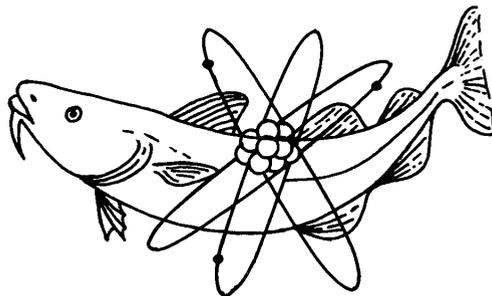


MINISTRY OF AGRICULTURE, FISHERIES AND FOOD
FISHERIES RADIOBIOLOGICAL LABORATORY



THE
DETERMINATION
OF RADIOCAESIUM
IN SEA AND FRESH WATERS

J.W.R. DUTTON

TECHNICAL REPORT FRL 6

HAMILTON DOCK
LOWESTOFT, SUFFOLK

OCTOBER
1970

In this paper John Dutton describes in detail the methods used at the Fisheries Radiobiological Laboratory for the determination of radiocaesium in natural waters. Further radiochemical methods will be published in this series, and the intention is to enable other workers to make a critical evaluation of our results and, if they wish, to apply the methods in their own studies.

A handwritten signature in black ink, reading "H. A. Cole" with a period at the end. The signature is written in a cursive style and is underlined with a single horizontal stroke.

H. A. Cole

Director of Fishery Research

CONTENTS

	Page
Abstract	1
1 AMP separation	1
1.1 Introduction	1
1.2 Analytical method	2
1.2.1 Reagents	2
1.2.2 Special filtration apparatus	3
1.2.3 Procedure	3
2 KCFC separation	4
2.1 Introduction	4
2.2 Analytical method	4
2.2.1 Reagents	4
2.2.2 Special filtration apparatus	5
2.2.3 Procedure	5
3 Measurement of radiocaesium	6
3.1 Special apparatus	6
3.2 Procedure	6
References	8
Reports in this series	9

THE DETERMINATION OF RADIOCAESIUM IN SEA AND FRESH WATERS

ABSTRACT

Two simple one-step separations of radiocaesium from sea and fresh waters are described, using either ammonium dodeca-molybdophosphate (AMP) or potassium cobalti-hexacyanoferrate (KCFC). Caesium-137 and -134 are measured by gamma-counting the dried material, using a sodium iodide (TI) crystal coupled to a gamma spectrometer. The methods are extremely simple, and enable caesium-137 at levels down to about 1 pCi/l (depending on the volume of water used) to be determined in rain, river, lake and sea waters without recourse to sophisticated chemical techniques.

1 AMP SEPARATION

1.1 Introduction

Ammonium molybdophosphate was first used as a reagent by Yamagata and Yamagata⁽¹⁾, who coprecipitated caesium with it as a method of separating caesium-137 from biological materials. Buchwald and Thistlethwaite⁽²⁾ studied the ion-exchange properties of AMP, by which the separation of caesium from other alkali metals could be achieved, and Miyake *et al.*⁽³⁾ and Yamagata⁽⁴⁾ applied the technique to the separation of caesium-137 from sea water, using gamma spectrometry to measure the caesium-137 content. Morgan and Arkell⁽⁵⁾ developed a method for the determination of caesium-137 in sea water, using an AMP/asbestos ion-exchange column; after dissolution of the AMP and adsorbed caesium in sodium hydroxide solution, a series of precipitations removed the traces of rubidium-86 which occur naturally in sea water; the caesium-137 thus separated was then measured by beta counting.

The alkali metal molybdophosphates are non-stoichiometric, and the metal:molybdophosphate ratio depends on the pH and the concentration of reagents during precipitation, as shown by Thistlethwaite⁽⁶⁾. Their solubility in water and acids decreases from sodium, which is very soluble, to caesium (and ammonium); they

are all soluble in alkaline solutions. The properties and uses of AMP are covered by a chapter in a monograph by Amphlett⁽⁷⁾ entitled "Inorganic Ion Exchangers", with twenty-six references.

The method described below is based on Yamagata's technique for the separation of caesium from sea water: after addition of caesium carrier to the filtered sample, ammonium nitrate is added to fresh waters to reduce the solubility of AMP⁽⁵⁾ without affecting the adsorption of caesium. The pH is then adjusted to between 1 and 1.5 with nitric acid, and scavenging of the caesium from the solution is carried out by adding 50 grammes of AMP and agitating vigorously; this removes more than 95 per cent of the caesium. The AMP is allowed to settle overnight and most of the supernatant liquor is then siphoned off. No experiments have been done to determine whether the agitation by itself removes all the caesium, or whether the settling also is required; settling overnight, however, is a useful analytical technique, being less time-consuming than filtering the whole sample.

