STRONTIUM-90 AND STRONTIUM-89: A REVIEW OF MEASUREMENT TECHNIQUES IN ENVIRONMENTAL MEDIA

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1. INTRODUCTION

There are only two radioactive isotopes of strontium of significance in radiological measurements in the environment: strontium-89 and strontium-90.

Strontium-90 is the more significant from the point of view of environmental impact. This is due mostly to its long half-life (28.1 years). It is a pure beta emitter with only one decay mode, leading to yttrium-90 by emission of a negative beta with E_{max} = 546 keV. Subsequently, the ^{90}Y daughter nucleus almost always decays be emitting a β^- (E_{max} = 2.27 MeV) with a 64 hour half-life, leading to stable zirconium-90. The beta energy spectra are shown in Figure 1 and Figure 2 (from Ref. 1).

Strontium-89 has a 52 day half-life, much shorter than that of ^{90}Sr but still quite long in its own right. It decays by nearly pure β^- emission to stable yttrium-89, the maximum beta energy being 1.463 MeV.

The main radiological impact of radiostrontium in man is due to its biochemical resemblance to calcium. When ingested, some of the strontium becomes lodged in the bones, where it remains for a long time (almost permanently). Its subsequent decay produces radiation dose directly at the site (the 2.27 MeV highest-energy beta of the daughter ^{90}Y has a maximum range of only about 1.0 g/cm^2). Because of this, the recommended maximum permissible concentrations (MPC) in air and water are quite small. For occupational exposure, the ICRP (Ref. 2) has recommended the following MPC's on a 168-hour-per-week basis for soluble strontium:

Isotope	168-hour-week Occupational MPC in air (pCi/m^3)	168-hour-week Occupational MPC in water (pCi/liter)
Strontium-90	100	1,000
Strontium-89	10,000	100,000

The maximum permissible body burdens (MPBB) are 2 μCi (for ^{90}Sr) and 4 μCi (for ^{89}Sr), both for burden in the *bone* (Ref. 2). For individuals of the general public, the MPC and MPBB levels are a factor of 10 smaller; and for a suitable average sample of a large general population, another factor of 3 smaller still.

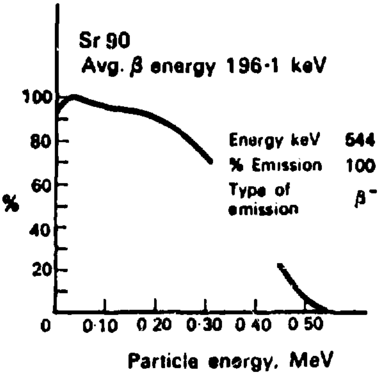

FIGURE 1. Spectrum of beta energies from decay of strontium-90 (from Ref. 1).

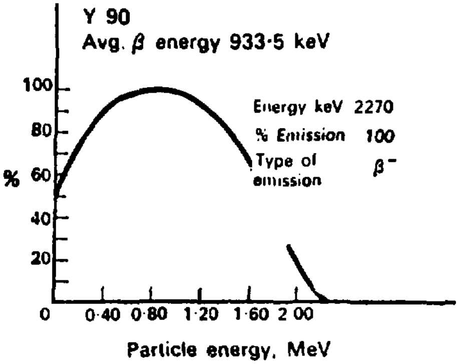

FIGURE 2. Spectrum of beta energies from decay of yttrium-90 (from Ref. 1).

2. SOURCES OF ENVIRONMENTAL RADIOSTRONTIUM

The two main sources of radiostrontium are from (i) nuclear reactors and their fuel reprocessing plants; and (ii) from fallout after atmospheric nuclear bomb tests. Both strontium radioisotopes are among the important fission products.

In *nuclear reactors*, there is a significant production of both ^{89}Sr and ^{90}Sr. Reference 3 projects that the *total* amounts of activity produced annually will increase dramatically in the coming decades because of growth in the nuclear power industry. In 1970 the total strontium-90 annual production rate was 4.0 megacuries/year; the projected figures for the years 1980, 1990, and 2000 are 227, 410, and 460 MCi/year, respectively. The integral (accumulated) strontium-90 activities in those three years are projected to be 960, 4600, and 9550 MCi, respectively. This is based upon an Oak Ridge National Laboratory projection whose detailed input is subject to revision, but the trend is clear. The strontium-89 production rates will grow similarly, although there is no long-term build-up of strontium-89 (because of its 52-day half-life).

