SPECTROMETRIC ANALYSIS OF ENVIRONMENTAL MATERIALS

1 Introduction

The major discharges of radioactive effluents into the aquatic environment arise from fuel re-processing and reactor sites operated by the United Kingdom Atomic Energy Authority (UKAEA) and from nuclear power stations operated by the Central Electricity Generating Board. The major radionuclides in the discharges, together with their concentration factors in various organisms, are shown in Table 1, and it can be seen that the determination of the extent of environmental contamination can be carried out by measurement of either beta or gamma activity of environmental materials. It has already been shown⁽¹⁾ that beta-counting can often provide a suitable check, but this method, albeit simple and rapid, suffers from several disadvantages:

- 1 the sample source causes considerable absorption of the low-energy beta emitters (e. g. niobium-95);
- 2 several of the radionuclides of interest either do not emit a beta particle or do so with very low yield (e. g. chromium-51 and zinc-65 respectively);
- 3 the identification of radionuclides present in the sample is not possible, and variations in levels of fallout and natural radioactivity may be great enough to mask any change in contamination from station operation.

The use of gamma spectrometry can often enable the radionuclides in environmental samples to be identified and quantitatively measured, and the method used at the Fisheries Radiobiological Laboratory since 1963 is described in this report and summarized below.

The gamma activity of the dried sample is measured with a 3 inch x 3 inch NaI (Tl) crystal/photomultiplier coupled to 200 channels of a pulse-height analyser. Suitable areas of the spectrum are chosen to characterize each gamma-emitting nuclide present (these areas are usually the total absorption peak of the major gamma photon from each nuclide), and their count rates in these areas are calculated by the solution of simultaneous equations using matrix inversion (the "matrix" method). The count rates thus obtained are converted to activity in picocuries by comparison with standard sources of each radionuclide identically mounted to preserve the same geometry. The analyser output, together with a numerical code describing the sample and counting details, is recorded on punched tape. The calculations described above, and others to convert the activity to unit wet weight at the time of sample collection, are carried out on an Elliott 803 computer in the Ministry's computer department at Guildford.

Table 1 Radionuclides in effluent; decay characteristics and concentration factors

Isotope	Mode of decay	Energy	E γ -MeV (major)	Half-life	Concentration factor**			
					Fish	Crustacea	Molluscs	Algae
³ H	β^-	0.018 MeV	-	12 years	1	1	1	1
⁴⁵ Ca	β^-	0.25 MeV	-	165 days	10 ⁻¹ -10	1-10	1-10 ²	10-10 ³
⁵¹ Cr	EC	5 keV	0.32 9%	28 days	10 ² -10 ³	10 ³	10 ³ -10 ⁵	10 ² -10 ³
⁵⁴ Mn	EC	6 keV	0.84 100%	314 days	1-10 ⁴	10 ² -10 ⁴	10 ² -10 ⁴	10 ³ -10 ⁴
⁵⁵ Fe	EC	6 keV	-	2.7 years	10 ² -10 ⁴	10 ² -10 ⁴	10 ² -10 ⁴	10 ³ -10 ⁴
⁵⁹ Fe	β^-	0.27 and 0.46 MeV	1.10 57%; 1.29 43%	45 days				
⁵⁸ Co	EC/ β^+	EC - 6 keV	0.81 101%	71 days	10-10 ³	10-10 ⁴	10 ² -10 ⁴	10-10 ³
⁶⁰ Co	β^-	0.31 MeV	1.17 100%; 1.33 100%	5.3 years				
⁶³ Ni	β^-	0.067 MeV	-	120 years	10-10 ²	10 ²	10 ² -10 ⁴	10 ² -10 ³
⁶⁵ Zn	EC/ β^+	EC - 8 keV	1.11 49%	245 days	10 ³ -10 ⁴	10-10 ⁴	10 ³ -10 ⁵	10 ² -10 ³
⁸⁹ Sr	β^-	1.46 MeV	-	51 days	10 ⁻¹ -1	10 ⁻¹ -10	10 ⁻¹ -10 ²	10 ⁻¹ -10 ²
⁹⁰ Sr/Y	β^-	0.54 and 2.27 MeV	-	28 years				
⁹⁵ Zr(+ ⁹⁵ Nb)	β^-	0.51-0.40 MeV	0.73-0.76 \approx 100%	65 days	10 ²	10 ² -10 ³	10 ² -10 ³	10 ² -10 ³
¹⁰³ Ru	β^-	0.21 MeV	0.50 88%	40 days	10 ²	10 ³	10 ³	10 ³
¹⁰⁶ Ru/Rh	β^-	3.6 MeV (others)	0.51 21%; 0.62 11%	1.0 year				
^{110m} Ag	β^-	0.085 and 0.53 MeV	0.66 93%; 0.89 72%	253 days	10 ² -10 ³	10 ² -10 ³	10 ² -10 ⁴	10 ² -10 ⁴
¹²⁴ Sb	β^-	0.61 MeV (others)	0.60 98%; 1.69 48%	60 days				
¹²⁵ Sb	β^-	0.30 MeV (others)	0.43 31%; 0.60 24%	2.7 years	10 ² -10 ³	10 ² -10 ³	10 ² -10 ³	10 ² -10 ³
¹³⁴ Cs	β^-	0.65 MeV (others)	0.61 97%; 0.80 91%	2.1 years				
¹³⁷ Cs	β^-	0.51 MeV	0.66 86%	30 years	10-10 ²	10-10 ²	10-10 ²	1-10
¹⁴¹ Ce	β^-	0.44 and 0.58 MeV	0.15 49%	33 days				
¹⁴⁴ Ce/Pr	β^-	2.98 MeV (others)	0.13 11%	285 days	10-10 ²	10 ⁴	10 ⁴	10 ² -10 ⁴
¹⁴⁷ Pm	β^-	0.23 MeV	-	2.6 years				

*spaces indicate that information is not available.

Four methods of unfolding the spectra were considered: all were based on an empirical approach using radionuclide standards, materials and source/detector geometries that would be encountered in analysis, rather than calculated detector responses.

(a) Spectrum stripping

This technique, although probably the simplest method of unfolding a complex spectrum, was rejected because the errors of stripping are cumulative and could lead to serious errors at the low energy end of the spectrum. This is particularly important in the measurement of cerium-144, which emits a 0.134 MeV gamma photon on decay.

(b) Reiterative procedures^(2, 3)

These techniques for unfolding the spectrum involve successive approximations using standard spectra, and are especially useful in the measurement of environmental gamma fluxes. The number of iterations required is about fifty⁽³⁾, however, and this would result in very long computer runs.

(c) The matrix inversion method⁽⁴⁾

This method seemed well suited to the small computer available at the time of application (1963) and had already been successfully applied in the UKAEA Chemical Services Department at Windscale⁽⁵⁾. The disadvantages of the method are that no direct evaluation of the imprecision of the result is possible and reliance has to be placed on the analysis of artificially prepared samples of known composition. Unfortunately, the levels of radioactivity encountered vary from less than 1 pCi to greater than 10^4 pCi per gramme, and the relative levels of the different radionuclides also vary; consequently, it is impossible to obtain comprehensive analytical quality control. As with most methods, the identity of the radionuclides present in the samples must be established before spectral analysis is possible, and the spectra must always be carefully checked for the presence of new radionuclides.

(d) Least-squares fitting⁽⁶⁾

Although probably the best method, this technique was rejected because the Ministry's Elliott 803 computer did not have sufficient storage capacity to enable all the samples to be handled by one comprehensive program. The position has changed, however, with the recent installation of an ICL 1907 computer at Guildford. A least-squares-fit program is being written, and it is hoped to carry out gamma-spectrometric analysis by this method in the near future.

