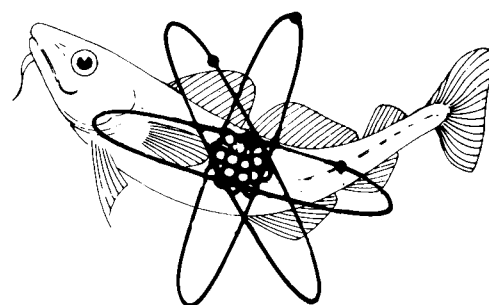


ISSN 0953-4466

MINISTRY OF AGRICULTURE FISHERIES AND FOOD
DIRECTORATE OF FISHERIES RESEARCH

AQUATIC ENVIRONMENT PROTECTION:
ANALYTICAL METHODS



Number 5

**Analytical procedures for the determination of strontium radionuclides
in environmental materials.**

B. R. Harvey, R. D. Ibbett, M. B. Lovett and K. J. Williams

Lowestoft 1989

MINISTRY OF AGRICULTURE, FISHERIES AND FOOD

DIRECTORATE OF FISHERIES RESEARCH

AQUATIC ENVIRONMENT PROTECTION : ANALYTICAL METHODS

NUMBER 5

**Analytical procedures for the determination of strontium radionuclides in
environmental materials**

B. R. HARVEY, R. D. IBBETT, M. B. LOVETT and K. J. WILLIAMS

LOWESTOFT, 1989

The authors:

B. R. Harvey, BSc, is a Grade 7 Officer, R. D. Ibbett is a Higher Scientific Officer, M. B. Lovett, LRSC, is a Senior Scientific Officer and K. J. Williams is an Assistant Scientific Officer within Aquatic Environment Protection Division 4 of the Directorate of Fisheries Research. All authors are based at the Fisheries Laboratory, Lowestoft.

Aquat. Environ. Prot.: Analyt. Meth., MAFF Direct. Fish. Res., Lowestoft, (5), 33 pp.

CONTENTS

	Page
Foreword	
1. Introduction	7
2. Analytical technique	8
2.1 Chemical separation of the element	8
2.2 Separative procedures	10
3. Yield determination	13
4. Radiometric assay	14
5. Sources of error	16
5.1 Analytical separation	16
5.2 Radiometry	17
6. Method performance	18
6.1 Decontamination	18
6.2 Chemical yield	19
6.3 Radiometric assay	19
6.4 Method validation	20
7. References	20
Appendix – Laboratory procedures	22
A1. Reagents	22
A2. Hazards	23
A3. Preparation of ^{85}Sr yield tracer	23
A4. Apparatus	23
A5. Practical analytical procedures	24
A6. Calculation of results	30
A7. Appendix reference	33

Foreword

As part of its responsibilities under various Acts of Parliament, MAFF Directorate of Fisheries Research has a duty to carry out a substantial programme of monitoring, surveillance and research in relation to the quality of the aquatic environment in and around the United Kingdom. In the course of that programme, a wide variety of methods of analysis are used for a wide variety of contaminants, both inorganic and organic, stable and radioactive. This series of publications describes the main methods used in the course of this work and parallels the existing Aquatic Environment Monitoring Report series, in which much of the resulting data is published. Regardless of whether the analytical procedure relates to a radionuclide or a non-radioactive contaminant, each report contains a step-by-step guide to analytical procedures and an explanation of the calculation of results.

A handwritten signature in dark ink, appearing to read 'H. W. Hill', with a long horizontal stroke extending to the right.

H. W. Hill
Director of Fisheries Research
Ministry of Agriculture, Fisheries and Food

1. Introduction

As part of its statutory role in the authorisation, monitoring and research relating to radioactive wastes discharged into the aquatic environment, the Aquatic Environment Protection Division of the Directorate of Fisheries Research (DFR), Lowestoft routinely carries out analyses for a substantial number of radionuclides in a wide range of environmental materials. Gamma-emitting nuclides can usually be determined with a minimum of preparative chemistry whereas alpha-emitting and pure beta-emitting nuclides require radiochemical separation for quantitative analysis. The Ministry of Agriculture, Fisheries and Food has for many years required information about the concentrations of strontium radionuclides in waters, sediments and biological materials. There are no absolute standard methods for such radiochemical analysis; indeed none are required because methodology is continually developing. Thus, a very considerable amount of expertise has been developed in the analysis of radiostrontium at the Laboratory since the late 1950s, when detailed analysis first commenced, and the procedures described in this report have been developed and tested over a long period of time with a view to achieving the highest analytical quality. Full details of the practical, analytical and computational procedures, as currently used, are given in the Appendix.

Historically, the determination of strontium radionuclides in environmental materials has been pursued with special interest from the very earliest days of the "nuclear age" (Martell, 1956; Bryant *et al.*, 1957; Shultz and Klement, 1963). Several factors have contributed to this interest: the high fission yield of strontium radionuclides, the bone-seeking nature of strontium, the relatively long half-life of ^{90}Sr and the fact that the environmentally important nuclides of strontium as well as the radioactive daughter product ^{90}Y , are all effectively pure beta emitters.

During the atmospheric testing of atomic weapons in the 1950's and 1960's, ^{90}Sr was reportedly the most persistent artificial source of internal radiation to man (Scott Russell, 1966). This situation arose from the combination of a number of factors. Firstly, in the fission of heavy element nuclei such as those of uranium and plutonium, both ^{89}Sr ($t_{1/2} = 50.5$ d) and ^{90}Sr ($t_{1/2} = 29$ yr) are produced in high yield - 4.9% and 5.8% respectively for the slow neutron irradiation of ^{235}U and 1.5% and 2.2% respectively for the fast neutron irradiation of ^{239}Pu (United Nations, 1962; Walker, Kirouac and Rourke, 1977). Furthermore, in these tests the mixed fission products were predominantly released into the atmosphere. Secondly, strontium enters the human diet via a complex series of routes in association with calcium and only limited discrimination against the heavier element occurs (Scott Russell, 1966). Thus, unlike other fission products of comparable yield and nuclear disintegration characteristics, such as ^{137}Cs ($t_{1/2} = 30$ yr), a major source of strontium radionuclides in human diet arises via plant root uptake from soils (Martell, 1956). Thirdly, like calcium, strontium becomes associated with human skeletal material and hence has a very long residence time in the body (about 50 years). Irradiation of the bone marrow represents the greatest radiological hazard from radiostrontium. Both ^{89}Sr and ^{90}Sr decay by beta-particle emission ($\beta\text{-max} = 1.49$ MeV and 0.545 MeV respectively) and, in the case of ^{90}Sr , its short-lived daughter product ^{90}Y ($t_{1/2} = 64.1$ h) is also radioactive and itself adds to the radiation dose ($\beta\text{-max} = 2.29$ MeV).

In the low-level aqueous wastes discharged from nuclear power plants and nuclear reprocessing facilities, strontium radionuclides have been of lower radiological significance than some other radionuclides. Not unexpectedly the greatest significance of strontium radionuclides in such wastes occurs in freshwater environments of very low calcium content (Hunt, 1987). What may seem more surprising is the fact that strontium nuclides did not feature amongst those responsible for the maximum risk to health following the accident at the USSR Chernobyl nuclear power plant in 1986. The reasons for the difference between the composition of these various emissions, and that of atmospheric fall-out debris from nuclear weapons testing, are due to the physical conditions obtaining. When a nuclear weapon is exploded in the atmosphere, the whole inventory is released to return to earth as finely divided debris. At Chernobyl, on the other hand, only some 4% of the ^{89}Sr + ^{90}Sr contained in the reactor was released (International Nuclear Safety Advisory Group, 1986), because of the relatively non-volatile nature of strontium compounds at the temperature of the fire, compared with elements such as caesium. In the case of spent reactor fuel storage in cooling ponds, it can be assumed that strontium remains in association with the fuel elements and their cladding as insoluble hydroxides or carbonates under the alkaline conditions of the ponds.

Radiochemical analysis for strontium radionuclides in environmental materials nevertheless remains an important part of radioactive waste management. Unlike many other important fission products, the total body burden of ^{89}Sr or ^{90}Sr cannot be assessed by whole-body gamma radiation monitors because no gamma emissions are associated with their beta decays. For the same reason, the detection and estimation of radiostrontium in environmental materials requires thorough radiochemical separation and purification from radionuclides of other elements, if reliable quantitative data are to be obtained. This need arises because of the relatively non-specific nature of beta counting compared with gamma spectrometry, and the rapid attenuation of beta particles by matter.

