LOW LEVEL ^{90}Sr (Cerenkov) AND ^{226}Ra (α/β LSC) ANALYSIS IN ENVIRONMENTAL SAMPLES USING AN AUTOMATED CHROMATOGRAPHY SYSTEM AND LSC

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Abstract

An automated method (8 columns in parallel) has been developed for the low-level (0.016 Bq MDA for a 200 minute count) determination of ^{90}Sr in milk and water samples. Water and milk ash samples (0.8L with 5mg Sr carrier) are adjusted to pH 5 in 2w/v% $(NH_4)_2$EDTA and then subjected to a pH gradient and the Sr fraction collected. At this point, the sample can be spiked with 2 mg Y carrier and held for ^{90}Y ingrowth. A final polishing is then performed on an automated ion chromatography system using a similar pH gradient where the ^{90}Y fraction is collected in a liquid scintillation vial and the aqueous solution subjected to Cerenkov counting on a low level liquid scintillation counter. Alternatively, the Sr fraction can be collected from the SCX manifold pretreatment, subjected to the final IC polishing, and the collected Sr fraction Cerenkov counted initially (to check for presence of ^{89}Sr). After ^{90}Y ingrowth, the sample can be Cerenkov counted again to determine the ^{90}Sr activity. The same pretreatment separation chemistry has also be used to determine ^{226}Ra in water samples with an MDA of about 0.002 Bq for a 100 minute count.

Introduction

^{90}Sr is a long-lived ($t_{1/2}$ = 28.5 years), high yield, beta emitting (E_{max} = 556 Kev) fission product which possesses a fairly high radiotoxicity owing to its long half-life, formation of a high energy beta daughter (^{90}Y, E_{max} = 2.27 Mev, $t_{1/2}$ = 64 hours), and tendency to accumulate in human bones. Environmental levels of ^{90}Sr peaked in about 1963 (with the moratorium on above ground nuclear testing) and have been steadily declining since.

Recently[1], a method was developed in our laboratories which enables the simultaneous [flow scintillation analyzer (FSA) for HPLC with 2-window counting; MDA ~ 0.2 Bq] determination of ^{89}Sr (higher E_{max} than ^{90}Sr but shorter half-life, 50.5 days) and ^{90}Sr in environmental samples for the purposes of emergency response. This method can determine both radionuclides at ^{89}Sr / ^{90}Sr ratios expected in an nuclear incident/accident (10-20/1) within about 24 hours.

The most recent development is an extension of the above method and is used where low levels of ^{90}Sr are of interest, and when the time required for ^{90}Y ingrowth is acceptable.

Objectives

Often in the field of environmental monitoring, it is desirable to be able to detect radionuclides at very low levels (well below action or guideline limits). In the field of radiochemistry, large samples are usually required in conjunction with long count times to achieve these low detection limits. In addition, the modern analytical laboratory relies heavily on; sample throughput (which implies an increasing role for automation), increased safety, minimization of chemical waste, greater precision, and simpler more robust methods of analysis. Our laboratory sought to modify the emergency response method to make it amenable to routine background ^{90}Sr monitoring (e.g. to be able to detect below current fallout levels in milk), and to reduce chemical waste by eliminating the need for liquid scintillation cocktail.

Experimental

An Ismatec IPC-24 multichannel peristaltic pump (Cole-Parmer), 18.5 mL polypropylene (PP) columns (Environmental Express), and 1.52 mm I.D. Tygon tubing transfer lines were employed in the open column pre-treatment manifold. The system is automated with the aid of National Instruments process control software (Lookout), data acquisition card (AT 232-4), and relays (FieldPoint). Stream selection is controlled by a series of electrically actuated solenoid valves (Takasago) and a multi-port switching valve (Hamilton).

A Waters HPLC system consisting of a 600 EF pump (0-45 $mLmin^{-1}$), 600 controller, 717 auto sampler, Waters column oven and fraction collector, Pharmacia (Model 18-1500-00) high range (0->100 $mScm^{-1}$) conductivity detector, and Waters BUS/LACE card and SATIN module (running Waters Millennium 32 chromatography software), was employed in the final polishing step. The high pressure ion chromatography (HPIC) column used was a Hamilton PRP-X400 cation exchange (250mm x 4.1 mm - @3.3 mL) column in a 12-20 μm particle size range (P/N 79563), with approximately 1.4 meq/mL exchange capacity.