Let the response of the analyser to m radionuclides $1 \dots j \dots m$ in regions (channel groups) $1 \dots i \dots m$ of the spectrum be denoted by a_{ij} . These sets of responses are normalized to $a_{ij} (i = j) = 1$ for each isotope. Let the measured count rate of a sample, corrected for background, in these regions be C_i , $i = 1 \dots m$. Let the sample count rate of each radioactive nuclide i in the region of the spectrum $j = i$ be x_i . We require to calculate x_i ($i = 1 \dots m$) and we have m simultaneous equations thus:

$$\begin{bmatrix} a_{11} (= 1) & a_{12} & \dots & a_{1m} \\ a_{21} & a_{22} (= 1) & \dots & a_{2m} \\ \vdots & \vdots & & \vdots \\ & & a_{ij} & \\ \vdots & \vdots & & \vdots \\ a_{m1} & a_{m2} & \dots & a_{mm} (= 1) \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_i \\ \vdots \\ x_m \end{bmatrix} = \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_i \\ \vdots \\ C_m \end{bmatrix}$$

$$\text{or } A x = C$$

$$\text{so } x = A^{-1} C ,$$

and expanding we have:

$$\begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_i \\ \vdots \\ x_m \end{bmatrix} = \begin{bmatrix} \alpha_{11} & \alpha_{12} & \dots & \alpha_{1m} \\ \alpha_{21} & \alpha_{22} & \dots & \alpha_{2m} \\ \vdots & \vdots & & \vdots \\ & & \alpha_{ij} & \\ \vdots & \vdots & & \vdots \\ \alpha_{m1} & \alpha_{m2} & \dots & \alpha_{mm} \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_i \\ \vdots \\ C_m \end{bmatrix}$$

So, from the inverted matrix derived solely from the response matrix of pure nuclides, we obtain sets of constants (α_{ij}) which, when applied to measured sample count rates in the selected channel groups (C_i), result in the sample count rates of the pure nuclides (x_i) in these channel groups. If the activity levels of the pure nuclides used to obtain the response matrix are known, then the comparison of the counting rates of the nuclides in the sample with those of the standards will enable the level of activities in the sample to be calculated.

The assembly is shown diagrammatically in Figure 1. The inside dimensions of the lead castle are 22 inches x 22 inches x 26 inches deep. The sodium iodide crystal is a 3 inch x 3 inch high-resolution assembly (Hilger and Watts Limited), with a minimum cobalt-60 peak-to-valley ratio for a test source of 5.5:1.

Samples are arranged round the crystal detector by packing them into 25 ml polythene tubes. These are fitted in an aluminium, copper or perspex "hat" (Figure 2) which is then placed over the crystal. The hat will hold up to fifteen polythene tubes, enabling any multiple between 1 and 15 times the weight in one tube to be analysed using only one calibration geometry.

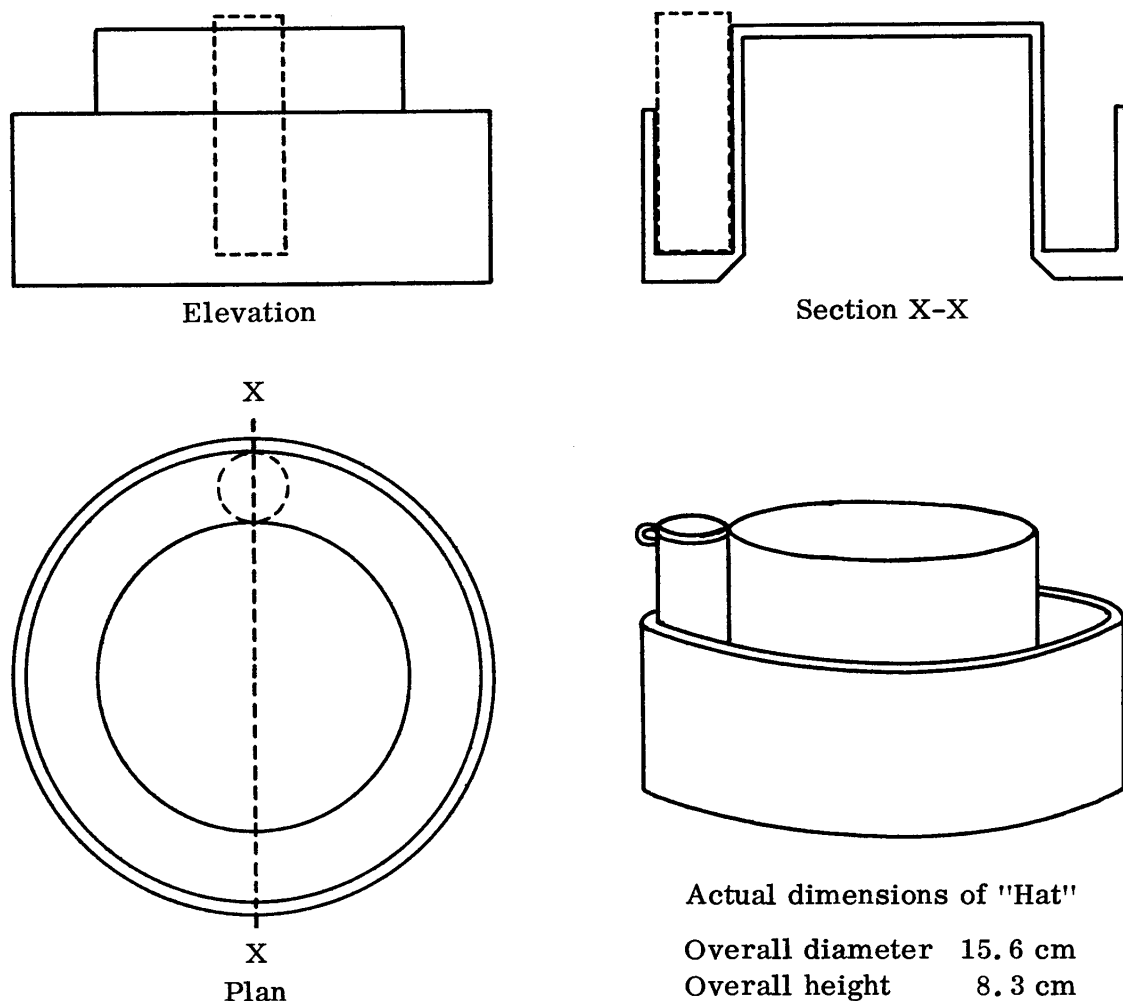


Figure 2 Aluminium sample container "Hat".

Two energy ranges are in use: 200 channels covering 0-1.7 MeV linearly, and 0-2.8 MeV logarithmically. The channel/energy relation is shown in Figure 3 and is checked twice daily using a ^{22}Na standard, the EHT being adjusted if necessary to maintain the 0.51 and 1.28 MeV peak positions. The day to day variation in stability of the assembly is ± 1.0 per cent at channel 199 and this small amount is due almost entirely to gain drifts.

