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DETERMINATION OF ^{90}Sr IN ENVIRONMENTAL AND BIOLOGICAL MATERIALS WITH COMBINED HDEHP SOLVENT EXTRACTION – LOW LIQUID SCINTILLATION COUNTING TECHNIQUE

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Low level ^{90}Sr in environmental and biological samples is determined using a combined HDEHP solvent extraction-liquid scintillation procedure. Yttrium-90 is selectively extracted from nitric acid solution into 5% di(2-ethylhexyl) phosphoric acid (HDEHP) in toluene, and ^{90}Y in the organic phase is measured directly using an ultra low level liquid scintillation spectrometer.

The working program of the Quantulus counter has been optimized. As the counting efficiency using liquid scintillation counting is high and the stripping and precipitation of Yttrium-90 oxalate is omitted, this procedure is simpler and more time-saving than traditional methods. The chemical recoveries of ^{90}Y were 85.1% for soil, 75.7% for milk and 65.3% for bone. The detection limit is 8 mBq.

INTRODUCTION

The presence of ^{90}Sr in environmental and biological materials is due to atmospheric nuclear weapon testing, nuclear waste discharges and nuclear accidents. This artificially-produced radionuclide has high ecological importance because it accumulates in bone tissues and has a long physical and biological half-life, 28.6 and 49.3 years, respectively. For this reason ^{90}Sr has been a principal subject for environmental monitoring and radioecological research.

The application of liquid scintillation counting (LSC) in environmental radioanalysis was originally used for monitoring radionuclides such as ^{3}H and ^{14}C. The use of LSC for both α and β-counting, instead of gas and solid scintillators has obvious advantages, however. Since the nuclides are homogeneously dispersed in the scintillator medium, the problems of sample self-

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absorption are avoided, allowing nearly 100% counting efficiency due to the 4^{a} geometry . Furthermore, the chemical isolation procedures for the nuclides of interest can be simplified. There are, however, many disadvantages with traditional LSC such as relatively high instrument background, a limited sample volume, quenching effects, and variable interferences from other radionuclides present in the sample.

Over the past ten years, however, a new generation of instruments have been developed, especially for low level counting. These liquid scintillation spectrometers (LSS) are equipped with different electronic devices to improve both the background rejection and the counting conditions for α- and β-spectrometry. The active guard detector, the pulse amplitude comparator (PAC) and the pulse shape analysis (PSA) minimize the background. Use of multichannel (MCA) and pulse shape-analysis (PSA) makes it easier to control quenching effects and interferences from nuclides of no interest present in the sample.

Several radiochemical procedures have been developed for the determination of ^{90}Sr in environmental and biological samples (1,2). However, the radioanalysis is most frequently carried out by isolating and counting the short-lived daughter nuclide ^{90}Y ($t_{\frac{1}{2}}$ = 64.oh) at radiological equilibrium. As natural matrixes of interest usually contain much higher concentration of divalent elements (e.g. Mg, Ca, and Ba) than Sr, it is more convenient to separate the daughter, having a valency of three. Solvent extraction systems which include HDEHP or Tributyl Phosphate (TBP) are often used. ^{90}Y is then stripped from the organic phase and usually precipitated in the aqueous solution as oxalate. Finally, the activity is measured using various detecting methods, e.g., β -counting, Cerenkov spectrometry and LSC.

The relatively short half-life of ^{90}Y is utilized to control the purity of the isolated sample by measuring the decay curve.

In the present work, Quantulus 1220, being an ultra low level liquid scintillation spectrometer, has been utilized for determining ^{90}Sr from the measurement ^{90}Y. Furthermore, a combined HDEHP solvent extraction low level liquid scintillation counting procedure has been developed for the determination of ^{90}Sr in environmental and biological samples. The recommended procedure has been examined for soil extracts, milk and bone samples.

EXPERIMENTAL

Reagents

Analytical grade reagents were used unless otherwise stated. Di(2-ethylhexyl) phosphoric acid (HDEHP, Bayer, FRG) 5% (V/V) was made from 50 ml of HDEHP in 950 ml of toluene.

^{90}Sr (carrier free) in 0.1 M HCl was used as tracer (Amersham, UK).

The scintillator (solid form) was a mixture of 91% PPO and 9% bis-MSB (PERMABLEND III, Packard Co., USA).

Strontium carrier (20 mg Sr ml^{-1}) was made from 61.2 g of $SrCl_2 \cdot H_2O$ in 1 liter of deionized H_2O. Yttrium carrier (10 mg Y ml^{-1}) was made from 15.4 of high purity yttrium oxide (99.99% purity) in 6 M HNO_3, then diluted to 1 liter.

