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LSC Handbook of Environmental Liquid Scintillation Spectrometry

Handbook of Environmental Liquid Scintillation Spectrometry

A Compilation of Theory and Methods

By

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Figures 2-2, 2-3, and 2-4 from: Cook, G. T., Scott, E. M., Wright, E. M., and Anderson, R. 1992. The statistics of low level counting using the new generation of Packard liquid scintillation counters. *Radiocarbon,* 34(3):362-364. Reproduced by permission of Radiocarbon.

Table 2-2 from: Prichard, H. M., Venso, E. A., and Dodson, C. L. 1992. Liquid scintillation analysis of ^{222}Rn in water by alpha-beta discrimination. *Radioactivity & Radiochemistry.* 3(1):28-36. Reproduced by permission of Radioactivity & Radiochemistry

Figures 5-1 and 5-2 from: Cook, G. T. and Anderson, R. 1993. Assessment of new features on a commercial liquid scintillation spectrometer for radiocarbon dating. *International Conference on Advances in Liquid Scintillation Spectrometry,* ed. Noakes, J. E., Schoenhofer, F. and Polach, H. A. Radiocarbon Publishers. p. 18. Reproduced by permission of Radiocarbon.

Figures 7-1, 7-2, and 7-3 from: Pates, J. M., Anderson, R., Cook, G. T., and MacKenzie, A. B. 1993. The determination of ^{234}Th in oceanic tracer studies by liquid scintillation spectrometry employing alpha/beta separation techniques. *International Conference on Advances in Liquid Scintillation Spectrometry,* ed. Noakes, J. E., Schoenhofer, F. and Polach, H. A. Radiocarbon Publishers. p. 419. Reproduced by permission of Radiocarbon.

Figures 8-4 and 8-5 from: Passo, Jr., C. J. and Floeckher, J. M. 1991. The LSC approach to radon counting in air and water. *Liquid Scintillation Counting and Organic Scintillators*, ed. Ross, H., Noakes, J. E., and Spaulding, J. D. Lewis Publishers, p. 380. Copyright 1992. Reproduced by permission of Lewis publishers, an imprint of CRC Press, Boca Raton, Florida.

Figures 8-6, 8-7, 8-8 and Table 8-1 from: Spaulding, J. D., and Noakes, J. E. 1993. Determination of ^{222}Rn in drinking water using an alpha/beta liquid scintillation counter. *International Conference on Advances in Liquid Scintillation Spectrometry,* ed. Noakes, J. E., Schoenhofer, F. and Polach, H. A. Radiocarbon Publishers. p. 375, 379, 380. Reproduced by permission of Radiocarbon.

Figure 9-1 from: Amano, H., and Yanase, N. 1990. Measurement of ^{90}Sr in environmental samples by cation-exchange and liquid scintillation counting. *Talanta*, 37(6):587. Reproduced by permission of Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington OX5 1GB, United Kingdom.

Figures 9-3 and 9-4 from: Dietz, M. L., Horowitz, E. P., Nelson, D. M., and Wahlgreen, N. 1991. An improved method for determining ^{89}Sr and ^{90}Sr in urine. *Health Physics*, 61 (6):875. Reproduced by permission of Williams and Wilkins, A Waverly Company, Baltimore, Maryland.

Table 9-5 from: Vajda, N., Ghods-Esphahani, A., Cooper, E., and Danesi, P. R. 1992. Determination of radiostrontium in soil samples using a crown ether. *J. Radioanal. Nucl. Chem.* 162. Reproduced by permission of the Journal of Radioanalytical and Nuclear Chemistry, Akadémiai Kiadó, Budapest, Hungary.

Figure 11-2 from: Silva, R. J., Evans, R., Rego, J. H., and Buddemeier, R. W. 1988. Methods and results of Tc-99 analysis of Nevada test site groundwaters. *J. Radioanal. Nucl. Chem.* 124(2):397-405. Reproduced by permission of the Journal of Radioanalytical and Nuclear Chemistry, Akadémiai Kiadó, Budapest, Hungary.

Figures 12-1 from: Pimpl, M. 1992. Increasing the sensitivity of ^{241}Pu determination for emission and immission control of nuclear installations by aid of liquid scintillation counting. *J. Radioanal. Nucl. Chem.* 161(2):431. Reproduced by permission of the Journal of Radioanalytical and Nuclear Chemistry, Akadémiai Kiadó, Budapest, Hungary.

Figure 12-2 from: Filss, P., and Enge, R. 1993. Detection of alpha emitters in solidified radioactive waste. *Nuclear Engineering and Design,* 147: p. 111-114. Reproduced by permission of Nuclear Engineering and Design.

Figures 13-1 and 13-4 from: Dietz, M. L. and Horowitz, E. P. 1993. Novel chromatographic materials based on nuclear waste processing chemistry. *LC•GC.* 11:(6). Reproduced by permission of LC•GC, Eugene, Oregon.

Table 13-1 from: McDowell, W. J., and McDowell, B. L. 1993. The growth of a radioanalytical method: alpha liquid scintillation spectrometry. *International Conference on Advances in Liquid Scintillation Spectrometry,* ed. Noakes, J. E., Schoenhofer, F. and Polach, H. A. Radiocarbon Publishers, p. 196. Reproduced by permission of Radiocarbon.

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Introduction

What Is Environmental Liquid Scintillation Counting?

Environmental liquid scintillation counting (LSC) measures radionuclides in the natural environment where radionuclide concentrations are low and the contribution of instrument background to the precision of the measurement is often important. During the last decade, a new generation of commercially manufactured liquid scintillation spectrometers was introduced. These instruments have been classified as "low level" instruments because their background reduction features have enabled the quantitation of much lower activities for a range of radionuclides, *i.e.*, the E^2/B factor is increased (where E = efficiency and B = background) or the MDA (Minimum Detectable Activity) is decreased. For example, increases in counting sensitivity have extended the effective age limit of radiocarbon dating from 50,000 years to approximately 60,000 years. In addition, levels of less than 1 Bq L^{-1} of water can be detected for environmental ^{3}H. Furthermore, the incorporation of Multichannel Analyzers (MCA's) and microcomputer technology has provided spectrometric and sophisticated data handling capabilities which have made LSC a much more attractive analytical tool for environmental analyses. Because of these advances, low level LSC is now commonly used for the following analyses:

1. Measurement of natural series radionuclides. Many are now routinely measured at natural environmental levels in a range of environmental sample matrices. These include isotopes of radium (Ra), uranium (U), ^{210}Pb, ^{222}Rn, ^{231}Pa, and ^{234}Th.
2. Monitoring the environment around establishments associated with the nuclear power industry for anthropogenic radionuclides - principally beta emitters without significant gamma emissions - such as ^{3}H, ^{14}C, ^{35}S, ^{55}Fe, ^{85}Kr, $^{89,90}Sr$, ^{99}Tc, and ^{241}Pu.
3. Nuclear weapons decommissioning; measurement of gross alpha activities in airborne particulates and surface wipes.
4. Radiocarbon dating.
5. Ground water/environmental ^{3}H.

Section I.

Basic Principles

Chapter 1: Low Level LSC Theory

Sources of Background

Background contributions come from many sources (Table 1-1). These sources can be divided into those produced in the liquid scintillator and sample, and those which result from events outside the scintillator solution. Background that results from within the liquid scintillation cocktail is often referred to as quenchable, while background originating outside the cocktail is referred to as unquenchable (Horrocks, 1985).

Sources of Background

Source	**Contributor**
Vial	Cosmic ray interactions with the glass to produce Cerenkov radiation, secondary electrons, and gamma rays. Natural radioactivity in the vial walls or cap. Static charge on the vial.
Photomultiplier (PMT) and surrounding materials	Cosmic ray interactions with the glass to produce Cerenkov radiation, secondary electrons, and gamma rays. Natural radiation in PMT construction materials. Crosstalk from electric discharges or Cerenkov events. Afterpulsing in the PMT due to residual gas discharges.

Quenchable Background Sources

Source	**Contributor**
Liquid scintillation cocktail	Cosmic ray interactions and radioactive contamination of solvent and scintillator chemicals. Chemiluminescence and/or bioluminescence produced by the interaction of certain solvents with the sample.
Sample	Radionuclide contamination. Chemiluminescence produced by impurities in the sample or the addition of organic/inorganic base.

Table 1-1.

Because quenchable background is primarily due to cosmic ray or other high energy radiation interacting with the scintillator solution, the pulse height spectra (energy) of this type of background extend beyond the ^{3}H and ^{14}C energy ranges. Quenchable background increases with increased cocktail volume and is reduced by any agent that quenches the cocktail.

High energy cosmic radiation interacting with vial and PMT glass surfaces is the primary source of unquenchable background. However, the resulting Cerenkov events are primarily confined to the ^{3}H and ^{14}C energy regions, but have a distribution that is flat over a broad energy range and are unaffected by cocktail quench.

Quenchable and Unquenchable Background

Approximately 32% of the total background spectrum is due to quenchable events, while approximately 68% is due to unquenchable events. Quenchable background results from interactions of external radiation with the liquid scintillation solution or from sample contaminants. The light pulses so produced are similar to those of true beta events (Figure 1-1A). Most quenchable background events are caused by external high energy radiation since the particles or photons must penetrate the lead shielding, the reflector and the glass wall of the vial before interacting with the scintillation cocktail. Unquenchable background results from the interaction of cosmic radiation or natural radioactivity in the counting vial wall, with the glass envelope of the PMT's, as well as with other material surrounding the vial. Such background can be distinguished electronically from valid scintillation events because the pulse pattern that results is characterized by a series of trailing low-photon-yield afterpulses or bursts following the initial prompt pulse. This trailing burst is due to Cerenkov events resulting from the cosmic ray or other radioactive interactions with the vial or PMT glass surfaces. A typical pulse pattern due to unquenchable background is shown in Figure 1-1B.

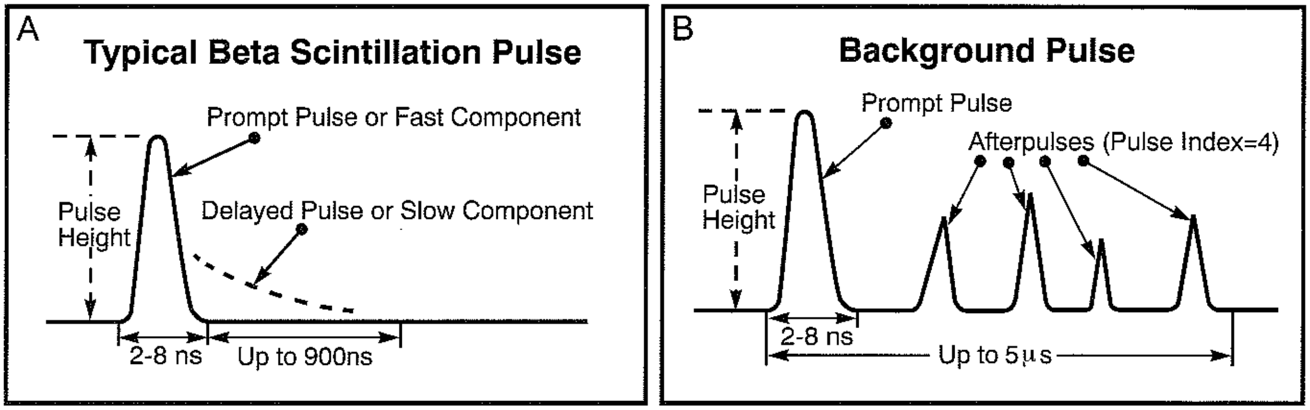

Figure 1-1.
Typical cocktail photoluminescence decay curve (A). Typical pulse pattern due to unquenchable background (afterpulse sizes are not to scale) (B).

Background Reduction Methods - Instrument Considerations

Until the introduction of commercially manufactured low level liquid scintillation counters, many background reduction methods were attempted by instrument users. They consisted mainly of modifications to existing instrumentation and included the following: increasing the amount of passive shielding, reducing the voltage applied to the photomultiplier tubes, masking the photomultiplier tubes or the vials to minimize crosstalk, or using alternative low background materials for vial construction (mainly quartz, delrin or Teflon™) (Tamers, 1965; Calf and Polach, 1974; Noakes, 1977; Haas, 1979; Gupta and Polach, 1985). In addition, a number of experimental devices incorporating cosmic guard detectors were fabricated (Pietig and Scharpenseel, 1964; Alessio et al., 1976; Punning and Rajamae, 1977; Iwakura et al., 1979; Jiang et al., 1983). However, it was not until background reduction features were combined with modern microprocessor technology that the full potential of low level LSC instrumentation was realized.

Modern low level instruments employ one or more of the following features to reduce background:

Enhanced Passive/Graded Shielding

Some instruments employ nearly 1000 kg of lead shielding. This reduces the background from environmental gamma photons associated with building materials and instrument construction materials, as well as the "soft" cosmic muon component of background. Such a shield may be lined internally with cadmium and copper to absorb secondary X-rays and thermal neutrons. Passive shielding does not remove the hard cosmic component.

Active Shielding

An active shield or guard detector consists of a volume scintillating material (*e.g.,* a plastic scintillator, such as NE-110, a mineral oil based scintillator, or even a large sodium iodide crystal) and two additional photomultiplier tubes, which surround the detector assembly, and are in anticoincidence with the sample PMT's. Events detected only by the guard detector or events simultaneously detected by the guard and sample PMT's are rejected. Typically, the guard will reject much of the residual environmental gamma radiation, the soft cosmic component, and the harder cosmic muon flux. This has the effect of reducing PMT crosstalk from Cerenkov light induced pulses which are primarily caused by the interaction of cosmic muons with the PMT's.

Pulse Discrimination Electronics

Pulse Shape Analysis (PSA)

A beta scintillation event is comprised of a fast (prompt) component and a delayed component. The majority of the light (derived from excited singlet states) is within the prompt component (typically 2-8 nanoseconds in duration). The delayed component (produced largely by the annihilation of triplet states) may persist for several hundred nanoseconds. The relative amounts of light in the prompt and delayed components has long been known to be dependent on the specific ionization induced by different types of particles. For example, the delayed component of an alpha induced pulse is typically longer in duration than a beta induced pulse. It is on this basis that PSA can be used for particle detection, which includes alpha/beta discrimination.

Although the most effective use of PSA is for alpha counting, the technique has also been used for background discrimination. The background of glass vials is characterized by long scintillation light pulses due to the interaction of cosmic or other environmental radiation with the vial. PSA is used to discriminate the long scintillation of the background from the shorter scintillations of true beta events.

PSA values are adjustable within a range of values. The optimum PSA (in which E^2/B is maximized) is determined by the user and specific for vial type and chemistry.

Pulse Amplitude Comparison (PAC)

This technique compares the ratio of the pulse amplitudes produced by the two PMT's. Photons produced in the cocktail during a decay event are evenly distributed and the number impinging on each photocathode will be similar; thus, the ratio of the pulse amplitudes will vary around a value of one. Photons produced in the vial wall or in the PMT's will show greater variation, *e.g.,* if a scintillation is produced through the interaction of a cosmic muon with a PMT, the amplitude of the pulse seen by one PMT will differ from that seen by the other, and the PAC ratio will deviate from unity. Therefore, the pulse amplitude ratios will be less evenly distributed.

Time-Resolved Liquid Scintillation Counting (TR-LSC®)

TR-LSC is a patented electronic technique used to reduce background count rates by discriminating out the unquenchable component of background from true beta events and the quenchable background on the basis of the number of afterpulses which follow a prompt pulse event.

TR-LSC Theory

Unquenchable background is the result of low photon yield Cerenkov events consisting of a prompt component followed by a delayed component comprised of a burst of afterpulses (of single photoelectron magnitude) which can continue for as long as five microseconds (Figure 1-1B) (Dressler and Spitzer, 1967; Jerde, Paterson and Stein, 1967; Roodbergen et al., 1972). Usually, a far greater number of afterpulses will result from an unquenchable background event than from a true scintillation event for a given energy. Valenta (1987) described burst counting circuitry to discriminate unquenchable background events from true beta events on the basis of the number of burst afterpulses which follow the prompt pulse. This is the basis of the TR-LSC background reduction feature employed in low level instruments manufactured by Packard Instrument Company. Each coincident event initiates a burst counter which counts the number of afterpulses occurring during a period of approximately five microseconds after the event. The total number of afterpulses is termed the pulse index. This is used to create a three dimensional spectral plot containing activity, energy, and time-resolved information for each detected event. Figure 1-2A demonstrates that a background sample produces a significant number of afterpulses or bursts at the low energy end of the spectrum. In contrast, an unquenched ^{3}H sample generates few afterpulses and only at the high energy end of the spectrum (Figure 1-2B). An air quenched ^{3}H sample prepared in the laboratory (Figure 1-2C) generates almost no afterpulses. By accepting only events with few or no afterpulses, a spectrum with a reduced background count rate may be obtained. Because there is a finite probability that sample events will cause afterpulses thereby leading to rejection of valid events, TR-LSC may reduce counting efficiency. In some applications rejection of valid events is more probable in: (1) deoxygenated samples, (2) long fluorescence life-time (slow) scintillators which produce a significant delayed component, and (3) higher energy beta emitters (energies greater than or equal to ^{14}C) where the delayed component persists, even in the presence of oxygen. The ability to optimize TR-LSC for all three of the above conditions is possible with the programmable feature of TR-LSC. Programmable TR-LSC is discussed in the next section under TR-LSC considerations.