A low background liquid scintillation counter (LSC), the Packard 2770TR was used for Cerenkov counting of the collected ^{90}Y fractions, and the ^{90}Sr fractions after ^{90}Y ingrowth. The ^{226}Ra fractions were also counted on the same LSC (which was equipped with the alpha/beta separation option) using a 2-phase aqueous/cocktail system with the ingrown ^{222}Rn distributing predominantly in the organic phase.

The resin employed in the open column pre-treatment was Dowex 50WX8 strong cation exchange (SCX), 1.7 meq/mL, 200-400 mesh. Ethylenediaminetetraacetic acid (EDTA), diammonium salt >99% (Fluka), Diaminocyclohexane-N,N,N,N'-tetraacetic acid (DCYTA) monohydrate 99% A.C.S. reagent (Aldrich), Ammonium chloride 99.5% (BDH Analar), Acetic acid (glacial) (Aldrich), HCl (trace metal grade, Fisher), Ammonium hydroxide (1+1) v/v (Fisher),. Sr, Y and Ba carrier stock solutions were prepared from A.C.S. reagent grade salts. The cocktail used for ^{226}Ra determination was Ultima Gold F.

NIST traceable ^{89}Sr and ^{90}Sr standards were obtained from AEA-QSA (formerly Amersham), with uncertainties of approximately 1% in their activities. The ^{226}Ra standard was obtained from

Isotope Products Laboratories.

Procedure

(1) Open Column SCX Pretreatment

Sample pretreatment for milk and water employs an open column ion exchange Diaminocyclohexanetetraacetic acid (DCYTA)/ Ethylenediaminetetraacetic acid (EDTA) pH gradient. The separation scheme is based on those of Wade/Seim[2], Povondra et.al.[3], and Diercks et. al.[4], with modifications. For an 0.8L water/1L milk ash sample, the sample is made 2 wt% in $(NH_4)_2$EDTA pH 5 and pulled through a 16 mL column at 3-4 $mLmin^{-1}$ with the aid of the peristaltic pump. For 0.8L water or 1L of milk ash made up to 0.8L, 5 mg Sr carrier is used. If Ra is being determined in water samples, 2 mg stable Ba is used as an isomorphous carrier.

The column is then washed with 10 column volumes (160 mL) of 0.06M DCYTA/0.04M acetic acid at pH 5, followed by 10 column volumes (160 mL) NH_4Cl (at ambient pH~5). The Sr is eluted with $(NH_4)_2$EDTA at pH 6.

The columns are then stripped with $(NH_4)_2$EDTA at pH 10 (Ra fraction), then re-equilibrated with $(NH_4)_2$EDTA at pH 5, when they are then ready for another separation cycle. The Ra fraction is then boiled dry, ashed, and taken up/transferred to a 20 mL LSC vial with 7 mL EDTA pH 10 solution. Finally 14 mL Ultima Gold F cocktail is added and the sample is capped, shaken, and held for Rn ingrowth.

The pH 6 fraction is then held for sufficient time to allow for ^{90}Y ingrowth, then boiled dry and ashed.

The open-column manifold has been sized to run 8 columns simultaneously, and the process has recently been automated and runs under the National Instruments Lookout process control software.

This open column pre-treatment leads to a good initial separation from most interferences of interest. The Sr fraction contains only a few mg Ca/Mg/K for a 1L milk sample. Decontamination factors [(DF) = number of atoms of element initially present in sample/number of atoms present in Sr fraction] (eg >12000 for Cs, >2800 for Ba) are fairly high for cations of radiological interest.

(2) HPIC polishing

After suitable ^{90}Y ingrowth, the ash from the pH 6 fraction of the open column pretreatment is dissolved in HCl, then boiled dry and taken up in a small volume (@2mL) of DCYTA pH 5. The sample is then filtered into a conical bottomed 3 mL polypropylene (PP) autosampler vial using a low hold-up volume (<20 µL) hollow fibre syringe filter. Virtually the entire sample is injected (1950 µL), and a similar DCYTA and EDTA pH 5 gradient is employed. The ^{90}Y fraction (unretained due to strength of DCYTA chelate - elutes in first 8' of run) is collected into

a 20 mL plastic scintillation vial and counted off-line on the 2770TR stand-alone counter. $(NH_4)_2$ EDTA at pH 10 is then employed to elute the Sr in a minimal volume for either on-line or off-line Cerenkov counting.

