

EXTRACTION CHROMATOGRAPHY AND LIQUID SCINTILLATION COUNTING FOR THE ANALYSIS OF LONG-LIVED RADIONUCLIDES

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ABSTRACT. The basic concepts of developing radiochemical procedures for analyzing long-lived radionuclides by liquid scintillation counting (LSC) are discussed. We briefly review procedures for determining ⁹⁰Sr, ⁸⁹Sr, ²¹⁰Pb, ⁹⁹Tc, ²⁴¹Pu, transuranium nuclides, ⁶³Ni, and ⁵⁵Fe. For extraction chromatography, we used commercially available columns of crown ether (Sr and Pb), supported quaternary amine (Tc), phosphonate derivative (Pu), di-phosphonate derivative (transuranium nuclides), or homemade columns of di-methyl-glyoxime and methyl-i-butyl-ketone (Ni and Fe, respectively). Difficulties arising during method development, as well as problems emerging during routine application, are discussed. The procedures were validated and applied for determining the above-mentioned long-lived radionuclides in radioactive wastes and/or environmental samples.

INTRODUCTION

Analyses of radionuclides emitting pure β or α particles or weak γ /X-rays (without accompanying easy-to-measure γ rays) are often performed by liquid scintillation counting (LSC). High counting efficiency and the absence of self-absorption are the general advantages that make LSC a widely applicable analytical tool and the exclusive technique for detecting weak energy emitters. The major problems of LSC originate from the poor resolution, the overlap between typical α and β spectra, the high background, and the dependence on quench. Additional difficulty arises from the continuous nature of the energy of β radiation. To identify the radionuclides in a complex sample matrix, chemical separations prior to LSC are necessary. The high efficiency of LSC can be combined advantageously with the selectivity provided by new, specific extraction chromatographic substances. The acquisition of LSC spectra instead of “counting” provides an additional tool for better identifying the radionuclides.

Extraction chromatography followed by LS spectrometry was used for analyzing several long-lived radionuclides in nuclear and environmental samples in the radiochemical laboratory of our institute. Our primary interest was to develop and adopt procedures for determining isotopes that are a major concern in nuclear power plant (NPP) waste processing technology and that might be released from nuclear facilities into the environment. A list of the most relevant “difficult-to-determine” nuclides in question and their nuclear properties are given in Table 1. Some attempts were also made to determine total α activity in power plant samples, which are regarded as a mixture of ²⁴²Cm, ²⁴⁴Cm, ²⁴¹Am, ²³⁹Pu, ²⁴⁰Pu, ²³⁸Pu, ²³⁸U, ²³⁵U, and ²³⁴U.

Details of the actual radiochemical procedure are given in the references. This paper focuses on general questions of method development, i.e. how extraction chromatography can be combined advantageously with liquid scintillation (LS) spectrometry. We discuss issues concerning selection of tracers and/or carriers, choice of chromatographic material, column design, inclusion of necessary preconcentration steps, final source preparation, and evaluation of spectra, as well as quality control.

DISCUSSION

The aim of the chemical procedure is the separation of the analyte, i.e. the chemical element, from other elements that contain radioisotopes that potentially interfere with those needing to be determined. Separation of the non-radioactive matrix components is also desirable because the organic

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Table 1 Radionuclides analyzed by radiochemical procedures using LS spectrometry.

Nuclide	Half-life	Decay mode	Radiation	Reference
⁹⁰ Sr	28 yr	β	E _{βMax} = 550 keV	Vajda et al. 1992; Moreno et al. 2004
<i>Progeny:</i>				
⁹⁰ Y	64 hr	β	E _{βMax} = 2.27 MeV	Vajda et al. 1992; Moreno et al. 2004
⁸⁹ Sr	50 days	β	E _{βMax} = 1490 keV	
²¹⁰ Pb	22 yr	β	E _{βMax} = 16 keV	Vajda et al. 1997
⁹⁹ Tc	2.13 × 10 ⁵ yr	β	E _{βMax} = 293 keV	Kabai et al. 2003
⁵⁵ Fe	2.7 yr	Electron capture	E _X = 5.9 keV	Kerkápoly et al. 2005
⁶³ Ni	100 yr	β	E _{βMax} ≈ 67 keV	Kerkápoly et al. 2005
⁵⁹ Ni	7.5 × 10 ⁴ yr	Electron capture	E _X = 6.9 keV	Kerkápoly et al. 2005
²⁴¹ Pu	14 yr	β	E _{βMax} = 20 keV	Moreno et al. 1998

