Approaches to ^{90}Sr determination in marine environmental materials

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Abstract. The determination of ^{90}Sr in seawater, sediment and biota is carried out by radiochemical analysis. The choice of method is dependent on the amount of sample to be analyzed, the Ca/Sr mass ratio and the natural Sr content of the sample. For large volumes of seawater and sediment samples (e.g., coral) of high Ca content, 1 g (minimum) of Sr carrier and ^{85}Sr tracer are used. The Sr fraction is separated and purified chiefly by $Sr(NO_3)_2$ precipitations. After 2 – 3 weeks, the ingrown ^{90}Y is separated from the parent ^{90}Sr, and the ^{90}Y beta activity is measured by a gas-flow proportional counter. The detection limits obtained are 36 μBq/L for seawater and 0.36 Bq/kg for corals. For sediment and biota samples of low to moderate Ca content and low natural Sr content, 10 – 20 mg of stable Sr carrier are used without ^{85}Sr. The Sr fraction is separated and purified using crown ether extraction chromatography. The purified Sr fraction itself (containing ^{90}Sr together with in-growing ^{90}Y) is measured immediately using liquid scintillation counting. The detection limit obtained is 0.66 Bq/kg for 10g of sediment or biota ash.

1. INTRODUCTION

The determination of the radiologically important pure beta-emitter ^{90}Sr in environmental samples has continued to be important since the beginning of the nuclear age. Its accurate measurement in water, sediment and biota represents a significant analytical challenge to radiochemists. Procedures for determination depend on many factors including availability of tracers (in particular, ^{85}Sr), type of matrix, sensitivity needed and measurement instrumentation at one's disposal. The very low concentrations of ^{90}Sr typically found in seawater and sediment require the analysis of a considerable amount of matrix to attain even modest precision in the result. In this paper, some selected methods are described in detail in order to illustrate various ways to carry out low level ^{90}Sr analyses in marine materials.

2. METHODS

2.1 Seawater

For adequate sensitivity, 100 – 500 liters of seawater are typically analyzed for ^{137}Cs, ^{241}Am and Pu radionuclides as well as for ^{90}Sr from the same sample [1]. Pre-concentration steps are carried out both on shipboard and in the laboratory in order to reduce the bulk of material that must be handled. **Figure 1** presents a schematic diagram of the separation stages. Spikes (^{85}Sr, ^{134}Cs, ^{242}Pu, ^{243}Am) and carriers (1000 mg Sr, 20 mg Cs) are added to acidified seawater. $KMnO_4$ is added to oxidize organic complexing species and to promote radiochemical exchange between Pu spike and analytes. After 1 hour or longer, Pu and Am are efficiently co-precipitated with MnO_2 [2]. The supernatant solution is transferred to a second tank, re-acidified, and solid ammonium molybdophosphate (AMP) powder is added. The AMP is an inorganic ion exchanger with a high selectivity for Cs compared to other cationic species [3]. After settling, the supernatant solution is transferred to another tank while the AMP with sorbed Cs is collected. From this AMP supernatant solution, a mixed Ca-Sr oxalate precipitation is carried out after adding oxalic acid (ca. 10 g/liter) and adjusting to pH 5 – 6 with 10M NaOH. The settled Ca-Sr oxalate precipitate is collected, and the supernatant solution is discarded.

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In the laboratory, the Ca-Sr oxalate is further processed by calcination, dissolution in HNO_3, precipitation of $Sr(NO_3)_2$ (separation from Ca) in concentrated nitric acid-nitrate medium [4], removal of Ra and ^{210}Pb by $BaCrO_4$ precipitation, and precipitation of iron hydroxide scavenges. The chemical recovery of the purified Sr fraction is measured by means of the added ^{85}Sr tracer (514 keV gamma-rays).