EDTA-solution 0.1 M (Titriplex III, Merck (FRG)) was used to determine the chemical yield of yttrium volumetrically. Xylenorange (tetra sodium salt) is used as an indicator.

Apparatus

A quantulus (Model 1220, LKB Wallac) ultra low level liquid scintillation spectrometer, was used for measuring the activity of radioyttrium.

A centrifuge, Model MSE (Measuring and Scientific Equipment Ltd., USA) and 100 ml centrifuge tubes were used at 2500 rpm.

Counting Vials

Low potassium glass vials (Packard Co., USA), polyethylene vials (Packard Co. 6000477), and teflon vials with heavy copper caps (LKB, Wallac, Finland) were tested.

Samples

Goat milk and reindeer bones were collected in 1987 from areas in Central Norway contaminated by the Chernobyl fallout.

Procedure

Weigh 5-20 g of sample ash into a porcelain crucible and add 50 mg of strontium carrier and 20 mg of yttrium carrier. Add 5-10 ml of conc. HNO_3 and 3 ml of H_2O_2 (30%). Evaporate it to near dryness on a hot plate and then ignite the sample in an electric furnace at 600°C until the ash becomes white. Transfer the calcined ash to a 500 ml conical beaker, add 50 ml of 2 M HCl, and boil the mixture on a hot plate for 30 minutes. Filter the leaching solution while hot through a glass-fiber membrane. Then wash the residue with three 20 ml portions of hot 2 M HCl, and combine the filtrates into a 250 ml beaker. Add 5 g of oxalic acid after heating, to dissolve the reagent and add ammonia to adjust the solution to pH 2.0-2.5 to precipitate the oxalates (3). Place the precipitate into a hot water bath and heat for 30 minutes. Filter the precipitate and wash it with two portions of 20 ml of oxalic acid. Discard the filtrate, dry and ignite the oxalate precipitate together with the filter in a crucible at 500°C for two hours.

After cooling, dissolve the ash with a small volume of 6 M HNO_3. Then add 40 ml of 0.5 M HNO_3 to dissolve the ash completely. Filter the solution with membrane filter into 100 ml

