APPLICATION NOTE

LSC

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Environmental Sample Preparation for LSC

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 above ground 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.

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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.

Table 1. Environmental radionuclides of specific interest.

Radionuclide	Environmental Location
^{3}H	Milk, crops, groundwater, 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
$^{134,137}Cs$	Milk, crops, animals and soil/sediments
^{238}Pu, $^{239,240}Pu$, ^{241}Pu, ^{241}Am	Milk, crops, animals and soil/sediments

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 efficienctly. In combination with 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.

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.

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

Method	Isotope	Emitter	Strip Volume (ml)	Eluent	Recommended Ultima Gold Cocktail
ACS06	$^{234-238}U$	α, γ	15	0.02 M HCl	AB/XR/LLT
	^{234}Th	β, γ	20	5 M HCl	AB[1]
ACW01	$^{234-238}U$	α, γ	20	0.02 M HCl	AB/XR/LLT
	^{134}Th	β, γ	20	6 M HCl	AB[1]/LLT[1]
ACW03	$^{234-238}U$	α, γ	15	0.01 M HCl	AB/XR/LLT
	^{241}Pu	β	10	0.1 M Ammonium Oxalate	AB/XR
	^{241}Am	α, γ	3 + 20	9 M + 4 M HCl	AB[1]/LLT[1]
ACW06	$^{234-238}U$	α, γ	15	0.02 M HCl	AB/XR/LLT
	^{234}Th	β, γ	15	5 M HCl	AB[1]
OTW01	^{210}Pb	β, γ	20	Water	LLT
SRW01	$^{89,90}Sr$	β	10	0.05 M HNO_3	AB/XR
SRS01	$^{89,90}Sr$	β	10	0.05 M HNO_3	AB/XR
TCS01	^{99}Tc	β	2	TEVA Resin	AB/XR/LLT
TCW01	^{99}Tc	β	2	TEVA Resin	AB/XR/LLT
SRU01	$^{89,90}Sr$	β	10	0.05 M HNO_3	AB/XR
ACW04	^{241}Am	α, γ	15	2 M HCl	AB[1]/LLT[1]
ACU02	$^{234-238}U$	α, γ	15	0.02 M HCl	AB/XR/LLT
	^{241}Pu	β	15	3 M HCl-0.25 M Ascorbic Acid	AB/LLT
	^{241}Am	α, γ	3 + 20	9 M + 4 M HCl	AB[1]/LLT[1]
ACW09	^{241}Pu	β	10	0.1 M Ammonium Oxalate	AB/XR
	^{241}Am	α, γ	3 + 20	9 M + 4 M HCl	AB[1]/LLT[1]
ACW07	^{241}Pu	β	10	0.1 M Ammonium Oxalate	AB/XR
H3W1	^{3}H	β	25	Non acidified water sample	LLT
	^{63}Ni	β	15	3 M HNO_3	AB[1]/LLT[1]

[1] Indicates limited sample uptake capacity (see Table 3 for further details)

Employing such technology has resulted in an accurate and reproducible sample preparation method for the determination of radionuclides in environmental samples. Eichrom has published methods for radionuclide separations using their chromatography technology and these can be conveniently explained as follows:

Method	Refer to:
ACW, ACS, ACU	Actinides in Water, Soil and Urine
SRW, SRS, SRU	Strontium in Water, Soil and Urine
TCW, TCS	Technetium in Water and Soil
H3W	Tritium in Water
OTW	Other (e.g. Lead in Water)

A summary of these methods together with the recommended PerkinElmer Cocktail for isotopic determination by LSC is presented in Table 2. Ultima Gold cocktails[9] are recommended for these applications due to the use of diisopropyl naphthalene (DIN) as the solvent base which enhances alpha/beta resolution in LSC[7]. 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[9] 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 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 TriCarb 3180TR (comparable with TriCarb B3180 TR/SL) including alpha/beta separation option 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 Isopropyl 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.

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

Eluent	Strip Volume (ml)	ml Sample/10 ml Ultima Gold AB @ 20 °C	ml Sample/10 ml Ultima Gold LLT @ 20 °C	ml Sample/10 ml Ultima Gold XR @ 20 °C
0,01 M HCl	15	10.0	8.0	10.0
0,02 M HCl	15-20	9.0	7.0	10.0
2,0 M HCl	15	3.5	3.5	1.0
5,0 M HCl	15	2.0	1.5	<0.5
6,0 M HCl	20	1.0	1.5	<0.5
4,65 M HCl (9 M + 4 M Mixture)	3 + 20	1.5	2.0	<0.5
9,0 M HCl	20	1.0	1.0	<0.25
3 M HCl/0,25 M Ascorbic acid	15	2.0	2.0	0.5
0,05 M HNO_3	10	8.0	7.0	9.0
3,0 M HNO_3	15	2.0	2.25	1.0
0,02 M HNO_3/0,02 M HF	10	8.0	10.0	10.0
0,1 M Ammonium oxalate	10	8.0	6.0	9.0
Water	25	10.0	10.0	10.0

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 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 is illustrated in Tables 4 and 5.

