

Counting Solutions

LSC Technical Tips from PerkinElmer

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Environmental Sample Preparation for LSC

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Introduction

The advance of the nuclear industry in all its forms coupled with growing concerns for possible environmental contamination has led to an increased interest in the quantification of radioisotopes in the environment. Radionuclides currently present in the environment originate from a variety of natural sources such as fallout from nuclear weapons testing, and in discharges from both nuclear and non-nuclear industries. Natural sources and fallout from nuclear devices provide the main input to terrestrial ecosystems, except for certain radionuclides emanating from nuclear installations. In the late 1950's and early 1960's, during and immediately after the period of most frequent aboveground nuclear weapons testing, numerous studies were performed to determine the distribution and movement of fallout radionuclides in air, precipitation, agricultural produce, animals and soils. Around this time the nuclear power industry was developing, and consequently, both the diversity and amount of radioactive species in the environment increased. Currently, the majority of the high level waste from the nuclear industry is stored for ultimate disposal in sites classified as stable, such as deep geological strata. However, as many nuclear facilities are situated in coastal areas, the bulk of low level radioactive waste is discharged to the sea.

Because of both nuclear fallout and discharges from the nuclear industry (including releases from the Chernobyl accident in 1986), certain radionuclides are studied more than others. This is due to either their radio-toxicity, increased presence in the environment or ease of entry into the food chain^{1,2,3,4,5,6,7}; a selection of these is presented in Table 1. The separation and isolation of these radionuclides from the complex sample matrices often encountered is presenting researchers with a myriad of problems; however many of these have been eased by the introduction of novel chromatographic separation technology (Eichrom Industries Inc. Darien, Illinois, USA). By employing this new technology, previously difficult and time consuming radionuclide separations are completed more effectively and efficiently. In combination with recent advances in liquid scintillation counting (LSC) technology by PerkinElmer it is now possible to consider LSC as an alternative screening tool to alpha spectrometry and gas flow proportional counting.

Radionuclide	Environmental Location
^3H	Milk, crops, ground water and precipitation
^{14}C	Milk, crops, animals and sea water
^{35}S	Milk, crops, animals and soil/sediments
^{90}Sr	Milk, crops, animals and soil/sediments
$^{134,137}\text{Cs}$	Milk, crops, animals and soil/sediments
^{238}Pu , $^{239+240}\text{Pu}$, ^{241}Pu , ^{241}Am	Milk, crops, animals and soil/sediments

Table 1. Environmental radionuclides of specific interest.

Chromatographic Sample Preparation

A range of products that employ the technique of extraction chromatography to efficiently pre-concentrate and separate radionuclides from a variety of different matrices have recently been introduced by Eichrom. Extraction chromatography combines the power and selectivity of solvent extraction with the ease of use of a chromatographic column. Through careful selection of the extractant, which is bound to the resin support, a material is produced which is highly specific for a particular radionuclide or group of radionuclides. In the majority of cases, either retention or elution of the radionuclide of interest is achieved by modification of the concentration of the acidic eluent used. Employing such technology has resulted in an accurate and reproducible sample preparation method for the determination of radionuclides in environmental samples.

Eichrom have published methods for radionuclide separations using their chromatography technology and these can be conveniently explained as follows:

ACW, ACS, ACU methods	refer to Actinides in Water, Soil and Urine
SRW, SRS, SRU methods	refer to Strontium in Water, Soil and Urine
TCW, TCS methods	refer to Technetium in Water and Soil
H3W methods	refer to Tritium (^3H) in Water
OTW methods	refer to Other (<i>e.g.</i> , Lead in Water)

A summary of these methods together with the recommended PerkinElmer Ultima GoldTM LSC cocktail for isotopic determination by LSC is presented in Table 2. Ultima Gold cocktails are recommended for these applications due to the use of di-isopropyl naphthalene (DIN) as the solvent base which enhances alpha/beta resolution in LSC.⁷