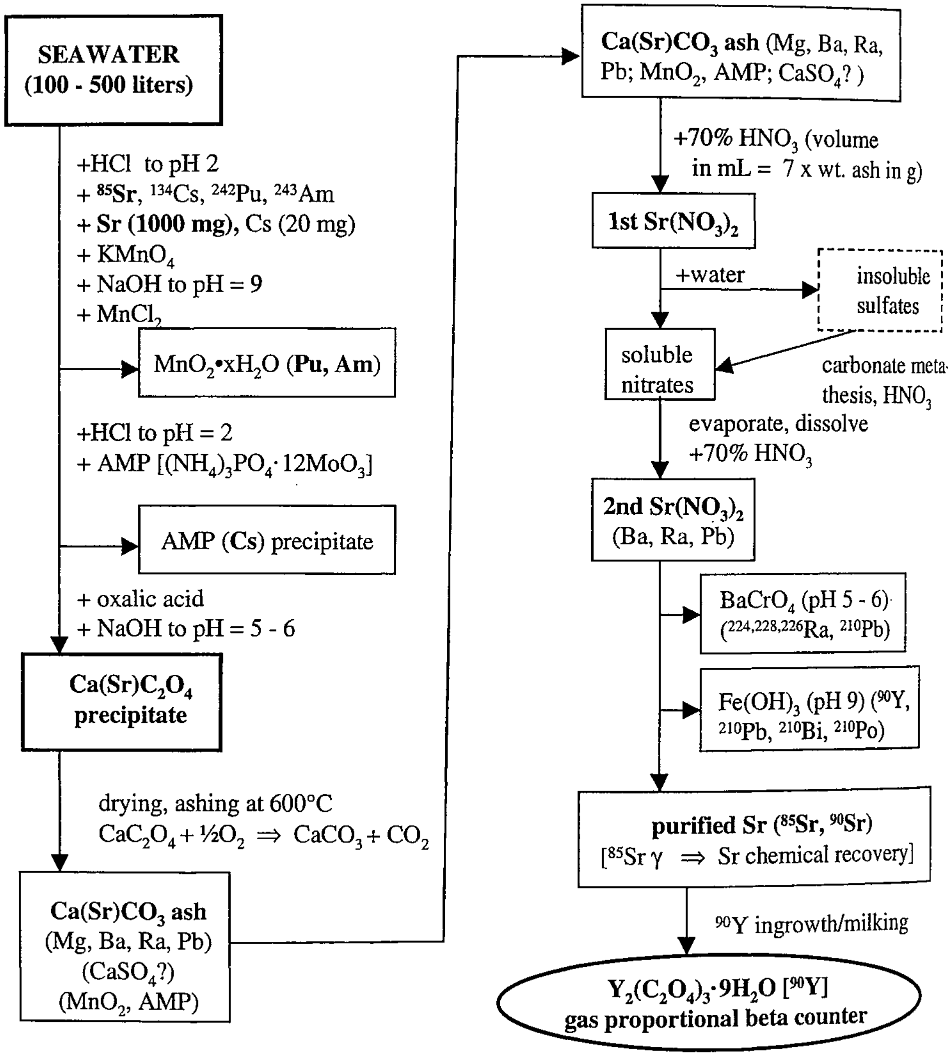

Figure 1: Scheme for separation, purification and measurement of $^{90}Sr(^{90}Y)$ from seawater

^{90}Y is allowed to grow into the Sr fraction for 2 weeks or longer to attain radioactive equilibrium with the parent ^{90}Sr. Ten mg of Y carrier are added to the purified Sr, Y is chemically separated from Sr, and a final yttrium oxalate precipitate $[Y_2(C_2O_4)_3 \cdot 9H_2O]$ is prepared. This yttrium oxalate nonahydrate serves as a gravimetric form to determine the Y chemical recovery and also as a solid source for radioactivity measurement.