Reactors can be designed and built so that most of the activities in the reactor fuel do not escape into the environment. At a reactor site itself, the average release rates of fission products are only very small fractions of the total fuel inventories. For example, at the Dresden Nuclear Power Station in Illinois, the ratios of released to produced activities in 1968 (Ref. 4) were 4×10^{-9} (for strontium-90) and 6×10^{-8} (for strontium-89). The average release rates in stack effluent were 700 pCi/second (strontium-89) and 3 pCi/second (strontium-90), while in liquid effluent the numbers were 8000 and 900 pCi/second, respectively.

The potential source for environmental release is mainly the nuclear fuel-reprocessing plants , where the fuel rods are dissolved and the radiostrontium is released from the cladding. However, sufficient precautions have been designed into the more recent plants to assure practically complete containment in normal operation. For example, the 150-day storage of fuel elements before reprocessing allows 86% of the ^{89}Sr to decay (but only 1% of the ^{90}Sr). At the Midwest Fuel Recovery Plant in Morris, Illinois, the design calls for *no* environmental release of radioactive waste in either solid or liquid form. A limit on emissions of gaseous gross beta (particulates in air) at 7.0 μCi/second has been suggested (Ref. 5), based upon strontium-90 as the limiting radionuclide. From this it can be seen that the total environmental emissions should be small indeed.

Fallout is, of course, the source of radiostrontium that has gained the widest cognizance in the minds of the general public. Indeed, strontium-90 was a household word in the early 1960's. This widespread concern in the era of large-scale atmospheric nuclear bomb tests led to a great deal of research into the environmental behavior of radiostrontium in its pathways from the nuclear fireball to man. Fallout concentrations were measured extensively, and are still being measured routinely (Ref. 6). The deposition was considerable. We quote from the Federal Radiation Council (Ref. 7), "On January 1, 1963, the accumulated levels of Strontium-90 deposited over the United States varied from about 100 to 125 millicuries per square mile in the 'wet' areas (areas of greatest annual precipitation) to 40 to 50 millicuries per square mile in the 'dry' regions." The recent French and Chinese nuclear tests have again deposited strontium-90 as fallout.

Studies of the fate of strontium-90 from fallout have revealed that an important measure of its impact on man is the ratio of strontium to calcium in the total diet. "The (Sr/Ca) ratio in new bone being formed is one-fourth of that in the average diet because the body selectively discriminates against strontium" (Ref. 8). Typical ^{90}Sr/Ca ratios in total diet in 1963 (Ref. 8) were 10 to 50 pCi/gram Ca (1 pCi of strontium-90 weighs about 7×10^{-15} grams). Activities in milk were 10 to 30 pCi/liter; and in flour about 40 pCi/kg. Strontium-89 in milk averaged 40 to 55 pCi/liter in 1963.

These figures indicate the range of activities requiring measurement. In biological and food samples, fallout measurements must be sensitive to a few pCi/liter of milk, and perhaps fractions of a pCi/kg of other foods such as vegetables and baked foods. In air-particulate samples from reactors or fuel-reprocessing plants, average release rates in the range from a few pCi/second to perhaps a *few μCi/sec* need measurement.

Finally, the standard "gross beta" measurements in both drinking water and respirable air are designed mainly to place upper limits on strontium-90 in these media. For example, the standard method for gross-beta in drinking water (Ref. 9) explicitly states that a limit of 10 pCi/liter is allowed for strontium-90, but if strontium-90 is known to be absent, then from the point of view of beta activity "the water supply would usually be regarded as radiologically acceptable provided that the gross beta concentration does not exceed 1,000 pCi/liter" (Ref. 9).

3. MEASUREMENT CONSIDERATIONS

A. Introduction

We shall discuss methods for strontium-90 and strontium-89 determination in *air, water, milk, and other media.* Either of two types of measurements is commonly required: In one type, a quantitative measurement of strontium-90 specific activity (e.g., pCi/g) is made, while in the second type it is merely necessary to determine an upper limit of activity to assure safety. In the second type, a gross-beta measurement is usually performed as a first screening step, since it is easier than elaborate strontium-isolation chemistry. Only when the gross-beta measurement exceeds guidelines, or when a strong suspicion of strontium contamination is present, is specific strontium analysis called for.