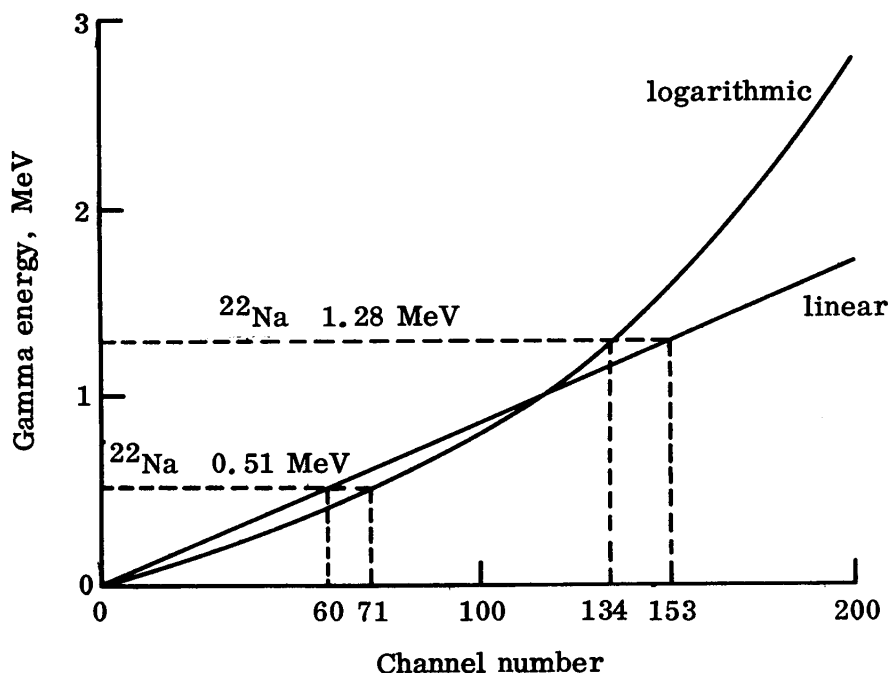


Figure 3 The relationship between gamma energy and channel number.

The background is checked daily over the whole spectrum by a 10 minute count, and each week by a long count (approximately 1 000 minutes).

5 Calibration of the gamma spectrometer

5.1 Preparation of standards

Radioactive standardized solutions are obtained from the Radiochemical Centre, Amersham, except for ^{40}K where A.R. potassium chloride is used. The standards for the spectrometer are made by adding accurately-known amounts (about $0.1 \mu\text{Ci}$) of standardized radioactive solutions (except ^{40}K , 6 g A.R. KCl in aqueous solution) to materials similar in gamma-scattering properties to those being analysed; thus sodium phosphate (25 grammes per tube) is used for sediments⁽⁷⁾, 4-amino-3-nitro-toluene (15 grammes per tube) is used for animal flesh, and A.R. sodium chloride (35 grammes per tube) for dried sea water. If, however, suitable inactive equivalents are not available, then environmental materials are used. In all cases, the amount of dry material spiked should pack into six polythene tubes.

After gentle drying of the spiked materials, each mixture is carefully homogenized, to ensure even distribution of the radioactivity, and packed into the tubes. The standards are then placed in the hat, interspersed with tubes of the unspiked material, and two counts made on consecutive days. The length of the counts varies between 100 and 500 minutes, except for those of the blank and ^{40}K standard which are of 3 000 minutes duration.

Thorium (4n) and uranium (4n+2) series standards are prepared by making solutions of Th(NO₃)₄·6H₂O (purified in 1906 and obtained from the Radiochemical Centre, Amersham) and uranium ore of known U content (obtained from UKAEA Springfields), and the solutions are then added to the inactive materials. The uranium series standard is counted 21 days after packing into the polytainer, this delay allowing the ²²²Rn and daughters to attain equilibrium with ²²⁶Ra.

5.2 Derivation of the inverted matrix

The channel groups characterizing the radionuclides are selected to make the most use of the spectrum in terms of counts in these groups, and it is obvious that the major total absorption peaks are the best areas of the spectrum to utilize. An example of a matrix is given in Table 2.

Table 2 The matrix used for the analysis of shellfish flesh from the environs of the UKAEA fuel-processing plant at Windscale

Nuclide (j)		Major γ emission (MeV)	Other γ photons (MeV) 10% of the major γ	Channel groups (i) (linear channel:energy)
¹⁴⁴ Ce	(1)	0.134	-	12- 15 (1)
¹⁰⁶ Ru	(2)	0.51	0.62	52- 66 (2)
¹³⁷ Cs	(3)	0.66	-	78- 82 (3)
⁹⁵ Zr/ ⁹⁵ Nb	(4)	0.72-0.76	-	89- 94 (4)
⁴⁰ K	(5)	1.46	(Bremsstrahlung)	164-182 (5)

After the duplicate measurements have been made, the counts of the standards in the selected channel groups are measured, converted to counts per minute, and the appropriate blank subtractions made. The count rates thus obtained* for each nuclide are normalized to the characteristic channel group ($a_{i=j}$) as unity.

These values constitute the response matrix of the spectrometer. The inversion of the response matrix is performed on the Elliott 803 computer.

5.3 Background

The background of the gamma-spectrometric assembly is determined by preparing 15 tubes of the inactive equivalent to the material being analysed and measuring the count rates in the channel groups used in the matrix.

*These count rates are used to determine isotope counting efficiencies (E_k), see paragraph 5.4.

$$E_k = \frac{\text{cpm in channel group k from isotope k}}{\text{pCi activity standard k}}$$

5.4 Radionuclide counting efficiencies

The efficiency E_k with which radioactivity of the nuclide k is measured in its characteristic channel group k is calculated as shown in the footnote on page 7.

The derived count rates x_k of the radionuclides in a sample are converted to pCi activity at the time of counting by the formula:

$$\text{pCi isotope } k = \frac{x_k}{E_k} .$$

5.5 Data inserted into program

The channel groups required in the calculations, the elements of the inverted matrix, the background counts, and isotope efficiencies are inserted into the computer program together with decay constants to enable the computer to correct for the radioactive decay of the different radionuclides.

6 Analysis of samples

6.1 Sample preparation

On receipt, the sample is examined and any portions considered unrepresentative removed; it is then transferred to a tared aluminium tray or glass bowl and weighed. Weeds are then oven-dried at 105-110°C. Silts and animal flesh are freeze-dried (Edwards High Vacuum Limited Vacuum Freeze Drier, Model 30P2T). The product in the case of silts is a friable powder; indeed, all freeze-dried materials are very easy to handle. The dried sample is then weighed and packed into the polythene tubes, the packing density varying with the type of material and drying technique. For example, any one tube will hold 15 g animal flesh, 25 g silt or 35 g dried seawater residue. For some silts, the density is required as well as the dry:wet ratio, and the sequence of weighing and transfer operations is given below.

Weight of sample container and sample ... W_1 g

Fill to brim with distilled water,

Total weight W_2 g

Weight of freeze-drying tray W_3 g

Transfer sample and water to tray,

Weight of empty sample container W_4 g

Fill container to brim with distilled water,

Total weight W_5 g

Dry the sample,

Weight of tray plus dry sample W_6 g

Then weight of wet sample = $W_1 - W_4$ g

volume of wet sample = $(W_5 - W_4) - (W_2 - W_1)$ cm³

so density of wet sample = $\frac{W_1 - W_4}{(W_5 - W_4) - (W_2 - W_1)}$ g/cm³

weight of dry sample = $W_6 - W_3$ g

so dry:wet weight ratio = $\frac{W_6 - W_3}{W_1 - W_4}$.

6.2 Counting

The sample tubes are then loaded into the hat, interspersed if necessary with tubes of the appropriate background material, and counted. There are no hard-and-fast rules applied in deciding the length of counting required; the duration is limited as much by the numbers of samples requiring analysis as by any other analytical parameter such as the counts accumulated in the photopeaks. At the end of the count, the 200 channel counts in the analyser are recorded in three ways:

by Addo printer on printer roll paper,

by Addo punch on 5 hole punched tape, and

on an Analogue recorder.