2. Analytical technique

Strontium is the middle member of the triad calcium, strontium and barium in group 2 of the periodic table of the elements (Walker, Kirouac and Rourke, 1977). Its chemistry, thus, is uncomplicated: it invariably displays a valency of 2+, and the formation of complexes is of limited importance. Nevertheless, a strong complex with oxine (8-hydroxyquinoline), $\log K = -20$, does offer a useful means of separating strontium by solvent extraction into chloroform (Stary, 1964); complexation with ethylenediamine tetracetic acid (EDTA), lactate and isobutyrate have also been employed successfully in the ion-exchange separation of strontium (Samuelson, 1963). For the radiochemist, the simple chemistry of strontium offers both advantages and disadvantages. On the one hand, it allows easier and more reliable equilibration of inactive strontium carrier and yield tracers with the sample radionuclides during analyses. On the other hand, the lack of complex species severely restricts the development of highly selective separative techniques for the element.

2.1 Chemical separation of the element

The purpose of a radiochemical separation scheme is to isolate, by a carefully selected series of steps, a chemical species of the element in a sufficiently pure state, such that the desired radionuclide(s) may be uniquely assayed or identified by a radiometric or other technique such as

mass spectrometry. Such procedures may involve precipitation, solvent extraction, ion-exchange, electrolysis or sometimes volatilisation steps depending on the nature of the element being sought. In the analysis of environmental samples, separation frequently has to be achieved from large quantities of an organic or inorganic matrix material as well as from a diversity of other radionuclides, particularly those of neighbouring elements in the periodic table. In many cases, interfering radionuclides must be reduced by factors well in excess of 10^4 before satisfactory quantification is possible. The general inorganic analytical literature, whilst helpful, is often not entirely suitable for radiochemical work where non-equilibrium conditions are common and the desired nuclides are present only in sub-trace (carrier free) quantities. Frequently, therefore, conventional analytical methods need to be modified to give maximum separation from specific undesirable elements.

The determination of radiostrontium in environmental materials presents a considerable challenge to the radiochemist; partly, as previously noted, because of the lack of highly specific separative procedures and partly because, in a number of cases, the determination involves the measurement of a small beta disintegration rate in the presence of a considerable mass of stable strontium. The problem is normally restricted to the measurement of ^{89}Sr , because the final assay for ^{90}Sr in environmental samples is most frequently carried out by separating and measuring the short-lived daughter product ^{90}Y after the radiochemical purification of strontium and subsequent grow-in of the daughter.

The very earliest identification and characterisation of the two environmentally important radionuclides of strontium seems almost to have been lost in the mists of time, probably because of the classified nature of the work on atomic weapons in the early 1940s. One of the earliest recorded identifications of ^{89}Sr and ^{90}Sr in environmental samples was in soil from Hiroshima and Nagasaki following the atomic bomb explosions in 1945 (Kimura *et al.*, 1956a). The initial analytical approach to this work involved group separations based on the classical scheme of qualitative chemical analysis, but with the addition of about 5 mg per element of appropriate carriers. It is also interesting to note that ion-exchange was used extensively in this early work as a means of further purification (Kimura *et al.*, 1956b). The alkaline earth elements, for example, were separated on Dowex 50 and Amberlite IR 120 cation exchangers as part of sequential elutions using 5% citrate solution at $\text{pH} > 4.1$. Yamada *et al.* (1956) also made use of the qualitative group separations in their extensive study of fish contaminated by fall-out debris from the 1954 hydrogen bomb test at Bikini Atoll.

For the analysis of strontium radionuclides in seawater, separation procedures have had to be designed to cope with large volumes - perhaps up to 200 l - which contain not only a substantial mass of inactive strontium (8 mg l^{-1}) but also large quantities of calcium (400 mg l^{-1}) from which the strontium must be at least partially separated. Such quantities of carrier strontium can seriously interfere with the radiometric assay of strontium nuclides if solid source (planchette) beta counting has to be used. It was for this reason that the idea of determining ^{90}Sr via its short-lived daughter ^{90}Y was first developed. This can be achieved if an initial radiochemical purification of the strontium is followed by storage to allow grow-in of the daughter which is then generally separated by the precipitation of an added yttrium carrier for radiometry (Martell, 1956). Other techniques, such as the separation of the ^{90}Y by solvent extraction, or by scavenging with iron hydroxide, have also been used. Direct extraction from the original sample and counting of ^{90}Y using thenoyl trifluoroacetone (TTA) in benzene was proposed and tried by Bowen and Sugihara in

1955 but proved to be completely impracticable for seawater samples, even of moderate size, because of the following reasons:

- (a) the short half-life of ^{90}Y ;
 - (b) the length of time required to carry out the solvent extraction;
- and
- (c) contamination of the extract by other beta-emitting nuclides, notably ^{234}Th (Bowen, 1970).

Some time after the initial development of the procedures for separating fission products in the early 1940s, a critical review of radiochemical separations for calcium, strontium and barium was carried out at the University of Michigan (Sunderman and Meinke, 1957). The purpose of this work was to establish the most favourable means of separating these elements. It was concluded that strontium and barium were best separated from calcium as insoluble nitrates in strong nitric acid solution and this still seems to be the most satisfactory initial radiochemical step for the isolation of strontium even today. The technique was first proposed by Rawson (1897) and was subsequently developed and quantified by Willard and Goodspeed (1936). Figure 1 has been drawn by combining the data of Sunderman and Meinke with that of Willard and Goodspeed. It shows how the percentage of strontium and barium precipitated varies with the strength of nitric acid present. It also shows that the solubility of calcium drops significantly as the strength of nitric acid is increased and that calcium will contaminate the precipitate unless the conditions are carefully selected so as to maximise the separation. From the data presented, it is clear that the optimum conditions for separating strontium from calcium lie in the range 70-75% w/w nitric acid. At 73% nitric acid, about 99% of the strontium is recovered. The method currently employed at this laboratory uses this concentration of nitric acid and the precipitation is normally repeated until the calcium concentration is reduced to an acceptable level.

Because of the unpleasant and somewhat tedious manipulations involved in the classical fuming nitric acid precipitation discussed above, several alternative separations of strontium from environmental matrices have been proposed. Most are based on the use of various complexing agents in conjunction with ion-exchange. The procedure devised by Ibbett (1967) uses mixed EDTA and citrate complexation along with ion exchange. This method works well especially when batches of similar biological or sediment samples are being processed. It does, however, require an experienced analyst for successful operation and is less convenient than the fuming nitric acid separation where groups of dissimilar samples are being handled. In its original form, it can cope with seawater samples of up to 1 litre only. At the present time, therefore, all radiostrontium analyses at DFR are carried out by the classical nitrate precipitation procedure.

2.2 Separative procedures

The analytical procedures can be divided into five sections:

- (1) yield tracer and carrier addition, solubilisation and/or preconcentration;
- (2) concentration of strontium as an insoluble nitrate;
- (3) purification of strontium from interfering radionuclides;
- (4) radiometric assay and analytical quantification of ^{89}Sr and ^{85}Sr yield tracer; and
- (5) separation and counting of the ^{90}Y daughter for the determination of ^{90}Sr .

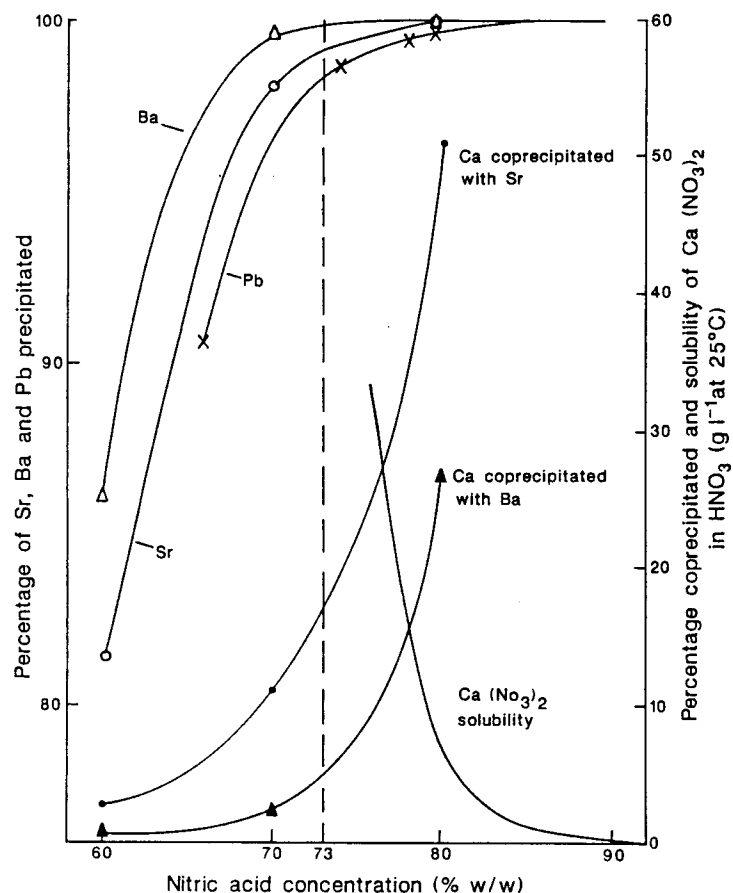


Figure 1. Precipitation of Ca, Sr and Ba as nitrates in nitric acid (10 mg in 10-15 ml nitric acid at 20°C). Data from Sunderman and Meinke (1957) and Willard and Goodspeed (1936).