Table 4. Suitability of Ultima Gold LLT for low level tritium measurements.

Water/Cocktail Ratio (ml)	Cocktail	^{3}H Efficiency (0,4 – 4,5 keV)	Background (CPM)	E^2/B	E^2V^2/B	MDA (Bq/l)
8:12	Ultima Gold LLT	24.6	1.15	526	33680	1.22
10:10	Ultima Gold LLT	21.2	1.11	405	40490	1.11
11:9	Ultima Gold LLT	18.1	0.95	345	41730	1.06

Table 5. Sample capacity of Ultima Gold LLT cocktail for different acids.

Temperature (°C)	1 M HCl (ml)	2 M HCl (ml)	1 M HNO_3 (ml)	2 M HNO_3 (ml)	1 M H_2SO_4 (ml)	2 M H_2SO_4 (ml)	1 M H_3PO_4 (ml)	2 M H_3PO_4 (ml)
14	4.0	2.0	3.0	2.25	5.5	3.5	4.5	4.0
16	4.0	2.5	3.5	2.25	6.5	4.0	5.0	4.0
18	4.0	2.5	3.5	2.25	7.0	4.0	7.0	4.0
20	5.0	3.0	3.5	2.5	7.0	4.0	4.0	4.0

Table 4 shows some of the properties of Ultima Gold LLT measured in Low Level Mode in a TriCarb 2770 TR/SL (comparable with TriCarb 3180 TR/SL) comparable with TriCarb B3180 TR/SL) at 15 °C. All samples were prepared in duplicates in polyethylene vials. The measurement time for the determination of the background was 500 minutes. The minimum detectable activity (MDA) was calculated using the formula from Currie[8].

Table 5 indicates that Ultima Gold LLT is capable to take up amounts of acids generally used for environmental samples. Ultima Gold LLT also shows a high sample capacity for urine samples, and therefore is ideally suited for bioassays with ^{3}H samples in urine. As a quick guide Table 6 shows the most important environmental radionuclides from nuclear power plants and the nuclear industry.

Conclusion

Environmental sample preparation encompasses a wide variety of techniques, including extraction chromatography, adic 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	Radionuclide	Half-life	Emitter	Energy (MeV)	Sources
Hydrogen	^{3}H	12.3 y	β	0.02	Fallout, nuclear industry
Carbon	^{14}C	5730 y	β	0.16	Fallout, nuclear industry
Phosphorus	^{32}P	14.3 d	β	1.71	Fallout, nuclear industry
Sulphur	^{35}S	88 d	β	0.17	Nuclear industry
Argon	^{41}Ar	1.83 h	β γ	1.20; 2.49 1.29	Nuclear industry
Calcium	^{45}Ca	165 d	β	0.26	Nuclear industry
Chromium	^{51}Cr	27.8 d	γ EC	0.32 0.75	Nuclear industry
Manganese	^{54}Mn	303 d	γ	0.84	Fallout, nuclear industry
Iron	^{55}Fe	2.6 y	EC	0.23	Fallout, nuclear industry
	^{59}Fe	45.1 d	β γ	0.27; 0.47 0.14-1.3	Nuclear industry
Cobalt	^{58}Co	71.3 d	β γ EC	0.47 0.81; 0.86 2.31	Nuclear industry
	^{60}Co	5.3 y	β γ	0.32; 1.49 1.17; 1.33	Fallout, Nuclear industry
Nickel	^{63}Ni	92 y	β	0.07	Nuclear industry
Zinc	^{65}Zn	244 d	β γ EC	0.33 1.11 1.11	Nuclear industry
Arsenic	^{76}As	1.1 d	β γ	0.35-2.96 0.51-2.66	Nuclear industry
Krypton	^{85}Kr	10.8 y	β γ	0.67 0.14	Fallout, Nuclear industry
Strontium	^{89}Sr	52 d	β	1.46	Fallout, Nuclear industry
	^{90}Sr	28.1 y	β	0.55	Fallout, Nuclear industry