Chemical yield of the Sr carrier (typically 95+%) is determined on-line with a high range conductivity detector. The Ca and Mg remaining in the IC Sr fraction for a 1L milk ash sample is several µg each, which represent overall DFs (from the combined 2 column clean-up) of approximately 10^5 and 10^4 respectively for milk.

The autosampler enables a large number of samples to be run overnight.

Discussion

Column sizing (16 mL) was based on a 1L ashed milk sample containing 40 mg Sr carrier. An 800 mL $(NH_4)_2$EDTA pH 5 sample load solution (<50 column volumes avoids any Sr breakthrough) is used. Subsequently, the carrier level was reduced to 5 mg Sr, which eluted in about 40 mL. A 125 mL pH 6 wash has been adopted to account for any variability in the ionic strength/pH of the load sample, or in the ion exchange resin. The new method can cope with higher amounts of Sr carrier particularly when the estimate of ^{89}Sr is performed off-line with Cerenkov counting.

A 1L milk ash sample represents approximately 1200 mg Ca, 135 mg Mg, 1600 mg K and 500 mg Na (major cations). Since the Ca is effectively complexed in $(NH_4)_2$EDTA pH 5, it does not interact with the resin, and can largely be ignored in a calculation of required capacity (assuming there is sufficient EDTA present stoichiometrically). The advantage of basing the method development on a 1L milk sample, is that if one can deal with a 1L milk ash sample, then one can certainly deal with a 1L fresh or surface water sample of almost any kind (from an ion loading standpoint).

The two-step separation based on the open column manifold in conjunction with the HPIC final polishing was adopted in order to decrease the cycle time for sample batches. Previous workers[4] have performed a similar separation (a straight EDTA pH gradient) using a completely instrumental two-column HPIC system. The first large column gives an initial clean-up, after which the sample is directed to a smaller column for final analysis via a switching valve. This in-series approach limits sample throughput since the dual-column separation requires about 4-5h, during which time, the HPIC system is entirely committed to a single sample. By running the first separation (the pretreatment step) in parallel on the open column manifold, multiple samples can be readied for the HPIC simultaneously for a final separation/analysis (approx 1h). This leads to decreased overall cycle times for sample batches.

Results

The method qualification is not quite finished for ^{89}Sr, but several blind radiological intercomparison water samples have been analyzed for ^{90}Sr by the new technique and found to agree well with the accepted values. The manifold was recently used to analyze a large number of archived samples for ^{90}Sr in milk and water (@160) and ^{226}Ra in drinking water (@90).

Table 1 – Intercomparison Results

Intercomparison Sample	^{90}Sr Present (Bq/L)	^{90}Sr Found by 2-Window LSC Method (Bq/L ± 1S error)	^{90}Sr Found by Cerenkov Method (Bq/L ± 1S error)
MAPEP 98 W6	39.5 ± 0.8	39.2 ± 1.3	42.8 ± 2.5
QAP 9909	1.72 ± 0.10	1.81 ± 0.26	1.69 ± 0.13
MAPEP 99 W7	8.19 ± 0.10	7.92 ± 0.38	8.17 ± 0.61
QAP 0003	3.39 ± 0.12	Not Determined	3.25 ± 0.27
QAP 0009	4.53 ± 0.12	Not Determined	4.69 ± 0.18
MAPEP 00 W8	Not Added-False Positive Test	Not Determined	0.09 ± 0.03*

* - result at method MDC due to limited sample size

Conclusions

The newly developed method shows promise for the determination of ^{90}Sr (and ^{89}Sr) in environmental samples. It is highly reproducible, automated, simple to set-up, results in a minimum of chemical waste, is much safer for personnel then the old fuming nitric acid technique, and is inexpensive from a reagent standpoint.

Future Work

The determination of ^{89}Sr in the same sample can be done using either on-line (using the FSA) or off-line (2770TR) Cerenkov counting of the IC Sr fraction. We hope to finalize the ^{89}Sr aspect of the Cerenkov method shortly.

References

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