Figure 2 summarises these procedures in the form of schematic diagrams. Seawater samples are first filtered through 0.45 μm or 0.22 μm membrane filters to separate-out suspended particulate matter. The filtrate is spiked with ^{85}Sr to act as a yield monitor and acidified to 0.1M HCl to assist equilibration. Alkaline-earth oxalates are then precipitated, filtered off and retained for further purification of strontium.

For suspended particulate matter and marine sediments, alkaline earth components are extracted from the ashed sample with nitric acid after the addition of ^{85}Sr yield tracer and inactive strontium carrier. The acid-insoluble residue is discarded and the filtrate retained for further purification of strontium. If refractory materials are being analysed then appropriate steps should be taken to bring the samples completely into solution (Bock, 1979). For the majority of environmental samples, the strontium nuclides are normally present in an acid-extractable form.

Samples of biological origin are first dried then ashed at $500 \pm 25^\circ\text{C}$ to remove the bulk of organic matter. The ash is spiked with ^{85}Sr and inactive strontium carrier then extracted with nitric acid as for sediments and, after filtering, the filtrate is retained for further strontium purification.

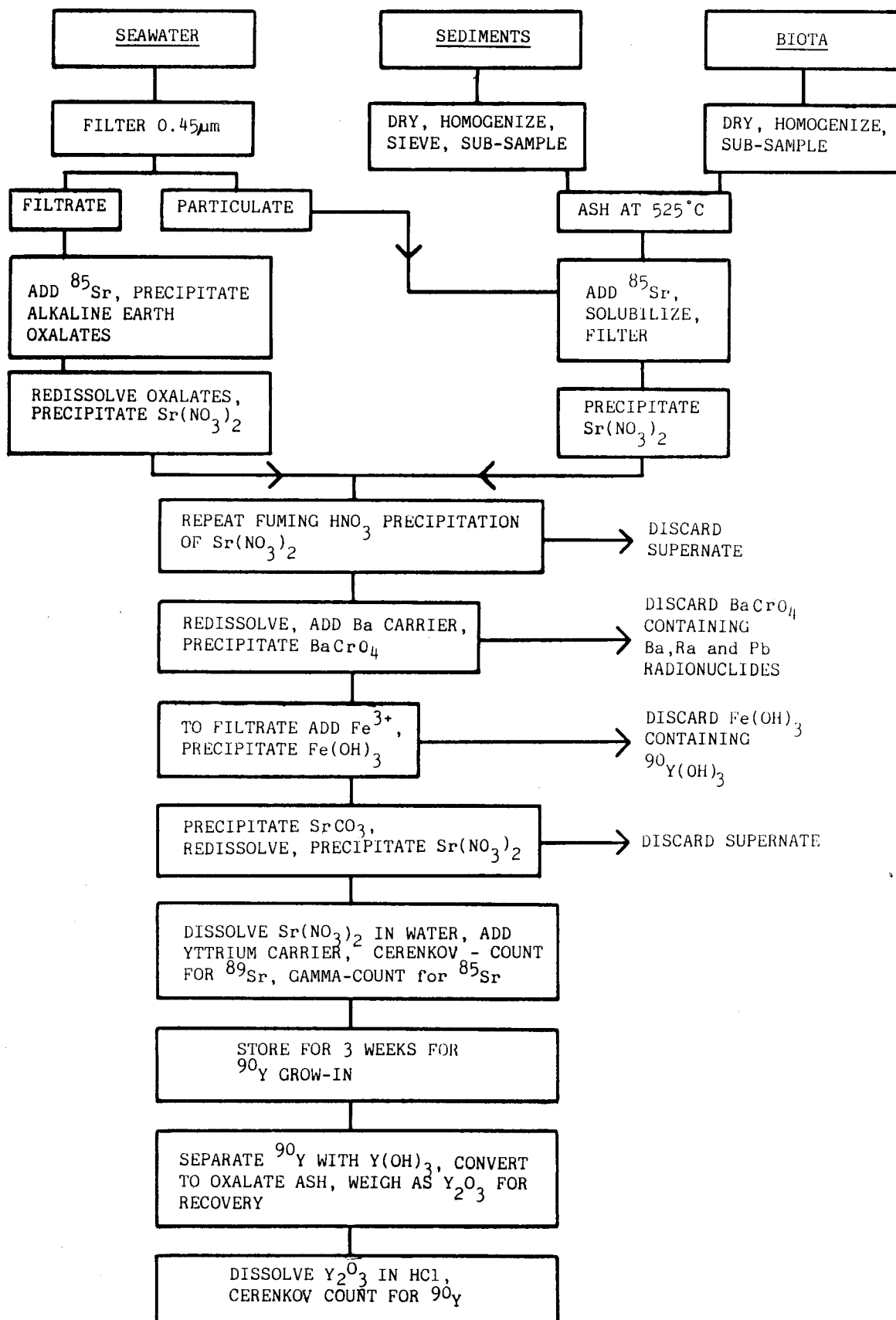


Figure 2. Schematic diagram of radiochemical separation of strontium nuclides.

In all cases, the first stage of strontium purification consists of precipitating oxalates which are insoluble in weakly-acid solution (pH4) followed by precipitation of insoluble nitrates from a nitric acid medium made 73% w/v by the addition of fuming nitric acid. From Figure 1, it can be seen that care is needed at this stage to ensure maximum decontamination from calcium (and with it many other interfering radionuclides) whilst retaining virtually quantitative recovery of strontium (typically 95%). The presence of sulphate in a sample would prejudice this nitric acid separation but should have been largely eliminated at the oxalate precipitation stage. When ^{85}Sr is being used as a yield tracer, complete separation of strontium from calcium is not necessary.

Figure 1 also shows that the fuming nitric acid separation achieves little or no decontamination from the later members of group 2 of the periodic table, namely barium and radium. Divalent naturally-occurring radionuclides, such as ^{210}Pb , may also largely accompany strontium in the insoluble nitrate precipitate. Purification from all of these nuclides is conveniently achieved by re-dissolving the nitrate precipitate in water and carrying out a scavenge with barium chromate (United States - Health and Safety Laboratory, 1962). Some authors recommend repeating the barium chromate scavenge, but this is not generally necessary for environmental samples.

To complete the purification, a ferric hydroxide scavenge is carried out followed by the successive precipitation of the strontium as the insoluble carbonate and nitrate. These steps progressively remove traces of interfering radionuclides and the coloured chromate ion which would interfere with subsequent Cerenkov counting for ^{89}Sr . But, most importantly, the final precipitation provides an unequivocal point in time at which the ^{90}Y daughter is completely removed from the ^{90}Sr parent. This time is needed for the radiometric assay as described in Sections 4 of the text and A6 of the Appendix.

The purified strontium extract is immediately assayed for ^{89}Sr content by Cerenkov counting, and then for ^{85}Sr recovery by gamma counting, and for $^{90}\text{Sr}/^{90}\text{Y}$ by Cerenkov or end-window beta counting.

Full laboratory working details are given in the Appendix, together with practical notes for the analyst.

3. Yield determination

Until about 1960, the chemical yield in strontium radionuclide analysis relied on the addition of an accurately known weight of stable strontium carrier (usually about 50 mg of Sr as SrCl_2 in dilute HCl) and gravimetric determination of the strontium recovered after radiochemical separation as the oxalate or carbonate. Such gravimetric determination of yield was complicated by the presence of stable strontium in the sample matrix (Bryant, Morgan and Spicer, 1959). Following the introduction by Butler (1960) of the gamma-emitting nuclide ^{85}Sr ($t_{1/2} = 62.8$ d; 0.51 MeV gamma photon from positron annihilation) as a method-development tracer, this nuclide was first used as a yield monitor in environmental radio-strontium analysis. It gives more precise results than gravimetric yield determination (Geiger, 1967), and was rapidly adopted by leading radioanalytical laboratories throughout the world. The tracer was first used at this laboratory in 1963. Supplies are now readily available (for example, from Amersham International plc).

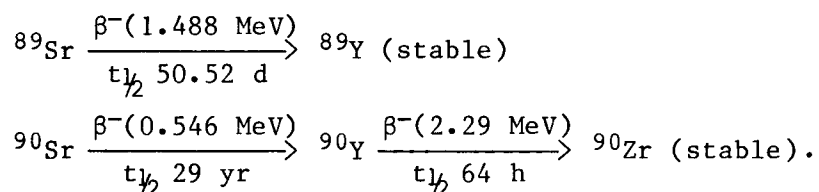
A suitable aliquot of tracer is added to the sample at the earliest appropriate stage in the analysis. After equilibration of the tracer with the sample, radiochemical purification of strontium is carried out and the recovery is determined by simple gamma counting of the ^{85}Sr against an ^{85}Sr standard.