LS cocktails may not be kept in solution in the presence of high salt/acid/base contents (phase separation). Thus, the simplified goal of the chemical treatment is the best possible separation of the analyte from any element in the sample.

Chemical Procedure

The general scheme of the separation procedures is shown below:

Destruction/Preconcentration → Extraction chromatography → LSC source preparation

Radioactive tracers and/or carriers (see Table 2) are added to the sample before beginning the chemical treatment. These radiotracers and non-radioactive carriers can be used for yield determination, but it should be noted that yield corrections are valid only if a chemical equilibrium between the analyte and the tracer/carrier has been established. Carriers are added to the samples whenever available (even if tracers are used) to reduce losses due to sorption, radio-colloid formation, or to enable a precipitation if preceding preconcentration steps are necessary.

Table 2 List of tracers added to the samples; radionuclide tracers used for recovery determination.

Nuclide	Half-life	Decay mode	Radiation to be detected
⁸⁵ Sr	60 days	Electron capture	E _X = 13.4 keV
²⁴² Pu	3.7 × 10 ⁵ yr	α	E _α ≈ 4.9 MeV
^{99m} Tc	6 hr	β	E _γ = 140 keV

For the determination of ⁹⁰Sr, ²¹⁰Pb, ⁵⁵Fe, and ⁶³Ni, carriers of the same element are added.

Destruction

Samples have to be destroyed to dissolve solid species and decompose organic material that might form complexes with the analyte, thus altering its chemical behavior. In large-volume liquid samples, the analyte is first preconcentrated, followed by the decomposition of organic material in the concentrate. For sample destruction, dry ashing (in an oven) and/or wet ashing (with oxidizing mineral acids on a heating plate) are applied.

Preconcentration

Preconcentration is often performed to remove potentially interfering isotopes and/or to remove undesired chemical matrix elements. In rare cases when the major separation step (extraction chro-

matography) provides sufficient selectivity, preconcentration can be omitted. This is, for instance, the situation for Pb separation using a highly selective crown ether (see Table 4). In other cases, a properly selected preconcentration procedure removes the matrix components as well as the major chemical interferences, which allows the concentrate to dissolve in a small volume and offers advantages in column separation. An interesting example is the case of Sr that is coprecipitated with Ca oxalate. Ca is a major interference in the classical Sr separation procedure using fuming nitric acid. Since the introduction of the Sr selective crown ether (Table 4), Ca is no longer an interfering component and it can be added to the sample before its effective separation. On the other hand, ^{40}K was not regarded as a major interference in the conventional procedures based on a sequence of alkaline earth precipitations, but it has become important due to the significant retention of K in the crown ether. Instead of preconcentration, preliminary separation of major interferences may be necessary, as in the case of removing Fe as hydroxide before the separation of Ni, while Ni can be kept in solution as an amino complex. Ferrous hydroxide is used for coprecipitation and as a reducing agent for preconcentration of actinides from many sample types. However, the procedure is not adequate for solutions of high phosphate or sulfate content. The preferred preconcentration procedure is often selected according to the mutual demand of the “tandem” procedures—e.g. for the simultaneous separation of ^{99}Tc and ^{129}I via sulfuric acid, destruction was followed by extraction of Tc with TBP. The applied preconcentration procedures are given in Table 3.

Table 3 Procedures for preconcentration of different analytes.