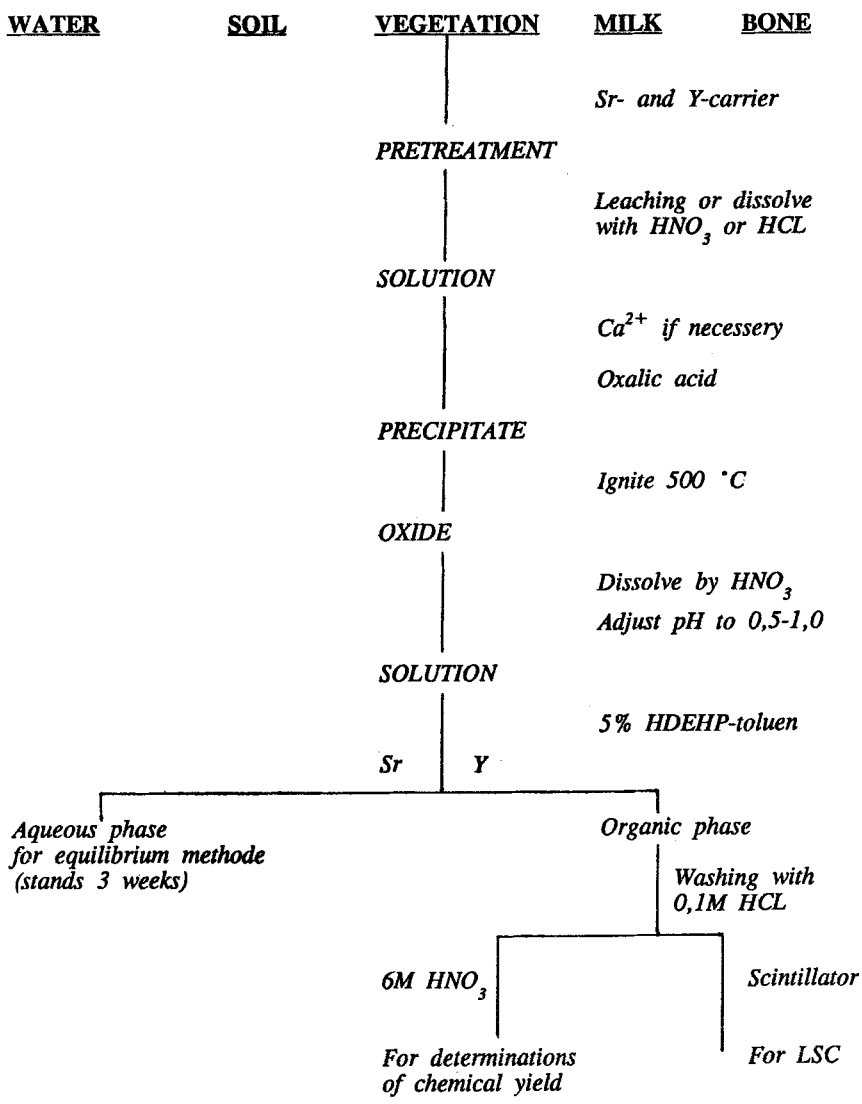

Figure 1. The chemical procedure for determination of ^{90}Sr from ^{90}Y by HDEHP extracton-LSC.

beaker, wash the residue and crucible with 10 ml of 0.5 M HNO_3 solution, combine the washing and filtrate, and control the pH (0.5-1.0). Transfer the solution into a 100 ml funnel, shake the aqueous phase with 20 ml of 5% HDEHP-toluene for five minutes and record the time of separation of yttrium from strontium. Transfer the aqueous solution into another separation funnel and shake it

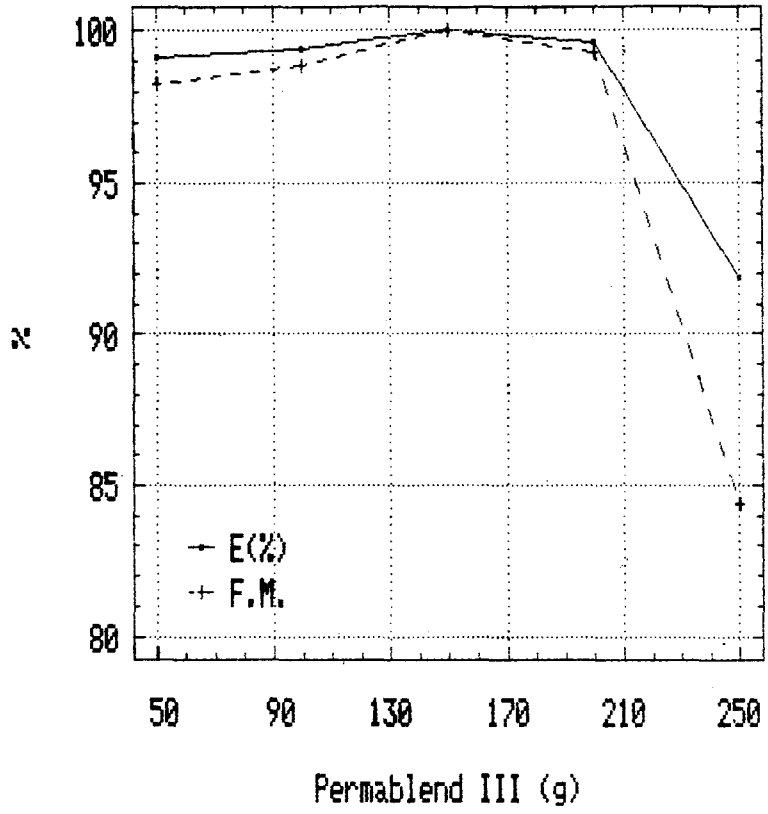

Figure 2. The influence of variable amounts of PERMABLEND III in 5% HDEHP on the counting efficiency (E (%) and Figure of Merit (F.M.). The data are normalized to 150 mg PERMABLEND III (E = 98.6%, F.M. 4948).

1.91 cpm/ch for spectrum B. The spectra in Figure 3 are presented logarithmically in accordance with the analog to digital conversion of the instrument.

The results indicate that the overall chemical yield for ^{90}Y using the recommended procedure, is in the range 79.8-91.7% with average 85.1% for soil, in the range 58.1-78.5% with average 75.5% for milk and in the range 53.4-70.0% with average 65.3% for bone. The detection limit is 8 mBq (3 α of blank 5% HDEHP extractive cocktail).

In addition, ^{90}Sr has been determined in biological samples, i.e., goat milk and reindeer bone from areas in Norway contaminated after the Chernobyl accident, using the present procedure (Tables 1 and 2, Figure 3). The results are in good agreement with those obtained by the routine

with 10 ml of 5% HDEHP-toluene for three minutes. Add 50 mg PERMABLEND III scintillator to 15-20 ml of the organic phase prior to the LSC measurement.