A particular benefit of this method of yield determination is the fact that complete isolation of strontium from the last traces of calcium is unnecessary. However, it must be borne in mind that radiochemical purification from the beta-emitter ^{45}Ca ($t_{1/2} = 163$ d; $\beta\text{-max} = 0.257$ MeV) may be necessary in some instances. This is considered in more detail in Section 5 in which sources of error are discussed.

A further benefit to the analyst is the ability to use the gamma-emitting ^{85}Sr for quick assessments of the progress of strontium throughout the course of the analysis.

4. Radiometric assay

Over 20 radionuclides of strontium have been identified, but most have short half-lives (10 h or less). For all practical purposes, therefore, only ^{89}Sr and ^{90}Sr are important as determinands in environmental radiochemical analysis. These nuclides decay as follows:



Because of the markedly different half-lives of the two nuclides, the ratio of ^{89}Sr : ^{90}Sr found in environmental samples will depend upon the time which has elapsed between their production in the fission event and the time of sampling (see Figure 3).

From decay schemes, it is clear that ^{90}Sr may be assayed independently of ^{89}Sr by separating and counting its short-lived ^{90}Y daughter. This clearly has a number of advantages apart from the obvious ability to make an accurate assessment of ^{90}Sr in the presence of ^{89}Sr . The chief practical advantage lies in the ability to carry out low-background, solid-source beta counting of the ^{90}Y after separating it from a substantial weight of stable strontium. The ^{90}Y scavenge can be repeated after the ^{90}Y daughter has been allowed to grow back into the purified strontium extract if necessary. As a check on purity, the rate of decay of the ^{90}Y can be followed.

With modern liquid scintillation counting equipment, however, a more convenient means of assaying for both ^{89}Sr and ^{90}Sr is by Cerenkov counting (Cerenkov, 1934; Frank and Tamm, 1937; Parker, 1974). In this procedure, which we now use for all but the very lowest level samples for ^{90}Sr analysis, ^{89}Sr is determined on the strontium solution immediately following the removal of ^{90}Y . Little or no interference arises from the ^{90}Sr present because the mean beta energy of the ^{90}Sr (0.1957 MeV) approximates to the threshold energy for the production of Cerenkov radiation from electrons in the aqueous solution. This can be calculated from the following equation:

$$E_T = 0.511 \frac{1}{\sqrt{1 - \frac{1}{\mu^2}}} - 1$$

where

E_T is the threshold energy in MeV and
 μ is the refractive index of the medium.

Thus using

$$\mu_D^{20^\circ\text{C}} = 1.33 \text{ for water,}$$

$$E_T = 0.263 \text{ MeV.}$$

Figure 4 shows that in practice the ^{90}Sr is detected with an efficiency of about 1% whilst the efficiency for ^{89}Sr approaches 30%. Any ^{90}Y present, such as that growing-in from the ^{90}Sr , counts with an even greater efficiency (> 50%). The contribution from both ^{90}Sr and ^{90}Y must be calculated once the ^{90}Sr content is established. This is achieved by allowing the ^{90}Y daughter to grow-in, preferably to equilibrium with the ^{90}Sr parent, at which point the ^{90}Y is separated and Cerenkov counted.

The chemical yield is determined by gamma counting the ^{85}Sr . In the procedure employed at the DFR, the strontium solution, contained in a

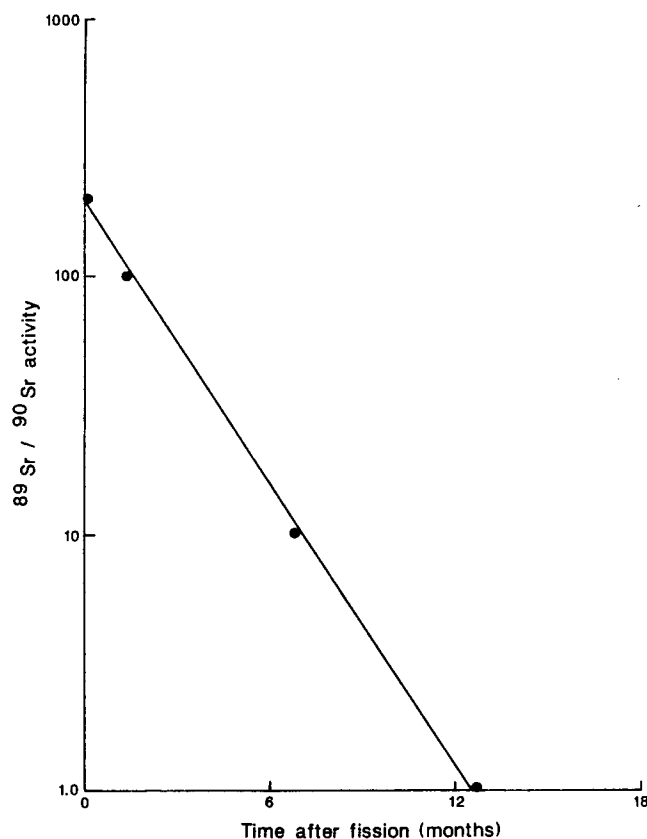


Figure 3. Relative activity of ^{89}Sr and ^{90}Sr in fission products assuming equal mass production of the two nuclides (redrawn from Mitchell and Eden, 1962).

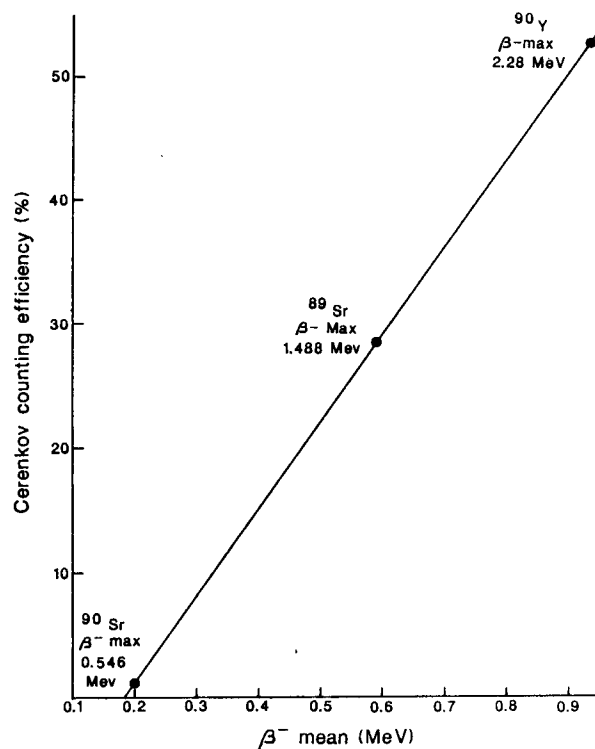


Figure 4. Variation of Cerenkov counting efficiency with beta energy (LKB 1217 Rackbeta liquid scintillation counter).

liquid scintillation counting vial (used for the Cerenkov counting), is placed in a NaI(Tl) well crystal and counted against an ^{85}Sr standard soon after the first Cerenkov count has been completed. Under normal circumstances, the ^{85}Sr may be measured without interference from ^{89}Sr , ^{90}Sr or ^{90}Y , but the analyst should be aware that high-energy beta particles generate a broad spectrum of pulses in gamma detectors known as Bremsstrahlung (see Section 5).

5. Sources of error

The analysis for strontium radionuclides is subject to a variety of possible errors which need to be understood if reliable results are to be achieved. The most important sources of error are discussed below and suggestions made about ways to eliminate or account for them.

5.1 Analytical separation

Incomplete extraction of the determinand nuclides from the matrix of environmental materials represents a common source of error. In the present method it is suggested that, for the majority of samples, complete extraction of strontium nuclides can be achieved by leaching with dilute nitric acid after the sample has been ashed in a muffle furnace to destroy organic matter. However, some refractory materials may need total dissolution in order to free all of the strontium from the sample matrix and the onus is on the analyst to decide which method to use. It must be remembered that a yield tracer does not account properly for losses until

complete equilibration between tracer and determinand nuclides has been achieved. Clearly, this cannot take place until all strontium nuclides are in solution. Fortunately, tracer/determinand equilibration is not complicated by oxidation state differences in the case of strontium.

5.2 Radiometry

The majority of potential errors can be expected to occur in the radiometric assay. The most obvious errors are likely to arise as a result of inadequate decontamination from other beta-emitting nuclides when these are not eliminated to a sufficient degree by the sequence of separation steps. Table 1 shows the nuclides which are most likely to cause interference in the analysis of environmental samples. The list is not exhaustive and the analyst should check the adequacy of decontamination when dealing with samples which have unusual nuclide composition (See Sub-section 6.1).

Very little can be done in practice to check specifically for the presence of interfering nuclides in the counting of ^{89}Sr (other than $^{90}\text{Sr}/^{90}\text{Y}$). The purity of the ^{90}Y source can, however, be established in the case of solid-source beta planchettes by re-counting several times in order to establish the half-life of the beta activity. Any deviation from $t_{1/2} = 64.1 \text{ h}$ should be looked upon as indicating the presence of contaminants - the most likely one being ^{90}Sr . If, instead of solid-source beta counting, the ^{90}Y is assayed by Cerenkov counting, then purity can be checked, but in this case the grow-in of ^{90}Y has to be followed.