Here we shall concern ourselves predominantly with the *quantitative analysis* of radiostrontium specific activity in various media. Because strontium must be determined at activity levels well below the permissible gross-beta levels in strontium's absence, *radiochemical separation techniques are invariably required.*

There is an extremely wide variety of methods for radiostrontium, but all follow a similar outline: chemical *concentration,* followed by *purification* and sample *preparation,* followed by *counting.*

Chemical techniques for radiostrontium have been tailored to the requirements of the various media to be measured. Since the chemical properties of yttrium play nearly as important a role as those of strontium itself, the procedures have generally depended upon multiple-step separations of yttrium as well as strontium from the bulk material. Also, media containing the radiostrontiums are frequently contaminated with radioactive cesium-137 (also a long-lived beta emitter), iodine-131, and perhaps other radionuclides as well, so that the radiochemistry can be complicated.

Here we shall give separate treatments to the various media: air, water, milk, and other media (principally foodstuffs and soil). The separate treatment is necessary because of the differences in the chemical techniques: for example, in both milk and urine yttrium forms an anionic complex which makes possible its separation by direct anion exchange. In air filters, the chemical techniques are quite different.

We shall not treat here measurements of strontium-90 activities in biomedical samples such as urine, bone, or soft tissue.

B. Counting

Beta counting is ultimately required in any of the methods. The final strontium sample has to be prepared properly for counting: for most of the counting instruments it must be a thin sample distributed reasonably uniformly over an area compatible with the instrument.

Counting is done with any of a number of instruments. Typical instruments include internal (or external thin-window) gas proportional counters; G-M tubes; semiconductor detectors; and less frequently liquid or plastic scintillation counters, which require different sample-preparation methods. The problems and differences which characterize the various beta counting techniques have been discussed elsewhere

C. Strontium-90/Strontium-89 Separation

The chemical separation techniques cannot, of course, separate the two strontium radioisotopes from each other or from stable strontium. Consequently the end product of the chemical separation contains all strontium isotopes, including carrier strontium and in some cases strontium-85 added as a tracer for chemical yield.

Separation of strontium-89 from strontium-90 is performed using one of two methods. The first is *beta spectrometry,* which relies upon the differences in the maximum energies of the beta spectra (E_{max} = 1.463 MeV for strontium-89; E_{max} = 546 keV for strontium-90; and E_{max} = 2.27 MeV for yttrium-90). This type of measurement is not well suited to the cases in which the strontium-89/strontium-90 ratio is either very large or very small.

The most commonly used spectrometry technique employs a succession of different absorbers to count selectively the highest-energy betas (yttrium-90). If yttrium has been separated out chemically, the strontium-89 betas are counted. Detection efficiencies *must* be calibrated using known activities of the individual radionuclide species (or for yttrium-90 an equilibrium mixture of strontium-90 and yttrium-90); since geometrical effects can produce quite wide variations, it is not safe to rely upon calculations of the fractional detection efficiency. Although this problem is most important in beta spectrometry, it holds as well for the

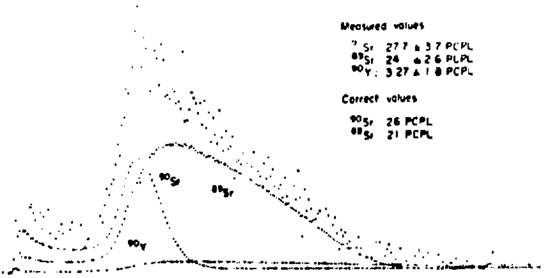

FIGURE 3. Beta pulse height spectra (from Ref. 11). PCPL = pCi/liter

determination of beta spectral efficiency in any of the methods being described.

The beta spectroscopy technique which shows the most promise is liquid scintillation spectroscopy, since after the sample is dissolved or suspended in a scintillator the geometrical efficiency factors are well understood. Direct counting of a sample with liquid scintillators suffers from severe limitations (Ref. 10). However, Piltingsrud and Stencel (Ref. 11) have described a technique which first separates strontium chemically as carbonate, using methods to be described later in this discussion. The $SrCO_3$ is then suspended in liquid scintillator using a gelling agent, and counted, typically for 2 to 12 hours, using a Packard 'Tri-Carb' system and a 512-channel analyzer. For a 12-hour counting period, the minimum detectable activity is about 1 pCi. A typical spectrum is shown in Figure 3; the unfolding of the three isotopic spectral shapes (^{90}Sr, ^{90}Y, ^{89}Sr) is done by computer. Another application of this technique is that of Kanada et al. (Ref. 12), who give detailed descriptions of the way the beta spectrum is unfolded.