If necessary, the aqueous solution containing ^{90}Sr can be retained for controlling purposes. Add 20 mg of yttrium carrier, extract ^{90}Y with 5% HDEHP, add PERMABLEND III to the organic phase, and determine ^{90}Y after two weeks of storage, i.e., when the ^{90}Sr and ^{90}Y has reached radiological equilibrium (See Figure 1).

RESULTS AND DISCUSSION

The LSC-instrument used in this study, Quantulus, combined with pulse height spectrum analysis provides a useful technique for the determination of ^{90}Sr, as other interfering nuclides, e.g., low energy β-emitters to a certain extent can be discriminated instrumentally (4).

However, when low level ^{90}Sr is determined in environmental and biological materials, separation of radiochemically pure yttrium from ^{90}Sr and other interfering β-emitters is still needed. Recently, selective LSC methods have been developed for the determination of plutonium by α-spectrometry (5,6,7). These techniques are mainly based on the combination of selective solvent extraction and direct liquid scintillation counting of plutonium in the organic phase. This technique has been found to be suitable also for ^{90}Sr, as HDEHP is a very effective agent for isolation of ^{90}Y from strontium and other interfering nuclides. Furthermore, the quenching effect in liquid scintillation counting of ^{90}Y (E^{β}_{max} = 2.27 MeV) is of minor importance (8).

The measuring conditions of LSC, including scintillation cocktail and ingredients, counting vial materials, sample volume and organic solvent have been optimized. The recommended preparation of a counting sample for LSC is commercial polyethylene vial (Packard 6000477) containing 150 mg of PERMABLEND III scintillator and 15-20 ml organic sample solution (5% HDEHP-toluene). Figure 2 illustrates the influence of different amounts of PERMABLEND III on counting efficiency (E %) and figure of merit (F.M.). Optimum conditions for E (%) and F.M. are obtained by adding PERMABLEND III in the range of 50-200 mg to the organic phase. For practical reasons 50 mg PERMABLEND III was chosen for the present procedure. The background levels obtained by the teflon and polyethylene vials are comparable (0.8 and 1.1 cpm, respectively) while essentially higher for the glass vials (12 cpm). For economic reasons, polyethylene vials are used in the procedure.

Tracer experiments (10 dpm level) using the combined HDEHP solvent extraction low level LSC have been performed. Soil, milk and bone were selected as representative materials. Figure 3 shows a LSS pulse height spectrum of ^{90}Y isolated from goal milk (A), and a spectrum from a standard solution of $^{90}Sr/^{90}Y$ at equilibrium (B). The scale for spectrum A is 0.042 cpm/ch while