Analyte	Preconcentration/Scavenging	Remark
^{90}Sr , ^{89}Sr	Coprecipitation with Ca oxalate (alkaline earth metal oxalates)	Separation of K (alkali metals)
^{210}Pb	None	
^{99}Tc	Extraction with TBP from sulfuric acid	In favor of a combined separation with ^{129}I
^{55}Fe	Precipitation of $\text{Fe}(\text{OH})_3$ with NH_3	Separation of Ni by forming amino complexes
^{63}Ni	Scavenging of Fe by $\text{Fe}(\text{OH})_3$ precipitation	Separation of Fe
^{241}Pu	Coprecipitation with $\text{Fe}(\text{OH})_2$	Addition of salting-out agent for extraction chromatography

Extraction Chromatography

Solvent extraction using organic solvents can be easily combined with LSC based on organic cocktails, while aqueous phases obtained in extraction chromatography have limited solubility in organic solvents. However, extraction chromatography has several advantages, such as requiring less time because it is equivalent with a set of extraction batches. Furthermore, the development of new scintillation cocktails results in high uptake of polar/aqueous liquids (due to emulgeators).

To separate the analyte, extraction chromatography was selected due to the improved separation offered by the chromatographic technique compared to batch ones, the relatively fast kinetics compared to the diffusion-controlled ion exchange, and the easy operation under laboratory conditions compared to solvent extractions.

When choosing the extractant, the most important factor is high selectivity (α) for the analyte compared to any other components. A high distribution coefficient (K_d) is also desirable, although for extremely high values ($K_d > 10^5$) removal of the retained component might be limited. The applied extraction chromatographic systems are given in Table 4.

Table 4 Extraction chromatographic systems for the separation of different nuclides. Types: IA = ion association; AE = anion exchange; Ch = chelating extraction.

Analyte		Chromatographic material		Media	
Primary	Others	Trade name ^a	Type	Loading	Stripping
⁹⁰ Sr, ⁸⁹ Sr		Sr.Resin	IA	3M HNO ₃	0.1M HNO ₃
²¹⁰ Pb	²¹⁰ Po	Sr.Resin	IA	2M HCl	6M HCl
⁹⁹ Tc	¹²⁹ I	TEVA	AE	pH = 5–6	8M HNO ₃
⁵⁵ Fe	⁶³ Ni	MIBK	IA	6M HCl	0.1M HCl
⁶³ Ni	⁵⁵ Fe	DMG	Ch	pH = 5–6	6M HCl
²⁴¹ Pu	U, Th/Np	UTEVA	IA	8M HNO ₃ (+Fe)	9M HCl/ 0.1M NH ₄ I
U + TRU		Actinide.Resin	IA	1M HCl	—

^aProduced by Eichrom Co. (US; www.eichrom.com); Sr.Resin = bis(-t-butylcyclohexano)-18,6-crown ether; TEVA = quaternary octyldecylmethyl-ammonium nitrate; MIBK = methyl-i-butyl ketone supported by Amberlite XAD; DMG = dimethylglyoxime supported by Amberlite XAD; UTEVA = di-pentyl-pentyl-phosphonate; Actinide.Resin = DIPEX = bis(2-ethylhexyl)methanediphosphonic acid.

The selective separation of Sr by the crown ether results in a modest K_d value (<100 in 3M HNO₃) but high selectivity. The same crown ether has a much higher K_d in a wide range of acidity for Pb; the high selectivity allows for a single-step separation procedure (without preconcentration). DMG is a highly selective chelating agent for Ni. Actinide resin has the highest K_d values for actinides in low acidic media, which prohibits the elution of the retained components. This material is recommended for concentrating actinides from large volumes of water, followed by direct counting in a mixture of the resin and LS cocktail. This procedure was tested for analyzing actinides in primary coolant samples of high concentrations of fission and activation products where it failed (see below). The measured activities from this experiment are compiled in Table 5.