By the very nature of radioactive decay - which is a random process - some uncertainty is always present in radiometric counting. Furthermore, where multiple calibrations are necessary and daughter products may be growing-in, as in the case when ^{89}Sr is to be measured in the presence of ^{90}Sr , cumulative errors can become considerable. Fortunately, however, this type of error can at least be identified and adequately allowed for providing the analyst is fully conversant with the subject.

Table 1. Decontamination factors for environmentally important interfering radionuclides

Nuclide	Half-life	β -max (MeV)	Decontamination factor
^{45}Ca	163d	0.257	2×10^3
^{91}Y	58.6d	1.544	10^5
$^{95}\text{Zr} (^{95}\text{Nb})$	64d (3.5d)	0.366, 0.398 (0.160)	2×10^4
$^{106}\text{Ru} (^{106}\text{Rh})$	368d (30s)	0.0394 (3.54)	5×10^4
$^{140}\text{Ba} (^{140}\text{La})$	12.8d (40.2h)	1.03 (1.68)	2×10^3
$^{210}\text{Pb} (^{210}\text{Bi})$	138.4d (5.0d)	0.061 (1.161)	10^3
$^{226}\text{Ra} (^{214}\text{Pb}/^{214}\text{Bi})$	1600yr (27min, 20min)	- (0.74, 3.28)	3×10^3

A counting error which is not necessarily obvious occurs in the measurement of the ^{85}Sr yield tracer. Unlike the standard solution of ^{85}Sr , with which it is to be compared, the sample solution contains varying amounts of relatively high-energy, beta-emitting nuclides - notably ^{89}Sr and ^{90}Y . Such high-energy beta particles can penetrate the casing of gamma detectors and give rise to a broad spectrum of pulses commonly referred to as Bremsstrahlung (Friedlander, Kennedy and Miller, 1964). The counting system is unable to distinguish the Bremsstrahlung pulses in the ^{85}Sr gate from those due to ^{85}Sr , with the result that chemical yield appears to be higher than it really is. With our detector, 1 Bq of ^{90}Y contributes about 0.3 counts per minute (ct min^{-1}) to the ^{85}Sr gamma count. The detector background count in the ^{85}Sr gate is some 200 ct min^{-1} and typically the ^{85}Sr added to samples as a yield tracer gives some 500 to 1000 ct min^{-1} above the background. Thus for most environmental samples, interference from Bremsstrahlung will be insignificant.

6. Method performance

The most important features of a good radiochemical separation are as follows:

- (1) it should be capable of producing good-quality sources for counting, free of unwanted interferences from a wide range of material types and nuclide concentrations;
- (2) the radionuclides of interest should be recovered with high yield (say not less than 75 percent overall); and
- (3) it should be possible to assay each nuclide accurately and unambiguously in the presence of other nuclides of the same element.

These features are discussed below.

6.1 Decontamination

Separation schemes should be designed to be as simple as possible, consistent with the required quality. As stated in Sub-section 5.2, Table 1 lists the nuclides which are considered to represent the greatest threat to purity in the present analysis. Thus decontamination factors are given for the other members of group 2 (Ca, Ba and Ra), for ^{91}Y , because ^{90}Y is used as a means by which the ^{90}Sr content is assayed, and for ^{210}Pb , because Pb precipitates efficiently along with Sr, Ba and Ra as an insoluble nitrate. Data for ^{95}Zr , ^{95}Nb and ^{106}Ru decontamination are included because they represent fission product elements which are produced in high yield and because they, or their daughter products, decay with the emission of high-energy, or relatively high-energy, beta particles.

Clearly, not every eventuality can be covered in an analytical scheme and difficulties may arise with some samples. If doubt exists about the quality of separation from interferences, then samples should be re-processed after radiometric counting. Any significant change in the strontium isotopic ratios after re-processing should be seen as indicating the possible presence of contaminants at the first radiometric assay.

6.2 Chemical yield

No stage should be included in a separation scheme if it consistently loses a significant proportion of the determinand. Table 2 shows that in the present method the chemical recovery of strontium can normally be expected to be above 80% overall. However, care is needed, especially at the fuming nitric acid stage, where losses may occur because of the presence of sulphate and chloride. In the case of sulphate, calcium sulphate precipitates along with the strontium nitrate and, unless its presence is recognised, subsequent efforts to reduce the bulk of the precipitate by further fuming nitric cycles can easily result in a substantial loss of strontium with little resultant loss of calcium. With chloride present the reverse problem occurs, the strontium remaining soluble when it should precipitate as an insoluble nitrate in the strong nitric-acid solution.

Table 2. Method performance for the separation of strontium radionuclides from environmental materials.

Analytical step	Strontium loss (percentage)			Number of determinations
	Mean	Medium	Range	
Initial and leach	0.9	0.9	0-7.1	54
BaCrO ₄ scavenge	2.1	2.7	0-7.3	46
Fe(OH) ₃ scavenge	1.6	1.4	0-8.8	61
Complete separation	21	17	8-72	59

6.3 Radiometric assay

⁹⁰Sr is quite easy to measure unambiguously via its short-lived daughter ⁹⁰Y. Standardized solutions of ⁹⁰Sr/⁹⁰Y are readily available and the choice of Cerenkov or end-window beta counting is a matter of availability or preference. Low background (say < 0.5 ct min⁻¹) gas-flow beta counters provide a detection limit up to 5 times better than Cerenkov counting.

⁸⁹Sr cannot be assayed uniquely in environmental samples. Cerenkov counting is undoubtedly the best approach because ⁹⁰Y can be largely removed and ⁹⁰Sr counts with very low efficiency. In practice, ⁸⁹Sr is likely to be of interest only when fresh fission product material is in the environment, and then its presence is often primarily of interest as a label of that material (see Figure 3).

Polythene liquid scintillation counting vials are preferred as they give background counts lower than those of glass vials.

6.4 Method validation

The method has been tested for reliability on a variety of environmental materials by analysing intercomparison samples (both national and international). In particular, it has been shown to give excellent results with a variety of nuclear power station effluents which contain a wide range of fission and activation products.

In-house quality assurance is also carried out on a regular basis with some 10 percent of samples analysed being quality assurance samples (quality control "standard" samples and reagent blanks).

Disclaimer: The reference to proprietary products in this report should not be construed as an official endorsement of these products, nor is any criticism implied of similar products which have not been mentioned.

7. References

- BOCK, R., 1979. Decomposition Methods in Analytical Chemistry. International Textbook Company, Glasgow, 444pp.
- BOWEN, V. T., 1970. Strontium analysis. In: Reference Methods for Marine Radioactivity Studies. Tech. Rep. Ser., Int. Atom. En. Ag., Vienna, (118): 1-70.
- BRYANT, F. J., CHAMBERLAIN, A. C., MORGAN, A. and SPICER, G. S., 1957. Radiostrontium fall-out in biological materials in Britain. AERE, Harwell, Report AERE HP/R 2056, 46pp.
- BRYANT, F. J., MORGAN, A. and SPICER, G. S., 1959. The determination of radiostrontium in biological materials. AERE, Harwell, Report AERE-R 3030, 35pp.
- BUTLER, F. E., 1960. Strontium-90 monitoring at the Savannah River plant. U.S Atomic Energy Commission, Savannah River Laboratory, Aiken, South Carolina, Doc. DP-473, 37pp.
- CERENKOV, P. A., 1934. [Visible light emissions from clear liquids under the influence of gamma radiation]. Dokl. Akad. Nauk. SSSR, 3: 451-454.
- FAIRES, R. A. and BOSWELL, G. G. J., 1981. Radioisotope Laboratory Techniques, 4th edition. Butterworths, London, 335pp.
- FRANK, I. and TAMM, I., 1937. Coherent visible radiation of fast electrons passing through matter. Dokl. Akad. Nauk. SSSR, 14: 109-114.
- FRIEDLANDER, G., KENNEDY, J. W. and MILLER, J. M., 1964. Nuclear and Radiochemistry. J. Wiley & Sons, London, 585pp.
- GEIGER, E. L., 1967. Strontium-85 tracer method for determination of strontium-90. Hlth Phys, 13: 607-612.
- HUNT, G. J., 1987. Radioactivity in surface and coastal waters of the British Isles 1986. Aquat. Environ. Monit. Rep., MAFF Direct. Fish. Res., Lowestoft, (18): 62pp.
- IBBETT, R. D., 1967. The determination of strontium-90 in environmental materials by ion-exchange and preferential chelation techniques. Analyst, 92: 417-422.
- INTERNATIONAL NUCLEAR SAFETY ADVISORY GROUP, 1986. Summary report on the post-accident review meeting on the Chernobyl accident. Saf. Ser., Int. Atom. En. Ag., Vienna, No.75-INSAG-1, 106pp.