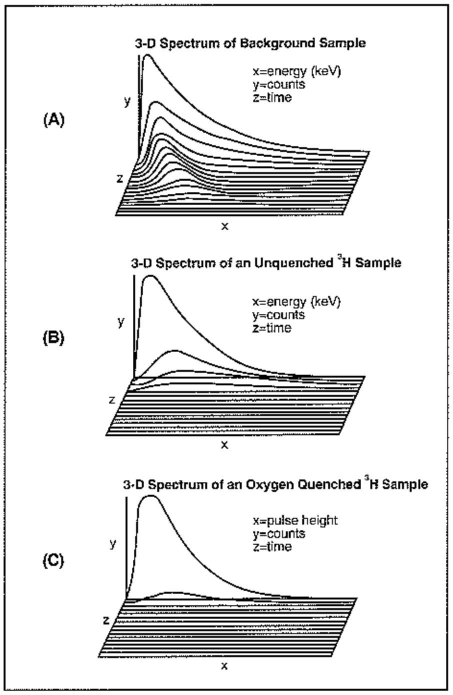

Figure 1-2.

Three dimensional plot of pulse height spectrum of background sample (A). The pulse index is the third dimension. Unquenched ^{3}H sample (B). Laboratory prepared ^{3}H sample (C).

TR-LSC Considerations

De-oxygenated Samples

Table 1-2 shows the effects on background and efficiency for ^{14}C-benzene which would be observed when samples are purged with nitrogen or oxygen. With TR-LSC (low level on), purging the samples with oxygen brings about a negligible change in efficiency within an open window but a considerable reduction within the optimum window due to quenching of the spectrum. Conversely, purging with nitrogen decreases efficiency, since the triplet states will not be quenched. This will have the effect of producing pulses with a significant delayed component; which in some cases are indistinguishable from background events. With the TR-LSC switched off (low level off), oxygen decreases efficiency in both the open and optimum windows while nitrogen has no effect. With TR-LSC switched on, nitrogen purging tends to reduce background count rates since the tailing of the pulses will be enhanced while oxygen will sharpen the pulses and so background will increase. With TR-LSC off, oxygen increases the background slightly. This is an effect of quenching rather than pulse shaping. Nitrogen has no effect on background with TR-LSC turned off.

	% Efficiency		Background (CPM)		
Purging	**(0-156 keV)**	**(11-90 keV)**	**(0-156 keV)**	**(11-90 keV)**	**tSIE**
A. Low level on					
None	89.70	71.60	6.50	2.19	595
Nitrogen	84.00	66.70	5.90	1.80	676
Oxygen	89.90	60.50	7.57	2.71	328
B. Low level off					
None	94.50	75.50	18.05	6.21	596
Nitrogen	94.50	75.20	17.93	6.18	675
Oxygen	91.50	61.90	19.18	6.74	329

Table 1-2.
Background count rates and efficiencies for ^{14}C-benzene from oxygen and nitrogen purged 20 mL vials using the Packard 2260 XL (4 g geometry).

The apparent constant efficiency for an oxygen purged sample, counted in an open window with low level enabled, is probably due to offsetting effects; oxygen quenches to lower efficiency while it also reduces the slow component and thereby increases efficiency in low level mode. The effects of purging may be further confirmed by examining the tSIE values. Predictably, nitrogen increases the tSIE while oxygen decreases it.

Cocktail Optimization

Rejection of some valid events can be brought about by long fluorescence life-time (slow) cocktails such as the di-isopropylnaphthalene (DIN) solvent based cocktails. Figure 1-3 demonstrates the differences in (average) pulse shape for ^{36}Cl which may be obtained from a slow (DIN based) and a fast (short fluorescence life-time) alkylbenzene based cocktail. The programmable feature of TR-LSC provides the ability to optimize the background rejection electronics to accommodate the pulse shaping effect of fast or slow solvent and fluor combinations. Refer to the section entitled Programmable TR-LSC for more details.

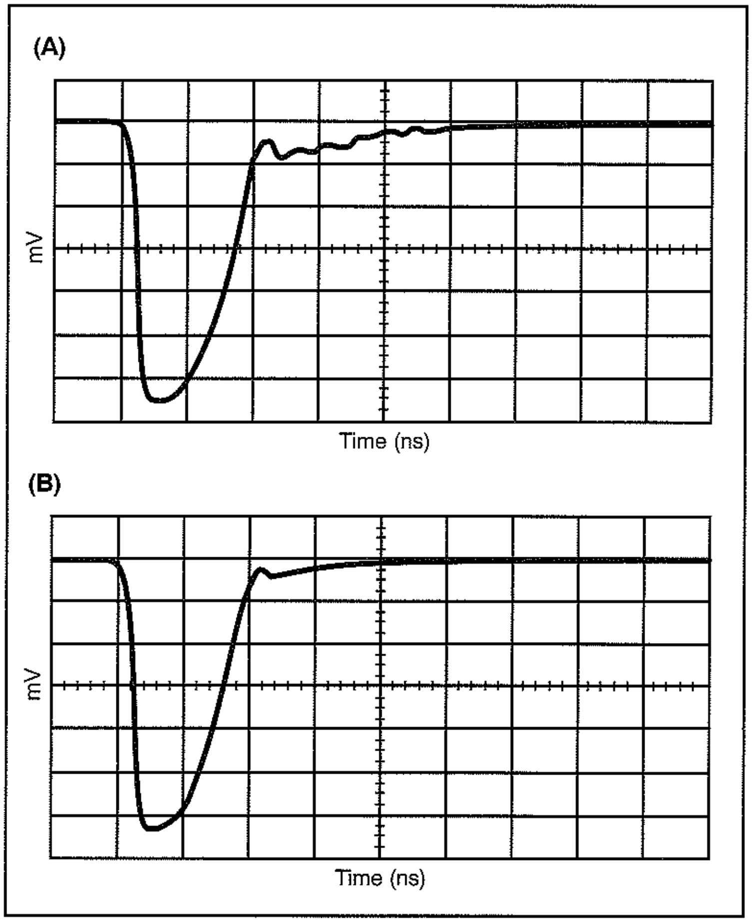

Figure 1-3.
Average ^{36}Cl pulse shape from a di-isopropylnaphthalene based (slow) cocktail (A).
Average pulse shape from an alkylbenzene based (fast) cocktail (B).

Isotope Energy

For higher energy beta emitters where the delayed component persists, rejection of valid events is more likely to occur. Figure 1-4 indicates pulse shapes derived for ^{3}H (A) and ^{36}Cl (B) in Insta-Gel® XF. The average ^{3}H and ^{36}Cl pulses represented in Figures 1-4A and 1-4B show that ^{36}Cl has a slightly longer pulse duration.

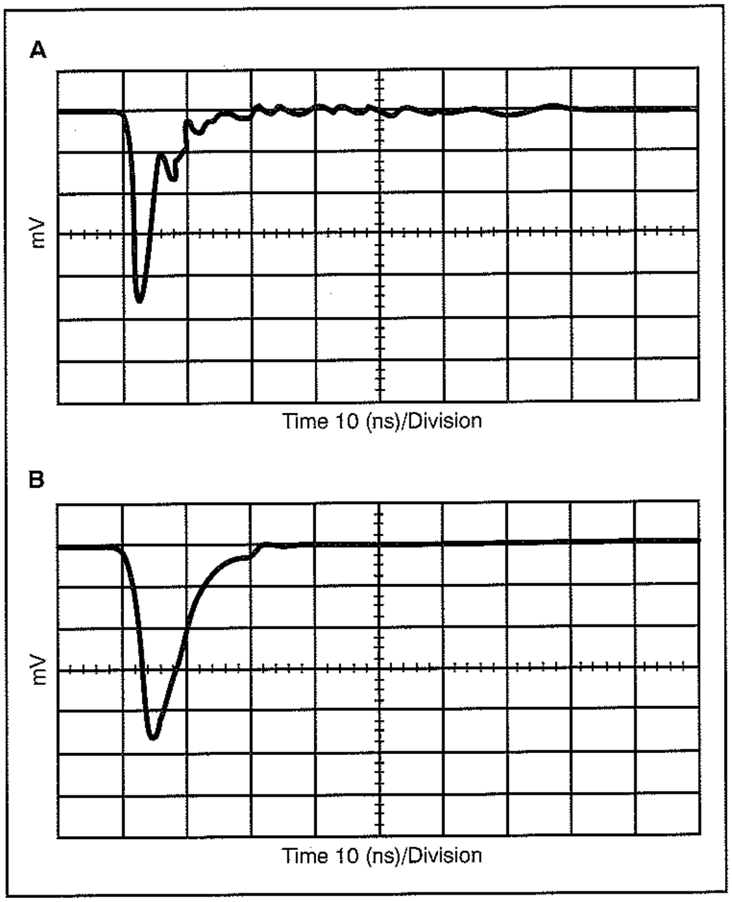

Figure 1-4.
Average pulse shape for ^{3}H (A) and ^{36}Cl (B) in Insta-Gel XF.

Programmable TR-LSC

TR-LSC has a preset delay of 75 nanoseconds (nsec) between the onset of the prompt pulse and the commencement of afterpulse or burst counting. Programmable TR-LSC, on the other hand, provides the ability to adjust the delay. This is particularly pertinent given the relatively recent introduction and current widespread use of environmentally safe cocktails based on DIN. As discussed previously, DIN pulses have much longer duration as demonstrated in Figure 1-3. Additionally, increasing the delay before counting afterpulses will compensate for the lowered counting efficiency of higher energy radionuclides. Graphic representations of non-programmable and programmable TR-LSC are shown in Figure 1-5.

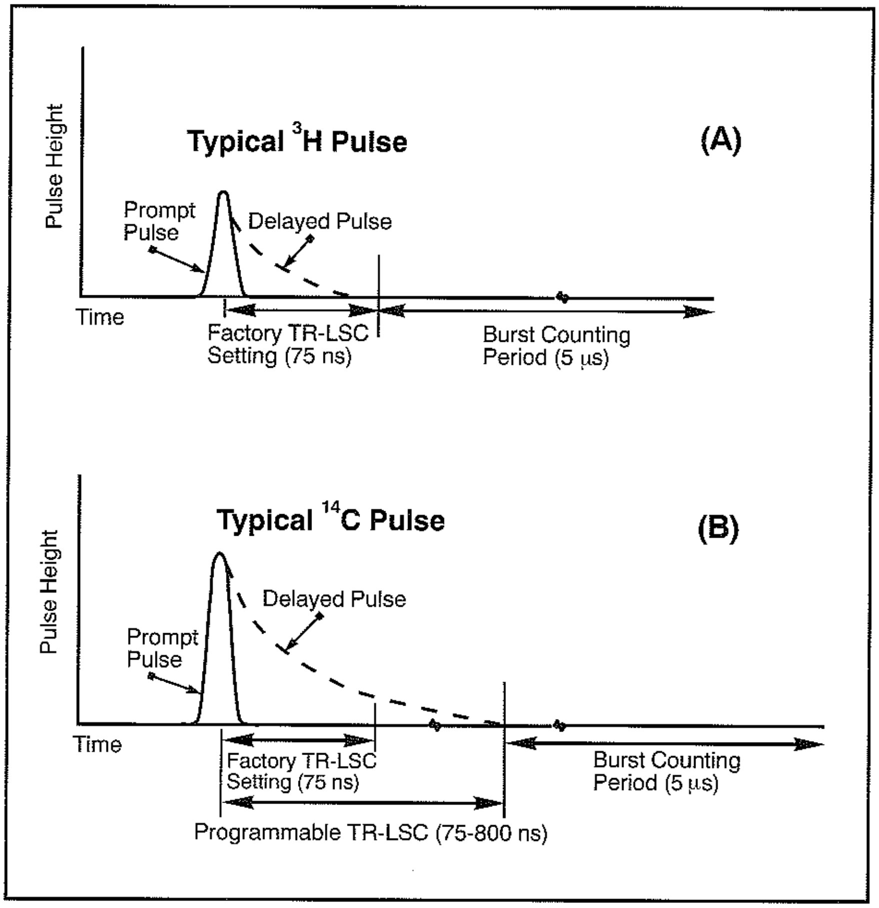

Figure 1-5.
Graphical representation of conventional TR-LSC (A) and programmable TR-LSC (B).

Programmable TR-LSC allows the user to adjust the delay from the preset value of 75 nsec to a maximum of 800 nsec to accommodate both slow cocktails and high E_{max} radionuclides. Figure 1-6 illustrates that for both ^{14}C and $^{90}Sr/^{90}Y$, the optimum burst delay setting provides a significant improvement in counting sensitivity over the preset value for both a fast (Insta-Gel XF) and a slow (Ultima Gold® XR) cocktail.

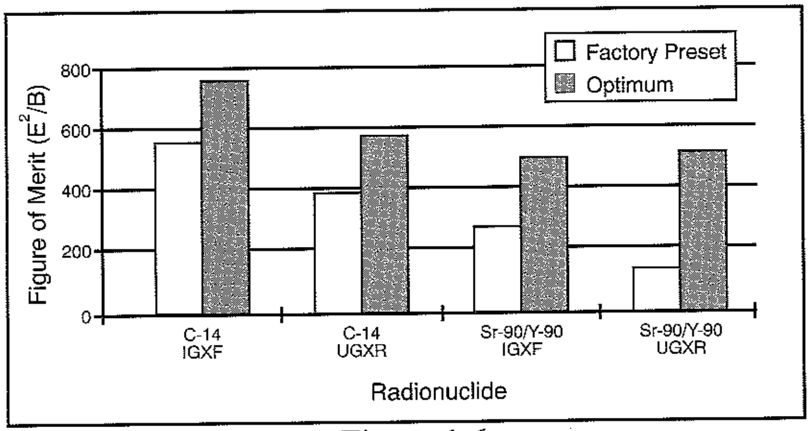

Figure 1-6.

Figure of merit at the factory and optimum TR-LSC settings. (All samples 50% water loaded, optimum windows).

TR-LSC Detector Guards

Slow Scintillating Plastic

An additional feature that reduces background is incorporated into extra low level (XL) LSC models employing TR-LSC. Currently this feature is in the form of a modified detector assembly which consists of a long fluorescence life-time scintillating plastic that surrounds the sample vial in the counting chamber (Valenta and Noakes, 1989). This plastic detector guard is optically coupled to the face of each PMT and is coated with a reflective material. It has very good optical transmission in the 4000-5000 Angstrom range and the decay time of the slower component of the scintillating plastic is approximately 250 nsec. When the slow fluor in the plastic (external to the sample) is excited by a high energy gamma or muon event which satisfies the instrument coincidence requirement, the phosphorescence of the slow fluor provides an extended burst of afterpulses which aids the background discrimination. Thus, the plastic acts as an active guard. This same plastic has also been used to produce vial holders which will accommodate 7 mL vials. The vial holders will enhance the background reduction even further when used in conjunction with the plastic guard; however, the vial holders may also be used effectively in a TR-LSC instrument which does not contain the guard. One factor which must be stressed when using the plastic guard is that the absorption spectrum of the guard should not match the emission spectrum of the cocktail. An appropriate secondary scintillator is suggested to ensure that the cocktail emission spectrum does not overlap the absorption spectrum of the guard.

Bismuth Germanate (BGO)

A new detector guard based on BGO ($Bi_4Ge_3O_{12}$) has been developed by Packard Instrument Company. BGO is a non-hygroscopic scintillator which exhibits low afterglow. Its high stopping power (Z = 83; density = 7.13 g/cm^3) makes BGO an effective cosmic guard. BGO gamma detectors were first introduced commercially (circa 1979) for use in Computerized Tomography (CT) applications. Because of its high gamma cross-section, BGO has also been used in Positron Emission Tomography (PET), high energy calorimetry, and medium energy physics (Bicron Product Bulletin SC-103A).

As a detector guard for LSC, BGO is used to discriminate against the gamma and muon components of cosmic background. Events that interact with BGO produce pulses that are of much longer duration than beta and alpha pulses in cocktail. If an event interacts with the detector and satisfies the coincidence requirement, time-resolved pulse decay electronics and TR-LSC are then used to discriminate the longer cosmic background pulses from beta or alpha pulses. Similar to the slow scintillating plastic guard already discussed, the BGO guard completely surrounds the sample vial in the modified detector assembly. In addition, BGO vial holders designed to accommodate 7 mL vials may be used to provide additional background discrimination. These vial holders work best in an instrument that has the BGO guard detector and electronics, but also perform quite well in other TR-LSC systems operating in the low level count mode.