The second, and today the more common technique for strontium-89/strontium-90 separation uses *the ingrowth of the daughter yttrium-90.* Figure 4 (from Ref. 9) shows the manner in which yttrium-90 and (yttrium-90 + strontium-90) activities grow in time from a pure strontium-90 sample. Counting rates (corrected for efficiency) can be compared from two measurements, the first immediately after strontium chemical separation (within a few hours, say) and the second 3 to 6 days later. Alternatively, chemical separation of the yttrium daughter can be performed after allowing for ingrowth. Both techniques are frequently used.

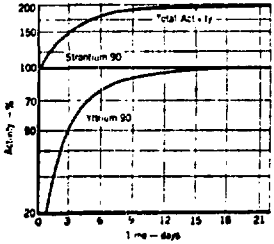

FIGURE 4. Yttrium-90 vs. strontium-90 activity as a function of time. (from Ref. 9)

Measurements of "total radiostrontium" usually refer to the total activity of a strontium fraction immediately after yttrium is separated chemically. The time elapsed before counting is critical, of course, because after strontium-90 and yttrium-90 reach parent/daughter equilibrium the "gross beta" counting rate represents exactly twice the activity of the parent strontium-90 itself.

4. CHEMICAL TECHNIQUES

A good summary of the various types of chemical separation techniques has been given by Bowen (Ref. 13). We shall quote from his work extensively below. In the quotation, Bowen refers to sea-water measurements, but his comments should apply to other liquids. He begins by discussing two attempts to extract yttrium-90 directly from environmental samples, using thenoyltrifuoroacetone (TTA) in benzene. He continues as follows:

"With the exception of these two ventures, all the procedures known to us for strontium-90 analysis in the oceans depend on the separation of most of the strontium, together with more or less of the calcium, followed by removal of all or most of the calcium and then by decontamination of the strontium fraction from other natural or artificial radionuclides by a series of ferric hydroxide and barium chromate scavenges; the cleaned strontium, usually after precipitation with ammonium carbonate for convenience, is then stored for enough time to allow yttrium-90 to come again to equilibrium with its parent, two weeks being a convenient time; yttrium-90 is separated with a minimum amount of iron, samarium or yttrium carrier, often with some additional scavenging steps, finally filtered, weighed and mounted for beta counting. Counting has been done using a variety of gas-filled Geiger-Müller or proportional counters, or with solid plastic beta scintillator. The amount of data obtained to confirm the shape of the expected 64-hr half-life decay curve has varied widely, in response largely to economic factors; although 'good radiochemical technique' dictates the use of repeated milkings of yttrium-90 and insistence on superimposable decay curves, this has been a nicety often omitted.

"In such a separation scheme, the number of variations available is not large:

"(a) Strontium may be initially precipitated as carbonate or as oxalate [Ref. 13b,c] and for the carbonate precipitation, sodium carbonate [Ref. 13d, e], sodium carbonate plus ammonium chloride [Ref. 13f], or ammonium carbonate [Ref. 13g] may be used. Although other reagents have been proposed: manganese dioxide by Shipman [Ref. 13h] or coprecipitation with rhodizonic acid, we know of no data reported to have been obtained by these or any other separation processes than those cited above.

"(b) The oxalate precipitate may be decomposed by dry ignition [Ref. 13e] or by wet combustion with nitric acid.

"(c) Strontium may be separated from such calcium and magnesium as accompany it in the initial precipitation by:

"(1) Selective complexation precipitation, followed by fuming nitric acid precipitations to obtain pure strontium nitrate [Ref. 13d, f].

"(2) Oxalate reprecipitation, followed by fuming nitric separations (Shvedov and Ivonova, referred to in [13f]).

"(3) Nitric acid precipitations without other treatment (cf. Ref. [13c, e]; many others).

"(4) Selective elution serially, from cation exchange columns [Ref. 13a].

"(d) The overall chemical yield of strontium in the separation procedure may be determined gravimetrically [Ref. 13b], by counting tracer strontium-85 (e.g., Ref. [13c]) by flame photometry or atomic absorption spectrophotometry, or volumetrically [Ref. 13a].

"(e) The final separation of daughter yttrium-90 may be made using ferric hydroxide [Ref. 13d, e, f] or yttrium hydroxide [Ref. 13c], or samarium hydroxide. In each case the choice has been based on the availability - or ease of preparation - of radiochemically pure carrier and of the physical properties of its dried hydroxide as a counting medium."

A. Air

In air, measurements of radiostrontium are nearly always made by examining particulate matter. The sampling technique is relatively straightforward: particulate matter is collected on a high-efficiency filter in a Hi-Vol sampler. Air sampling rates of 1000 m^3/day are typical.