- KIMURA, K., MINAMI, E., SAITO, N., SASAKI, Y. and KOKUBU, N., 1956a. Radiochemical interpretation of the radioactive fallout at Nagasaki. In: Research in the Effects and Influences of the Nuclear Bomb Test Explosions. Pt. I. Japan Society for the Promotion of Science, Ueno, Tokyo. pp.529-536.
- KIMURA, K., MINAMI, E., HONDA, M., YOKOYAMA, Y., IKEDA, N., FUWA, K., NATSUME, H., ISHIMORI, T., SASAKI, Y., MIZUMACHI, K., ASADA, M., ABE, S., MABUCHE, H., SUZUKI, Y., KOMATSU, K. and NAKADA, K., 1956b. Radiochemical analysis of falling dust on the fishing boat "Fukuryu Maru" on 1st March, 1954. In: Research in the Effects and Influences of the Nuclear Bomb Test Explosions. Pt.I. Japan Society for the Promotion of Science, Ueno, Tokyo, pp.497-519.
- MARTELL, E. A., 1956. The Chicago sunshine method; absolute assay of strontium-90 in biological materials, soils, waters and air filters. The University of Chicago, Illinois, Rep. AECU-3262, 59pp.
- MITCHELL, N. T. and EDEN, G. E., 1962. Radioactive strontium in the River Thames. *J. Instn. Wat. Engrs*, 16: 175-187.
- PARKER, R. P., 1974. Cerenkov counting and other special topics. In: M. A. Crook and P. Johnson (Eds.) Liquid Scintillation Counting, Vol. 3. Heyden, London, pp.237-252.
- RAWSON, S. G., 1897. The quantitative and qualitative separation of barium, strontium, and calcium. *J. Soc. Chem. Ind.*, 16: 113-115.
- SAMUELSON, O., 1963. Ion Exchange Separations in Analytical Chemistry. John Wiley & Sons, London, 474pp.
- SCHULTZ, V. and KLEMENT, A. W. Jr., Eds., 1963. Radioecology. Proceedings of the 1st National Symposium on Radioecology, Colorado, September 10-15, 1961. Reinhold Publishing Corporation, New York and American Institute of Biological Sciences, Washington, 746pp.
- SCOTT RUSSELL, R., 1966. Radioactivity and the Human Diet. Pergamon Press, Oxford and London, 552pp.
- STARY, J., 1964. The Solvent Extraction of Metal Chelates. Pergamon Press, Oxford and London, 240pp.
- SUNDERMAN, D. and MEINKE, W., 1957. Evaluation of radiochemical separation procedures. *Analyt. Chem.*, 29: 1578-1589.
- UNITED NATIONS, 1962. Report of the scientific committee on the effects of atomic radiation. UN, New York, 17th Session, Suppl. 16 (A/5216), 442pp.
- UNITED STATES - HEALTH AND SAFETY LABORATORY, 1962. Radiochemical determination of strontium-90. USAEC Health and Safety Laboratory, New York, NYO-4700 (Rev), pp.E-38-01-01 to 39.
- WALKER, F. W., KIROUAC, G. J. and ROURKE, F. M., 1977. Nuclides and Isotopes. 12th edition. Educational Relations, General Electric Co. Schenectady, New York, 12pp.
- WILLARD, H. and GOODSPEED, E., 1936. Separation of strontium, barium and lead from calcium and other metals. *Ind. Engng. Chem.*, 8: 414-418.
- YAMADA, K., TOZAWA, H., AMANO, K. and TAKASE, A., 1956. Studies on the radioactivity in certain pelagic fishes. II. Group separation of radioactive element in fish tissues. In: Research in the Effects and Influences of the Nuclear Bomb Test Explosions. Pt.II. Japan Society for the Promotion of Science, Ueno, Tokyo, pp.849-854.

Appendix - Laboratory procedures

A.1 Reagents

Analytical grade reagents are suitable unless otherwise stated. Prepared reagents can be stored in polythene bottles unless alternative container materials are specified.

A.1.1 Water

Distilled or deionized water should be used throughout.

A.1.2 Hydrochloric acid

Concentrated HCl is that which has a specific gravity of 1.18.

A.1.3 Nitric acid

Fuming HNO_3 has a specific gravity of 1.5. Concentrated HNO_3 has a specific gravity of 1.42. To prepare 4 M of HNO_3 dilute 250 cm³ of the HNO_3 to 1 litre with distilled water.

A.1.4 Oxalic acid

For seawater, approximately 250 g of $(\text{COOH})_2$ are dissolved in 1 litre of hot, distilled water immediately prior to use. For other analyses, prepare saturated $(\text{COOH})_2$ by dissolving about 110 g in 1 litre of distilled water.

A.1.5 Acetic acid

To prepare 6M of CH_3COOH , dilute 345 ml of glacial CH_3COOH to 1 litre with distilled water.

A.1.6 Ammonia solution

Concentrated ammonia solution is that which has a specific gravity of 0.880.

A.1.7 Ammonium acetate 3M

Dissolve 230 g of $\text{CH}_3\text{COONH}_4$ in 1 litre of distilled water.

A.1.8 Sodium carbonate solution

A saturated solution contains 70 g of Na_2CO_3 per litre of water at 20°C.

A.1.9 1.5M sodium chromate solution

Dissolve 510 g of $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ in 1 litre of water.

A.1.10 Ferric chloride solution

Dissolve 4.8 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 1 litre of 3M HCl to give a carrier solution of 1 mg Fe ml^{-1} .

A.1.11 Strontium carrier

Dissolve 153 g of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ in 1 litre of water to give a carrier solution of 50 mg Sr ml^{-1} .

A.1.12 Barium carrier

Dissolve 18 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 1 litre of water to give a carrier solution of 10 mg Ba ml^{-1} .

A.1.13 Methyl red indicator

Dissolve 0.5 g of methyl red in 100 ml of industrial methylated spirit.

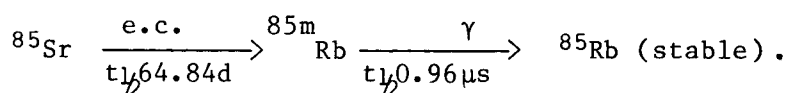
A.2 **Hazards**

In addition to observing normal standards of safety in the chemical laboratory, particular care is needed in handling fuming nitric acid. The handling of radionuclides in analytical laboratories is now governed by the Ionizing Radiation Regulations 1985 (Great Britain - Parliament, 1985) to which reference should be made before using the radioactive tracers and standards recommended in this booklet.

A.3 **Preparation of ^{85}Sr yield tracer**

^{85}Sr is available from, for example, Amersham International plc, as a tracer solution (2MBq or 54 μCi per 5 ml).

The nuclide decays by electron capture (EC) as follows:



Counting is conveniently carried out using the gamma photon at 0.514 MeV (50.4%) (positron annihilation peak). Because the half-life of the nuclide is relatively short, dilute small aliquots at a time in order to give a working tracer solution of about 50 Bq $^{85}\text{Sr ml}^{-1}$ in 0.1M HCl solution. Inactive strontium carrier should be added to stabilize the tracer solution at about $100 \mu\text{g Sr ml}^{-1}$.

A.4 **Apparatus**

- 1) A centrifuge capable of handling 1 litre sample containers is required. Adaptors to enable 100 ml centrifuge tubes to be used in this machine are also required unless a separate machine is available for 100 ml capacity containers.

- 2) A well crystal NaI(Tl) gamma counter, capable of accepting 20 ml liquid scintillation counting vials, is most suitable for ^{85}Sr recovery counting.
- 3) A liquid scintillation spectrometer is a requisite.
- 4) A low-background, end-window beta-counter is also needed.