The AMP is then filtered from the residual liquor and, after washing with an acid solution of 0.025 M ammonium nitrate and a 0.01 M nitric acid solution, can be oven-dried and gamma-counted. A single-gate gamma count is suitable only if caesium-137 alone is present. The use of a gamma spectrometer enables any contamination to be detected - a possible contaminant is zirconium-95/niobium-95 (12 per cent adsorbed)⁽⁴⁾ from nuclear weapon test fallout or effluent discharge - and of course is necessary when caesium-134 is present from effluent discharge.

1.2 Analytical method

1.2.1 Reagents

Ammonium dodeca-molybdophosphate (AMP): the normal material obtained from Messrs BDH Chemicals Limited, Hopkin and Williams Limited, etc. is satisfactory.

Acid 0.025 M ammonium nitrate solution: 2 g/l ammonium nitrate and sufficient nitric acid (AR) to adjust the pH to between 1 and 1.5.

Caesium-137 and -134 standard solutions: obtained from RCC, Amersham, and accurately diluted until the activity levels are approximately 1000 pCi/ml.

Carrier solution of caesium chloride: 1 ml \equiv 30 mg Cs.

1.2.2 Special filtration apparatus

- (a) Millipore filtration assembly, comprising a pressure vessel and a filter press capable of taking 293 mm diameter millipore filter papers with 0.22 μm pore size (type GS).
- (b) Buchner filtration assembly, comprising a 1 litre buchner flask and glass sinter filter-funnel (porosity 4). A suitable size funnel has 700 ml capacity and a 120 mm diameter filter.

1.2.3 Procedure

- (1) Take about 50 litres of the sample and, if it has not been filtered on collection, filter through the millipore filter assembly into a polythene carboy.
- (2) Measure the volume of the filtered solution; let this be V litres.
- (3) Add 1 ml of the caesium carrier solution.
- (4) For freshwater samples only: add 100 g ammonium nitrate (AR).
- (5) Commence bubbling air into the carboy.
- (6) Add concentrated (SG 1.42) nitric acid (AR) until the pH is between 1 and 1.5 (use multirange pH paper).
- (7) Add 50 g dry AMP. (The AMP should be dried at 105°C and kept in a desiccator until required for use.)
- (8) Bubble air through the sample for 1 hour.
- (9) Allow the AMP to settle by standing the sample overnight. (Tipping the container is inadvisable because the AMP may then stick to the side while settling.)
- (10) Siphon off about 45 litres of the supernate. (The AMP is easily disturbed.) If a strontium-90 determination is required then retain the supernate.
- (11) Transfer the precipitate by swirling the remaining liquor and tipping part of the slurry into a 3 litre beaker.
- (12) Filter the slurry through a large-capacity glass sinter filter-funnel (porosity 4) into a buchner flask; add the filtrate to the supernate (stage 10) if required for further analysis.
- (13) Continue to transfer the slurry as in stages 11 and 12, keeping the final 2 litres of filtrate and returning them as often as necessary to the carboy in order to remove as much of the AMP as possible.
- (14) Wash the AMP with 50 ml of the acid 0.025 M ammonium nitrate solution.

- (15) Wash the AMP with 50 ml of 0.01 M nitric acid.
- (16) Suck air through the precipitate to remove most of the residual wash liquor.
- (17) Transfer as much as possible of the AMP to a porcelain bowl and dry in an oven at 105°C to constant weight. (The apparatus may be cleaned by dissolving the small amount of AMP left in 7 M ammonium hydroxide, followed by rinsing well with water.)
- (18) Transfer the dry AMP to a tared petri dish (a suitable disposable type is available, 75 mm in diameter, made of polystyrene) and reweigh. Let the weight of recovered AMP be W g. The AMP should be free from lumps and the surface should be smoothed to ensure reproducibility of counting geometry. Seal the dish with adhesive tape.
- (19) Prepare a background dish, using 50 g of clean AMP. A new background dish should be prepared each time a fresh batch of AMP is used.

2 KCFC SEPARATION

2.1 Introduction

The ion-exchange absorption of caesium by potassium cobalti-hexacyanoferrate, $K_2[CoFe(CN)_6]$, was first reported by Prout, Russell and Groh⁽⁸⁾, and almost immediately applied to the analysis of radiocaesium in sea water by Boni⁽⁹⁾. The method described below is based directly on that of Boni: the sea water - after acidification to pH 1.5 with hydrochloric acid - is passed through a KCFC column, and the caesium-137 (and caesium-134) determined by gamma spectrometry. A high flow rate (approximately 10-15 l/hour) and the low pH help to minimize the possibility of contamination.