Results using the BGO detector guard show greatly improved performance versus low level or low level with the plastic guard. Table 1-3, 1-4, and 1-5 show the performance of the BGO detector in the low level count mode (LLCM). Table 1-3 shows the results for ^{3}H and ^{14}C in LLCM for the normal reflector system and the BGO guard system for a 10 mL PPO/dimethyl POPOP O_2 quenched toluene cocktail in a 20 mL, flame-sealed, borosilicate glass ampoule (Noakes and Valenta, 1994). The BGO results for ^{3}H and ^{14}C yield a 127% and 300% increase, respectively, in E^2/B versus the normal reflector system. ^{3}H BGO performance for a 6 mL water sample in 9 mL of Ultima Gold AB cocktail in a plastic 20 mL vial is shown in Table 1-4.

		Normal Reflector			**BGO Detector**		
Samples	**Window (keV)**	**Efficiency (%)**	**Background (CPM)**	**E^2/B**	**Efficiency (%)**	**Background (CPM)**	**E^2/B**
H-3	1-18.6	54.48	5.46	543.60	53.97	2.36	1234.2
C-14	14.5-97.5	63.88	2.56	1594.00	62.94	0.63	6306.0

Table 1-3.
Comparison of beta counting performance in LLCM
for a normal reflector versus a BGO detector.

^{3}H Window (keV)	**Efficiency (%)**	**Background (CPM)**	**E^2/B**
0.50-6.50	27.30	1.25	596.23

Table 1-4.
^{3}H counting performance for a 40% water loaded sample using the BGO detector.

The results in Table 1-4 are significant because the sample:cocktail ratio is more representative of an environmental ^{3}H application which requires a large sample:cocktail volume ratio. In addition, an E^2/B of 596 is more than twice the previously reported value (approximately 260) by Dr. Gordon Cook in an unpublished study for a similarly prepared sample (40% water load) in a plastic vial. In that study, Dr. Cook reported a background of 2.68 CPM and a counting efficiency of 26.4% for an optimum window.

Table 1-5 compares the ^{14}C counting performance between LLCM, LLCM with the scintillating plastic guard (with and without the plastic vial holders), and the BGO guard (with and without BGO vial holders). 3 mL benzene samples were prepared in 7 mL low ^{40}K glass vials with Teflon® (E.I. DuPont, Wilmington, Delaware) cap liners (Valenta, 1994). The samples contained a primary fluor of butyl PBD (10.54 mg L^{-1} benzene) and a secondary fluor of bis-MSB (3.52 mg L^{-1} benzene). ^{14}C samples were counted for 60 minutes and backgrounds for 960 minutes.

The results in Table 1-5 indicate a 50% increase in E^2/B for a TR-LSC instrument equipped with the BGO detector guard, versus a TR-LSC instrument with a plastic guard. Comparing a BGO guard and holder to a plastic guard and holder, the BGO yields a 100% increase in E^2/B. Results from the combined BGO guard and vial holder yield approximately a 400% E^2/B increase over LLCM alone with no guard and no vial holder.

Packard Tri-Carb configuration	Window (keV)	Background (CPM)	Efficiency (%)	E^2/B
LLCM (No guard, no vial holder)	19.5-95.5	0.76	54.05	3837
With plastic vial holder	12.5-89.5	0.63	61.00	5906
With plastic detector guard	10-81	0.51	66.20	8593
With plastic vial holder and plastic detector guard	11.5-81	0.43	64.00	9526
With BGO detector guard	15.5-95	0.35	67.00	12826
With BGO vial holder and BGO detector guard	18.5-92	0.20	62.00	19220

Table 1-5.
^{14}C low level counting performance with various LLCM configurations.

Counting Region Optimization

The limit of detection of a measurement is determined by the signal-to-background ratio. In liquid scintillation counting, the signal-to-background ratio is expressed as the square of the detection efficiency divided by the background (E^2/B) and is termed the Figure of Merit (FOM). Counting region optimization is used to maximize the E^2/B to improve the limit of detection.

Even without background pulse discrimination, optimizing the counting regions can provide significant gains in FOM. The effect of region setting is shown in Table 1-6 for data acquired in both normal and low level count mode using a Packard Tri-Carb® LSC.

	Region Settings (keV)			
	5-156	10-102	18-102	30-100
Normal Count Mode				
% Efficiency	92.02	81.87	67.17	46.76
Background	12.04	7.07	3.83	2.05
E^2/B	703	948	1178	1067
Low Level Count Mode				
% Efficiency	78.89	70.10	57.99	40.82
Background	2.93	1.38	0.90	0.60
E^2/B	2124	3561	3736	2777

Table 1-6.
The effect of optimizing the region setting on FOM for ^{14}C benzene, 3.5 mL small vial, 6 g L^{-1} PPO, 0.1 g L^{-1} POPOP.

Region Optimization Procedures and Requirements

Constant Quench Conditions

A blank and a standard sample containing the radionuclide of interest are required to optimize the counting region for that radionuclide.

Requirements for proper region optimization include:

1. The standard containing the radionuclide of interest should have sufficient known activity, and must be in the same cocktail and quenched to the same degree as the unknown samples. Equivalent quench assures that the appropriate region is chosen for the sample which gives the optimum E^2/B. Different quench levels will shift the counts in or out of the region and thus affect the counting efficiency in that region. The assumption is made that the unknown(s) will be quenched to the same degree. In reality, there will be slight differences in quench. For this reason, once the optimum region is determined, quench correction should be applied to calculate absolute activity (DPM). A quench curve encompassing the optimum region should be used to account for the minor quench variations in the samples.

2. The blank should be quenched to the same degree as the standard and the unknown samples. Minor fluctuations in the quench will result in only small changes in the blank activity. Therefore, it is generally not necessary to construct a quench curve for the blank. Small changes in the blank spectrum will not adversely affect the optimum window determination.

By using a representative standard and an appropriate blank, a reasonable approximation of the optimum counting window can be determined for unknown samples near background levels. In some cases, it may be possible to use the unknown sample as the standard if the activity is several times the background. In this case, the count time should be long enough to minimize the error associated with the measurement. However, counting efficiency must still be determined.

Region optimization can be performed automatically through the software on the Packard Tri-Carb 2500 and 2700 series LSC's using an appropriate blank and a representative radionuclide standard.

If automatic region optimization is not available, a reasonable approximation of an optimum window can be made by viewing the sample and background spectrum, and performing a manual calculation of E^2/B from the CPM in the chosen regions of interest.

Variable Quench Conditions

For samples that have highly variable quench, it may not be practical to maintain a fixed counting region and still maintain maximum counting sensitivity. A practical solution is to determine the equivalent unquenched spectral endpoint by counting the least quenched sample in the batch of unknowns or by counting the least quenched standard of the quench set (reverse region compensation is a Packard Tri-Carb feature that can determine the equivalent unquenched endpoint of an unknown automatically). Quench standards and samples are counted using this region setting with Automatic Efficiency Compensation (AEC) or an equivalent technique. AEC adjusts the upper limit of the counting region to the observed spectral endpoint of the quenched sample. By adjusting the region in this manner, background is reduced and high counting efficiency is maintained. For variably quenched samples, using AEC represents the best choice for maintaining high sensitivity. AEC is available on all Packard Tri-Carb LSC's.

Background Reduction Methods - Environment

Temperature

Temperature plays an important role in the operation of early liquid scintillation counters. The noise rate of earlier PMT's was much greater than today's PMT's and very dependent on operating temperature. For this reason, older instruments were refrigerated to reduce noise, even though the coincidence circuit significantly reduced the amount of noise that contributed to the background count rate. Refrigeration is not as critical in modern instruments because of the introduction of bialkali tubes and improvements in tube manufacturing. If the noise rate exceeds about 30,000 CPM per tube, the actual chance coincident rate contribution to the background is approximately 0.6 CPM. This value is calculated by the following formula: $N_c = 2(\tau/60) \times N_1N_2$ where τ is the resolving time of the coincidence circuit in nanoseconds (typically 20) and N_1 and N_2 are the singles rates observed in PMT 1 and 2 in CPM. Today, refrigeration is often used for reasons other than cooling the PMT tubes. Temperature control may be necessary either for special sample preparation or severe operating conditions.

Counting Room

High energy radiation can interact with materials in the vicinity of the liquid scintillator or the PMT's. These interactions result in the production of Cerenkov radiation, secondary electrons, and low energy gamma and X-rays. Low energy electrons will contribute to the background only when they are produced in the liquid scintillator. Low energy X-rays have more influence because of their greater penetration. Shielding material can be a source of these X-rays because of the high cross section for high energy cosmic rays. Thus the lead shield will be a source of Pb X-rays. For this reason, some manufacturers use enhanced passive graded shielding in which the shielding is lined with cadmium or copper to eliminate these secondary X-rays. Graded shielding is not required on Packard liquid scintillation analyzers because TR-LSC electronic background reduction is very effective at eliminating the background which is caused by the interaction of secondary X-rays with the counting chamber. In addition, background due to Cerenkov radiation, which is the result of the slowing of high energy cosmic electrons in the glass surfaces of the PMT's or the counting vial, is also effectively eliminated by TR-LSC.

However, the amount of cosmic or other environmental radiation will affect the background observed. Specially shielded or below ground level counting rooms may be effective at reducing instrument background. If practical, choosing a location that provides additional shielding against cosmic or environmental radiation will reduce the background.

Vial Type

Any natural radioactivity in the walls or cap will obviously increase the background count rate. For this reason, glass vials containing very little ^{40}K are desirable. Plastic vials display lower background than glass. However, care must be exercised when choosing certain cocktails when using plastic vials. Typically, cocktails based on di-isopropylnaphthalene (DIN) and phenyl-ortho-xylylethane (PXE) will not attack the plastic vial. Refer to section II, chapter 4 on ^{3}H for more detail.

Cocktail Choice

Overall, liquid scintillators should be prepared with reagents that are low in natural radioactivity. Cocktails that exhibit low background and high sample loading capacity are desirable for environmental counting. Table 1-5 contains some ^{3}H background and efficiency data on three cocktails used in environmental counting: Pico-Fluor LLT (PFLLT), Ultima Gold XR (UGXR), and Ultima Gold LLT (UGLLT). PFLLT is an environmental cocktail with special application for high volume ^{3}H counting; UGXR is a new generation safer cocktail capable of 50% water load capacity; and UGLLT is a new environmental cocktail designed for high sample loads, versatility and high efficiency. Results are reported in Table 1-7 for both normal count mode and low level count mode using TR-LSC background reduction.

Normal Count Mode

Cocktail	Vial	Water Load %	Background (0-18.6 keV)	Background (0.5-5.0 keV)	Efficiency (0-18.6 keV)	Efficiency (0.5-5.0 keV)
PFLLT	Plastic	0.5	9.65	3.56	27.19	26.11
UGLLT	Plastic	0.5	10.15	3.88	31.71	29.31
UGXR	Plastic	0.5	12.4	NA	26.9	NA
PFLLT	Glass	0.5	16.32	7.79	31.23	29.34
UGLLT	Glass	0.5	16.87	8.04	30.95	28.91
UGXR	Glass	0.5	19.5	NA	25.9	NA

Low Level Count Mode

Cocktail	Vial	Water Load %	Background (0-18.6 keV)	Background (0.5-5.0 keV)	Efficiency (0-18.6 keV)	Efficiency (0.5-5.0 keV)
PFLLT	Plastic	0.5	6.22	2.91	25.58	24.68
UGLLT	Plastic	0.5	5.76	3.65	26.06	24.58
UGXR	Plastic	0.5	6	NA	23	24.58
PFLLT	Glass	0.5	6.72	3.52	29.24	27.68
UGLLT	Glass	0.5	5.75	3.32	25.73	24.45
UGXR	Glass	0.5	6.8	NA	22.6	NA

NA = Data not available in this study.

Table 1-7.

Normal and low level count mode (TR-LSC) performance for several types of cocktails in plastic and glass vials.

References

Alessio, M., Allegri, L., Bella, F. and Improta, S. 1976. Study of background characteristics by means of high efficiency liquid scintillation counter. *Nuclear Instruments & Methods.* 137: 537- 543.

Bicron Corporation. 1988. *BGO ($Bi_4Ge_3O_{12}$) Product Bulletin SC-103A.* Newbury, Ohio.

Calf, G. E. and Polach, H. A. 1974. Teflon vials for liquid scintillation counting of carbon-14 samples. In *Liquid Scintillation Counting: Recent Developments*, ed. Stanley, P. E., and Scoggins, B., 224-234. New York, Academic Press.

Dressler, K. and Spitzer, L. 1967. Photomultiplier tube pulses induced by rays. *Review of Scientific Instrumentation.* 38: 436-438.

Gupta, S. K. and Polach, H. A. 1985. Radiocarbon Dating at ANU, *Radiocarbon Laboratory.* ANU.

Haas, H. 1979. Specific problems with liquid scintillation counting of small benzene volumes and background count rate estimations. In *Proceedings of the 9th International ^{14}C Conference*, ed. Berger, R. and Suess, H. E., 246-255. Berkeley, University of California Press.

Horrocks, D. L. 1985. Studies of background sources in liquid scintillation counting. *Int. J. Appl. Radiat. Isot.* 36: 609- 617.

Iwakura, T., Kasida, Y., Inoue, Y. and Tokunaga, N. 1979. A low-background liquid scintillation counter for measurement of low level tritium. In *Behavior of Tritium in the Environment*, IAEA Proceedings Series, 163-171. IAEA, Vienna.

Jerde, R. L., Paterson, L. E. and Stein, W. 1967. Effect of high energy radiations on noise pulses from photomultiplier tubes. *Review of Scientific Instrumentation*, 38: 1387-1395.

Jiang, H., Luu, S., Fu, S., Zhang, W., Zhang, T., Ye, Y., Li, M., Fu, P., Wang, S., Peng, Ch. and Jiang, P. 1983. Model DYS low level liquid scintillation counter. In *Advances in Scintillation Counting*, ed. McQuarrie, S. A., Ediss, C. and Wiebe, L. I., 478-493. University of Alberta, Alberta Press.

Noakes, J. E. 1977. Considerations for achieving low level radioactivity measurements with liquid scintillation counters. In *Liquid Scintillation Counting*, ed. Crook, M.A. and Johnson, P., 4:189-206. London, Heyden.

Noakes, J. E. and Valenta R. J. 1994. The role of $Bi_4Ge_3O_{12}$ as an auxiliary scintillator for α, β, γ liquid scintillation counting and low level counting. Paper presented at the International Conference on *Advances in Liquid Scintillation Spectrometry (LSC '94)* Glasgow. *Radiocarbon*, in press.

Pietig, F. von. and Scharpenseel H. W. 1964. Alterbestimmung mit flussigheits-scintillations-spectrometer, uber die wirksamkeit von abschirmungsabnahmen. *Atompraxis*, 7: 1-3.

Punning, J. M. and Rajamae, R. 1977. Some possibilities for decreasing the background of liquid scintillation beta-ray counter. In *Low Radioactivity Measurements and Applications*, ed. Povinec, P. and Usacev, S., 169-171. Bratislava, Slovenske Pedagogicke Nakladatelstvo.

Roodenberg, S., Kroondijk, R. and Verhuel, H. 1972. Cerenkov radiation in photomultiplier windows and the resulting time shift in delayed coincidence time spectra. *Nuclear Instruments and Methods in Physics Research*, 105: 551-555.

Tamers, M. A. 1965. Routine carbon-14 dating using liquid scintillation techniques. In *Proceedings of the 6th International Conference on Radiocarbon and Tritium*, ed. Chatters, R. M. and Olson, E. A., 53-67.

Valenta 1987. Reduced background scintillation counting. U.S. Patent No. 4,651,006.

Valenta, B. 1994. Personal Communication, Packard Instrument Company. Meriden, Connecticut.

Valenta & Noakes 1989. Liquid scintillation measurement system with active guard shield. U.S. Patent No. 4,833,326.

Chapter 2: Statistics of Low Level Counting

The %2s Value and Why It Is an Important Consideration in Nuclear Counting

Radioactive decay is a random event. The number of decay events per unit time is variable. Counting statistics provide the means to describe the average behavior of all nuclear decays in a sample and are used to express the probability of obtaining a given count within a certain confidence limit. By applying counting statistics, the validity of a single count determination as being representative of the true count rate may be determined.

For example, if a sample is counted ten times, the CPM values obtained would not all be the same (Table 2-1). If the individual observed values are plotted in CPM intervals on the x-axis and the frequency of occurrence of each value in the interval is plotted on the y-axis, there would be a distribution similar to the one shown in Figure 2-1. The familiar bell-shaped curve that is superimposed on the actual count data represents what is known as a normal or Gaussian distribution.[1] In a normal distribution, the mean, median (the middle value in the distribution), and the mode (the most frequent value) are all the same. Notice also that this type of distribution is symmetrical and has only one mode. If the sample were counted more than ten times, the data would more closely approximate the normal curve shape and the mean value would more closely approximate the true count value. As with all distributions, this one is continuous for all values of X.