A.5 Practical analytical procedures

<u>Step</u>	<u>Experimental procedure</u>	<u>Notes</u>
	<u>Preliminary treatment of samples of seawater</u>	
1	Collect a known volume of seawater.	a. The quantities described in this method relate to a 50 l sample.
2	Filter through a 293 mm diameter 0.45 μm membrane filter to remove suspended particulate matter.	b. Retain membrane for the analysis of suspended particulate matter starting at step 4 of the sediment stage
3	Add an appropriate amount of ^{85}Sr to act as a yield tracer to the filtrate whilst it is being stirred with compressed air.	c. The addition of inactive carrier is unnecessary because seawater already contains 8 mg of Sr per litre. Inactive carrier should not contain less than 100 mg of Sr.
4	Whilst the sample is still being stirred, add 500 ml of concentrated HCl followed by 250 g of $(\text{COOH})_2$ as a solution in 1 litre of hot, distilled water.	
5	When thoroughly mixed, add 575 ml of concentrated NH_4OH solution to precipitate alkaline earth oxalates.	d. Check that the pH is approximately 4 ± 0.2 .
6	Filter the sample through a 293 mm diameter 0.45 μm membrane filter. Wash the precipitate with distilled water to remove the bulk of the chloride ions. Discard the filtrate.	
7	Scrape the precipitate from the filter membrane into a 1 litre polythene centrifuge pot. Then transfer any remaining precipitate from the filter to the pot with the aid of 200 ml of distilled water.	e. The volume of water is critical for the next stage in the process. Optimum separation of Sr from Ca is achieved when the

<u>Step</u>	<u>Experimental procedure</u>	<u>Notes</u>
		nitric acid concentration is approximately 73% HNO_3 , w/w.
8	Add 450 ml of fuming HNO_3 and cool the container to room temperature.	
9	Centrifuge and discard the supernate.	
10	Dissolve the $\text{Sr}(\text{NO}_3)_2$ precipitate in 200 ml of distilled water and repeat steps 8 and 9.	f. Repeat precipitation is needed to reduce the amount of $\text{Ca}(\text{NO}_3)_2$ in the precipitate.
11	Proceed to the purification stage.	
<u>Preliminary treatment of samples of sediments</u>		
1	Dry the sample to constant weight either by freeze-drying or by oven-drying at 110°C .	g. Freeze-drying gives samples which are more easily handled if appreciable amounts of clay are present.
2	Homogenize the dry sample until all of the material will pass through a $63\mu\text{m}$ sieve.	
3	Cone and quarter the sieved sample to give a sub-sample of about 100-200g dry weight.	
4	Weigh-out suitable portions of the dry sample for analysis.	h. Aluminium trays make ideal containers for muffle ashing at this temperature.
5	Ash the sample in a muffle furnace at $500 \pm 25^\circ\text{C}$ for at least 6 hours	i. Samples of 10 g-20 g are commonly suitable amounts.
6	Place the ashed sample in a 1 litre Pyrex glass beaker. Then add 100mg of inactive strontium carrier and an appropriate amount of ^{85}Sr tracer solution	j. By not having excess liquid present, the problem of bumping is avoided. In some exceptional cases (e.g. shell sand), more HNO_3 may be needed to dissolve all of the alkaline earth components.
7	Moisten with concentrated HNO_3 and evaporate on a hot plate to remove chloride.	

<u>Step</u>	<u>Experimental procedure</u>	<u>Notes</u>
8	Repeat the moistening process with HNO_3 and evaporate to dryness. Then add 4M HNO_3 (10 ml g^{-1} of original sample should be sufficient) and digest for 60 minutes on a hotplate.	
9	Filter through a 47 mm diameter 0.45 μm membrane filter mounted in a suitable vacuum filtration rig.	k. Millipore-type rigs are suitable (250 ml capacity).
10	Transfer the filtrate to a 1 litre polythene centrifuge pot and dilute to approximately 700 ml. Add sufficient saturated $(\text{COOH})_2$ solution to ensure complete precipitation of Ca and Sr when the pH is adjusted to 4 by the addition of 0.880 sp. gr. ammonia solution. Centrifuge and discard the supernate.	
11	Add water to bring the volume of precipitate to 100 ml. Then add 225 ml of fuming HNO_3 , slowly and with stirring, to ensure initial dissolution of the Ca and Sr oxalates. Cool for 1 hour. Centrifuge and reject the supernate.	
12	Proceed to the purification stage.	
<u>Preliminary treatment of samples of biota</u>		
1	Dry the sample to constant weight either by freeze-drying or by oven-drying at 110°C.	
2	Homogenise the sample by grinding or another suitable method.	
3	Sub-sample as appropriate to provide suitable-sized samples for the analysis.	l. Sufficient dry material to provide 20 g of ash is commonly a suitable amount.
4	Muffle-ash at $500 \pm 25^\circ\text{C}$ to remove the bulk of the organic matter present.	m. This is conveniently carried out in a 1 litre Pyrex glass beaker.
5	Cool and add an appropriate quantity of ^{85}Sr solution and 100 mg of inactive Sr carrier.	n. The Sr concentration of biota is very variable. It is better

<u>Step</u>	<u>Experimental procedure</u>	<u>Notes</u>
		to add an excess of Sr rather than have an insufficient amount for the separation scheme.
6	Moisten the ash with concentrated HNO_3 and evaporate to dryness in order to remove residual carbonaceous material and chloride.	
7	Repeat the moistening process with HNO_3 and evaporate to dryness then add sufficient 4M HNO_3 to solubilise all but siliceous matter when digested for 60 minutes on a hotplate.	
8	Filter through a 47mm diameter 0.45 μm membrane filter mounted in a suitable vacuum filtration rig.	
9	Transfer the filtrate to a 1 litre polythene centrifuge pot and dilute to approximately 700 ml. Add sufficient saturated $(\text{COOH})_2$ solution to ensure complete precipitation of Ca and Sr when the pH is adjusted to 4 by the addition of 0.880 sp. gr. ammonia solution. Centrifuge and discard the supernate.	
10	Add water to bring the volume of precipitate to 100 ml. Then add 225 ml of fuming HNO_3 , slowly and with stirring, to ensure initial dissolution of the Ca and Sr oxalate precipitates. Centrifuge and discard the supernate.	o. These volumes can be doubled if the sample type and size warrant them.
11	Proceed to the purification stage.	

Purification

1	Dissolve the $\text{Sr}(\text{NO}_3)_2$ precipitate in 20ml of distilled water and transfer the solution to a 100 ml centrifuge tube.	
2	Add 45ml of fuming HNO_3 , cool and centrifuge. Discard the supernate.	
3	Dissolve the precipitate in 15 ml of distilled water.	p. If any insoluble matter remains, dilute to 50 ml, add 5 g of Na_2CO_3 and digest on a

<u>Step</u>	<u>Experimental procedure</u>	<u>Notes</u>
		water bath for 1 hour as the precipitate may contain SrSO_4 . Centrifuge and discard the supernate then dissolve in the minimum amount of dilute HCl.
4	Add 1 ml of Ba carrier solution and one drop of methyl red indicator. Adjust to neutral pH by the dropwise addition of NH_4OH solution until the indicator changes from red to yellow. Then add 1 ml of 6M CH_3COOH and 2 ml of 3M $\text{CH}_3\text{COONH}_4$.	q. The pH of the solution at this point is critical. BaCrO_4 precipitates incompletely in more acid conditions.
5	Dilute the solution to 30 ml and heat in a boiling-water bath.	r. If the solution is too concentrated, loss of Sr will occur in the following step.
6	Add 1 ml of 1.5M Na_2CrO_4 solution and continue heating for a further 5 minutes, before centrifuging.	
7	Without disturbing the precipitate, add a further 1 ml of Ba carrier solution and heat to coagulate the second precipitate. Centrifuge and then transfer the precipitate to another tube. Discard the BaCrO_4 precipitate which contains radionuclides of Ba, Ra and Pb.	
8	To the supernate add 5 ml of FeCl_3 solution. Mix and add concentrated NH_4OH solution, dropwise, until the solution is alkaline. Centrifuge and transfer the supernate to a clean centrifuge tube. Reject the $\text{Fe}(\text{OH})_3$ precipitate.	s. The $\text{Fe}(\text{OH})_3$ scavenge removes remaining traces of ^{90}Y , ^{91}Y and radium daughters.
9	To the supernate add 2 g of Na_2CO_3 . Heat in a water bath to coagulate SrCO_3 , then centrifuge and discard the supernate.	
10	To the precipitate add 20 ml of distilled water and 45 ml of fuming HNO_3 . Cool and reject the supernate.	t. The highly-coloured chromate ion has to be thoroughly removed to avoid quenching problems in subsequent Cerenkov counting.
11	Record the date and time at which the supernate is separated. This is the beginning of ^{90}Y grow-in.	

<u>Step</u>	<u>Experimental procedure</u>	<u>Notes</u>
	<u>Source preparation and radiometric assay</u>	
1	Dissolve the $\text{Sr}(\text{NO})_3$ in 1M HCl and transfer to a 20 ml plastic scintillation phial which contains 10 mg of Y carrier.	
2	If ^{89}Sr is to be determined or a check made for the presence of ^{89}Sr , count the sample immediately in a liquid scintillation counter optimised for Cerenkov counting. Note the time of the count for the calculation of ^{90}Y grow-in.	u. See text (Figure 4) for an instrument energy calibration.
3	Measure the chemical yield of Sr by counting the phial in a well crystal NaI(Tl) gamma detector against an ^{85}Sr standard (and background) sample, both presented in an identical geometry to that of the sample.	
4	Store the sample for up to 3 weeks to enable the ^{90}Y to grow-in.	v. See Table A1 for ^{90}Y grow-in factors.
5	Transfer the contents of the phial, carefully, to a 50 ml centrifuge tube. Add a slight excess of carbonate-free 0.880 sp. gr. ammonia solution and centrifuge. Note the time for the purpose of calculating the ^{90}Y grow-in factor (see note v). Transfer the supernate to a labelled 100 ml beaker. Dissolve the precipitate in a few drops of 11.3M HCl, dilute to ~ 30 ml with water, add a slight excess of 0.880 sp. gr. ammonia solution and centrifuge. Add the supernate to the 100 ml beaker.	w. The supernates which contain the Sr fraction are acidified and stored to enable a second "milking" of ^{90}Y to be made, should it prove to be necessary.
6	Dissolve the precipitate in a minimum of 6M HNO_3 . Add 20 ml of 8% $(\text{COOH})_2$ solution, heat in a water bath to coagulate, then filter onto a 47 mm millipore membrane filter.	x. If end-window counting is employed, mount the filter on a 5 cm planchette and count against a standard and background sample as soon as possible. Determine Y recovery as in step 7.