2.2 Analytical method

2.2.1 Reagents

Potassium cobalti-hexacyanoferrate, 30-60 mesh, obtainable from Westo Industrial Products Limited, 5 Addison Avenue, London W.11.

Caesium-137 and -134 standardized solutions, obtainable from RCC, Amersham, and accurately diluted until the activity levels are approximately 1000 pCi/ml.

2.2.2 Special filtration apparatus

- (a) Millipore filtration assembly, as detailed in the AMP section.
- (b) Ion-exchange columns. Barrels of disposable polystyrene syringes (capacity 20 ml) with a disc of terylene or polyamide resin-bonded fibre at the bottom. A suitable material is the air filtration sheet type T3/290, produced by Bondina Limited, Greetland, Halifax, Yorkshire.

2.2.3 Procedure

- (1) Take about 50 litres of the sample and, if it has not been filtered on collection, filter through the millipore filter assembly into a polythene carboy.
- (2) Measure the volume of the filtered solution; let this be V litres.
- (3) Add concentrated (SG 1.18) hydrochloric acid (AR) until the pH is between 1 and 1.5 (use multirange paper).
- (4) Weigh 6.0 g KCFC into the prepared ion-exchange column. The fines should be removed by adding distilled water to fill the column, which is then gently inverted a few times; the heavy fraction quickly settles and the supernatant liquid is decanted; the procedure is repeated until the supernate is virtually clear. The column should be used the same day; if it is kept for a longer period, the washing should be repeated.
- (5) Siphon the acidified sample through the column. A head of 1 metre results in a flow rate of over 10 litres per hour.
- (6) If a suitable well-crystal is available the column can be counted directly; if not, transfer the KCFC to a polystyrene container (capacity 75 ml, dimensions 50 mm diameter x 40 mm high). The transfer is facilitated by drilling 8 holes (1.5 mm diameter) in the base of the tub and cementing a disc of glass fibre paper (Whatman grade C) over the base with a ring of polystyrene cement around the edge. The KCFC can then be transferred to the tub by water washing and vacuum filtration. The surface of the damp KCFC should be smoothed to ensure reproducibility of counting geometry.
- (7) Prepare a background tub by carrying out the procedure detailed in paragraphs 4 and 6. A new background tub should be prepared each time a fresh batch of KCFC is used.

3 MEASUREMENT OF RADIOCAESIUM

3.1 Special apparatus

Gamma-counting assembly: a 75 mm x 75 mm NaI (Tl) crystal coupled to a 200-channel gamma spectrometer.

3.2 Procedure

- (1) The assembly is calibrated by the counting of caesium-137 and -134 standards, which are prepared as follows:

Take 1 ml aliquots (or weigh accurately about 1 gramme) of the diluted standard solutions (P_{137} and P_{134} pCi respectively) and carefully spread them on individual 50 gramme portions of AMP. Dry in an oven at 105°C and mix well until the radioactivity is homogeneously distributed throughout the AMP. Transfer to a petri dish. The KCFC standards are made by placing 6 grammes of KCFC in an unmodified polystyrene tub and adding a 1 ml aliquot of the diluted standard radiocaesium solution; the KCFC is gently stirred with a glass rod and smoothed.

- (2) Measure the count rates of the standards over the 0.662 MeV caesium-137 and 0.80 MeV caesium-134 photopeak areas, both for the caesium-137 and -134 standards and the background, ensuring that the channels chosen around 0.66 MeV are sufficient to include the 0.60 MeV caesium-134 peak. The spectrum covered by the FRL-assembly is about 0-1.7 MeV⁽¹⁰⁾, and the channels used are 61-85 and 87-102.

Let the count rates (corrected for background) in the two channel groups be a_1 and b_1 for the caesium-137 standard, and a_2 and b_2 for the caesium-134 standard. The efficiency of the assembly to caesium-137 and -134 is given by:

$$E_{137} = \frac{a_1}{P_{137}} \text{ cpm/pCi}$$

$$\text{and } E_{134} = \frac{b_2}{P_{134}} \text{ cpm/pCi .}$$

- (3) Measure the count rates of the sample and background over the channel groups 61-81 and 87-102.