Although actinides strongly adsorb onto Actinide.Resin, the high fraction of other radioisotopes on the resin (e.g. retained activity of ⁵⁴Mn is 5 orders of magnitude greater than those of all actinides) results in reduced selectivity and prohibits the use of the procedure for determining actinides in highly active coolant samples without using further separation steps between β and α emitters. (The α/β discrimination unit of the LSC facility overestimated the α activity due to false counting of the intensive beta radiation.) For Tc, Fe, and Pu separations by TEVA, MIBK, and UTEVA, respectively, separation by chromatography is improved by the preconcentration procedure.

Extraction chromatographic materials can be divided into 3 groups: 1) those forming chelate complexes; 2) neutral ion association complexes; and 3) quaternary amines that can be regarded as liquid anion exchangers. According to the mechanism of extraction, the conditions may vary significantly. In the previous case, the load solution should be only slightly acidic, while for the latter cases a high acid concentration (with adding salting-out agents) is favored.

Optimal chromatographic parameters (column sizes, volumes of load and strip solutions, flow rate) are determined by the amounts and the distribution coefficients of the analyte and the components retained by the column. Tracer amounts of retained materials do not need long, wide column filling (e.g. 34-mm-long, 3-mm-inner-diameter UTEVA columns are appropriate for Pu separation). TEVA columns of similar sizes are used to purify carrier-free Tc, while bigger columns (~10 cm long, 1 cm diameter) are used to separate about 10–30 mg of Sr, Pb, Fe, or Ni species. Columns should not be overloaded.

Table 5 Retention of various radionuclides originating from primary coolant sample on actinide resin. Conditions of separation: 800 mL of coolant acidified to 0.01M with HCl was equilibrated with 0.5 g of Actinide resin for 3 hr. The resin was filtered, washed, and analyzed by gamma spectrometry; the filtrate as well as the load solution were analyzed by alpha and gamma spectrometry.

Nuclide	Retained activity on resin (Bq)	Retained fraction of load (%)
Fission and activation products		
²⁴ Na	2.58E+01	0.1
⁴² K	2.50E+02	0.1
¹³⁴ Cs	—	0
¹³⁷ Cs	4.2	0.2
¹⁴⁰ Ba	6.07E+01	
⁷ Be	1.75E+03	
¹⁴⁴ Ce	4.37E+02	
¹³¹ I	1.73E+01	7.3
¹³³ I	1.82E+02	9.1
Corrosion products		
¹²⁴ Sb	25.46	
⁵⁹ Fe	16.71	
⁵⁴ Mn	4.18E+03	84
⁵⁸ Co	5.89E+01	20
⁶⁰ Co	2.51E+02	32
⁹⁹ Mo	6.63E+02	74
<i>Total activity retained</i>	<i>7.92E+03</i>	
Actinides		
²⁴² Cm	6.34E-02	
²⁴⁴ Cm	5.32E-02	
^{239,240} Pu	1.53E-02	
<i>Total alpha activity retained</i> ^a	<i>1.32E-01</i>	

^aAverage actinide retention in model experiments: Am (Cm) - 93%, Pu - 83%, Th - 89%, U - 93%.

Reuse of the columns is generally not recommended, in order to avoid cross-contamination. Nevertheless, in the case of reversible retention, columns can be effectively decontaminated, e.g. crown ether columns are purified by EDTA that forms strong complexes both with Pb and Sr.

LSC Source Preparation

Separated analyte is usually precipitated or coprecipitated to obtain a solid source. This procedure serves as a final purification step and allows for a well-defined precipitate gravimetric yield determination to be carried out (e.g. for Sr oxalate, Pb oxalate). From tracer amounts of Tc and Pu, coprecipitated sources are also prepared. These precipitates are dissolved in a fixed small volume of diluted acid—which assures constant quench for the source—that is finally mixed with a fixed volume of an LS cocktail solution. A list of the chemical compositions of the final sources is given below.

Ferric ions and Ni complexes have intensive colors that cause strong color quench. To reduce the color, Fe(III) is reduced by ascorbic acid, and Ni complexes are decomposed directly in the LS vials. The quench indicating parameter (tSIE) is determined before sample counting and the efficiency-tSIE calibration function is a priori determined.