Method No.	Analyte	Emitter	Strip Volume	Eluent	Recommended Ultima Gold Cocktail
ACS06	²³⁴⁻²³⁸ U ²³⁴ Th	Alpha, gamma Beta, gamma	15 ml 20 ml	0.02M HCl 5M HCl	AB / XR / LLT AB*
ACW01	²³⁴⁻²³⁸ U ²³⁴ Th	Alpha, gamma Beta, gamma	20 ml 20 ml	0.02M HCl 6M HCl	AB / XR / LLT AB* / LLT*
ACW03	²³⁴⁻²³⁸ U ²⁴¹ Pu ²⁴¹ Am	Alpha, gamma Beta, gamma Alpha, gamma	15 ml 10 ml 3+20 ml	0.01M HCl 0.1M Ammonium H Oxalate 9M+4M HCl	AB / XR / LLT AB / XR AB* / LLT*
ACW06	²³⁴⁻²³⁸ U ²³⁴ Th	Alpha, gamma Beta, gamma	15 ml 15 ml	0.02M HCl 5M HCl	AB / XR / LLT AB*
OTW01	²¹⁰ Pb	Beta, gamma	20 ml	Water	LLT
SRW01	^{89,90} Sr	Beta	10 ml	0.05M HNO ₃	AB / XR
SRS01	^{89,90} Sr	Beta	10 ml	0.05M HNO ₃	AB / XR
TCS01	⁹⁹ Tc	Beta	0.7g (2 ml)	TEVA Resin	AB / XR / LLT
TCW01	⁹⁹ Tc	Beta	0.7g (2 ml)	TEVA Resin	AB / XR / LLT
SRU01	^{89,90} Sr	Beta	10 ml	0.05M HNO ₃	AB / XR
ACW04	²⁴¹ Am	Alpha, gamma	15 ml	2M HCl	AB* / LLT*
ACU02	²³⁴⁻²³⁸ U ²⁴¹ Pu ²⁴¹ Am	Alpha, gamma Beta, gamma Alpha, gamma	15 ml 15 ml 3+20 ml	0.02M HCl 3M HCl-0.25M Ascorbic Acid [#] 9M+4M HCl	AB / XR / LLT AB / LLT AB* / LLT*
ACW09	²⁴¹ Pu ²⁴¹ Am	Alpha, beta Alpha, gamma	10 ml 3+20 ml	0.1M Ammonium H Oxalate 9M+4M HCl	AB / XR AB* / LLT*

ACW0 7	²⁴¹ Pu	Alpha, beta	10 ml	0.1M Ammonium H Oxalate	AB / XR
H3W1	Tritium	Beta	25 ml	Non-acidified water sample	LLT
----- -	⁶³ Ni	Beta	15 ml	3M HNO ₃	AB* / LLT*

Table 2. Compatibility of Ultima Gold cocktails with Eichrom eluents.

* Indicates limited sample uptake capacity (see Table 3 for further details).

Ascorbic acid causes yellowing upon storage (> 2 days).

The information presented in Table 2 shows both the eluent used in the final stripping of the radionuclide from the chromatographic column and the appropriate Ultima Gold cocktail which will accommodate either all, or at least a sizeable aliquot of the eluent. Table 2 should be used in conjunction with Table 3 which demonstrates the maximum capacity of each of the Ultima Gold cocktails with the each of the eluents. It should be remembered that the use of alpha/beta LSC for alpha determination will only provide a gross alpha measurement and is capable of limited alpha-alpha resolution. An example of such an alpha/beta LSC is the PerkinElmer Tri-Carb® 2770TR/AB which uses Time-Resolved Pulse Decay Analysis (TR-PDA)⁷ technology to separate the alpha spectrum from the beta spectrum.

An alternative method to acidic stripping of the radionuclide from the column is to elute with Iso-propyl alcohol (IPA). IPA effectively strips the resin coating (containing the radionuclide) and this can be counted with 4π geometry in a suitable Ultima Gold cocktail. The information in both these tables is presented to help researchers investigate the use of LSC as an alternative technology for gross alpha determination.

Eluent	Strip Volume	Ultima Gold AB ml/10 ml @ 20 °C	Ultima Gold LLT ml/10 ml @ 20 °C	Ultima Gold XR ml/10 ml @ 20 °C
0.01M Hydrochloric Acid	15 ml	10.0 ml	8.0 ml	10.0 ml
0.02M Hydrochloric Acid	15-20 ml	9.0 ml	7.0 ml	10.0 ml
2.0M Hydrochloric Acid	15 ml	3.5 ml	3.5 ml	1.0 ml
5.0M Hydrochloric Acid	15 ml	2.0 ml	1.5 ml	< 0.5 ml

6.0M Hydrochloric Acid	20 ml	1.0 ml	1.5 ml	< 0.5 ml
4.65M Hydrochloric Acid 9M + 4M mixture	3+20 ml	1.5 ml	2.0 ml	< 0.5 ml
9.0M Hydrochloric Acid (concentrated HCl 1.16 S.G.)	20 ml	1.0 ml	1.0 ml	< 0.25 ml
3M HCl / 0.25M Ascorbic Acid	15 ml	2.0 ml	2.0 ml	0.5 ml
0.05M Nitric Acid	10 ml	8.0 ml	7.0 ml	9.0 ml
3.0M Nitric Acid	15 ml	2.0 ml	2.25 ml	1.0 ml
0.02M HNO ₃ / 0.02M HF	10 ml	8.0 ml	10.0 ml	10.0 ml
0.1M Ammonium H Oxalate	10 ml	8.0 ml	6.0 ml	9.0 ml
Water	25 ml	10.0 ml	10.0 ml	10.0 ml

Table 3. Sample capacity of Ultima Gold cocktails for chromatographic eluents.