<u>Step</u>	<u>Experimental procedure</u>	<u>Notes</u>
7	Transfer the filter to a tared platinum crucible. Burn off the paper carefully then ignite over a Meker-type burner. Cool in a dessicator and weigh as Y_2O_3 to determine the Y recovery.	
8	Dissolve the Y_2O_3 in 2 ml of 6M HCl and transfer to a plastic liquid scintillation phial with water. Count immediately, on a liquid scintillation counter optimised for Cerenkov counting, against a ^{90}Y or $^{90}Y/^{90}Sr$ standard and a background sample in the same geometry to that of the sample. Note the time so that the decay of ^{90}Y after separation can be calculated.	

A.6 Calculation of results

A6.1 Chemical yield

Record the counts, S_Y for the sample, X_Y for the ^{85}Sr standard and B_Y for the background, on the γ detector. Sufficient counts should be taken to enable the recovery to be established with good precision. Then, provided that:

- (i) the counts are carried out within 4 h of one another so that the error due to ^{85}Sr decay may be ignored;
- (ii) an equal quantity of ^{85}Sr is taken for both the sample and the standard;
- (iii) all counts are made over an equal period of time; and
- (iv) interference from Bremsstrahlung arising from the beta-emitting nuclides has been shown to be insignificant or has been allowed for in the chemical recovery;

then R_Y is given by

$$R_Y = \frac{S_Y - B_Y}{X_Y - B_Y}$$

and the 1 σ percentage error, P_Y is given by

$$P_Y = 100 \sqrt{\frac{X_Y + B_Y}{(X_Y - B_Y)^2} + \frac{S_Y + B_Y}{(S_Y - B_Y)^2}}$$

A6.2 Determination of ^{90}Sr

^{90}Sr is determined by counting the separated ^{90}Y daughter. Counting is carried out by end-window or Cerenkov counting and the counter efficiency is determined with a ^{90}Y standard or, alternatively, with a $^{90}Sr/^{90}Y$ standard (allowing for the small contribution for the ^{90}Sr) in

the case of Cerenkov counting. Record the counts, S_β for the sample, X_β for the ^{90}Y standard and B_β for the background, obtained on the beta counter over the same counting time.

The ^{90}Sr content, $A_{90\text{Sr}}$, of the sample in Bq kg^{-1} is given by

$$A_{90\text{Sr}} = \frac{S_\beta - B_\beta}{T} \times \frac{1}{R_\gamma} \times \frac{1}{R_\beta} \times \frac{1}{E_{90\text{Y}}} \times f \times G \times \frac{1}{W}$$

where

T is the counting time in seconds;

R_γ is the chemical recovery of ^{90}Sr (see Sub-section A6.1);

R_β is the chemical recovery of ^{90}Y ; determined gravimetrically in the case of Y addition or assumed to be unity where ^{90}Y is coprecipitated on $\text{Fe}(\text{OH})_3$;

$E_{90\text{Y}}$ is the counting efficiency for ^{90}Y , given by $\frac{\text{count rate}}{\text{disintegration rate}}$;

f is the decay correction for ^{90}Y , given by $e^{\lambda t}$, where t is the time lapse between the Sr/Y separation (prior to counting) and the mid-time of the count;

G is that fraction of the ^{90}Y which has grown-into the ^{90}Sr in the time, t , between the virtual Sr/Y separation (prior to counting) and equals $\frac{1}{1 - e^{-\lambda t}}$. Table A1 gives values for easily calculating this fraction. (G will be approximately unity when $t > 20$ days);

W is the weight in kilograms of the sample taken for analysis.

The 1σ percentage counting error P_β is given by

$$P_\beta = 100 \sqrt{\frac{X_\beta + B_\beta}{(X_\beta - B_\beta)^2} + \frac{S_\beta + B_\beta}{(S_\beta - B_\beta)^2}}$$

The overall 1σ percentage error on the ^{90}Sr result attributable to counting will be $\sqrt{E_\gamma^2 + E_\beta^2}$.

Other sources of error, for example certificated calibration errors of the standard, can be readily incorporated into this latter expression if required.

It is worth noting that, in samples where ^{89}Sr is known to be absent, the overall procedure for ^{90}Sr estimation can be considerably simplified as follows:

- (i) no final Sr/Y separation (prior to counting) need be carried out, thus eliminating the need for the chemical recovery of Y ;
- (ii) provided that the ^{90}Sr and ^{90}Y have reached equilibrium (~ 20 days) the ^{90}Y grow-in factor, G , approximates to unity and the sample can be counted against a $^{90}\text{Sr}/^{90}\text{Y}$ standard removing the need for preparation of a ^{90}Y standard.

The expression for the calculation of ^{90}Sr activity can be reduced to

$$\frac{(S_\beta - B_\beta)}{R_\gamma} \times \frac{1}{E_{90\text{Sr}+90\text{Y}}} \times \frac{1}{W} \times f$$

where

$$E_{90\text{Sr}+90\text{Y}} = \frac{\text{count rate from } ^{90}\text{Sr} + ^{90}\text{Y}}{\text{distinguishing rate of } ^{90}\text{Sr} + ^{90}\text{Y}}.$$

Table A1. The grow-in of ^{90}Y into ^{90}Sr :
relationship between grow-in factor (G)
and time (t)

t		G ($^{90}\text{Sr}/^{90}\text{Y}$)
Hours	Days	
1		94.007
2		47.255
3		31.672
4		23.880
5		19.206
6		16.090
7		13.864
8		12.195
9		10.898
10		9.8596
20		5.1931
30	1.25	3.6436
40		2.8732
50		2.4145
60	2.50	2.1116
70		1.8976
80		1.7393
90	3.75	1.6180
100		1.5225
200		1.1335
300	12.5	1.0421
400		1.0141
500		1.0048
600	25	1.0016

A6.3 Determination of ^{89}Sr

After completion of the Sr purification (final fuming nitric acid treatment), the Sr is encapsulated in a plastic scintillation phial and immediately Cerenkov counted. The resultant beta count (S_T) is a total of four components - the ^{89}Sr count, $S_{89\text{Sr}}$; the ^{90}Sr count, $S_{90\text{Sr}}$; the count $S_{90\text{Y}}$ arising from the ^{90}Y grown-in since separation; and the background, B_β .

Thus

$$S_{89\text{Sr}} = S_T - B_\beta - S_{90\text{Sr}} - S_{90\text{Y}}.$$

$S_{89\text{Sr}}$ and $S_{90\text{Y}}$ can be calculated from the subsequently determined ^{90}Sr content, $A \text{ Bq kg}^{-1}$, of the sample and are given by the following expressions:

$$S_{90Sr} = A \times W \times R_Y \times E_{90Sr} \times T$$

$$S_{90Y} = A \times W \times R_Y \times E_{90Y} \times T \times F$$

where

E_{90Sr} and E_{90Y} are the Cerenkov counting efficiencies for ^{90}Sr and ^{90}Y respectively;

F is the grow-in factor for ^{90}Y given by $1 - e^{-\lambda t}$;

where

t is the time lapse between the mid-time of counting and the final fuming nitric acid treatment.

The ^{89}Sr content, A_{89Sr} , in $Bq\ kg^{-1}$ of the sample is given by:

$$A_{89Sr} = S_{89Sr} \times \frac{1}{R_Y} \times \frac{1}{E_{89Sr}} \times \frac{1}{W} \times \frac{1}{T}$$

where

E_{89Sr} is the counter efficiency for ^{89}Sr .

Provided that all of the counts were taken or calculated for the same counting period and, where the count of the ^{89}Sr standard is given by X_{89} , the 1σ percentage error (P_{89Sr}) associated with the beta counting of ^{89}Sr can be given by:

$$P_{89Sr} = 100 \sqrt{\frac{S_T + B_\beta + S_{90Sr} + S_{90Y}}{(S_T - B_\beta - S_{90Sr} - S_{90Y})^2 + \frac{X_{89} + B_\beta}{(X_{89} - B_\beta)^2}}$$

and the overall 1σ percentage error attributable to counting in the estimation of ^{89}Sr is given by $\sqrt{P_{89Sr}^2 + P_Y^2}$.

Note: Corrections for activities back to sampling date, etc. have not been included in the above calculations.

A7. Appendix reference

GREAT BRITAIN - PARLIAMENT, 1985. The Ionising Radiations Regulations 1985. Her Majesty's Stationery Office, London, 83pp.