The measurement of ^{90}Y beta activity is made with a proportional counter (Riso National Laboratory model GM-25-5, Roskilde, Denmark). The yttrium oxalate source (diameter = 15.5 mm) loaded on a 22 mm membrane filter (0.2 μm porosity) is centered on a 23.5 mm plastic disk and covered with a thin Mylar plastic film (ca. 0.8 mg/cm^2 thickness). A metal retaining ring fits over the plastic disk and secures the assembly. In the proportional counter, the covered source can be positioned adjacent to the detector window, which allows a beta detection efficiency of up to 48% for ^{90}Y. The combination of lead shielding with an anti-coincidence guard detector produces background counting rates of 0.1 to 0.2 counts/minute (cpm).

2.2 Sediments and biota

We have divided these materials into two general groups of samples:

- Group I: clay/sand sediments and biota ash with a low to moderate Ca concentration range and low Sr concentration;
- Group II: coral sediments with high Ca concentrations and significant natural Sr concentrations.

Again, a combined procedure for the analysis of Am-241 and Pu radionuclides is usually made together with the ^{90}Sr analysis. **Figure 2** illustrates the radiochemical procedures used for sediments and biota. For Group I, after tracer (but not ^{85}Sr) and Sr carrier additions to the 600°C ash, hot digestions are carried out with concentrated HF, HNO_3 and HCl. Reduction-oxidation steps lead to Pu(IV), which is separated by anion exchange column chromatography. Sr and Am are then twice co-precipitated with Ca oxalate at pH 5 - 6 to separate them from PO_4, Al, Fe, Ti and other common mineral elements. Purification of the Ca-Sr-Am fraction is made by passing the solution in 10M HCl through a "double ion exchange column" consisting of anion and cation exchangers. This removes especially Fe(III) and Po(IV) [Po-210], which form strong chloro-complexes that are retained by the anion exchanger. Am(III) is then separated from Ca(II) and Sr(II) by either (1) liquid-liquid extraction of Am from 12M HNO_3 into dibutyl-N,N-diethylcarbamylphosphonate (DDCP) or (2) extraction chromatographic separation of Am using EiChrom TRU resin™.

The further separation and purification of Sr in the Group I procedure depends on the mass ratio of Ca to Sr. For ratios equal to or exceeding 100, one or two fuming HNO_3 precipitations of $Sr(NO_3)_2$ are performed to decrease this ratio before going to the Sr crown ether extraction chromatography column (EiChrom Sr resin™) for the final Sr separation from Ca. When the Ca/Sr ratio is under 100, the Sr resin column is used directly for Sr purification. The bed volume of the Sr resin column will depend critically on the amount of Sr carrier to be retained and less significantly on the amount of Ca present. Generally 10 mg of Sr carrier and a bed volume of ca. 10 cm^3 are used. Ba and Ra, which have significantly lower distribution coefficients than Sr, are washed out of the Sr resin column along with Ca in 3M HNO_3. Traces of Pb [Pb-210], which sometimes accompany the Sr strip solution (mainly due to bleeding of organic extractants containing Pb from the column), can be removed after wet-ashing with concentrated HNO_3 and $HClO_4$ by co-precipitation with a small amount of $Fe(OH)_3$ from pH 8 – 9. The purified Sr is precipitated as $SrC_2O_4{\cdot}H_2O$ at basic pH, filtered, washed, dried at low temperature (50°C) and weighed to obtain the Sr chemical recovery gravimetrically. The amount of stable Sr contributed by the sample matrix itself must be taken into account. This $SrC_2O_4{\cdot}H_2O$ (ca. 10 – 20 mg) is dissolved in 1M HNO_3 (2 ml) and mixed with liquid scintillation cocktail (e.g., 15 ml of Packard InstaGel Plus™). It is measured in a Quantulus model 1220 liquid scintillation analyzer, where the signals coming from both ^{90}Sr and ^{90}Y are counted [5].