Aqueous Sample Preparation

Many of the radioactive species of interest to low level researchers are present in an aqueous medium, usually water. Therefore, any suitable LSC cocktail must not only have a high capacity for water but also be compatible with water from a variety of different sources. These include distilled, deionized, tap, rain, river and even sea water. In addition to high sample capacity, other preferred requirements for liquid scintillation counting include a very low background contribution and high counting efficiency. Ideally the LSC cocktail should also be based on the high flash point, safer solvent DIN. Ultima Gold LLT is such a cocktail and is primarily designed for the low level tritium (LLT) monitoring and research sectors. Additionally, Ultima Gold LLT has other unique performance characteristics that set it apart from currently available cocktails. Ultima Gold LLT meets additional requirements for a low level counting cocktail such as long term stability and sub-ambient temperature stability, and it can accept the important mineral acid species normally encountered in alpha/beta counting applications. A selection of the more important properties of Ultima Gold LLT are illustrated in Tables 4 and 5.

from either nuclear devices or the nuclear industry are summarized in Table 6.

Conclusion

Environmental sample preparation encompasses a wide variety of techniques, including extraction chromatography, acid extraction, ashing and solvent extraction, and chemical separation. Advances in liquid scintillation technology, together with new and emerging sample preparation techniques, now enable researchers to consider LSC as an alternative environmental sample radionuclide counting method, or as a potentially useful screening tool.

Table 6. The main radionuclides originating from nuclear devices and the nuclear industry.

Element	Radio - nuclide	Half-life	Type of emission	Energy (MeV)	Sources
Hydrogen	³ H	12.3 y	Beta	0.02	Fallout, nuclear industry
Carbon	¹⁴ C	5730 y	Beta	0.16	Fallout, nuclear industry
Phosphorus	³² P	14.3 d	Beta	1.71	Fallout, nuclear industry
Sulphur	³⁵ S	88 d	Beta	0.17	Nuclear industry
Argon	⁴¹ Ar	1.83 h	Beta Gamma	1.20,2.49 1.29	Nuclear industry
Calcium	⁴⁵ Ca	165 d	Beta	0.26	Nuclear industry
Chromium	⁵¹ Cr	27.8 d	Gamma EC	0.32 0.752	Nuclear industry
Manganese	⁵⁴ Mn	303 d	Gamma	0.84	Fallout, nuclear industry
Iron	⁵⁵ Fe ⁵⁹ Fe	2.6 y 45.1 d	EC Beta Gamma	0.232 0.273,0.475 0.142-1.29	Fallout, nuclear industry Nuclear industry

Cobalt	⁵⁸ Co	71.3 d	Beta Gamma	0.474 0.810,0.864	Nuclear industry
	⁶⁰ Co	5.3 y	EC Beta Gamma	2.31 0.315,1.49 1.17,1.33	Fallout, nuclear industry
Nickel	⁶³ Ni	92 y	Beta	0.07	Nuclear industry
Zinc	⁶⁵ Zn	244 d	Beta Gamma EC	0.325 1.11 1.11	Nuclear industry
Arsenic	⁷⁶ As	1.1 d	Beta Gamma	0.35-2.96 0.51-2.66	Nuclear industry
Krypton	⁸⁵ Kr	10.8 y	Beta Gamma	0.67 0.14	Fallout, nuclear industry
Strontium	⁸⁹ Sr	52 d	Beta	1.46	Fallout, nuclear industry
	⁹⁰ Sr	28.1 y	Beta	0.546	Fallout, nuclear industry
Yttrium	⁹⁰ Yr	2.67 d	Beta	2.27	Nuclear industry
	⁹¹ Yr	58.8 d	Beta Gamma	0.33,1.55 1.21	Nuclear industry
Zirconium	⁹⁵ Zr	65 d	Beta Gamma	0.36-1.13 0.236,0.723	Fallout, nuclear industry
Niobium	⁹⁵ Nb	35.1 d	Beta Gamma	0.160 0.766	Fallout, nuclear industry
Technetium	⁹⁹ Tc	2.12 x 10 ⁵ y	Beta	0.29	Fallout, nuclear industry

Table 6. continued.