Count #	**CPM**	**Histogram**	
1.	46704	CPM interval	Frequency
2.	46685	1. 46400-46499	1
3.	46685	2. 46500-46599	1111
4.	46495	3. 46600-46699	111
5.	46827	4. 46700-46799	1
6.	46566	5. 46800-46899	1
7.	46514		
8.	46557		
9.	46548		
10.	46625		
mean	46615		

Table 2-1.
Count data summary of counting a sample ten times.

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[1] Count data are actually defined by another type of distribution called a Poisson distribution. However, given a sufficient number of events, the Poisson distribution and the normal distribution are approximately the same.

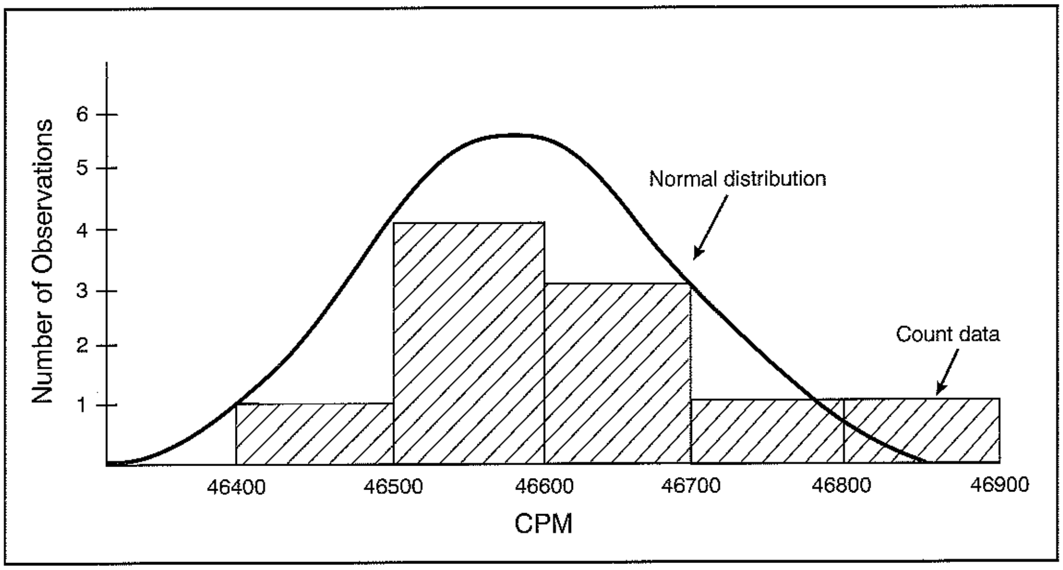


Figure 2-1.
Frequency distribution of counts for a sample counted ten times.

There is a probability of observing values in selected intervals under the curve. It is reasonable to conclude that the probability of observing a value with an interval being the entire area under the curve is 1.00.

Therefore, an observed count will fall somewhere on the x-axis. In nuclear counting, one can use these probabilities to estimate the counting error associated with any determination or to what degree the observed value deviates from the true value (mean). This is achieved by calculating a value called the standard deviation (abbreviated as "s"). For a normal distribution, the probability of an observed value falling within ±1s is 68%. This is the confidence limit. In nuclear counting, it is desirable to work with a higher confidence limit of ±2s from the mean or 95.5% confidence. This means that the probability of the observed count being within ±2s from the mean will be 95.5% and that 4.5% of the time the observed count will fall outside of this range (recall that the mean is an approximation of the true count value; the more counts accumulated, the more accurate the approximation). Stated another way, 95.5% of the time, the observed count will be within ±2s of the true count. This concept may be applied to nuclear counting by calculating the standard deviation from the total counts observed in one determination. From basic statistics, the master equation for counting statistics is the following:

Equation 1. $s = (\text{total counts})^{1/2}$

From the above discussion, it is clear that the observed count may be expressed as that value ± 2s. Substituting real numbers, a sample counted for one minute to 9500 counts gives an s value of

$$s = (9500)^{1/2} = 97.5$$

$$\text{and } 2{*}s = 2(97.5) = 195$$

The observed counts can then be described as 9500 ±195 counts. Reporting the data in this way gives an indication of the error associated with an individual determination (95.5% of the time the observed count will be within ± 195 counts of the true count). It is obvious that the standard deviation can be a relatively large number. For this reason, the %2s value is normally used to report counting errors.

Stated simply, the %2s value is the 2s value expressed as a percentage of the total counts. Mathematically this is represented by Equation 2.

Equation 2. $\%2s = \frac{2 * s * 100}{\text{total counts}}$

Substituting the previously used numbers...

$$\%2s = (2*97.5*100)/9500 = 2.05\%$$

Equation 2 may be mathematically altered to derive the familiar formula for computing %2s shown in Equation 3.

Equation 3. $\frac{2 * s * 100}{\text{total counts}} = \frac{2 * \text{total counts}^{1/2} * 100}{\text{total counts}^{1/2} * \text{total counts}^{1/2}} = \frac{200}{\text{total counts}^{1/2}}$

Net Count Rate Statistics

Since data are normally acquired as CPM, it is often necessary to report %2s as a function of count rate. Therefore, total counts are related to count rate (CPM) by the expression:

Total Counts= CPM * time(minutes), therefore %2s for count rate becomes Equation 4.

Equation 4. $\%2s\ (\text{count rate}) = \frac{200}{(\text{CPM} * \text{time})^{1/2}}$

For situations in which the sample count rate is very near the background (for instance, a low level environmental sample), the background contributes more significantly to the overall count rate. In this situation, the statistics of net count rate must be considered to adequately assess the counting statistics of the sample. The net count rate is therefore obtained by subtracting the observed background from the observed count rate, as shown in Equation 5.

Equation 5. net counts = observed sample counts - observed background counts

The net counting error (standard deviation or s) is then the square root of the sum of the squares of the background standard deviation and the sample standard deviation. Mathematically, this is expressed as:

Equation 6. $S_{Net} = (s^2_{gross} + s^2_{background})^{1/2}$

These two factors are applied to the count data as follows:

Equation 7. $s = (\text{CPM}_{sample}/T_{sample} + \text{CPM}_{bkg}/T_{bkg})^{1/2}$

where T_{sample} = counting time of the sample

T_{bkg} = counting time of the background

Substituting 50 for CPM_{sample}, 60 for T_{sample}, 10 for CPM_{bkg} and 100 for T_{bkg}:

$$s = (50/60 + 10/100)^{1/2} = 0.97$$

The net CPM ± is then expressed as (50 CPM - 10 CPM) or 40 ± 0.97 CPM.

To calculate the %2s, we substitute the values into Equation 8.

Equation 8. $\%2s = 100*2*s/(\text{CPM}_{sample} - \text{CPM}_{bkg})$

$\%2s = 100*2*0.97/(50 - 10)$

$\%2s = 4.85\%$

Thus, the result is expressed as 40 CPM ± 4.85%.

Note that this error is larger than it would be if the background counts were not considered:

$$\%2s = 200/(\text{total counts})^{1/2} = 200/(3000\ )^{1/2} = 3.65\%$$

For samples with activity near background levels, the net count rate %2s error calculation (Equations 7 and 8) must be used.

Time Required to Achieve a Desired %2s Error

For paired sample measurements of sample and background, the counting time required to achieve a desired error is defined in Equation 9.

Equation 9. $$T_s = \frac{(40000)(CPM_S + CPM_b)}{(\%2s)^2\,(CPM_s\text{-}CPM_b)^2}$$

where CPM_s = CPM of sample

CPM_b = CPM of background

%2s = desired %2s of analysis

T_s = count time (minutes) required to analyze the sample and the background to the required %2s precision level.

As an example, consider a sample which contains a total activity of ten CPM with a background of three CPM and a required %2s error of 5%. Substituting these values in the equation gives the following:

$$T_s = 40{,}000 * (10+3)/(5)^2 * (10\text{-}3)^2$$

$$T_s = 424 \text{ minutes}$$

If background is not considered, then the calculation becomes:

$$T_s = 40{,}000 * (10)/(5)^2 * (10)^2$$

$$T_s = 160 \text{ minutes}$$

If the background is not considered, then the time to achieve the desired error is underestimated. Equation 9 is a mathematical derivation of Equation 8.

Limit of Detection

Various mathematical expressions have been described to define limit of detection. Many terms are often used interchangeably such as lower limit of detection, sensitivity, minimum detectable activity, and others. In fact, depending on the expression used, the detection limit can actually encompass three orders of magnitude (Currie, 1968). The confusion persists in the literature such that the mathematical working expression used to determine a detection limit should be given in order to avoid ambiguity. This is absolutely essential if one is to compare detection limits for different instruments and methods. However, many standards and regulations have accepted Currie's expressions for limit of detection. Thus, the definition for limit of detection that will be discussed in this document is the one proposed by Currie.

Currie defines two fundamental aspects of detection. The first is that of deciding whether an observed signal is indeed a detected "true" signal (an *a posteriori* or after-the-fact decision). This is a qualitative decision and is subject to two kinds of errors: concluding that the signal is true when it is not (α or error of the first kind or Type I error), and failing to conclude that it is true when it is true (β or error of the second kind or Type II error). Type I errors (α) are used to establish the concept of the Critical Level, L_c (the level above which an observed signal would be detected). In nuclear counting, 5% is an acceptable value for α. This means that there is a 5% probability of falsely concluding that the signal is true when it is not. The correct conclusion is made 95% ($1-\alpha$) of the time. The working mathematical expression from Currie for L_c is:

$$L_c = 2.33\ B^{1/2}$$

where B is the total counts of an appropriate blank counted for the same time as the sample. An appropriate blank is defined as a sample which is identical, in principle, to the sample of interest, except that the substance of interest is absent or small when compared to the standard deviation of the blank (Currie, 1968). Once L_c is established with its established error level for α, the true net signal that can reliably be detected (the Detection Limit) is defined as:

$$L_d = 4.65\ B^{1/2}$$

This expression is derived from the L_c and an acceptable level of β (Type II error). An acceptable value for β is 5%; a 5% probability that a true signal will be missed. Conversely, $1-\beta$ or 95% of the time the conclusion that a signal was true will be correct. Thus, L_d is determined by L_c and accounts for both Type I and Type II errors. The 4.65 factor is derived from statistics and accounts for a 5% probability of making a Type I and a Type II error. Refer to Currie, 1968, for a discussion of this derivation. For radioactivity calculations, 2.71 is often added to the L_d term to account for the zero blank case which corresponds to a 5% probability of a false negative. Sometimes, the number is simply rounded to 3. ANSI N13.30, *Performance Criteria for Radiobioassay,* uses the above mentioned formula with 3 instead of 2.71.

The term "lower limit of detection" (LLD), as often referred to in literature, is used to report the L_d in terms of units and accounts for any other factors that will influence the calculation. Expressed mathematically, the equation for LLD for a paired sample and blank is:

$$LLD = L_d/K$$

where K = a series of factors multiplied together and grouped as one:

K = {(activity units)(efficiency)(aliquot size)(abundance)(count time)(chemical yield)(decay correction)} and applied where appropriate.

Specifically, the LLD is the smallest concentration of material that yields a net count above background with a 95% probability (5% chance of a false negative) with no more than a 5% probability of concluding that a blank is a true signal (false positive). Essentially, LLD is equivalent to minimal detectable activity (MDA).

Further modification of the LLD expression has been used when the total background acquired is less than 70 counts (Prichard et al., 1992) which also accounts for systematic errors in B (blank) and in any calibration factor that may be applied. A more conservative expression for LLD becomes

$$LLD = 1.1\ L_d/K$$

where $L_d = 0.1B + 4.65B^{1/2} + 2.71$

The above formulae apply to the background and sample counted as pairs. If the background is well known, the expressions for L_c, L_d and LLD will change only slightly. Table 2-2 summarizes the working expressions for L_c, L_d and LLD.

	Background and sample counted as pairs (*i.e.*, at the same time)	**If background is well known**
	Background < 70 counts	
L_c	$0.1B + 2.33B^{1/2}$	$0.1B + 1.64B^{1/2}$
L_d	$1.1(2.71 + 4.65B^{1/2} + 0.1\ B)$	$1.1(2.71 + 3.29B^{1/2} + 0.1B)$
LLD	$L_d/(K)$	
	Background > 70 counts	
L_c	$2.33B^{1/2}$	$1.64B^{1/2}$
L_d	$4.65B^{1/2}$	$3.29B_{1/2}$
LLD	L_d/K	

Table 2-2.
Working expressions for L_c, L_d and LLD (Prichard et al., 1992).

The question is often asked "How many counts must I acquire to achieve a calculated LLD?" To answer this question, a specific example for a ^3H water sample is presented.

The following data refer to a ^3H water sample and background counted as pairs:

Count time	1000 minutes
Counting efficiency	25%
Background counts	3000 counts (3 CPM x 1000 minutes)
Sample volume	10 mL

Using the expressions for a sample and background counted as pairs with the total background greater than 70 counts gives the following values:

L_c	127 counts
L_d	254 counts
LLD	46 pCi/L

A 1000 minute count would require 3127 gross counts {(127 (L_c) + 3000 (B)} to conclude that ^3H had been detected. 46 pCi/L may be detected for a 10 mL sample with a 1000 minute count with 95.5% confidence if 3254 counts {L_d(254) + B(3000)} or more are observed.

Factors that Influence LLD

Certainly, factors that influence the background will have a profound effect on the detectable limit. Any improvement made to lower the background will most likely increase sensitivity. There are several ways that this reduction can be achieved. These were discussed in chapter one and fall into two categories: instrument considerations and environment considerations.

As discussed earlier, the principle instrument modifications that will help reduce background include:

1. Background pulse discrimination electronics.
2. Additional passive shielding.
3. Active or quasi-active shielding (guard detector).
4. Optimizing counting regions.
5. Cooling the sample chamber.
6. Using low noise photomultiplier tubes.

Environmental considerations include:

1. Cocktail components that are prepared and purified to result in low levels of radioactive contaminants.
2. Use of a specially designed, highly shielded counting room.
3. Using plastic counting vials.

Certainly, cocktails that are resistant to quenching effects and have the capacity to hold large amounts of water are desirable because counting efficiency and sample size influence detectability. Several Packard cocktails have such properties.

Ultima Gold XR	XR for extended range sample capacity of up to 50% aqueous loads; a universal non-gelling environmental type cocktail.
Ultima Gold LLT	LLT for low level tritium, suitable for all low level work and capable of 55% aqueous loads; a non-gelling environmental type cocktail.
PicoFluor LLT	LLT for low level tritium, suitable for 47-55% distilled water samples.
Insta-Gel XF	A universal classical gelling type cocktail capable of holding up to 50% water.

Table 2-3.
Recommended cocktails for environmental work.

Another factor that influences LLD is the counting time. Depending on the counting efficiency and background count rate, a longer count time will result in a lower LLD, up to a limit. An *a priori* calculation (before counting) should be performed to determine if the detectable limit can be achieved in the desired count time.

Count Time Intervals Versus One Long Count Time

Several count time intervals equal to the intended total count time are desirable over a single long count. Statistically, the acquisition of data in intervals is equivalent to counting for one long time period. In addition, acquiring the data over several count periods instead of one long count time provides the ability to eliminate data acquired in one period which deviate, or are unusual for unknown reasons, from the rest of the group. The decision to reject a value for no apparent reason seems unscientific when the rules of science dictate to include all data. However, to include an odd value may significantly alter the conclusions being drawn from the data. Since there is no obvious basis (experimental or instrumental) to reject the value, some other reasonable basis is needed to reject data. In order to deal with this dilemma, a data rejection procedure has been suggested by Chauvernet, and his procedure is known as "Chauvernet's criterion" (Kobayashi and Maudsley, 1974). This criterion has been accepted by many as the means of rejecting unusual data. Chauvernet's criterion states that any data point in a series may be rejected if the magnitude of its deviation from the mean of n values (including the suspect value) is such that the probability of occurrence of all deviations from this value or larger is less than 1/2n. For example, if 20 determinations are made and one value is suspect, then the criterion for rejection is whether the value exceeds the mean ± the deviation equivalent to:

$$p \leq 1/2n = 1/2(20) = 0.025$$

A p value of 0.025% significance is reached by any value outside the range of the mean ± 2.24 mean$^{1/2}$ or ± 2.24 sigma. Therefore, according to Chauvernet's criterion, any of the 20 values that are outside this range may be rejected. If a value is rejected, the mean and standard deviations are recomputed. Chauvernet's criteria for various numbers of observations are listed in Table 2-4.

n	k	n	k	n	k
2	1.15	7	1.80	20	2.24
3	1.38	8	1.86	25	2.33
4	1.54	9	1.91	30	2.40
5	1.65	10	1.96	35	2.45
6	1.73	15	2.13	40	2.50

* n is the number of observations and k is the factor that, when multiplied by the standard deviation, defines the range from the mean beyond which values may be rejected for that n.

Table 2-4.

Chauvernet's criterion for rejecting a value*.

Kobayashi and Maudsley point out that the main objection to the use of this criterion is that for a small number of observations, values are rejected too easily. An alternative criterion that is often used is to reject values greater than three times the standard deviation. Several other criteria have been used for the rejection of outliers. These include the rule of the Huge Error, the Dixon Test and the Grubbs Test (Taylor, 1990). There is no universal procedure for the rejection of a suspect value from a series of measurements.