Chemical separation is required because of the normal presence of other beta-emitting radionuclides in the particulate matter: for example, naturally-occurring radon daughters can adhere to particulate matter and produce sizeable beta activities. The compilation of *Methods of Air Sampling and Analysis* (Ref. 14) recently issued by the Intersociety Committee contains tentative methods for measuring both strontium-90 and strontium-89 in air. The chemical separation is the same for both radiostrontium isotopes, and this method is likely to be adopted as a "standard Method" in the near future.

The filter is ashed in a muffle furnace prior to the chemical procedure. We quote from Ref. 14:

> "Strontium is separated from calcium, other fission products, and natural radioactive elements. Nitric acid separations remove the calcium and most of the other interfering ions. Radium, lead, and barium are removed with barium chromate. Traces of other fission products are scavenged with iron hydroxide. After the strontium-90 + yttrium-90 equilibrium has been attained, the yttrium-90 is precipitated as the hydroxide and converted to the oxalate for counting. Strontium chemical yield is determined gravimetrically as strontium carbonate. 0.5 pCi strontium-90 can be determined by this method with an error of less than ±10% at the 95% confidence level under usual conditions (counter background of less than 1 cpm and a 60-minute count)."

Another technique for air filters has been developed at Atomic Energy of Canada Limited (A.E.C.L.) (Ref. 15). The first stages of the separation are described as follows:

> "The ashed air filter is fumed with hydrofluoric and perchloric acids to remove silica. After extraction with nitric acid and fusion with sodium carbonate, an anion exchange column is used to separate plutonium from iron and other elements. The column effluent is retained for the estimation of barium (140), strontium (89, 90) and cesium (137)."

An alternative separation method, also described in the A.E.C.L. Manual (Ref. 15), is applicable when the ashed air filters contain little acid-insoluble material. In this method, "plutonium is separated from barium, strontium, and cesium by hexone extraction from a saturated ammonium nitrate solution" (Ref. 15). Hexone is methyl isobutyl ketone. This method is shorter and easier than either of the others mentioned, making it attractive where the conditions for its use are applicable. Use of either A.E.C.L. separation method must be followed by another stage to isolate radiostrontium from barium and cesium.

B. Water

Two types of water are of most concern: Drinking water and waste water. We have already referred above to the U.S. Public Health Service Drinking Water Standards (Ref. 16). The limit for strontium-90 is 10 pCi/liter, when other sources of intake are not considered. No explicit limit is given for strontium-89, but the maximum permissible level for it would be significantly higher: for example, the ICRP's maximum permissible concentration for strontium-89 in water is a factor of 100 higher than for strontium-90.

In *Standard Methods* (Ref. 9) the method for total radiostrontium and strontium-90 in water applies to either drinking water or filtered raw water. We quote from Ref. 9:

> "It is applicable to sewage and industrial wastes, provided that steps are taken to destroy organic matter and eliminate other interfering ions. In this analysis, a known amount of inactive strontium ions, in the form of strontium nitrate, is added as a "carrier". The carrier, alkaline earths and rare earths are precipitated as the carbonate to concentrate the radiostrontium. The carrier, along with the radionuclides of strontium, is separated from other radioactive elements and inactive sample solids by precipitation as strontium nitrate from fuming nitric acid solution. The strontium carrier, together with the radionuclides of strontium, is finally precipitated as strontium carbonate, which is dried, weighed to determine recovery of carrier, and then measured for radioactivity. The activity in the final precipitate is due to radioactive strontium only, because all other radioactive elements have been removed....
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> "Radioactive barium (^{140}Ba, ^{140}La) interferes in the determination of radioactive strontium inasmuch as it precipitates along with the radioactive strontium. This interference is eliminated by adding inactive barium nitrate carrier and separating this from the strontium by precipitating barium chromate in acetate buffer solution. Radium isotopes are also eliminated by this treatment....
>
> "Two alternate procedures are given for the separation of ^{90}Y. In the first method, ^{90}Y is separated by extraction into tributyl phosphate from concentrated nitric acid solution. It is back-extracted into dilute nitric acid and evaporated to dryness for beta counting. The second method consists of adding yttrium carrier, separating by precipitation as yttrium hydroxide, and finally precipitating yttrium oxalate for counting."

A similar technique, not identical in all respects but following the same general lines, is described in the A.E.C.L. Manual (Ref. 15).