Element	Radio - nuclide	Half-life	Type of emission	Energy (MeV)	Sources
Ruthenium	¹⁰³ Ru	39.6 d	Beta Gamma	0.203-0.90 0.04-0.61	Fallout, nuclear industry
	¹⁰⁶ Ru	367 d	Beta Gamma	0.039 0.512-2.64	Nuclear industry

Silver	^{110m} Ag	253 d	Beta Gamma	0.087,0.529 0.657,0.818	Nuclear industry
Antimony	¹²⁴ Sb	60.3 d	Beta Gamma	0.06-2.32 0.044-2.30	Nuclear industry
	¹²⁵ Sb	2.7 y	Beta Gamma	0.10-0.619 0.036-0.671	Fallout, nuclear industry
Tellurium	^{125m} Te	58 d	Gamma	0.035,0.110	Nuclear industry
	¹³² Te	3.25 d	Beta Gamma	0.22 0.049-0.228	
Iodine	¹²⁹ I	1.7 x 10 ⁷ y	Beta Gamma	0.189 0.040	Fallout, nuclear industry
	¹³¹ I	8.07 d	Beta Gamma	0.257-0.806 0.080-0.723	Fallout, nuclear industry
Xenon	^{131m} Xe	11.8 d	Gamma	0.164	Nuclear industry
	¹³³ Xe	5.27 d	Beta Gamma	0.267,0.347 0.080,0.382	Nuclear industry
Cesium	¹³⁴ Cs	2.05 y	Beta Gamma	0.089,0.410 0.475-1.40	Nuclear industry
	¹³⁶ Cs	13 d	Beta Gamma	0.341,0.560 0.067,1.24	Fallout
	¹³⁷ Cs	30.2 y	Beta Gamma	0.511,1.18 0.662	Fallout, nuclear industry
Barium	¹⁴⁰ Ba	12.8 d	Beta Gamma	0.47-1.02 0.139-0.537	Fallout
Lanthanum	¹⁴⁰ La	1.67 d	Beta Gamma	1.25-2.17 0.110-2.55	Fallout, nuclear industry
Cerium	¹⁴¹ Ce	33 d	Beta Gamma	0.444,0.582 0.145	Fallout, nuclear industry
	¹⁴⁴ Ce	285 d	Beta Gamma	0.175-0.309 0.034-0.134	Fallout, nuclear industry
Neodymium	¹⁴⁷ Nd	11.1 d	Beta Gamma	0.38,0.82 0.091-0.69	Fallout
Promethium	¹⁴⁷ Pm	2.5 y	Beta	0.23	Nuclear industry

Europium	¹⁵⁴ Eu	16 y	Beta Gamma	0.27-1.86 0.060-1.60	Nuclear industry
	¹⁵⁵ Eu	1.81 y	Beta Gamma	0.10-0.25 0.043-0.105	Nuclear industry

Table 6 continued.

Element	Radio - nuclide	Half-life	Type of emission	Energy (MeV)	Sources
Polonium	²¹⁰ Po	138.4 d	Alpha Gamma	5.30 0.803	Nuclear Industry
Thorium	²³⁴ Th	24.1 d	Beta Gamma	0.100,0.191 0.030-0.094	Nuclear Industry
Uranium	²³⁴ U	2.47 x 10 ⁵ y	Alpha Gamma	4.60,4.72 0.053-0.580	Nuclear Industry
	²³⁵ U	7.1 x 10 ⁸ y	Alpha Gamma	4.16-4.60 0.074-0.367	Nuclear industry
	²³⁶ U	2.39 x 10 ⁷ y	Alpha Gamma	4.33,4.44 0.050	Nuclear industry
	²³⁸ U	4.51 x 10 ⁹ y	Alpha Gamma	4.14,4.15 0.048	Nuclear industry
Neptunium	²³⁷ Np	2.14 x 10 ⁶ y	Alpha Gamma	4.40-4.87 0.020-0.240	Nuclear industry
Plutonium	²³⁸ Pu	86 y	Alpha Gamma	5.36,5.46,5.50	Fallout, nuclear industry
	²³⁹ Pu	2.44 x 10 ⁴ y	Alpha Gamma	0.044 5.01-5.16	Fallout, nuclear industry
	²⁴⁰ Pu	6580 y	Alpha Gamma	0.039-0.769 5.02,5.12,5.17	Fallout, nuclear industry
	²⁴¹ Pu	13.2 y	Alpha Beta	0.045,0.104	Fallout, nuclear industry
	²⁴² Pu	3.79 x 10 ⁵ y	Alpha	4.80-5.05 0.021 4.86,4.90	Nuclear industry
Americium	²⁴¹ Am	458 y	Alpha Gamma	5.39-5.55 0.026-0.060	Fallout, nuclear industry

Curium	²⁴² Cm	163 d	Alpha Gamma	5.97-6.11 0.044	Nuclear industry
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