Table 6. Continued

Element	Radionuclide	Half-life	Emitter	Energy (MeV)	Sources
Yttrium	^{90}Y	2.67 d	β	2.27	Nuclear industry
	^{91}Y	58.8 d	β γ	0.33; 1.55 1.21	Nuclear industry
Zirconium	^{95}Zr	65 d	β γ	0.36-1.13 0.24; 0.72	Fallout, Nuclear industry
Niobium	^{95}Nb	35.1 d	β γ	0.16 0.77	Fallout, Nuclear industry
Technetium	^{99}Tc	$2.12 \cdot 10^5$ y	β	0.29	Fallout, Nuclear industry
Ruthenium	^{103}Ru	39.6 d	β γ	0.226 0.04-0.61	Fallout, Nuclear industry
	^{106}Ru	367 d	β γ	0.04 0.51-2.64	Nuclear industry
Silver	^{110m}Ag	253 d	β γ	0.09; 0.53 0.66; 0.82	Nuclear industry
Antimony	^{124}Sb	60.3 d	β γ	0.06-2.32 0.04-2.3	Nuclear industry
	^{125}Sb	2.7 y	β γ	0.10-0.62 0.04-0.67	Fallout, Nuclear industry
Tellurium	^{125m}Te	58 d	γ	0.04; 0.11	Nuclear industry
	^{132}Te	3.25 d	β γ	0.22 0.05-0.23	Nuclear industry
Iodine	^{129}I	$1.7 \cdot 10^7$ y	β γ	0.19 0.04	Fallout, Nuclear industry
	^{131}I	8.07 d	β γ	0.26-0.81 0.08-0.72	Fallout, Nuclear industry
Xenon	^{131m}Xe	11.8 d	γ	0.16	Nuclear industry
	^{133}Xe	5.27 d	β γ	0.27; 0.35 0.08; 0.38	Nuclear industry
Cesium	^{134}Cs	2.05 y	β γ	0.09; 0.41 0.48-1.4	Nuclear industry
	^{136}Cs	13 d	β γ	0.34; 0.56 0.07; 1.24	Fallout
	^{137}Cs	30.2 y	β γ	0.51; 1.18 0.66	Fallout, Nuclear industry
Barium	^{140}Ba	12.8 d	β γ	0.47-1.02 0.14-0.54	Fallout
Lanthanum	^{140}La	1.67 d	β γ	1.25-2.17 0.11-2.55	Fallout, Nuclear industry
Cerium	^{141}Ce	33 d	β γ	0.44; 0.58 0.15	Fallout, Nuclear industry
	^{144}Ce	285 d	β γ	0.18-0.31 0.03-0.13	Fallout, Nuclear industry
Neodymium	^{147}Nd	11.1 d	β γ	0.38; 0.82 0.09-0.69	Fallout
Promethium	^{147}Pm	2.5 y	β	0.23	Nuclear industry
Europium	^{154}Eu	16 y	β γ	0.27-1.86 0.06-1.6	Nuclear industry
	^{155}Eu	1.81 y	β γ	0.10-0.25 0.04-0.11	Nuclear industry
Polonium	^{210}Po	138.4 d	α γ	5.30 0.80	Nuclear industry
Thorium	^{234}Th	24.1 d	β γ	0.10; 0.19 0.03-0.09	Nuclear industry
Uranium	^{234}U	$2.47 \cdot 10^5$ y	α γ	4.60; 4.72 0.05-0.58	Nuclear industry
	^{235}U	$7.1 \cdot 10^8$ y	α γ	4.16-4.60 0.07-0.37	Nuclear industry
	^{236}U	$2.39 \cdot 10^7$ y	α γ	4.33; 4.44 0.05	Nuclear industry
	^{238}U	$4.51 \cdot 10^9$ y	α γ	4.14; 4.15 0.05	Nuclear industry

Table 6. Continued

Element	Radionuclide	Half-life	Emitter	Energy (MeV)	Sources
Neptunium	^{237}Np	$2.14 \cdot 10^{6}$ y	α γ	4.40-4.87 0.02-0.24	Nuclear industry
Plutonium	^{238}Pu	86 y	α γ	5.36; 5.46; 5.50 0.04	Fallout, nuclear industry
	^{239}Pu	$2.44 \cdot 10^{4}$ y	α γ	5.01-5.16 0.04-0.77	Fallout, nuclear industry
	^{240}Pu	6580 y	α γ	5.02; 5.12; 5.17 0.05; 0.10	Fallout, nuclear industry
	^{241}Pu	13.2 y	α β	4.80-5.05 0.02	Fallout, nuclear industry
	^{242}Pu	$3.79 \cdot 10^{5}$ y	α	4.86; 4.90	Nuclear industry
Americium	^{241}Am	458 y	α γ	5.39-5.55 0.03-0.06	Fallout, nuclear industry
Curium	^{242}Cm	163 d	α γ	5.97-6.11 0.04	Fallout, nuclear industry

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