The analysis of ^{90}Sr in **Group II** materials takes into consideration the large Ca amount (mainly $CaCO_3$) and significant natural Sr content (1 – 5 mg Sr/g). Referring to Figure 2, if Pu and Am are to be analyzed, and little or no phosphate is present, they may be co-precipitated with $Fe(OH)_3$ by ammonia at pH 8 – 9 leaving Ca and Sr in solution. Then Ca and Sr are conveniently precipitated as carbonates from the ammoniacal solution. The remaining procedure closely follows that of the seawater Sr analysis: precipitation of $Sr(NO_3)_2$ with concentrated HNO_3 additions; a $BaCrO_4$ precipitation from acetate-buffered solution to remove Ra and Pb; and one or more $Fe(OH)_3$ scavenging precipitations. If ^{85}Sr tracer is not available, the Sr chemical recovery can in principle be determined by a gravimetric Sr measurement (e.g., $SrCO_3$); however, care must be taken to include any stable Sr contribution to the carrier from natural Sr contained in the sample matrix. (This natural Sr content is usually determined by a separate experiment.)

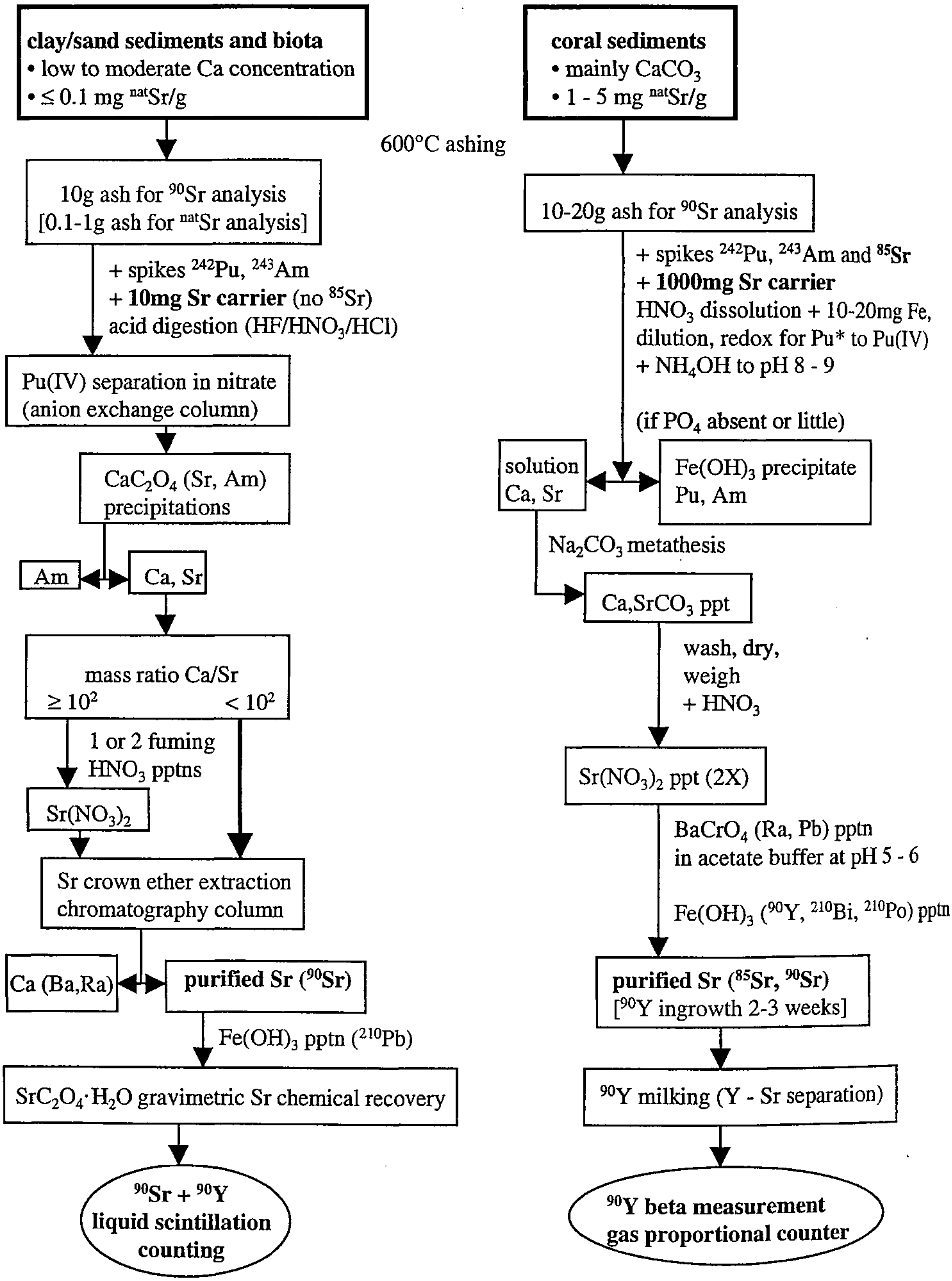

Figure 2: Schemes for separation, purification and measurement of $^{90}Sr(^{90}Y)$ from sediment and biota

3. RESULTS AND DISCUSSION

For the seawater/coral sediment procedure, a detection limit of 3.6 mBq of ^{90}Sr has been calculated using the formula of Currie [6], $L_D = 2.71 + 4.65(\text{background counts})^{1/2}$. This considers the following characteristics: a proportional counter background of 0.11 cpm; source counting time of 60 hours (beginning 8 hours after the Y-Sr separation time); decay of the ^{90}Y activity during the 60-hour counting period; 50% Sr chemical recovery; 90% Y chemical recovery; 40% beta counting efficiency for ^{90}Y in the counting configuration. This leads to a limit of detection of 36 μBq/liter for 100 liters of seawater, and 0.36 Bq/kg for 10g of sediment.