C. Milk

Milk is one of the most important pathways to man for environmental strontium. The U.S.P.H.S. Pasteurized Milk Network has developed a standard analytical procedure (Ref. 18-22) which will be discussed here as typical of several other methods. The method removes strontium (and other alkaline and alkaline earth ions) by passing a liter of milk through a cation exchange resin, followed by removal of yttrium in an anion exchange resin.

We quote from Ref. 20:

> "The procedure consists of storing the milk samples with formaldehyde preservative for the ingrowth of the yttrium-90 daughter of strontium-90, adding yttrium carrier, and then passing the milk consecutively through cation and anion exchange resin columns. The alkaline earth ions in milk are replaced by sodium ions in the cation exchange column, after which the yttrium is retained as an anionic complex - probably of citrate - in the anion exchange column. The effluent milk is discarded and the yttrium complex on the anion exchange resin is destroyed with hydrochloric acid. The yttrium, eluted with the acid, is precipitated as the oxalate, and the radio-yttrium is measured with a low-background beta counter....
>
> Initially, the maximum yttrium yield was 65% and average yields were 55%. Yttrium retention on the resin was improved from 80 to 90% by adding sodium citrate to the milk. The per cent eluted in 35 ml of hydrochloric acid was increased from 81 to 96% by decreasing the amount of anion exchange resin and by thoroughly stirring the resin during elution. Other losses were minimized by small procedural changes, so that the overall average yield was increased to 86%."

The U.S. Public Health Service manual (Ref. 21) describes other methods for milk analysis. Their "reference method", used mainly for quality control, is not applicable for routine analysis. The method uses strontium-85 as a tracer; strontium is separated by successive carbonate precipitation and HNO_3 washing, and the yttrium-90 ingrowth occurs in solution. The special feature is separation of ingrown yttrium from contaminating lanthanum-140 using tributyl phosphate. A similar method is described in the *Procedures Manual* of the USAEC Health and Safety Laboratory (Ref. 32).

Another method in the U.S.P.H.S. manual (Ref. 21) removes milk proteins by precipitation with trichloroacetic acid (TCA); precipitates the alkaline earths as oxalates, subsequently converted to nitrates; and separates strontium from calcium by solubility. When working in humid climates, care is required since the sample is counted as strontium nitrate on a stainless steel planchet, which can corrode the counting chamber if nitric acid is formed at high humidities. The *Handbook* of the Environmental Protection Agency's National Environmental Research Center (Las Vegas) (Ref. 24) describes a method very similar to this last (TCA) technique.

D. Other Media

Chemical separation techniques have been developed for a wide variety of media besides air, water, and milk. The techniques are as varied as the problems, since media such as food or biological samples can have any of a large number of (radioactive or stable) impurities. Here we shall only mention briefly a few methods.

In most biological samples, the first procedure is to convert the sample to *ash* in a muffle furnace (500° to 800°C). This eliminates the large organic substrate, which might originally contain strontium or yttrium in complexed form. Ashing is also performed on milk and bone samples. For some samples, which are volatile at dry-ashing temperatures, it is preferable to perform *wet ashing* with nitric acid, followed by an equal-volume mixture of perchloric and nitric acids (Ref. 25). The U.S.P.H.S. manual (Ref. 21) contains good outlines of the procedures for both dry and wet ashing.

Fusion is used for those samples (e.g., soil, silt) which are not easily dissolved by acid digestion because of their high silica content. The fusion procedure in the U.S.P.H.S. manual is typical: the sample, with carrier plus 5 g of NaOH pellets per gram of sample, is fused over a Meeker burner for 20-30 minutes. Then 0.5 g of anhydrous Na_2CO_3 per sample gram is slowly stirred in and heated again. The melt is cooled, taken up in water, centrifuged, heated again after $3\underline{N}$ Na_2CO_3 is added and centrifuged again. The precipitate is dissolved in $6\underline{N}$ HCl, ready for analysis (Ref. 21).

Once ashing or fusion has provided a dissolved sample, the radiochemical methods are quite similar to those already described. There are some differences, but we refer the reader to the appropriate references for details.

The U.S.P.H.S. manual (Ref. 21) contains radiostrontium techniques for urine, bone, bone ash, tobacco, vegetation, soil, and silt.