Table 6 LS sources of various analytes.

Analyte	Chemical form of LS source	Quench parameter
^{90}Sr , ^{89}Sr	Sr oxalate + 1M HNO_3	Constant
^{210}Pb	Pb oxalate + 1M HNO_3	Constant
^{99}Tc	Tc/MnS	Constant
^{55}Fe	Fe nitrate reduced by ascorbic acid	Varying
^{63}Ni	NiDMG destroyed with HNO_3	Varying
^{241}Pu	Pu/ NdF_3 + boric acid + ethanol + 1M HNO_3	Constant

Chemical Recovery Determination

Chemical yield is determined in the final source either by gravimetry (e.g. Sr and Pb) or by analyzing the stable carrier of the analyte via an independent element analytical method before and after chemical treatment (e.g. Fe, Ni content is measured by TXRF) or by detecting the known amount of tracer in the final source (e.g. measuring $^{99\text{m}}\text{Tc}$ and ^{242}Pu by gamma and alpha spectrometry, respectively).

Liquid Scintillation Counting

LS sources are counted in well-calibrated facilities against a sample specific background (blank composition) and a set of calibration sources (efficiency–tSIE). In each case, LS spectra are collected and analyzed to check sample purity. Typical LS spectra obtained by analyzing radioactive waste samples are shown in Figure 1.

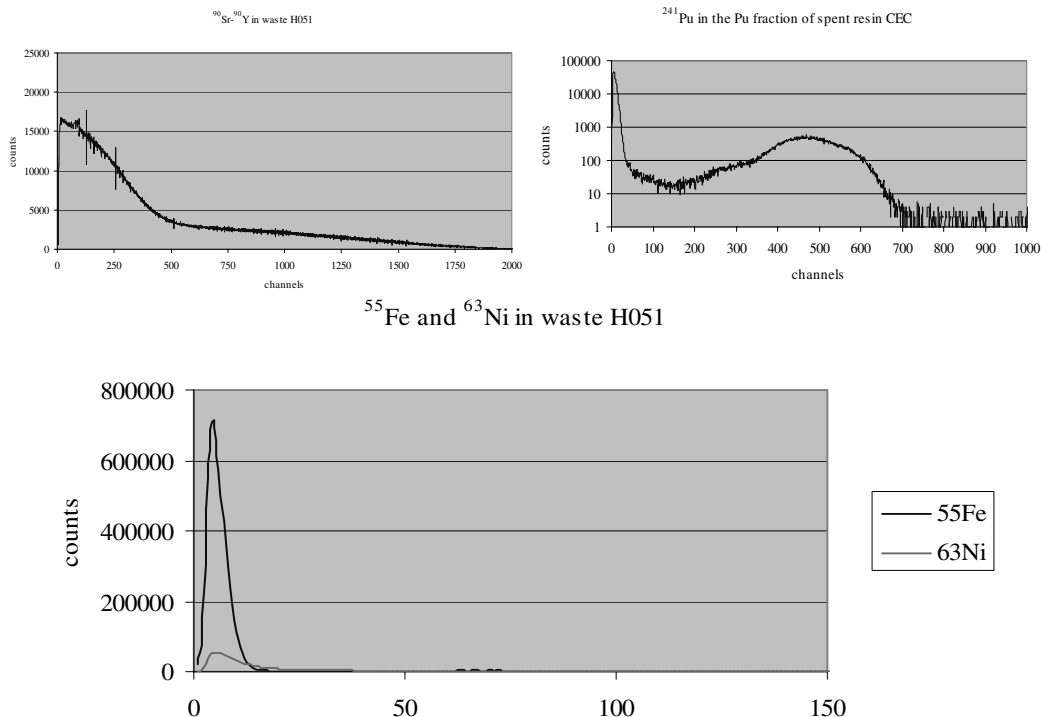


Figure 1 LS spectra of various LS sources prepared from radioactive samples: a) LS spectrum of ^{90}Sr separated from waste concentrate from a nuclear power plant (NPP); b) LS spectrum of ^{241}Pu separated from waste concentrate from a NPP; c) LS spectrum of ^{55}Fe and ^{63}Ni separated from waste concentrate from a NPP.