6.3 Tape heading

Before the recording of the analyser channels, the tape is headed using the Addo punch, the following details being inserted:

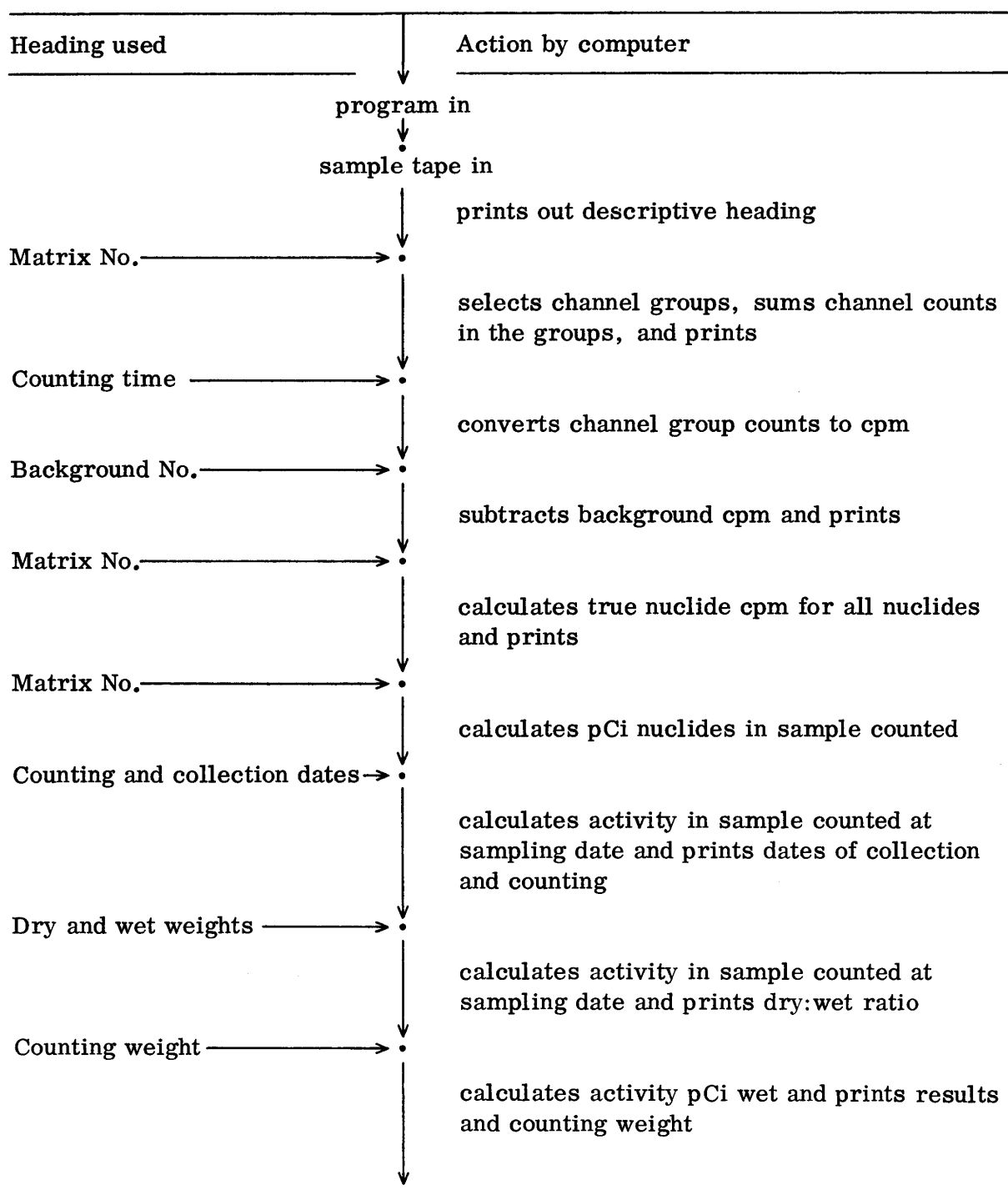
	INPUT	OUTPUT
	Tape headed	Computer prints
Introduction	Tape identification number	Number
Analysar No.	1 or 2	-
Sample group	Numerical code	Word equivalent
Sample definition	"	"
Sample subgroup	"	"
Frequency	"	"
Site	"	"
Station No.	Number	Number
Number of collection dates	"	"
Collection (up to a maximum of four dates)	Day Month Year	Date As punched
Counted	Day Month Year	"
Matrix No.	Number	"
Background No.	"	"
Counting time	As counted	"
Dry weight	"	
Wet weight	"	Dry:Wet weight (ratio)
Counted weight	"	As punched
Heading check	Code	-

This heading ensures firstly that the full description of the sample is printed with the results, and secondly that the correct analytical procedure is carried out by the computer.

After the 200 channel output has been printed, a further tape check code is printed to indicate the end of the tape.

7 Computer calculation of results

The computer calculations and the incorporation of the tape headings are shown in the following diagram:



The computer program is an Elliott 803 auto code program (A207) written for this laboratory by T. F. Hughes and R. S. Huttley of the Ministry's 803 Data Processing Unit at Guildford. The final results, together with the descriptive heading, are produced by the computer on paper sheets of approximately 8 x 25 cm in size.

The dry and wet weights of animal flesh and weed samples are incorporated in the tape headings as indicated, but silt and seabed samples are generally required to be reported as pCi/g dry matter. Conversion of the activity into pCi/cm³ if necessary is effected by the following calculation:

$$\text{pCi/cm}^3 = \text{pCi/dry} \times \text{dry:wet weight ratio} \times \text{density of wet sample} \\ \text{(as determined in paragraph 6.1).}$$

8 Examples of gamma spectra

Some typical gamma spectra are shown in Figures 4 to 12 to give some indication of the wide variety of materials and radionuclides encountered during surveys of the aquatic environment. The radionuclides present and the energies of the total absorption peaks used in the analysis are shown.