The A.E.C.L. manual (Ref. 15) has techniques for animal and fish flesh, cereals, eggs, fats, and various vegetation as well as bone. The HASL *Procedures Manual* (Ref. 22) contains methods for vegetation, tissue, soil, and urine. The British A.E.R.E. has published radiostrontium methods in bone ash, milk ash, vegetable matter, human teeth, and soil (Ref. 26). Porter et al. (Ref. 27) have developed a method using excess ethylenediaminetetraacetic acid (EDTA) which is applicable in samples with very large calcium/strontium ratios, yet still permits strontium yield (as carbonate) to be determined gravimetrically. It has been used for a wide variety of organic media. Finally, Baratta and Reavey (Ref. 28) have described a method used by the U.S. Food and Drug Administration for food and other biological samples, which uses tributyl phosphate extraction and analysis of yttrium-90.

This is only a partial list of the many radiochemical analysis techniques in the literature; for more complete coverage, the reader is referred to the literature cited.

E. Yttrium Recovery after Ingrowth

The chemical separation of radiostrontium is often followed by ingrowth of yttrium-90, yttrium separation, and counting of yttrium-90. This method is especially useful to determine strontium-90 in the presence of strontium-89.

One critical parameter is the specificity of this yttrium-90-separation scheme for strontium-90. This specificity has been studied by Goldin et al. (Ref. 25), whose procedure, after purifying $SrCO_3$ precipitate, is described as follows:

> "After ingrowth of yttrium, the strontium carbonate precipitate is dissolved with hydrochloric acid, neutralized to methyl orange with ammonia, and buffered at pH 5. The yttrium is extracted into 2-thenoyltrifluoroacetone solution. After the organic phase is washed with water buffered at pH 5, the yttrium-90 is stripped by extraction with 1N hydrochloric acid. The hydrochloric acid extract is evaporated on copper planchets, heated thoroughly to destroy residual organic matter, and counted, correcting for decay of the yttrium-90 between its extraction and the counting time."

The yield of strontium-89 is *very small* in this procedure: only 4 x 10^{-6} of the strontium-89 is counted as yttrium-90, while the strontium-90 yields are typically 85% and the yttrium yield in the solvent extraction is greater than 95%.

Proper analytical procedure demands that calibrations be taken periodically to check the *64-hour half-life* of yttrium-90 measured from the final yttrium sample. This half-life is in the range where such measurements are easy, yet they are omitted in some laboratories for reasons of economics or inconvenience. This check is one of the easiest ways to exercise internal quality control on a modest scale.

F. Interferences

When chemical separation is performed, the main interferences in environmental samples are *stable calcium, barium-140, and stable phosphates*. The chemical considerations have been well discussed by Goldin, Velten and Frishkorn (Ref. 25), from whom we quote:

> "*Calcium.* Strontium as an alkaline earth element is chemically similar to the other members of this family. Its resemblance to calcium, barium, and radium is especially marked. Calcium, which is widely distributed in nature, is one of the inert elements whose separation from radiostrontium has been most studied. Such separation is necessary if the strontium radiations are to be measured directly in samples of moderate or high calcium content, or if the final precipitate is weighed to determine the chemical recovery of strontium. Occasionally calcium is present in such large quantities as to give unmanageable amounts of precipitate unless it is removed.
>
> "The precipitation of strontium (and barium) nitrate in concentrated nitric acid also separates strontium from calcium. The concentration of nitric acid is critical, as too dilute a nitric acid solution will solubilize too much strontium, while too strong a nitric acid will precipitate calcium with the strontium. The most favorable range is from 65 to 75% nitric acid. Concentrated nitric acid will suffice. If the sample is in aqueous solution, fuming nitric acid probably will be needed to take care of the dilution....
>
> "*Barium and Radium.* The fission product barium-140, also a member of the alkaline earth group, is carried along with strontium as carbonate.

It must be removed whether the strontium or its daughter is to be counted, as there is a radioactive daughter, lanthanum-140, which will contaminate the yttrium. It is precipitated, with carrier barium, as chromate from a solution buffered at pH 5. Radium, which follows barium in this procedure, can be determined, although rather crudely, by alpha-counting the barium chromate precipitate....

"*Phosphates*. Phosphates interfere by causing precipitation of strontium when the solution is made basic in the hydroxide scavenging step. Although the phosphate content of water is usually too low to be of consequence, this interference is very troublesome in the analysis of biological samples, whose ash is largely calcium phosphate. Phosphates are removed in the nitric acid treatment already described, being converted to phosphoric acid, which is removed with the supernate. Several treatments usually are necessary to ensure complete removal."

G. Calibration Techniques

There are a number of problems in performing accurate measurements using the chemical techniques discussed above. Among them are losses of radiostrontium, losses of yttrium, and counting errors.