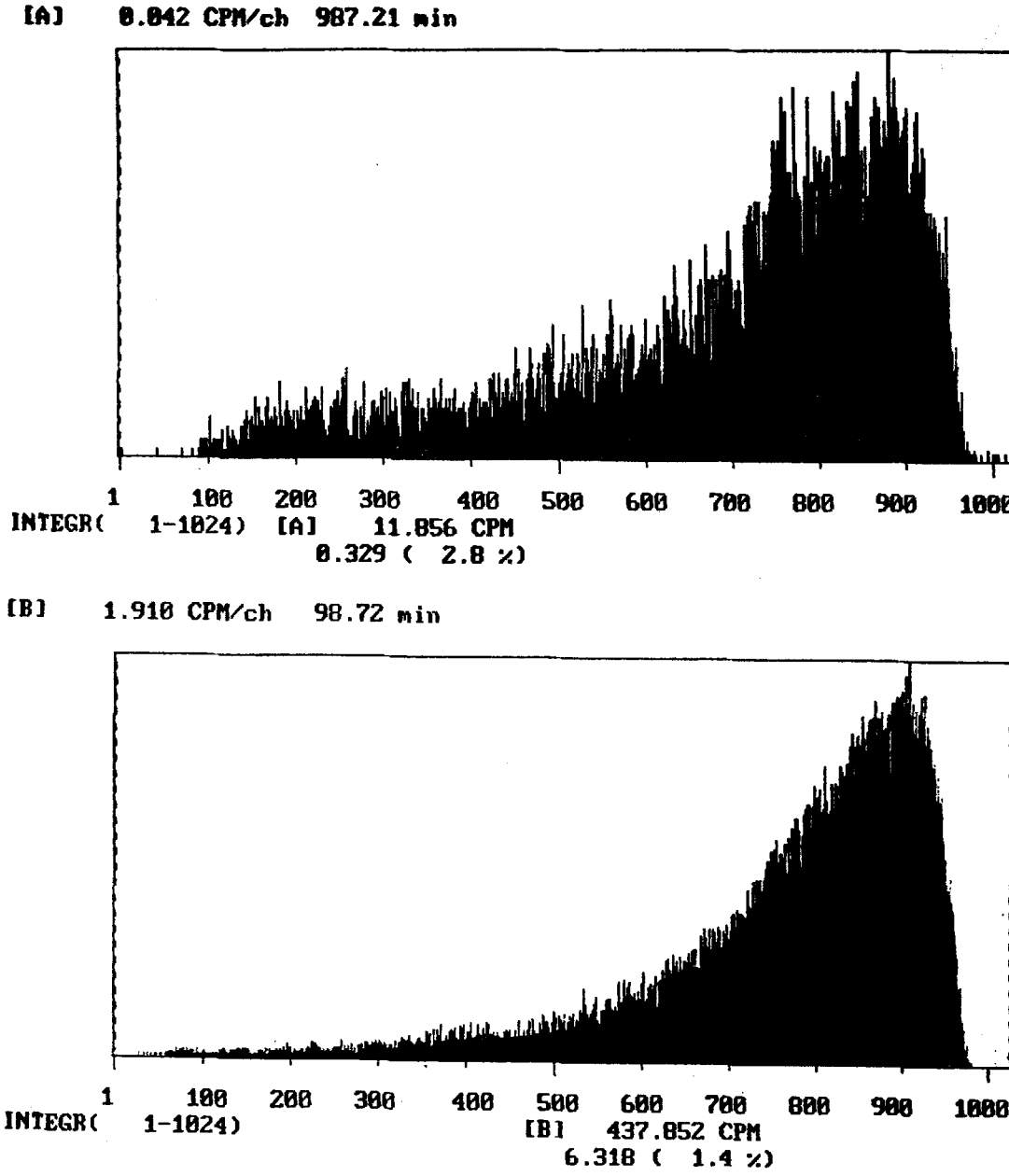

Figure 3. LSS-pulse height spectrum of ^{90}Y:
(A) goat milk
(B) ^{90}Y isolated from standard solutions (^{90}Sr and ^{90}Y in equilibrium)

Table 1.
^{90}Sr in Goat Milk Determined by HDEHP Solvent
Extraction Low Level Liquid Scintillation Counting.

Sample Number	Weight (g)	Chemical Yield (%)	Present Method Bq/kg	Cerenkov's* Bq/kg
1	131.8	78.5	1.7 ± 0.1	1.68
2	127.8	69.1	1.73 ± 0.09	1.88
3	152.7	68.1	1.9 ± 0.1	1.94
4	137.9	58.5	1.6 ± 0.1	1.64

Table 2.
^{90}Sr in Reindeer Bone Determined by HDEHP Solvent
Extraction Low Level Liquid Scintillation Counting.

Sample Number	Weight (g)	Chemical Yield (%)	Present Method Bq/kg	Cerenkov's* Bq/kg
1	2.25	55.6	1.76 ± 0.06	1.68, 1.65
2	2.25	53.4	1.64 ± 0.05	1.63, 1.59
1	1.67	64.1	1.97 ± 0.07	1.89, 1.92
2	1.67	57.1	2.18 ± 0.08	2.02, 2.06

*A Cerenkov counting technique whereby Y is stripped into 6 M HNO_3 from organic phase, precipitated with NH_4OH, dissolved in diluted HNO_3 and counted, is also used as a routine technique in our laboratory. This technique has been checked by IAEA standard materials (IAEA 152, milk powder, and IAEA 154, whey powder) and showed good precision and accuracy.

procedure based on the Cerenkov counting technique. The detection limit of the present method is comparable with that obtained by the Cerenkov method. However, the present procedure is more time saving than the Cerenkov technique as the organic phase with scintillator can be counted directly.

CONCLUSION

The ultra low level liquid scintillation spectrometer, Quantulus, is a powerful system for monitoring trace ^{90}Sr in environmental and biological samples. The present procedure which combines the HDEHP solvent extraction with low level LSC has three main advantages:

1) ^{90}Sr can be determined immediately after extraction of ^{90}Y using direct LSC, thereby eliminating several chemical steps including stripping and precipitation.
2) The liquid scintillation counting efficiency for ^{90}Y is much higher than traditional β-counting.
3) The problems associated with counting solid samples (e.g. $^{90}Y_2(C_2O_4)_3$) such as self-absorption, nonuniformity of the sample mounting, and variation in counting efficiency are avoided.

The procedure can preferentially be used for determination of low level ^{90}Sr in environmental and biological samples in both routine and emergency cases. In emergency cases, the degree of equilibrium between ^{90}Sr and ^{90}Y must be controlled.

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