If C_1 cpm = measured sample count rate in 1st channel group

C_2 cpm = measured sample count rate in 2nd channel group

X cpm = true caesium-137 count rate in 1st channel group

Y cpm = true caesium-134 count rate in 2nd channel group

g_1 and g_2 cpm = true background count rates in each channel group,

then

$$C_1 - g_1 = X + \frac{a_2}{b_2} Y$$

and

$$C_2 - g_2 = \frac{b_1}{a_1} X + Y$$

from which

$$X = \frac{1}{1 - \frac{b_1 a_2}{b_2 a_1}} (C_1 - g_1) - \frac{\frac{a_2}{b_2}}{1 - \frac{b_1 a_2}{b_2 a_1}} (C_2 - g_2)$$

and

$$Y = -\frac{\frac{b_1}{a_1}}{1 - \frac{b_1 a_2}{b_2 a_1}} (C_1 - g_1) + \frac{1}{1 - \frac{b_1 a_2}{b_2 a_1}} (C_2 - g_2)$$

The caesium-137 and -134 activities present are then given by

$$\frac{X}{E_{137}} \quad \text{and} \quad \frac{Y}{E_{134}} \quad \text{pCi respectively.}$$

- (4) Yields of the KCFC method have been shown to be between 90 and 100 per cent, and with each group of columns a series of yield determinations is carried out. Known amounts (about 1000 pCi) of caesium-137 are added to batches of sea water which has already been passed through KCFC, and the average percentage recovery, = R, say, is measured. This factor is applied to all subsequent determinations.

- (5) The caesium-137 and -134 activities in the water as determined by the KCFC method

$$= \frac{X \times 100}{E_{137} \times V \times R} \quad \text{and} \quad \frac{Y \times 100}{E_{134} \times V \times R} \quad \text{pCi/l respectively.}$$

The caesium-137 and -134 activities in the water as determined by the AMP method

$$= \frac{X \times 50}{E_{137} \times V \times W} \quad \text{and} \quad \frac{Y \times 50}{E_{134} \times V \times R} \quad \text{pCi/l respectively}$$

(W is the weight of the recovered AMP).

REFERENCES

- 1 YAMAGATA, N. and YAMAGATA, T., Bull. chem. Soc. Japan, Vol. 31 (1958), p. 1063.
- 2 BUCHWALD, H. and THISTLETHWAITE, W. P., J. inorg. nucl. Chem., Vol. 5 (1958), p. 341.
- 3 MIYAKE, Y., SARUHASHI, K., KATSURAGI, Y., and KANAZAWA, T., Jnl Radiat. Res., Vol. 2, No. 1 (1961), pp. 25-28.
- 4 YAMAGATA, N., Nature, Lond., Vol. 200 (1963), p. 157.
- 5 MORGAN, A. and ARKELL, G. M., Hlth Phys., Vol. 9 (1963), p. 857.
- 6 THISTLETHWAITE, W. P., J. inorg. nucl. Chem., Vol. 28 (1966), p. 2143.
- 7 AMPHLETT, C. B., Inorganic Ion Exchangers, Monograph II in "Topics in Inorganic and General Chemistry". Elsevier Publishing Co. (1964).
- 8 PROUT, W. E., RUSSELL, E. R. and GROH, H. J., J. inorg. nucl. Chem., Vol. 27 (1965), p. 473.
- 9 BONI, A. L., Hlth Phys., Vol. 38 (1966), p. 89.
- 10 DUTTON, J. W. R., Ministry of Agriculture, Fisheries and Food, Fisheries Radiobiological Laboratory, Technical Report FRL 4 (1969), 18 pp.

FOOTNOTE

The reference to proprietary products in this report should not be construed as an official endorsement of those products, nor is any criticism implied of similar products which are not mentioned.

REPORTS IN THIS SERIES

Radioactivity in surface and coastal waters of the British Isles, by N. T. Mitchell.
Technical Report FRL 1. October 1967. 45 pp.

Radioactivity in surface and coastal waters of the British Isles 1967, by
N. T. Mitchell. Technical Report FRL 2. September 1968. 41 pp.

Gross beta counting of environmental materials, by J. W. R. Dutton. Technical
Report FRL 3. October 1968. 13 pp.

Gamma spectrometric analysis of environmental materials, by J. W. R. Dutton.
Technical Report FRL 4. November 1969. 18 pp.

Radioactivity in surface and coastal waters of the British Isles 1968, by
N. T. Mitchell. Technical Report FRL 5. November 1969. 39 pp.

Determination of radiocaesium in sea and fresh waters, by J. W. R. Dutton.
Technical Report FRL 6. October 1970. 9 pp.