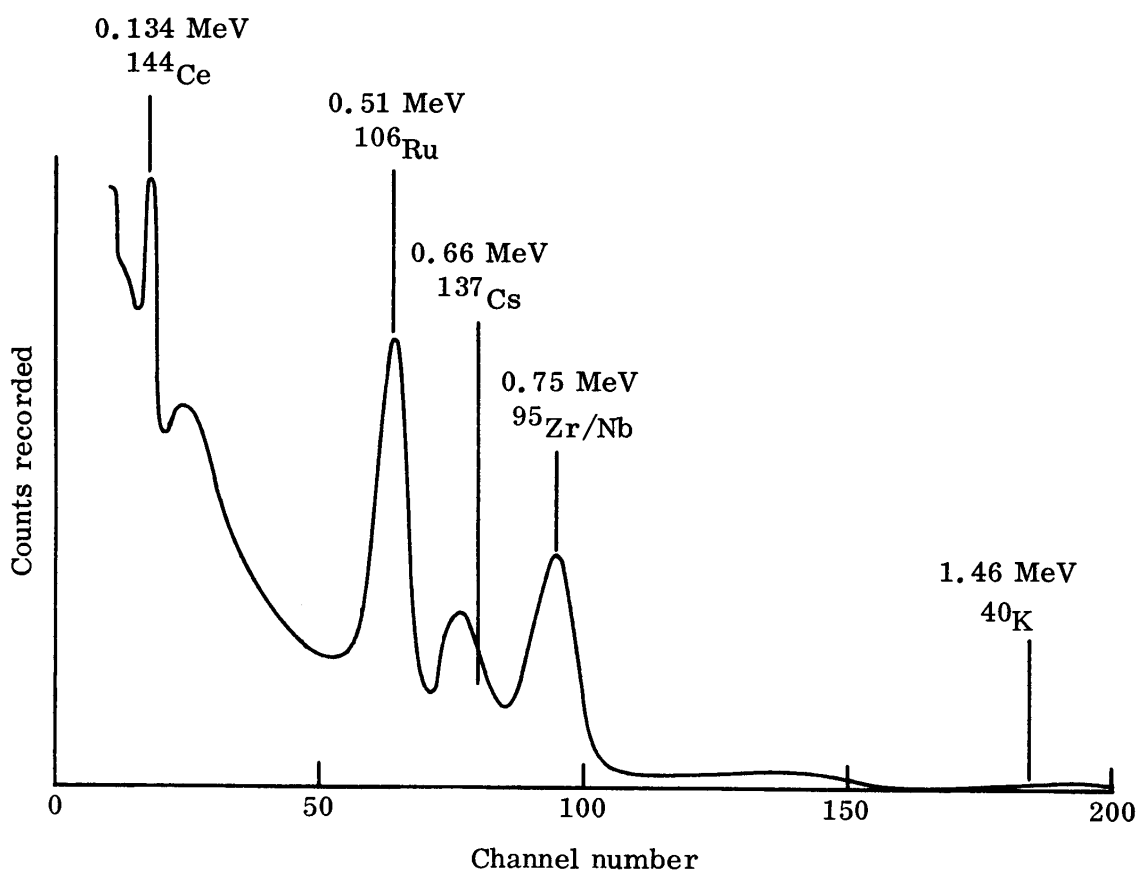


Figure 4 Mytilus edulis (mussel) soft parts, from Braystones (Cumberland).

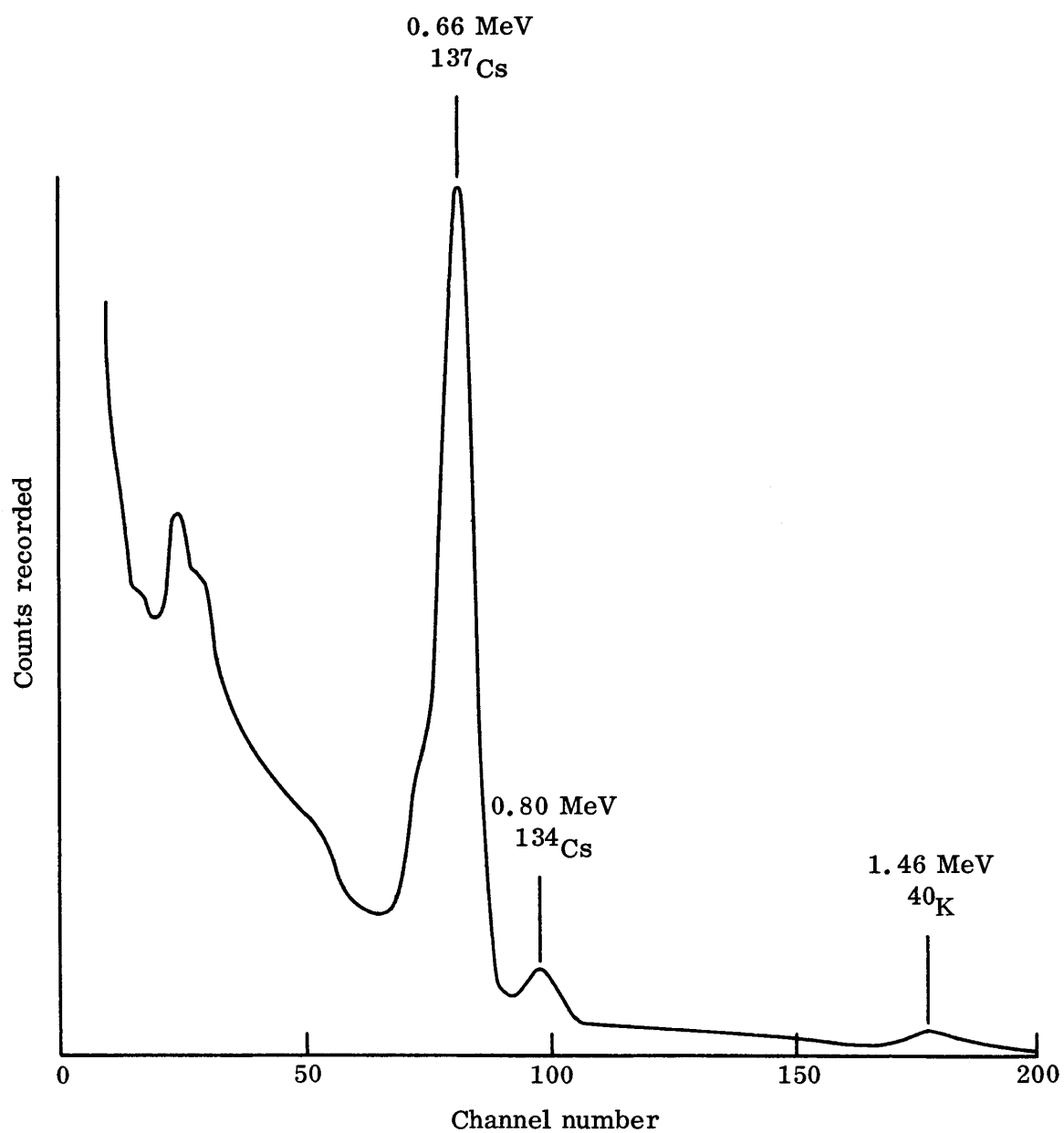


Figure 5 Salmo trutta (brown trout) flesh, from Trawsfynydd (North Wales).