Instrument Stability

Environmental counting requires that background measurements are precise. Any instability in the instrument will certainly result in excess variability in background which will lead to imprecise and inaccurate measurements.

In nuclear counting, Poisson counting statistics are applied. The basic premise of Poisson statistics is that the variance is equal to the mean of the observed counts. In non-counting experiments, the variance is based on the deviation of replicates from the mean (Cook et al., 1992). Cook et al. have demonstrated the applicability of Poisson counting statistics to the variability observed in background counts acquired with Packard low level liquid scintillation analyzers. In this study, 12 background samples (both commercially purchased scintillation-grade benzene and benzene synthesized from "infinite age" material) representing three groups of four were counted for 50 minutes each. A summary of the counting experiments is shown in Table 2-5.

Group	Counter	Number of Samples	Sample Geometry	Determinations
1	Tri-Carb 2000CA/LL	4	2 g C-6 H-6	100
2	Tri-Carb 2260XL	4	2 g C-6 H-6	100
3	Tri-Carb 2260XL	4	0.5 g C-6 H-6	50

Table 2-5.

Counting experiments performed to measure background stability.

Each sample was counted for ten cycles of ten determinations. Each cycle for a particular sample is considered a subgroup. Figure 2-2 is a typical plot of the ratio of the Poisson error to the standard deviation about the mean for blocks (subgroups); each subgroup consists of ten in a single batch where there is no evidence of extra Poisson deviation, except for subgroup 9. In subgroup 9, the batch of ten counts should be re-examined. The ideal value of 1.00 is represented by the horizontal line. If the Poisson error was identical to the standard deviation, then all ratios would be equal to 1.00. Two conclusions are clear from the data: (1) the scatter of points is fairly evenly distributed above and below the ideal value, except for subgroup 9, and (2) the Poisson error is approaching the ideal value which would be the case if the actual count data are tending toward a normal distribution. Long term background stability has been demonstrated with Packard Tri-Carb low level LSC's by Cook in this same study. Two control charts (Switsur, 1990) were used to track long term stability: the $\bar{x}$ chart to assess the process mean level, and the s chart to assess the process variability. For the s chart, the standard deviation of each subgroup is plotted against the subgroup number; a horizontal line representing the average standard deviation is superimposed, and two lines representing lower (LCL) and upper (UCL) control limits are drawn. Lower and upper control limits are defined as:

$$\text{LCL} = \frac{\underline{s}}{C_4} \{\chi^2(n\text{-}1, 0.25)/\ n\text{-}1\}^{1/2}$$

$$\text{UCL} = \frac{\underline{s}}{C_4} \{\chi^2(n\text{-}1, 0.975)/\ n\text{-}1\}^{1/2}$$

C_4 is tabulated (Ryan, 1989). χ^2 is the Chi-square statistic which is discussed below.

A typical s chart is shown in Figure 2-3 showing data for sample 8 in the Cook study.

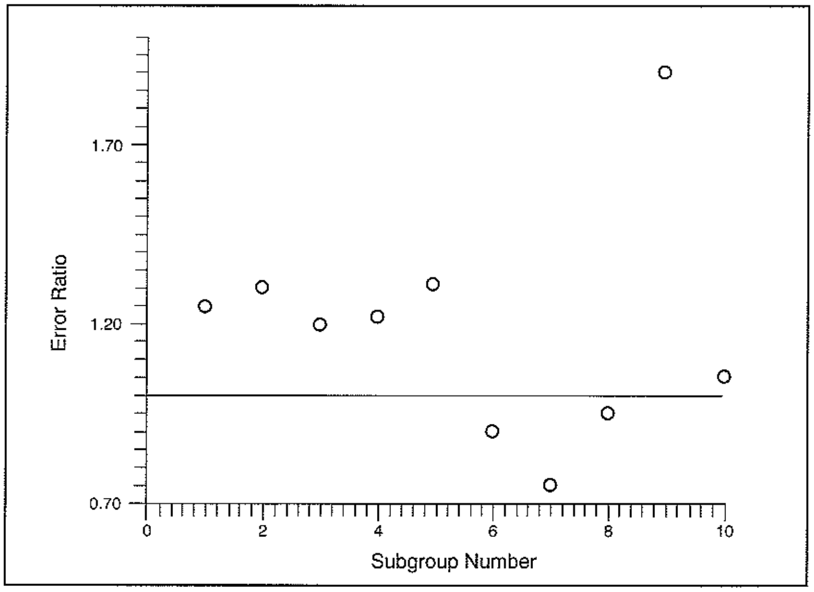


Figure 2-2.
Ratio vs. subgroup number for sample 5 (Cook et al., 1992).

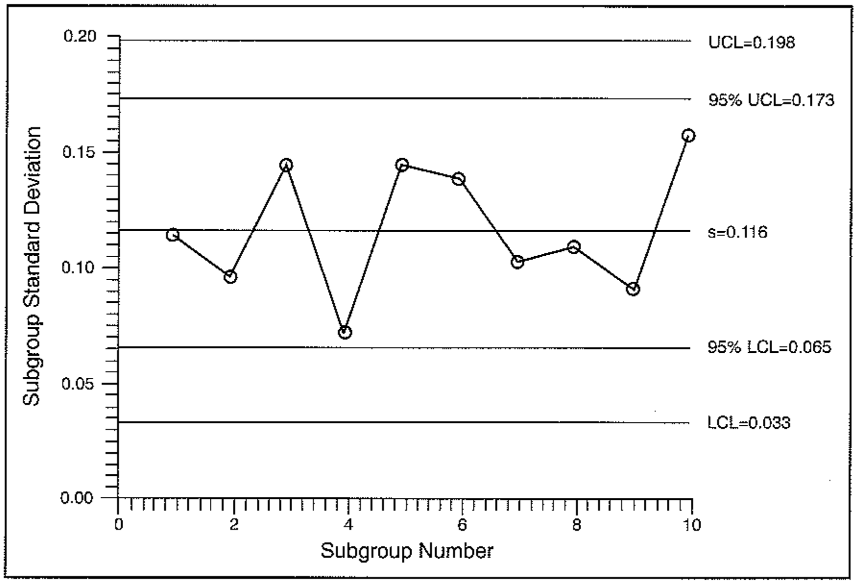


Figure 2-3.
S chart for sample 8 (Cook et al., 1992).

Figure 2-3 indicates that the process variability is in control since none of the points lie outside the control limits. The $\bar{x}$ (mean) chart is constructed similarly, with subgroups being plotted against subgroup number, the overall mean $\bar{\bar{x}}$ superimposed, and the control limits of $\bar{\bar{x}} \pm A_3 s$ (A_3 are tabulated, Ryan, 1989). The $\bar{x}$ chart for sample eight is shown in Figure 2-4. The process mean appears in control. These charts are intended to demonstrate substantial oscillations or large-scale drift, but any significant small-scale drift within the defined control limits may not be detectable.

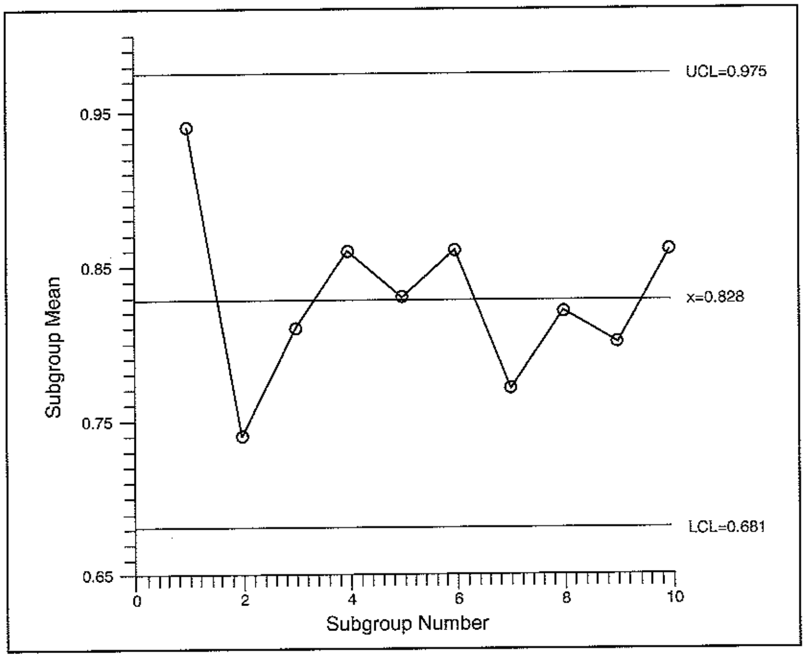


Figure 2-4.
$\bar{x}$ chart for sample 8 (Cook et al., 1992).

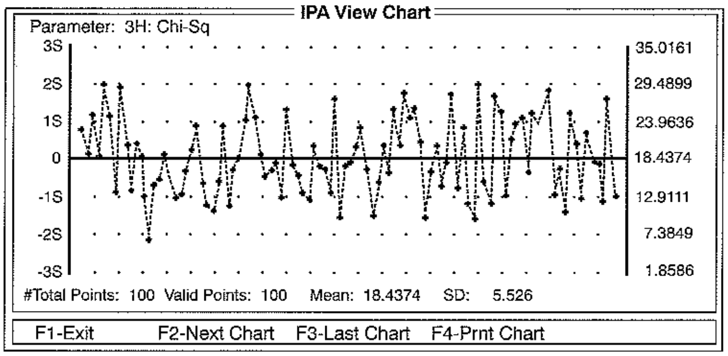
Again, A_3 are tabulated (Ryan, 1989).

Instrument Performance Assessment

Since instability in a counting system would most likely result in excess variability in the background count rate, it is advantageous to monitor performance over time for various parameters including background. Most Packard Tri-Carb normal and low level liquid scintillation analyzers provide this capability with Instrument Performance Assessment (IPA). IPA automatically creates a version of the $\bar{x}$ chart for up to 100 individual Chi-square statistical values for ^{3}H and ^{14}C. The Chi-square statistic is commonly used to assess excess variability. If given a number of observations (at least ten are required), the distribution of observed values does not conform to the Poisson distribution, then the calculated Chi-square value will be outside the probable distribution of such values. A table of calculated Chi-square values is used to determine the probability of the value falling in the range as a function of the number of observations or alternatively, degrees of freedom (n-1, number of observations -1). Values falling outside this range do not necessarily indicate an instrument malfunction, since there is a statistical probability that a value will fall outside the range. The Chi-square limits set for Packard low level LSC's predicts that 1 in 20 measurements will be outside these limits. For Packard counters, 20 individual, 0.5 minute determinations are used to calculate the Chi-square statistic. The Chi-square statistic is calculated as:

$$X^2 = \frac{\sum (N-\bar{N})^2}{\bar{N}}$$

A typical IPA chart of Chi-square values for ^{3}H is shown in Figure 2-5.



#Total Points: 100 Valid Points: 100 Mean: 18.4374 SD: 5.526

Figure 2-5.
IPA chart ^{3}H Chi-square values.

In addition to Chi-square values for ^{3}H and ^{14}C reference standards, up to 100 individual values for background, counting efficiencies, and Figure of Merit (FOM = Efficiency^2/Background or E^2/B) may be plotted. IPA data are presented in either table or chart format.

How Are the IPA Data Acquired and What Do They Mean?

IPA data are acquired automatically as part of the instrument calibration routine with factory supplied, NIST traceable ^{3}H, ^{14}C, and background sealed standards. The data and date of acquisition are automatically logged into the IPA database for later retrieval. IPA files can be exported to external computers or databases via the RS-232 port or through a network. In addition, IPA results including measurement parameters, date and time are automatically printed every time new data are added to the database. Chart data are plotted as values ± 3 standard deviations from the mean. As new data are acquired the mean and standard deviation values are recomputed.

Performance baselines and error limits are established after five initial IPA determinations. Once established, the baselines and error limits remain until the baseline is reset. If the baselines are reset, then five IPA determinations are required to re-establish the new baseline and error limits. Baselines typically are reset only after a major repair. Baselines and error limits are established for ^{3}H background, ^{14}C background and ^{3}H efficiency. If the background exceeds the baseline value by four times statistical counting error (Poisson error), a message is printed.

If IPA data are within the performance limits established, the system is operating according to specification, which means that instrument performance is stable.

References

American National Standards Institute, Inc. 1989. Draft American national standard for performance criteria for bioassay. N13.30.

Cook, G. T., Scott, E. M., Wright, E. M., and Anderson, R. 1992. The Statistics of Low Level Counting Using the New Generation of Packard Liquid Scintillation Counters. *Radiocarbon*. 34(3): 360-365.

Currie, L. A. 1968. Limits for detection and quantitative determination. *Analytical Chemistry*. 40(3): 586-593.

Kobayashi, Y. and Maudsley, D. V. 1974. *Biological Applications of Liquid Scintillation Counting*. New York: Academic Press, Inc.

Prichard, H. M., Venso, E. A., and Dodson, C. L. 1992. Liquid scintillation analysis of ^{222}Rn in water by alpha-beta discrimination. *Radioactivity & Radiochemistry*. 3(1): 28-36.

Ryan, T. P. 1989. *Statistical Methods for Quality Improvement*. New York: John Wiley & Sons, Inc.

Switsur, R. 1990. Statistical Quality Control Graphs in Radiocarbon Dating. In Proceedings of the International Workshop on Intercomparison ^{14}C Laboratories. ed. Scott, E. M., Long, A., and Kra, R. S., *Radiocarbon*. 32(3): 347-354.

Taylor, J. K. 1990. Statistical Techniques for Data Analysis. Boca Raton, Florida: CRC Press.

Chapter 3: Alpha/Beta Discrimination

Alpha/Beta Separation Theory

The ability to measure the activity of alpha emitting radionuclides by LSC has been recognized for many years. It has also been established that alpha and beta emitting radionuclides produce different shapes at the PMT anode and may be separated on this basis (Thorngate, McDowell and Christian 1974; McKlveen and Johnson 1975). Much of the early pioneering work on alpha/beta separation was carried out by W. J. McDowell, G. N. Case and the late John W. McKlveen. McDowell has carried this on to the present day and much of it is discussed in McDowell and McDowell (1994) which has a comprehensive bibliography. In order to understand how the separation of alpha events from beta events is accomplished, it is necessary to examine the processes at a molecular level. Alpha and beta events may be distinguished from one another in a liquid scintillator by examining the electronic pulses that are produced at the PMT anode of the detector. These pulses are made up of two components: the prompt component and the delayed component (Horrocks, 1974). These components occur in different proportions in alpha and beta pulses, with the result that alpha pulses are longer than beta pulses (see Figure 3-1). The photons incident on the cathode of the PMT originate from the radiative decay of excited singlet and triplet states of the fluor molecules in the cocktail. The prompt component arises from the fast, exponential decay of excited singlet states (< 80 nsec). Triplet states can produce photons only upon collision with another molecule in the triplet state, resulting in a longer lifetime (> 300 nsec) and this produces the delayed component of the pulse (Brooks, 1979). The higher specific ionization of alpha particles causes a greater proportion of excited molecules to be in triplet states and, hence, alpha pulses have a longer duration. The longer duration of alpha pulses is the basis of alpha/beta separation by pulse shape discrimination. Figure 3-1 demonstrates the difference in pulse shape between ^{36}Cl (beta emitter) and ^{241}Am (alpha emitter) in Insta-Gel with 20% weight/volume naphthalene added. These pulse shapes were measured at the PMT anode of a Packard Tri-Carb 2500TR/AB using a storage oscilloscope set on averaging mode to produce an average pulse shape.

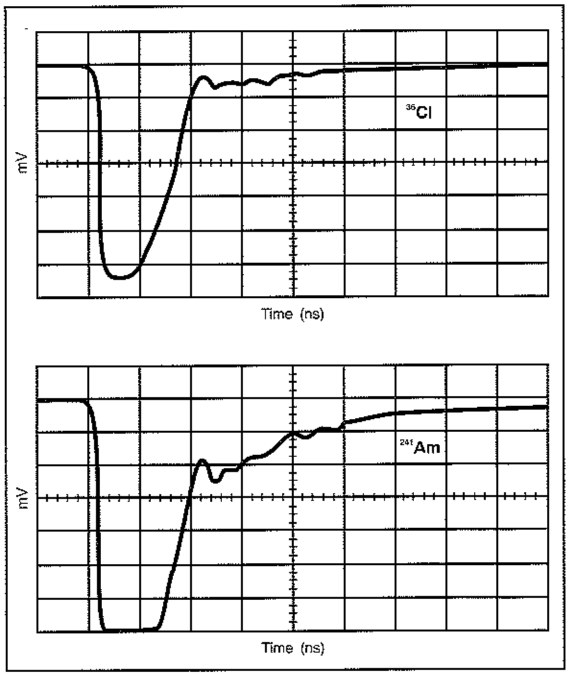


Figure 3-1.
^{36}Cl and ^{241}Am pulse shapes from the PMT anode.