An alternative to proportional counter measurement of ^{90}Y can be liquid scintillation counting. In particular, Cerenkov counting of ^{90}Y [7] in 10 ml of aqueous medium has an efficiency of about 60% and a background of ca. 0.6 - 0.8 cpm with the Quantulus 1220 liquid scintillation analyzer in our laboratory. The higher background necessarily leads to a poorer detection limit under the same sample conditions as above.

Advantages of the seawater procedure using ^{85}Sr tracer include the capability to handle large volumes of water and tens of grams of coral sediment, use of generally available reagents, and high sensitivity from ^{90}Y measurement. Some disadvantages can be the need for ^{85}Sr (unless Sr chemical recovery is based on stable Sr), the use of a considerable quantity of concentrated HNO_3, and the time required for ingrowth of ^{90}Y prior to milking (often 2 weeks).

For the clay/sand sediment and biota procedure, a detection limit of 6.6 mBq of ^{90}Sr has been calculated from Currie's formula based on the following characteristics: liquid scintillation counting (LSC), beginning 24 hours after the final Sr-Y separation, with a sample measurement of 4 hours per day for 5 consecutive days (24 hours between the start of each measurement); LSC background counting rates of 1.6 cpm and 0.3 cpm for low-energy and high-energy window spectral regions, respectively; LSC total counting efficiencies of 92% and 100% for ^{90}Sr and ^{90}Y, respectively; a low-energy/high-energy window counting rate ratio of 0.71 ± 0.02 for ^{90}Y; 50% Sr chemical recovery. This results in a detection limit of 0.66 Bq/kg for 10g of sediment or biota ash. Advantages of this procedure include the ability to handle difficult matrices, avoidance of ^{85}Sr tracer, the very selective Sr separation by means of column chromatography (without using large amounts of concentrated HNO_3), and no need to wait for ^{90}Y ingrowth from purified Sr before measurement. Disadvantages are the necessity to determine the stable Sr content of the sample, the relatively expensive Sr crown ether resin, and the reduced sensitivity compared with ^{90}Y measurement by proportional counting.

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