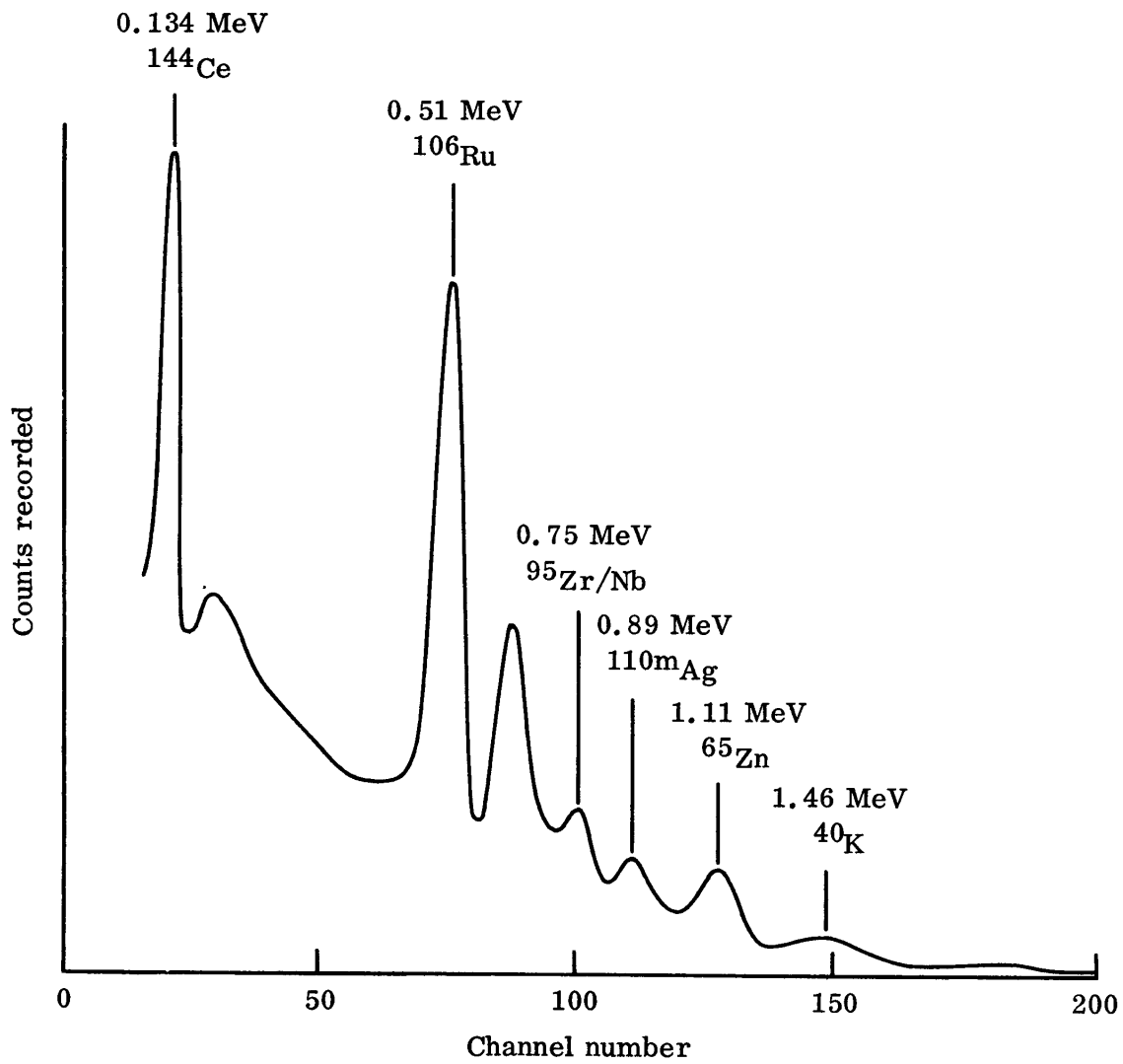


Figure 6 Ostrea edulis (native oyster) soft parts, from the north-east Irish Sea.

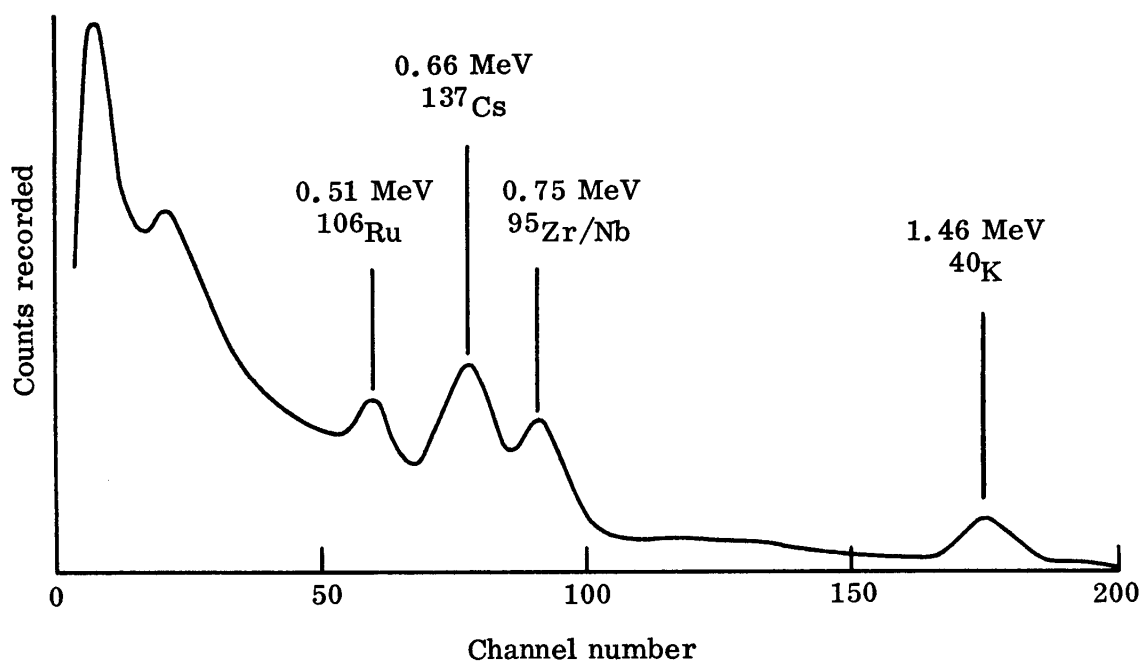


Figure 7 Seawater residue from Braystones (Cumberland).

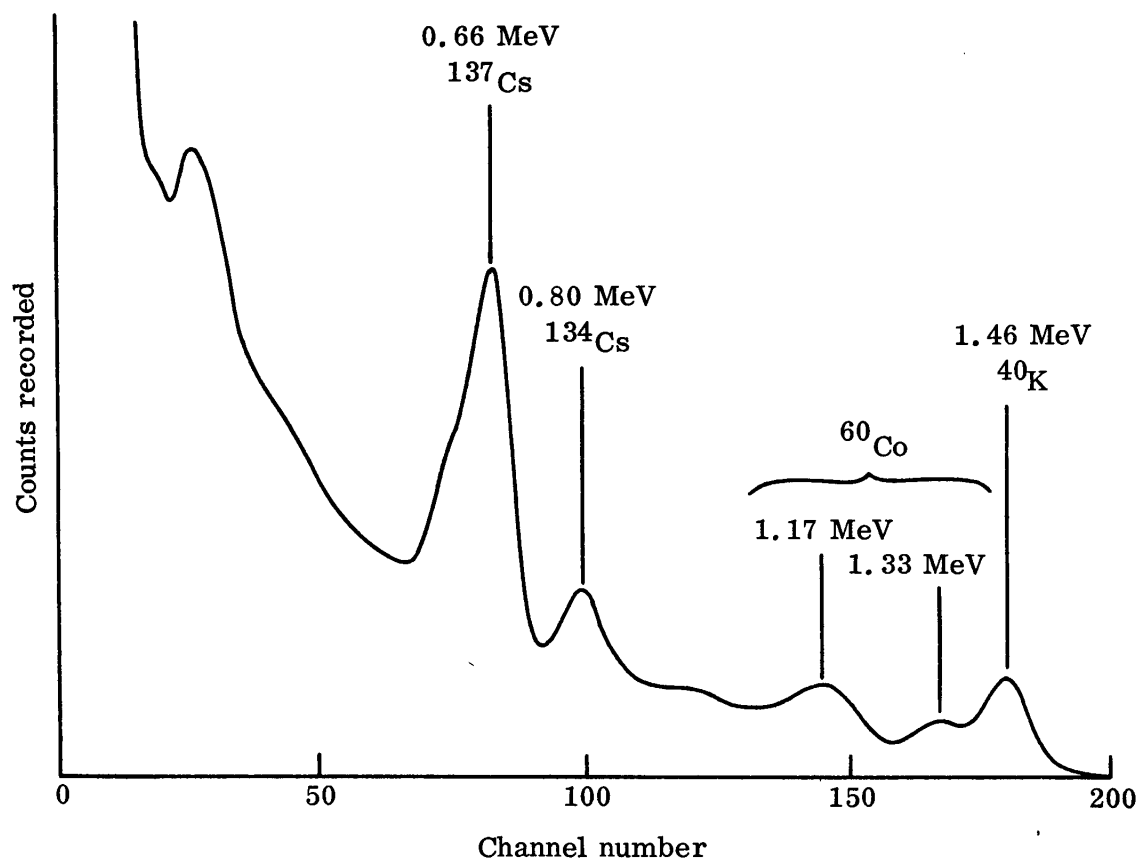


Figure 8 *Fucus vesiculosus* (bladder wrack) from Bradwell Waterside (Essex).