Most of the environmentally significant alpha emitting radionuclides emit particles in the 4-6 MeV energy region, while the betas of interest typically have E_{max} values below 2.5 MeV. Separation of alpha from beta events is necessary because the energy to light conversion yield from alpha particles is approximately a factor of ten lower than from betas, lowering their spectra into the beta region. Figure 3-2 illustrates the spectral overlap which is observed between ^{241}Am which produces alpha particles in the 5.4 to 5.5 MeV region and ^{36}Cl which has an E_{max} of 710 keV.

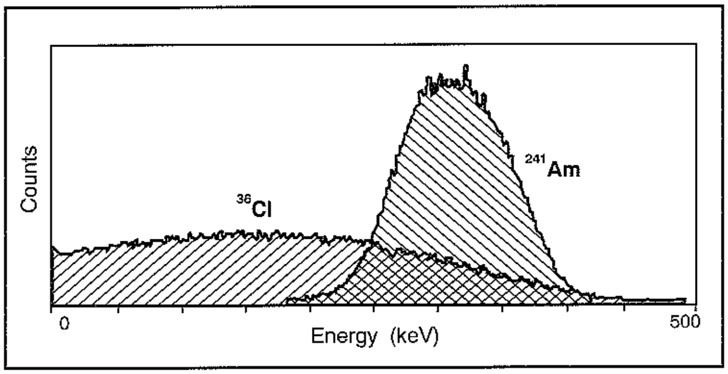


Figure 3-2.
Multichannel analyzer display, alpha/beta interferences.

Alpha/beta separation discrimination is a comparatively recent feature on commercially available, conventional LSC's. The 4 π counting geometry of LSC results in approximately 100% counting efficiency for alpha emitting radionuclides, which, coupled with the low alpha background count rates, provides an alternative to gross alpha/beta via gas flow proportional counting. Alpha/beta LSC can also be a very useful alternative to conventional alpha spectrometry using PIPS (passivated implanted planar silicon) and SSB (silicon surface barrier) detectors for certain applications. However, the much poorer resolution of LSC relative to semiconductor detectors can be a major disadvantage. This is brought about principally because of the relatively large amount of energy required to produce a single photoelectron at the PMT photocathode and, to a much lesser extent, by the inefficient light production by alpha particles relative to betas.

Pulse Shape Discrimination Electronics

Pulse shape discrimination techniques are well known and have been extensively applied to the rejection of gamma background in neutron spectrometry (Horrocks, 1970; Winyard, et al., 1971) and to the isolation of fission events in liquid scintillation counting (Horrocks, 1963). Such techniques are often referred to in the literature by different instrument manufacturers as either pulse shape discrimination, pulse shape analysis, or pulse decay analysis. Different names arise because the techniques of pulse shape discrimination can vary, but all are based on electronic circuits that measure some aspect of pulse decay time.

Pulse Shape Analysis (PSA)

Pulse Shape Analysis is a pulse shape discrimination technique that is based on a method that integrates the charge of the "tail" of the scintillation pulse and compares it with the total charge in the same pulse. Different settings of the PSA level assign the pulse into either a long (alpha-like) or short (beta-like) category. Thus, different PSA settings allow pulses to be categorized according to their length (shape). Typically, increasing the PSA setting will direct more pulses toward the long or alpha category. However, depending on how the technique is implemented, the reverse can also be true, *i.e.*, increasing the setting may direct more alpha counts into the beta category.

There are several methods of accomplishing pulse shape analysis including slow crossover timing, fast crossover timing, and constant fraction of pulse-height trigger. The unique approach used in Packard Tri-Carb LSC's is termed Pulse Decay Analysis (PDA).

Pulse Decay Analysis (PDA)

The higher percentage of triplet states produced by alpha particles translates into electronic pulses at the PMT anode which may be as much as 30 nsec longer than those derived from beta particles and gamma photons produced in the sample cocktail. A graphical representation of this is shown in Figure 3-3.

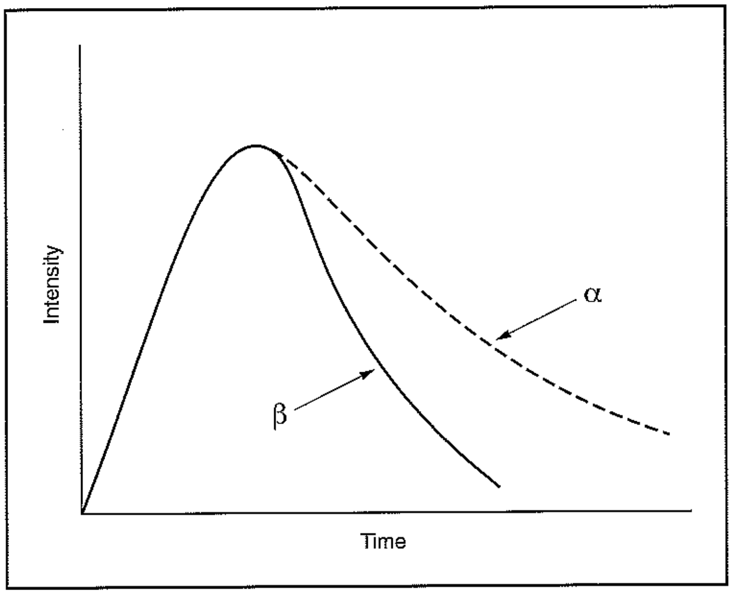


Figure 3-3.
Characteristic light pulse shapes of alpha and beta pulse in a liquid scintillator.

Pulse Decay Analysis is based on the zero-cross pulse timing technique. In general, a zero-crossing sensing circuit has consistently proven to provide excellent alpha/beta separation (McDowell and McDowell, 1994). The zero-cross method is illustrated in Figures 3-4 and 3-5. To further optimize the separation of alpha from beta/gamma events, the anode pulses are integrated, slowed and further shaped by passing through a low pass filter. This stretches the pulses as represented graphically in Figure 3-4.

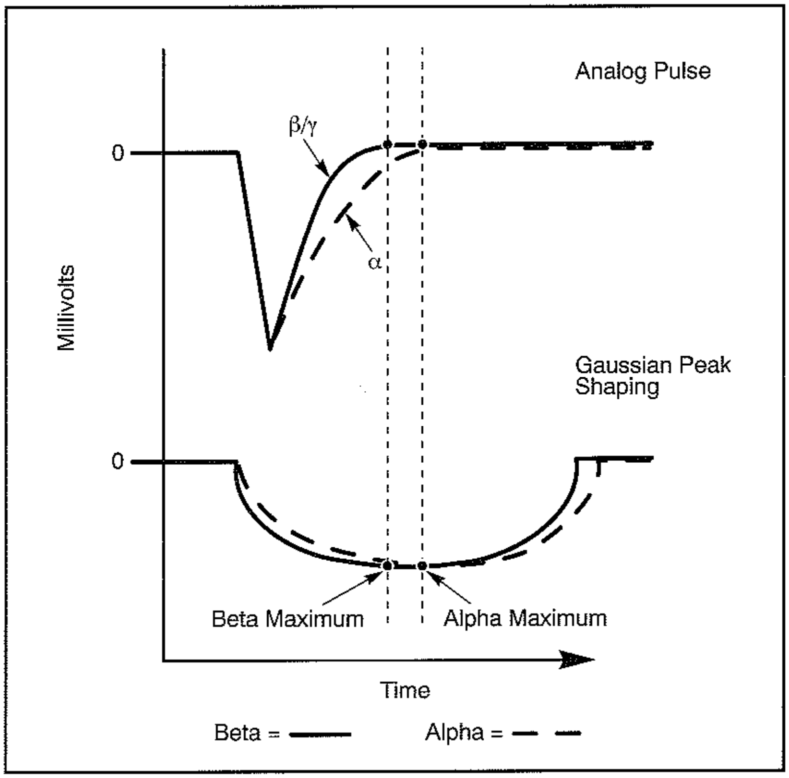


Figure 3-4.
Low pass filtered pulse processed with pulse decay analysis.

A derivative of this wave function produces a zero crossover pulse as indicated in Figure 3-5. From this information, an optimum pulse decay discriminator (PDD) may be set between the zero-cross time points of the two types of pulses.

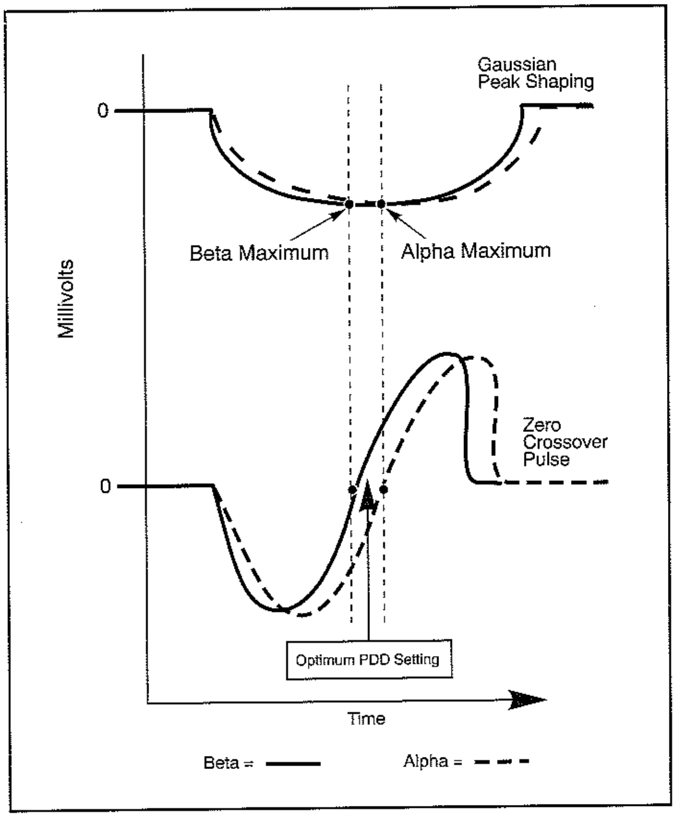


Figure 3-5.
Zero crossover for determining PDD for pulse processed with PDA.

<u>Time-Resolved Pulse Decay Analysis (TR-PDA)</u>
TR-PDA is the combined use of TR-LSC background discrimination and pulse decay analysis. By applying TR-LSC to PDA, alpha events that are misclassified as beta are discriminated by TR-LSC since the long "tails" (delayed component) of alpha pulses resemble background events. Thus, alpha events misclassified as beta will be eliminated from the beta MCA. In addition, the misclassification of beta events will also be reduced since the TR-PDA causes a shift to a higher optimum PDD value. At higher PDD values, fewer beta events can satisfy the time requirement for an alpha pulse which reduces the beta spill into the alpha MCA. The net result of TR-PDA is a reduction of two to five fold in the misclassification of beta and alpha events. An added benefit of TR-PDA is that TR-LSC background discrimination allows for simultaneous low level beta counting. The effects of TR-PDA on alpha/beta misclassification are illustrated in Figure 3-6A and B which compares the misclassification curves without and with TR-PDA.

Alpha/Beta Calibration

Percent Misclassification Curves

In order to optimize alpha/beta separation performance, it is essential to determine the correct PDD setting as described above. On Packard Tri-Carb models with alpha/beta discrimination, the optimum setting is the setting where there is equal and minimum spill of alpha pulses into the beta MCA and beta pulses into the alpha MCA. Figure 3-6A illustrates the percent spillover or percent misclassification of ^{241}Am and ^{36}Cl samples in Packard Ultima Gold AB, a cocktail specifically designed for alpha/beta separation. The determination of an optimum PDD requires two standards: one of the pure alpha emitter of interest and one of the pure beta emitter of interest. For the most accurate results, the standards must be as near identical as possible to the unknown samples in their chemistry, volume, vial type, etc. Separate optimum PDD settings should also be derived for unique alpha and beta standard pairs. For gross alpha and gross beta measurements where the particular radionuclides may not be known, an alpha and beta standard of similar energy to the alpha and beta in the samples is desirable. To arrive at the optimum setting, each standard is counted individually at a range of PDD settings and the percent misclassification of alphas into the beta MCA and vice versa are plotted against PDD on the same graph. Figure 3-6A is a typical misclassification plot for unpurged samples of ^{36}Cl and ^{241}Am using a long fluorescence lifetime cocktail. The instrument determines the optimum setting that results in the minimum misclassification of alpha and beta activity, and will generate the percent misclassification plot on demand. When only the beta emitter is of interest, a PDD value below the instrument determined optimum may be used, which minimizes the misclassification of alpha activity into the beta MCA at the expense of reducing the beta efficiency. Similarly, when only the alpha emitter is of interest, a PDD value greater than the optimum can be used. This minimizes the misclassification of beta events into the alpha MCA at the expense of reduced alpha counting efficiency. The effect of TR-PDA on the misclassification curve is shown when one compares the ^{241}Am and ^{36}Cl misclassification curve in Figure 3-6A (without TR-PDA), with the curve shown in Figure 3-6B, which was acquired with the same standards and TR-PDA. As mentioned previously, the instrument determined optimum PDD is at the intersection of the two curves which corresponds to the minimum misclassification of alpha and beta events. Several observations can be made by comparing these two curves. The first observation is the obvious shift in the instrument determined optimum PDD to a slightly higher value with TR-PDA (Figure 3-6B) than without TR-PDA (Figure 3-6A). The next observation is the flattening of the alpha curve. The flattening of the alpha curve is the cause of the shift in the intersection of the curves and results in a higher optimum PDD value. The flattened shape of the alpha curve is due to TR-LSC discrimination of misclassified alpha events in the beta MCA. At this higher value, beta misclassification is also reduced. Manual adjustment of the discriminator to a higher or lower value than the optimum will further reduce either beta or alpha misclassification at the expense of some loss of alpha or beta counting efficiency, respectively.

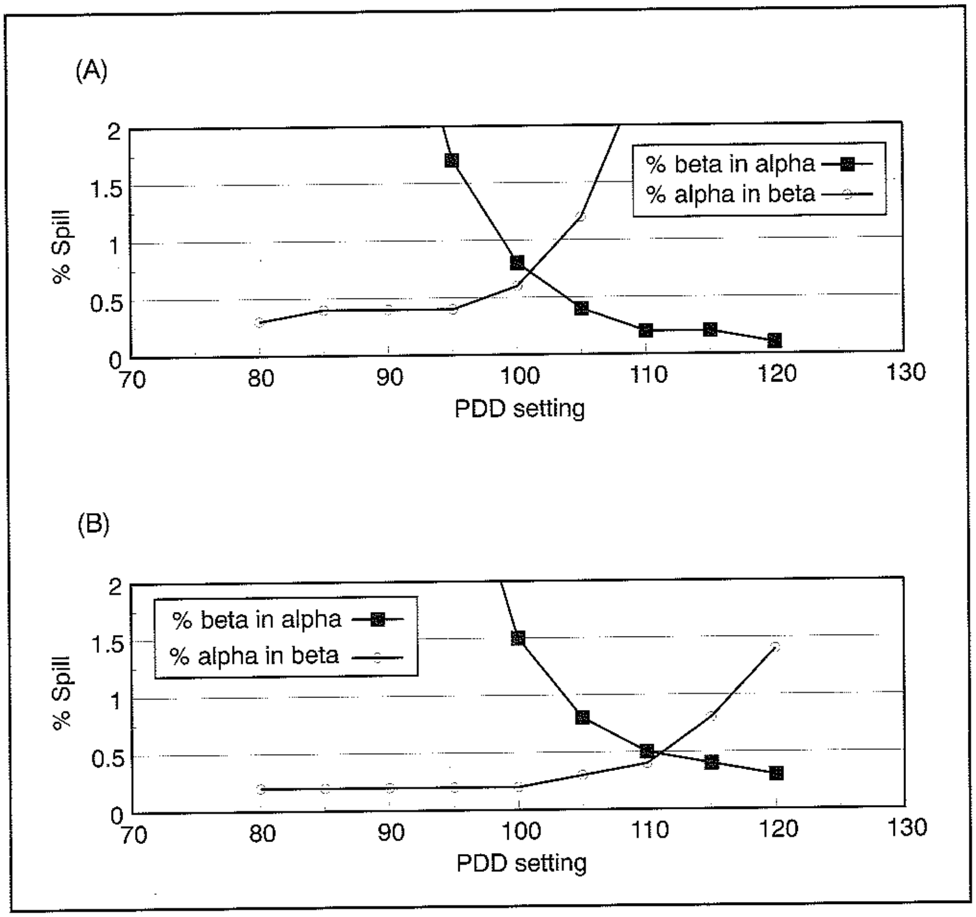


Figure 3-6.

Typical alpha/beta misclassification plot, ^{241}Am and ^{36}Cl (A).
Alpha/beta misclassification plot using TR-PDA (B).