The LS spectrum shape of ^{99}Tc is basically similar to that of ^{63}Ni , but count rates in waste samples are orders of magnitude lower, and very often traces of impurities prohibit correct spectrum evaluation.

Nuclear Interferences

After chemical processing, there may be 3 types of nuclear interferences in the source: 1) other radionuclides of the analyte element; 2) impurities due to insufficient decontamination; and 3) daughter nuclides of any radionuclide present in the source. Because the objects of chemical procedures are chemical elements, radionuclides of the same element are not separated, and since chemical separations are never complete, some impurities might remain in the source. Radioactive daughters of any parent nuclide accumulate in the source. For high-efficiency LSC, these interferences must be taken into correction. A list of interfering nuclides is given in Table 7.

Table 7 Nuclides interfering in LS spectrometry and actions for correction.

Analyte	Interfering nuclide	Characteristics of the interference	Corrective action
^{90}Sr	^{90}Y	Daughter, pure β emitter, Half-life: 64 hr	- ^{90}Y ingrowth calculation - Channel-ratio correction for ^{90}Y spectrum
^{90}Sr	^{90}Y	Daughter, pure β emitter, Half-life: 64 hr	- Repeated counting, channel-ratio correction or spectrum deconvolution
	^{89}Sr	pure β emitter, Half-life: 50 d	- Repeated separation of Y after attaining secular equilibrium, ^{90}Y counting as well
	$^{91}\text{Sr}, ^{92}\text{Sr}$	β, γ emitter	- Cooling, delayed separation
^{210}Pb	^{210}Bi	Daughter, β emitter, Half-life: 64 hr	- ^{210}Bi ingrowth calculation - Channel-ratio method for ^{210}Bi spectrum
	^{212}Pb	From natural decay series β, γ emitter, half-life: 10 hr	- Waiting for decay, delayed counting
^{99}Tc	Colloids	Impurities β, γ emitter	- γ spectrometry, activity correction by calculation
^{55}Fe	^{59}Fe	β, γ emitter, half-life: 45 d	- γ spectrometry, activity correction by calculation
^{63}Ni	^{59}Ni	Electron capture, half-life: 76,000 yr	- X spectrometry, activity correction by calculation
^{241}Pu	Other Pu	α emitter, long-lived	- Channel-ratio correction (α cross talk)

LS spectrometry instead of LS counting offers a good opportunity for correction. Cross-talking can be corrected by the channel-ratio method, and radionuclides also emitting γ radiation can be corrected via spectrometry. Short-lived chemical analogues of the analyte can be eliminated by waiting for decay (cooling, reactor materials) before counting/separation.

APPLICATION OF THE METHODS: PERFORMANCE CHARACTERISTICS

The methods have been validated, and the procedure for ^{90}Sr analysis was successfully tested in an intercomparison exercise as well as in proficiency tests. Unfortunately, reference materials for the other nuclides are not available.

Methods were used for determining the studied nuclides in radioactive waste samples, waste concentrates, exhausted ion exchange resins, and occasionally for the analysis of environmental samples. To illustrate the capabilities of the methods, detection limits are given below.

Table 8 Typical detection limits of various nuclides in different sample types.

Analyte	Sample type	Sample mass	LD Bq/kg
⁹⁰ Sr	Well water	100 L	0.00001
	Waste concentrate	0.1 L	1
²¹⁰ Pb	Soil	10 g	10
⁹⁹ Tc	Soil	10 g	100
⁵⁵ Fe	Waste concentrate	0.1 L	200
⁶³ Ni	Waste concentrate	0.1 L	500
²⁴¹ Pu	Soil	10 g	10

Among the procedures listed above, only 2 are involved in the standard operating procedures of the laboratory (Sr nuclides in well water and radioactive wastes).

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