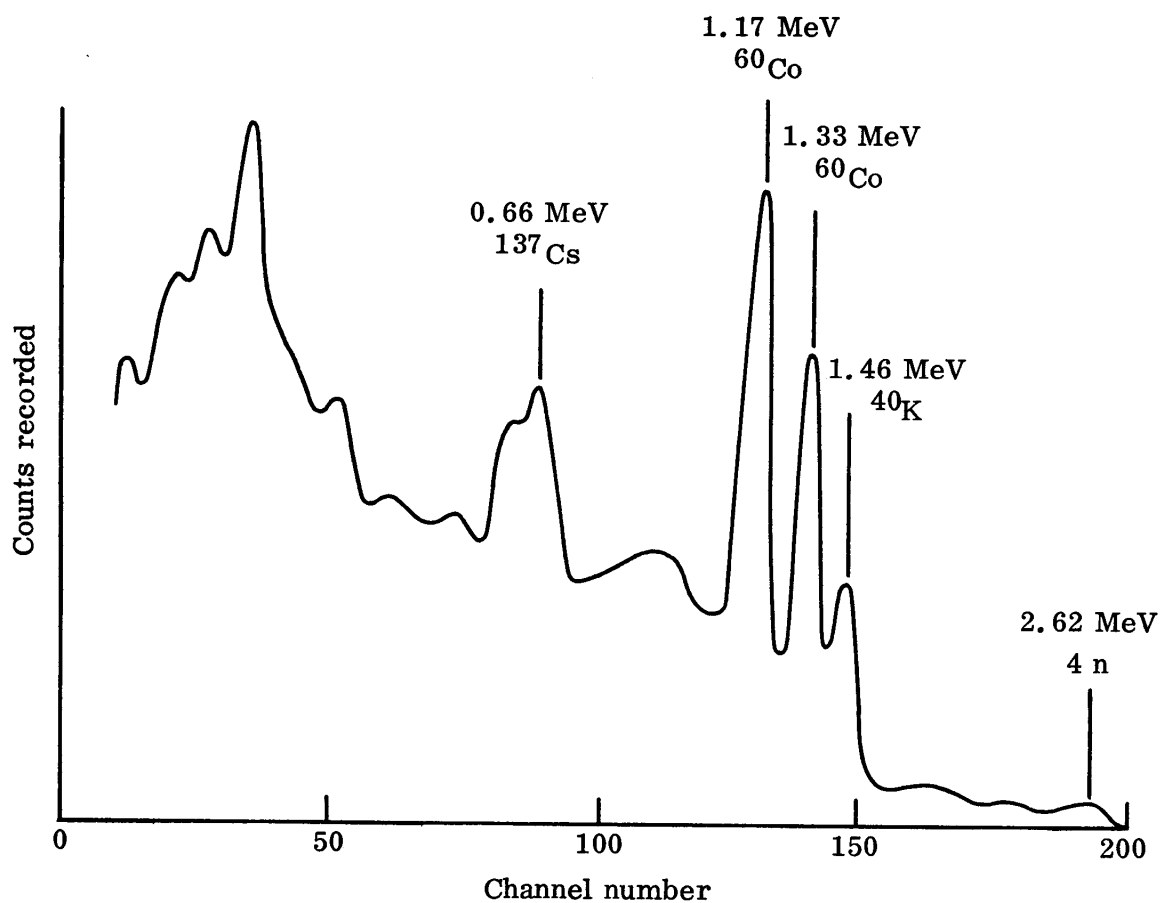


Figure 9 Sediment, grab sample from the River Clyde, Scotland.

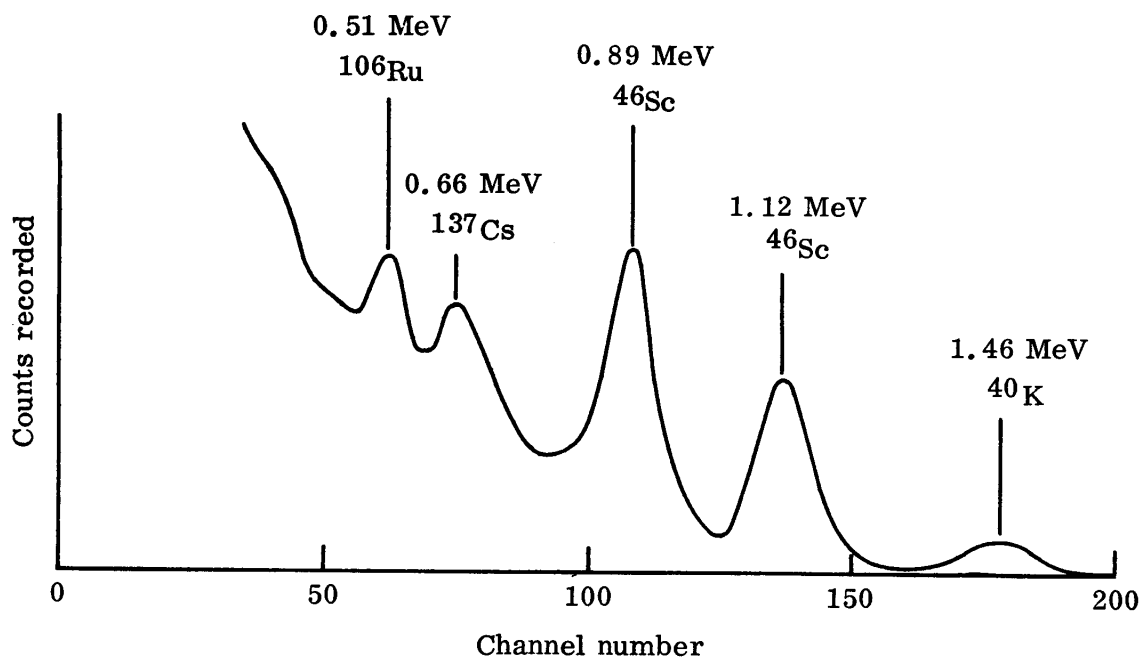


Figure 10 Sediment from the Firth of Forth, Scotland.