Misclassification Calculations

The calculation required to determine the actual CPM is essentially the same as that used in dual label studies and can be defined as follows:

X_α = alpha misclassification as beta
X_β = beta misclassification as alpha
A_T = true count rate due to alpha disintegrations
B_T = true count rate due to beta disintegrations
A_O = observed count rate in alpha MCA
B_O = observed count rate in beta MCA

Alpha into beta misclassification (X_α) is defined as the ratio of counts accumulated in the beta MCA to counts accumulated in both the alpha and beta MCA's as measured with the alpha standard.

$$X_\alpha = B_o / (A_o + B_o)$$

Similarly, beta into alpha misclassification (X_β) is defined as:

$$X_\beta = A_o / (A_o + B_o)$$

as measured with the beta standard.

It is important to understand that the count rate observed in each MCA is a function of both alpha and beta disintegrations because of the occurrence of some misclassification. This relationship can be defined as:

$$A_o = A_T - A_T X_\alpha + B_T X_\beta$$
$$B_o = B_T - B_T X_\beta + \cancel{B}_T X_\alpha \quad A_T$$

The first equation defines that the observed count rate in the alpha MCA (A_O) is mainly due to counts from alpha disintegrations (A_T); however, this value will be reduced by the total number of alpha disintegrations counted in the beta MCA ($A_T X_\alpha$). Furthermore, beta counts falling into the alpha MCA must also be taken into account. This is accomplished by adding the $B_T X_\beta$ term. The calculation of the observed beta count rate (B_O) is the reverse of the calculation for the observed alpha count rate.

Solving for A_T and B_T and substitution of the A_T expression into the B_T expression and vice versa we obtain the final equations for A_T and B_T:

$$A_T = \frac{A_o - A_o X_\beta - B_o X_\beta}{1 - X_\beta - X_\alpha}$$

and similarly

$$B_T = \frac{B_o - B_o X_\alpha - A_o X_\alpha}{1 - X_\alpha - X_\beta}$$

Examples of Misclassification Calculations

The calculation is further illustrated by counting mixtures of ^{36}Cl and ^{241}Am (Tables 3-1 and 3-2) ranging from approximately 500 DPM of ^{36}Cl and 50000 DPM of ^{241}Am to approximately 50000 DPM of ^{36}Cl and 500 DPM of ^{241}Am in a total volume of 10 mL of cocktail (with appropriate background samples) at the optimum PDD value.

The results were as follows:

Optimum PDD = 105

Misclassification of alphas into the beta MCA (as a fraction) = 0.0071 = X_α
Misclassification of betas into the alpha MCA (as a fraction) = 0.0063 = X_β
Background in alpha-MCA = 0.69 CPM (0-2000 keV)
Background in beta-MCA = 39.6 CPM (0-2000 keV)

Table 3-1 shows the gross and background corrected raw instrument data. Table 3-2 compares the actual alpha and beta activities in the vial with the calculated spill corrected activities derived from the raw data.

Sample No.	Observed Gross Counts Beta-MCA	Observed Gross Counts Alpha-MCA	Net Counts (Background Subtracted) Beta-MCA	Net Counts (Background Subtracted) Alpha-MCA
1	48545	684	48506	683
2	46533	2731	46494	2730
3	44254	5313	44215	5312
4	24435	25323	24395	25332
5	5208	46131	5168	46130
6	2833	47160	2793	47159
7	811	50775	771	50774

Table 3-1.
Gross and background-corrected raw data.

Sample No.	Actual (Vial) CPM Values Cl-36	Actual (Vial) CPM Values Am-241	Spill Corrected CPM Values Cl-36	Spill Corrected CPM Values Am-241
1	48684	449	48811	378
2	46694	2496	46771	2453
3	44187	5004	44459	5068
4	24315	24847	24369	25348
5	4961	45118	4869	46429
6	2425	47626	2472	47481
7	507	49595	411	51135

Table 3-2.
Results of performing misclassification correction on the net counts.

Quench Correction of Percentage Misclassification

As stated above, actual samples must be prepared in an identical manner to the standards, *i.e.*, same volume, composition (acid strength, etc.), cocktail, and vial type. Where the samples differ from the standards in terms of the degree of quenching, the quenching of the standards should be modified to better reflect the samples. Where sample quenching is variable, corrections to the spill calculation may be made and this process will be described in the following section.

Factors Influencing Alpha/Beta Discrimination

Quenching

Figures 3-7A and 3-7B represent misclassification plots for the same type of standards but under different quench conditions. Figure 3-7A represents relatively unquenched conditions compared to Figure 3-7B. Both the optimum PDD value and the percentage misclassification of events change under these different conditions. It should be noted, however, that this effect will vary according to the isotopes being measured and may also vary, in a more limited fashion, from instrument to instrument.

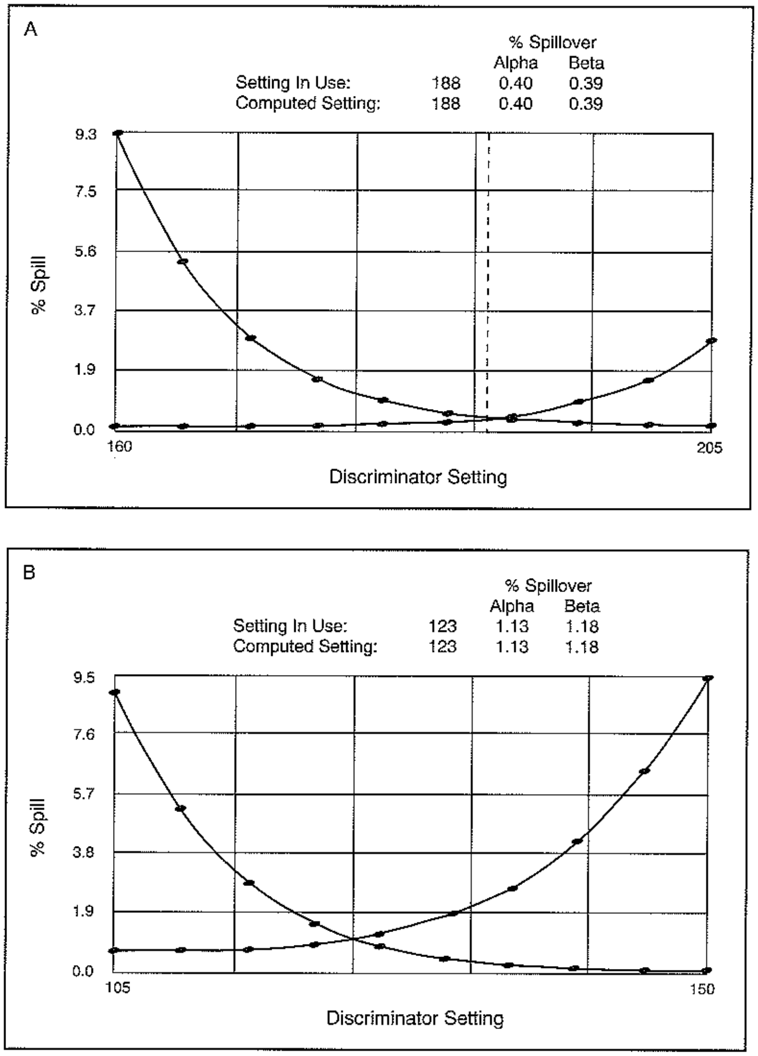


Figure 3-7.

Misclassification plot for ^{36}Cl and ^{241}Am under relatively unquenched conditions (A).
Misclassification plot for ^{36}Cl and ^{241}Am under quenched conditions (B).

When the degree of quenching for a particular set of samples varies, there are two possible approaches. The first approach is to produce a single pair of alpha/beta standards which are similar in their quench (tSIE) value to the least quenched sample; then, progressively quench them and re-optimize the PDD at each quench level. This produces a series of PDD values and percentage misclassifications for a range of quenching (tSIE values). The degree of sample quenching in each sample may then be measured by making a short count on each sample to determine the value of the tSIE quench indicating parameter. Then, samples have to be counted at their individual optimum PDD conditions, which could conceivably require a separate protocol for each sample. The alternative approach is again to prepare a pair of standards which are equivalent in quenching to the least quenched samples, determine the optimum PDD and then progressively quench the standards. However, in this approach, the misclassification is always determined at the original PDD setting. This allows the construction of a plot of percentage misclassification versus tSIE for a single PDD setting. All samples may then be counted within a single protocol and a correction for misclassification as a function of quench is applied. This approach would be in addition to a quench curve which relates quenching to detection efficiency. Figure 3-8 demonstrates the construction of such a correction plot.

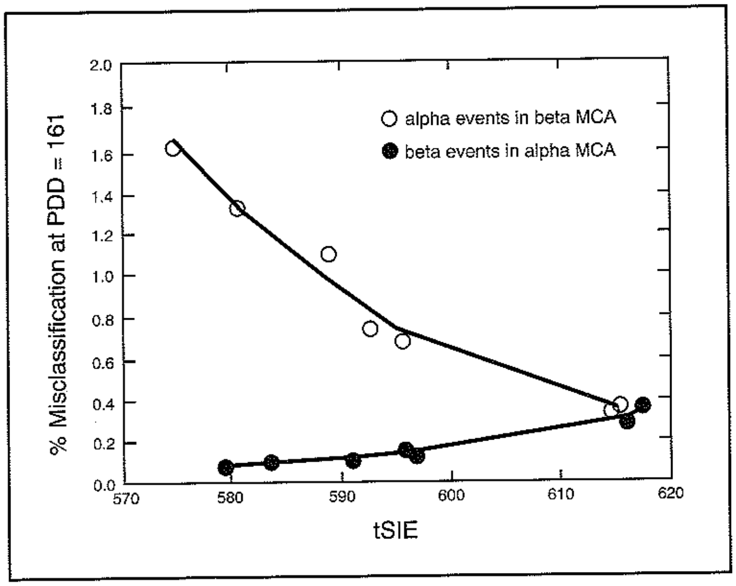


Figure 3-8.
The effect of quenching (tSIE) on percent misclassification of alpha and beta events using Ultima Gold AB.

Cocktails
Standard cocktails for beta counting applications which employ fast solvents, such as xylene, pseudocumene, toluene and alkylbenzenes, are less efficient for separating alpha from beta activity. Figure 3-9 illustrates the misclassification of ^{238}Pu and ^{90}Sr/^{90}Y which was achieved using Insta-Gel (xylene solvent). This would be a typical misclassification value for a cocktail employing a fast solvent.

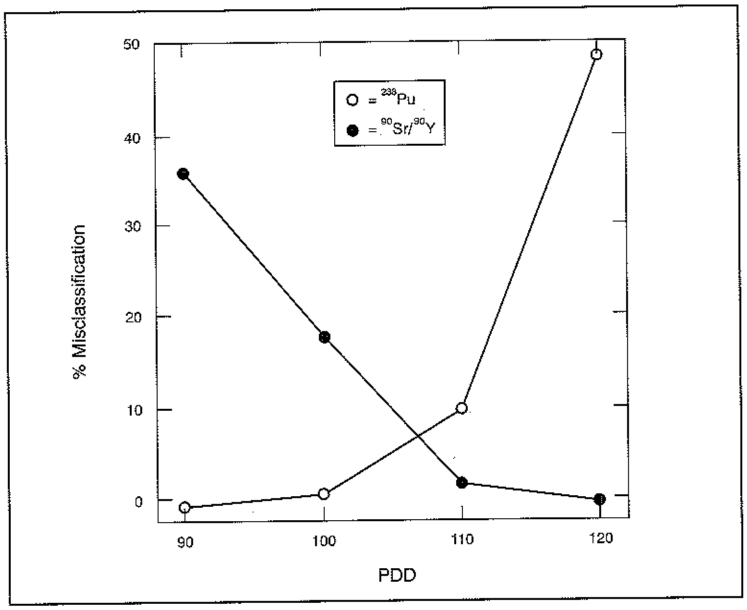


Figure 3-9.
Crossover plot for ^{238}Pu and ^{90}Sr/^{90}Y in Insta-Gel.

To overcome the poor separation, 20% naphthalene has been added to standard cocktails for alpha/beta separation applications (Oikari et al., 1987). Figure 3-10 illustrates the improvement in separation which is obtained when 20% naphthalene is added to Insta-Gel. Naphthalene improves alpha/beta separation by acting as an intermediate in the energy transfer process between the solvent and fluor (Brooks, 1979; McDowell, 1986). This more energetically favorable route increases the production efficiency of excited fluor molecules. The production rate of fluor triplet states is especially enhanced because energy transfer to triplet states relies on a physical approach, and is affected by the concentration of both the fluors and the intermediate, naphthalene, in the cocktail. As more triplet states become occupied, the delayed component of the PMT anode pulse increases, with the effect of stretching the alpha pulses relative to the beta pulses. The ability of naphthalene to act as an intermediate in this way is the result of the extensive delocalization of its electrons.

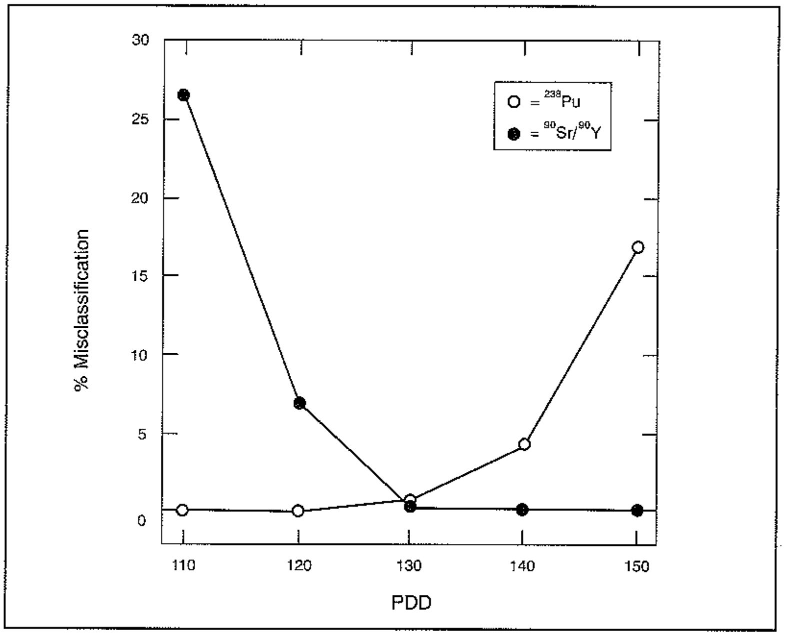


Figure 3-10.
Crossover plot for ^{238}Pu and ^{90}Sr/^{90}Y in Insta-Gel + 20% weight/volume naphthalene.

Recently, Packard Instrument Company introduced a scintillation cocktail (Ultima Gold AB) designed specifically for alpha/beta separation in aqueous samples. This cocktail is based on the solvent di-isopropylnaphthalene (DIN) which has many advantages over fast cocktails with 20% naphthalene. It is nontoxic, nonflammable and biodegradable, and is therefore preferable in cocktail manufacture to naphthalene (Thomson, 1991). Ultima Gold AB has also exhibited superior alpha/beta separation compared to fast cocktails with 20% naphthalene, and has an excellent water and acid holding capacity.

Sample Volume

Several experiments have been performed to determine the effect of sample volume on alpha/beta separation. Alpha/beta misclassification plots were acquired with ^{36}Cl and ^{241}Am in Insta-Gel +20% weight/volume naphthalene (both approximately 5000 DPM per mL) in cocktail volumes ranging from 1 mL to 16 mL. The percentage misclassification and optimum PDD values are presented in Table 3-3. These demonstrate virtually constant PDD over the entire volume range and only a small increase in the misclassification at the 1 and 2 mL volumes. However, this can be accounted for by the increasing importance of the background count rate in the misclassification calculation since background subtraction is not performed in the calculation of the misclassification spill plot.

Sample Volume (mL)	Alpha Spill (%)	Beta Spill (%)	Optimum PDD
16	0.69	0.70	101
10	0.65	0.62	101
8	0.64	0.57	101
4	0.68	0.67	101
2	0.85	0.74	100
1	1.14	1.02	98

Table 3-3.

Percent misclassification and optimum PDD values for various sample volumes.

Vial Type

Table 3-4 illustrates the change in percentage misclassification of events over a period of 24 days using alpha and beta standards prepared in 7 mL and 20 mL glass vials, 20 mL plastic vials and 20 mL low diffusion plastic vials (Packard low diffusion vials are specially prepared polyethylene vials with a micron thin, Teflon-like inner coating). The 20 mL vials contained 10 mL of Ultima Gold AB and 0.2 mL sample loading while the 7 mL vials contained 5 mL of Ultima Gold AB and 0.1 mL of sample loading. There appears to be no significant difference in performance between standard 7 mL and 20 mL glass vials, and no change in misclassification with time. On the other hand, the misclassification from standard plastic vials systematically increases throughout the time-course of the experiment. The effect seems to be caused by a stretching of the beta pulses. Table 3-4 demonstrates the misclassification of events using the various vial types.