The use of standard radiostrontium preparations can help to reduce counting efficiency errors. The detection efficiency over the spectrum of strontium-90 (and it daughter yttrium-90) must be understood, and for this purpose low-level solid $SrCO_3$ sources have been prepared by the USAEC Health and Safety Laboratory (Ref. 29) by dilution of primary sources from the National Bureau of Standards. Standard sources for strontium-90 in milk have also been prepared (Ref. 30).

Chemical yields can be studied using strontium-85 as a chemical tracer: it decays ($T_{1/2}$ = 64 days) by electron capture followed by emission of a 514-keV gamma ray. Its routine use is uncommon partly because of its own intrinsic radiological hazard, but it serves a valuable function in periodic quality control. Other methods for determining chemical yield rely on classical chemical techniques, such as gravimetric measurements of carrier strontium or of possible interfering radionuclides.

Another quality control measurement, mentioned above, is the observation of yttrium-90's 64-hour half-life in counting of the yttrium fraction.

As in any analytical procedure, much of the success of radiostrontium assay depends upon the care of the analyst ... an obvious point but one which cannot be overemphasized.

H. Quality Control

Quality control is one of the most important elements of any radionuclide-analysis program. Unfortunately, quality-control checks have usually revealed significant variations among laboratories analyzing for ^{90}Sr at low levels. These variations are a cause for concern since they demonstrate the fundamental difficulty in making routine, reliable, accurate ^{90}Sr measurements in environmental media.

We shall discuss one recent study as an example ... others show comparable results. In 1971, the EPA Office of Radiation Programs carried out a study of analysis capabilities in *milk* (Ref. 31). Thirty-five participating laboratories made triplicate determinations of unknown concentrations of ^{89}Sr, ^{90}Sr, ^{131}I, and ^{137}Cs at activity levels (±2%) of 31, 42, 69, and 52 pCi/liter, respectively. Unfortunately, *nine* laboratories reported results whose mean exceeded the 'control level' of about ±10% for ^{90}Sr. [For ^{89}Sr, ^{131}I, and ^{137}Cs the outlying laboratories numbered 4, 6, and 2 respectively.] For many of the outlying laboratories in the ^{90}Sr study, the range of reported results for the triplicate analyses exceeded 25%. This study seems to show that, while many laboratories can perform ^{90}Sr analyses well, a significant minority cannot.

3. SUMMARY AND CONCLUSIONS

In this section we have attempted to give an overview of the present status of radiostrontium measurements in environmental media.

Perhaps the key point to make first is that, at the low levels which concern us here, the only methods for *specific radiostrontium analysis* involve *analytical chemistry* followed by *beta counting*. We have therefore emphasized the considerations characteristic of the chemical techniques in common use.

One difficulty in comparing different chemical techniques is that so much rests in the hands (and mind) of the analyst himself. A choice among the various 'commonly used' techniques may depend more on the particular equipment and skills available than on the differences among the techniques themselves.

This point has been made extremely well by Bowen, from whom we quote (Ref. 13):

> "In the extensive series of studies of strontium-90 in sea-water choice among these various possibilities has been made partly on the basis of prejudice, partly on economics, partly on the basis of which other radionuclides were to be sought on the same samples, partly on the basis of which alternative used fewest reagents known or suspected to be significant contributors to the radiochemical blank and partly on the basis of safety. In most of these variations the decisions have been legitimate ones, but we feel of even more importance have been questions which one can still only describe as those of art: in the hands even of very competent and experienced analysts, no one method, whether of trace element or of low-level radiochemical analysis, appears ever to have been uniformly superior in quality of results. For this reason, we strongly resist the suggestion that a single 'standard' method be selected and recommended."

In support of his viewpoint, Bowen cites interlaboratory calibration analyses in which nearly the full spectrum of possible radiochemical procedures was represented. We quote Bowen again:

> "... it is clear, we believe, that in suitable hands each method was capable of delivering data of high quality; it is also clear from some of the entries ... that these well-established methods were capable in unsympathetic hands of yielding some pretty bizarre sets of numbers, indeed."

We agree with this general viewpoint. Apparently, none of the techniques suffers from critical intrinsic flaws; yet equally apparently, the results obtained with a particular method seem to depend upon a specific skill of the analyst rather than upon his general competence. This situation is *not* satisfactory or necessary. Much can be done in the development of these or other methods to make them less dependent upon individual talents.

We can summarize by stating first that sensitivity is adequate in the methods commonly used; second, that further research and development in this field is most needed in simplifying, standardizing, and automating the methods; but finally, that the market for a fully automated system (even if available) is probably insufficient to justify its development.

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