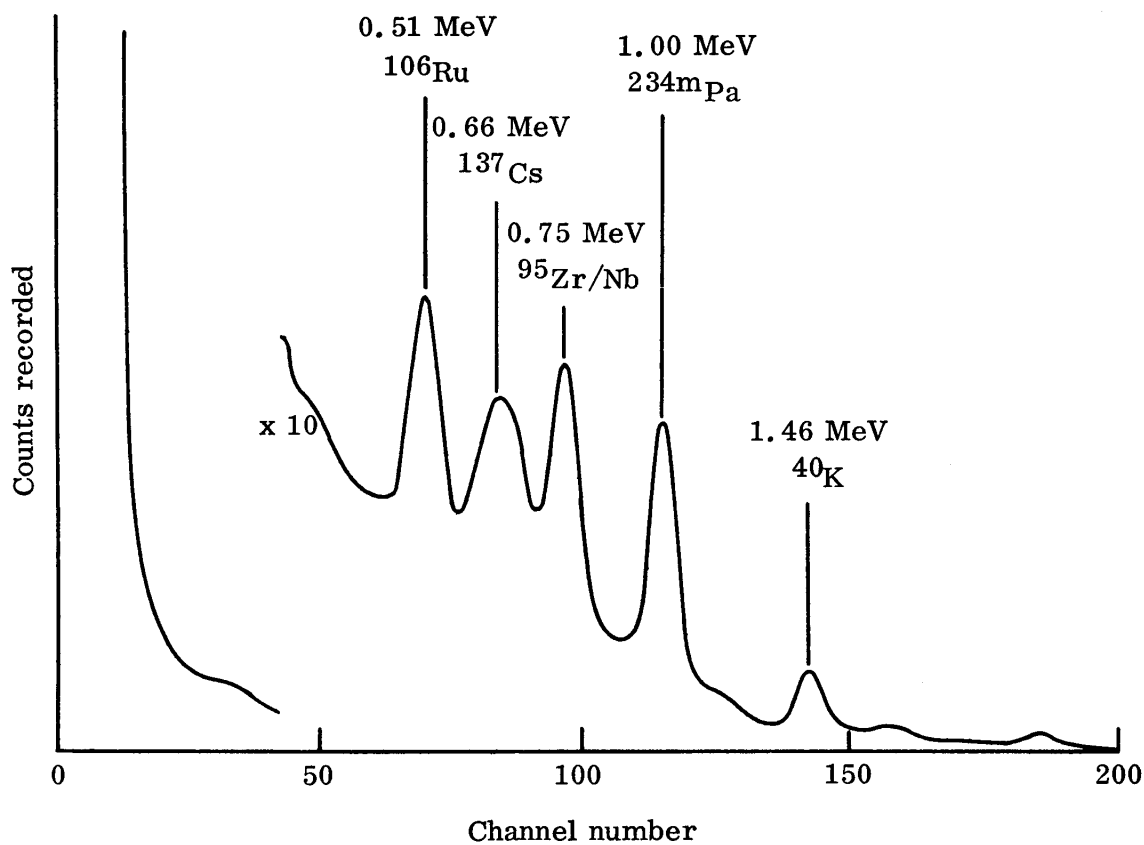


Figure 11 Sediment from the River Ribble, Lancashire.

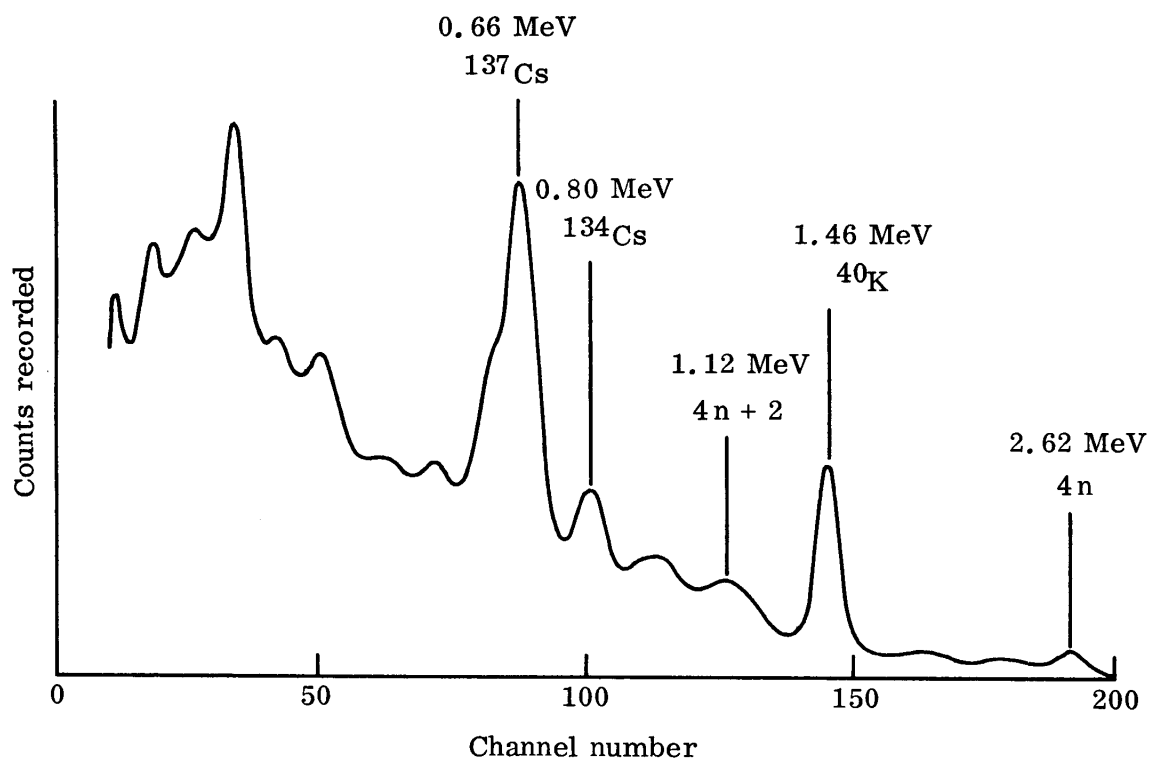


Figure 12 Sediment from the Bristol Channel.

REFERENCES

- 1 DUTTON, J. W. R. Gross beta counting of environmental materials. Ministry of Agriculture, Fisheries and Food, Fisheries Radiobiological Laboratory. Technical Report FRL 3 (1968), 13 pp.
- 2 SCOFIELD, N. E. A technique for unfolding gamma-ray scintillation spectrometer pulse-height distributions. US NRDL-TR-447 (1960), 41 pp. US Naval Radiological Defense Laboratory, San Francisco 24, California.
- 3 MOLLENAUER, J. F. A computer analysis for complex sodium iodide gamma spectra. UCRL-9748 (1961), 30 pp. University of California, Lawrence Radiation Laboratory, Berkeley, California.
- 4 HUBBELL, J. H. and SCOFIELD, N. E. IRE transactions on nuclear science, NS-5 (1958), pp. 156-8.
- 5 UKAEA The determination of ruthenium-103, caesium-137, zirconium/niobium-95 and cerium-144 in shore sand and sea silt samples. PG Report 312W (1962), 17 pp. HMSO, London.
- 6 SALMON, L. Analysis of gamma-ray scintillation spectra by the method of least squares. Nuclear Instruments and Methods, 14 (1961), pp. 193-9.
- 7 GUSTAFSON, P. F., MARINELLI, L. D. and BRAR, S. F. Natural and fission-produced gamma-ray emitting radioactivity in soil. Science, Vol. 127 (1958), pp. 1240-2.

REPORTS IN THIS SERIES

Radioactivity in surface and coastal waters of the British Isles, by N. T. Mitchell. Technical Report FRL 1. October 1967.

Radioactivity in surface and coastal waters of the British Isles 1967, by N. T. Mitchell. Technical Report FRL 2. September 1968.

Gross beta counting of environmental materials, by J. W. R. Dutton. Technical Report FRL 3. October 1968.

Gamma spectrometric analysis of environmental materials, by J. W. R. Dutton. Technical Report FRL 4. November 1969.

Radioactivity in surface and coastal waters of the British Isles 1968, by N. T. Mitchell. Technical Report FRL 5. November 1969.

Determination of caesium-137 in sea and fresh waters, by J. W. R. Dutton. Technical Report FRL 6. December 1969.