Days After Sample Formulation	Percentage Misclassification alpha in beta/beta in alpha			
	20 mL glass	7 mL glass	20 mL plastic	20 mL low diff. plastic
0	0.47/0.51	0.56/0.58	0.56/0.65	0.46/0.53
1	0.42/0.51	0.49/0.62	0.59/0.90	0.43/0.61
2	0.49/0.51	0.48/0.62	0.96/1.01	0.53/0.63
6	0.41/0.55	0.47/0.55	1.39/1.51	0.68/0.81
9	0.38/0.51	0.43/0.54	1.61/1.78	0.96/0.95
16	0.41/0.49	0.46/0.56	1.94/2.24	1.22/1.28
24	0.49/0.51	0.49/0.54	2.18/2.53	1.40/1.67

Table 3-4.

Alpha/beta misclassification as a function of time and vial type.

The low diffusion vials are similar in response to plastic vials except that there is a lag period of about two days before there is an increase in misclassification. Apparently the effect of the plastic vials is due to diffusion of some component into the vial wall since decanting the vial contents into a glass vial restores the misclassification to that which is typically observed in a glass vial. Alpha/beta separation with glass vials can be improved significantly by etching the outside wall of the vial. Figure 3-11A demonstrates the shape of an ^{241}Am spectrum which may be observed in a glass vial. The double peak is a purely optical effect of the glass. Figure 3-11B demonstrates the same sample spectrum after the vial has been etched. In addition, the percentage misclassification of events is also decreased by etching. A decrease from 0.67/0.69 to 0.44/0.44 was observed for ^{241}Am/^{36}Cl. Etching the vial improves the light output and thus improves the ability to separate alpha and beta events.

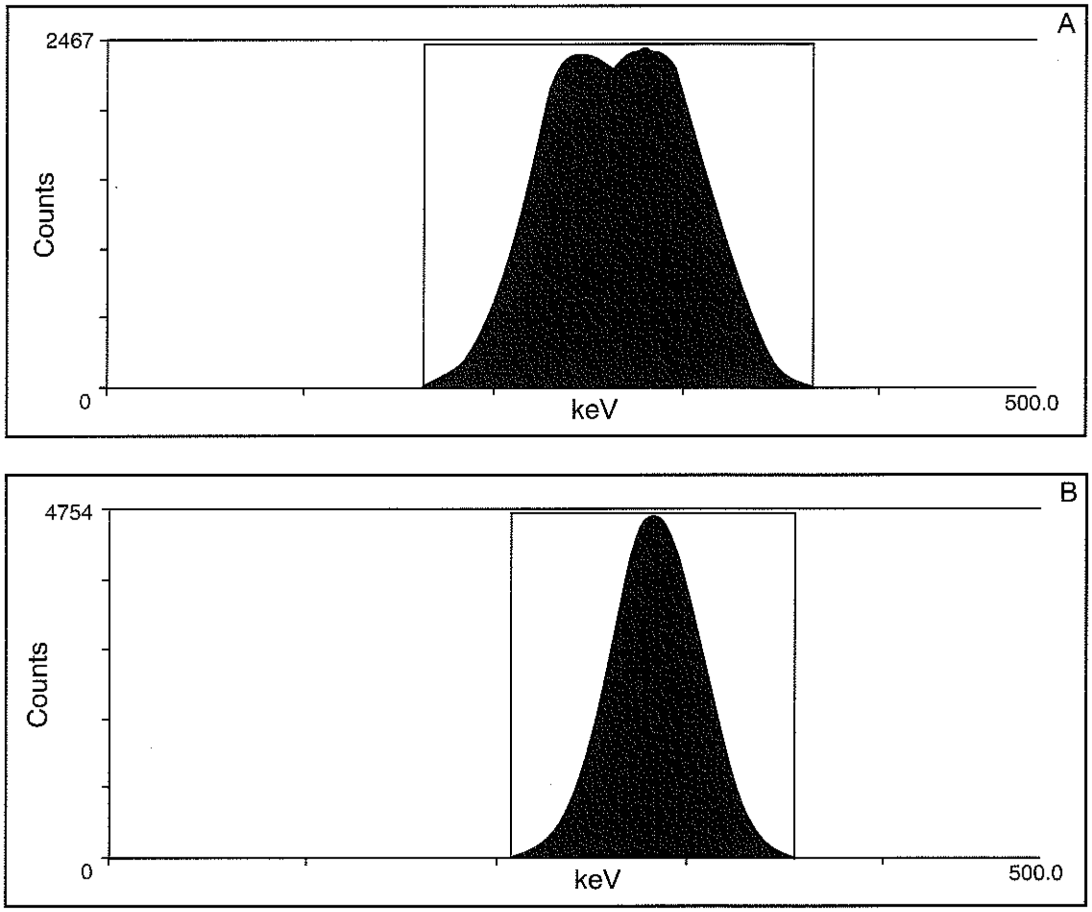


Figure 3-11.
^{241}Am spectrum in a 20 mL glass vial (A). ^{241}Am spectrum in a 20 mL glass vial with an etched outer surface (B).

Applications of Alpha/Beta LSC

The separation of alpha from beta activity is one of the most rapidly growing areas of interest in LSC. In particular, the measurement of gross alpha and gross beta activities in processes associated with nuclear fuel processing and disposal is common. Much of this interest is due to increasing pressures to address safety, regulatory compliance, and disposal issues. Gross alpha/beta techniques are now used to monitor smears (Hochel, 1993), air filters (Hinton et al., 1990) and liquid samples associated with nuclear fuel processing. Leyba (1992) suggests this method for screening relatively “clean” samples prior to disposal while Yang et al., (1990) propose its use for process stream analysis. Yang et al., (1991) have used extractive scintillators to separate the actinides from most of the beta emitting nuclides prior to alpha/beta separation and this combination of techniques enables alpha emitters to be measured in the presence of much higher beta activity. In terms of environmental measurements of natural radionuclides, several interesting methodologies have recently been developed. Saarinen and Suksi (1992) have developed a method for ^{231}Pa measurement from rock samples using a beta emitting tracer (^{233}Pa). The measurement of ^{231}Pa in this instance is to aid in the interpretation of uranium series data obtained in the context of natural analog studies on radionuclide migration. Pates et al., (1993) use alpha/beta separation to study ^{234}Th/^{238}U disequilibria in the context of marine productivity studies. The beta emitting ^{234}Th is measured in the presence of an alpha emitting yield tracer (^{230}Th). Venso et al., (1993) use a combination of solvent extraction and alpha/beta separation to measure ^{234}U / ^{238}U isotopic activity ratios in drinking water.

References

Brooks, F. D. 1979. Development of organic scintillators. *Nuclear Instruments and Methods.* 162: 477-505.

Hinton, E. R., Adams, T. T. and Burchfield, L. A. 1990. Gross alpha counting of air filters using a pulse shape discriminating alpha liquid scintillation counter. *36th Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry.* Oak Ridge, TN.

Hochel, R. C. 1993. Direct characterization of smears by alpha-beta liquid scintillation spectroscopy. *39th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry.*

Horrocks, D. 1970. Appl. Spectros. 24: 397.

Horrocks, D. 1963. Rev. Sci. Instrum. 34: 1035.

Horrocks, D. L. 1974. *Applications of Liquid Scintillation Counting.* New York: Academic Press.

Leyba, J. D. 1992. Gross alpha/beta determination by liquid scintillation counting. Westinghouse Savannah River Company, *WSRC-TR-92-079.*

McDowell, W. J. 1986. *Alpha Counting and Spectrometry Using Liquid Scintillation Methods.* Nuclear Science Series on Radiochemical Techniques.

McDowell, W. J. and McDowell, B. L. 1994. *Liquid Scintillation Alpha Spectrometry*, CRC Press.

McKlveen, J. W. and Johnson, W. R. 1975. Simultaneous alpha and beta particle assay using liquid scintillation counting with pulse shape discrimination. *Health Physics* 28 (Jan.): 5-11.

Oikari, T., Kojola, H., Nurmi, J., Kaihola, L. 1987. Simultaneous counting of low alpha and beta particle activities with liquid scintillation spectrometry and pulse shape analysis. *Journal of Applied Radiation and Isotopes.* 38: 875-878.

Pates. J. M., Anderson, R., Cook, G. T. and MacKenzie, A. B. 1993. In *Advances in Liquid Scintillation Spectrometry 1992,* ed. Noakes, J. E., Schoenhofer, F. and Polach, H. A., 417-423, Radiocarbon Publishers.

Saarinen, L. and Suksi, J. 1992. Determination of uranium series radionuclide ^{231}Pa using liquid scintillation counting. In *Advances in Liquid Scintillation Spectrometry,* ed. Noakes, J. E., Schoenhofer, F. and Polach, H. A., 209-215, Radiocarbon Publishers.

Thomson, J. 1991. Di-isopropylnaphthalene - a new solvent for liquid scintillation counting. *In Liquid Scintillation Counting and Organic Scintillators,* ed. Ross, H., Noakes, J. E., Spaulding, J. D., 19-34, Lewis Publishers.

Thorngate, J. H., McDowell, W. J., Christian, D. J. 1974. An application of pulse shape discrimination to liquid scintillation counting. *Health Physics*, 27: 123-126.

Venso, E. A., Prichard, H. M. and Dodson, C. L. 1993. Measurement of isotopic uranium in Texas drinking water supplies by liquid scintillation with alpha-beta discrimination. In *Advances in Liquid Scintillation Spectrometry 1992,* ed. Noakes, J. E., Schönhofer, F. and Polach, H. A., 425-430, Radiocarbon Publishers.

Winyard, R., Lutkin, J. and McBeth, G. 1971. Nuclear Instrumentation and Methods 95: 141.

Yang Dazhu, Zhu Yongjun and Möbius, S. 1991. Rapid method for alpha counting with extractive scintillator and pulse shape analysis. *Journal of Radioanalytical and Nuclear Chemistry, Articles.* 147: 177-189.

Yang Dazhu, Zhu Yongjun, Möbius, S, and Keller, C. 1990. Simultaneous determination of alpha and beta-emitting nuclides by liquid scintillation counting. *Journal of Radioanalytical and Nuclear Chemistry, Letters.* 144: 63-71.

Section II.

Environmental Radionuclide Analysis - Cosmogenic Beta Emitting Radionuclides

Chapter 4: Tritium

^{3}H in the Environment

Tritium has a half-life of 12.43 years and decays by beta emission (E_{max} = 18.6 keV) to ^{3}He. ^{3}H is produced naturally in the upper atmosphere as a result of cosmic ray induced spallation and particle interactions with atmospheric nitrogen and oxygen (Libby, 1946; Grosse et al., 1951; Geyh and Schleicher, 1990). The production rate is 0.25 atoms $cm^{-2} sec^{-1}$, approximately two thirds of which occurs in the stratosphere and one third in the troposphere. ^{3}H is oxidized to water and enters the hydrological cycle where it has a residence time of about two years (Geyh and Schleicher, 1990). The global inventory of this naturally occurring tritium is estimated to be about 1×10^{18} - 1.3×10^{18} Bq (Momoshima, Takashima and Okai, 1990). Tritium activities are commonly described in terms of Tritium Units (TU) where 1 TU = 1 atom of tritium per 10^{18} atoms of hydrogen or 1 TU = 0.118 Bq L^{-1} of water. The natural activity of tritium in precipitation varies from around 25 TU at high latitudes to about 4 TU at the equator (Geyh and Schleicher, 1990). Anthropogenic tritium is principally from nuclear weapons testing or from activities associated with the nuclear fuel cycle and tritium geophysical research. The world's inventory of tritium falls into two distinct time periods: the natural tritium or pre-thermonuclear test period, and the artificial or hydrogen bomb test period (Libby, 1963). The dividing line between these two periods is about March 1954 when the first significant activity of artificial ^{3}H was added to the atmosphere during the "Castle test series" in the Pacific. Detonation of the first thermonuclear device roughly doubled the world's inventory of natural tritium. In the northern hemisphere, the concentration of tritium in precipitation passed through a maximum of several thousand TU around 1963. The present day activity in precipitation is approximately 20 TU.

^{3}H Monitoring Applications

The relatively constant cosmogenic production of tritium makes short term age measurement studies feasible, *e.g.*, the dating of agricultural produce. The assumptions here are that plants derive most of their water from recent rainfall and cease uptake when they are harvested. The age estimation of wines is another good example of this technique. Here, tritium exchange with the atmosphere is ceased by bottling. The tritium in both of the above examples then decays according to its 12.43 year half-life. This classic concept of age measurement lost its significance with the commencement of thermonuclear weapons tests. However, many other applications were enhanced or made possible by the advent of thermonuclear derived tritium since its placement in time was accurately known and the activities were much greater than that of natural production. As in radiocarbon, much of the early pioneering work came from Willard Libby and coworkers.

Tritium has been used in many hydrological studies, including: (1) the age of precipitation in ice; (2) a study of the circulatory rates of waters in the northern hemisphere; (3) well water studies to assess supplies and make predictions of their susceptibility to drought as well as depletion by pumping and their replenishment from rain and snow; and (4) surface ocean water currents and mixing times (Kaufman and Libby, 1954; Begemann and Libby, 1957; Roether et al., 1980). Apart from hydrological studies, many of the current environmental applications are associated with measurements in and around facilities associated with nuclear power production and the cleanup of sites formerly used in the production of nuclear weapons (Noakes and De Filippis, 1988; Amano, 1992; Hofstetter and Wilson, 1993).

Cocktail Choices

Insta-Gel XF (sold as Insta-Gel Plus in Europe) is popular gelling cocktails (Packard Instrument Company) capable of accepting up to 50% water. The XF (xylene free) version was introduced because it has a lower vapor pressure and a higher flash point, as well as lower toxicity. Pico-Fluor LLT was formulated specifically for low level tritium work and it is capable of accepting approximately 55% water provided the sample is of low ionic strength (distilled water is required for maximum holding capacity). It causes less quenching than the Insta-Gel products and consequently produces higher counting efficiencies. More recently, in response to environmental, health and safety pressures, di-isopropylnaphthalene (DIN) based cocktails for liquid scintillation analysis have been introduced. Packard Instrument Company produces the Ultima Gold series of DIN-based cocktails. Ultima Gold has an aqueous holding capacity of approximately 25% while Ultima Gold XR has a 50% holding capacity. These cocktails have several major advantages:

1. DIN has not been identified as hazardous by the Environmental Protection Agency of the United States. Because it is widely used in the manufacturing of carbonless copy paper, its toxicological properties have been extensively studied - the results of these studies are summarized by Thomson (1989).
2. DIN has a very high flash point (152 °C) and is therefore classified as non-dangerous in accordance with national and international traffic regulations.
3. DIN is considered biodegradable (Yoshida and Kojima, 1978; Addison, 1983).

Table 4-1 indicates the performances of four of the main Packard cocktails used for tritium analysis. The following points should be noted. Ultima Gold gives the highest efficiency because it produces less quenching due to a lower surfactant content. However, because it could only retain approximately 25% aqueous loading in this experiment, the E^2V^2/B factor is always the lowest among the four cocktails for the same experimental conditions (the V^2 factor in the E^2/B expression is often included when comparing results between samples of different volumes). The combination of plastic vials with the low level option enabled always produces the highest E^2V^2/B factor. Ultima Gold XR does not differ significantly in performance from Insta-Gel or Pico-Fluor LLT, and of course has the major safety advantages described previously and much slower diffusion rates into plastic vials. The latest product in this range is Ultima Gold LLT, which is specifically designed for low level environmental sample counting.

Cocktail	Vial	BCC*	Efficiency (0-18.6 keV) (%)	Background (0-18.6keV) CPM	E^2V^2/B** (Opt. Region)
Insta-Gel XF	Glass	Off	27.6	22.5	7640
Insta-Gel XF	Glass	On	25.6	8.8	14400
Insta-Gel XF	Plastic	Off	27.6	12.6	19800
Insta-Gel XF	Plastic	On	25.4	7.6	22000
Pico-Fluor LLT	Glass	Off	28.2	22.5	7360
Pico-Fluor LLT	Glass	On	26.7	9.2	15700
Pico-Fluor LLT	Plastic	Off	28.1	12.6	19400
Pico-Fluor LLT	Plastic	On	26.8	7.6	24300
Ultima Gold	Glass	Off	44.1	21.4	2060
Ultima Gold	Glass	On	36.5	6.7	4510
Ultima Gold	Plastic	Off	45.6	11.0	5940
Ultima Gold	Plastic	On	37.5	5.6	6160
Ultima Gold XR	Glass	Off	25.9	19.5	8710
Ultima Gold XR	Glass	On	22.6	6.8	14900
Ultima Gold XR	Plastic	Off	26.9	12.4	19000
Ultima Gold XR	Plastic	On	23.0	6.0	20700

*Burst counting circuitry on (low level option)

**(Efficiency^2 x Volume^2)/Background

Table 4-1.

Background and efficiencies for ^{3}H (0-18.6 keV) and optimum region E^2V^2/B values using a Packard 2250CA with Insta-Gel XF, Pico-Fluor LLT, Ultima Gold XR (50% loading), and Ultima Gold (25% loading).

Sample Preparation and Measurement

In the early years of ^{3}H measurement at environmental concentrations, gas proportional counting was the most commonly used analytical technique since the background from commercially available LSC instruments was relatively high and counting efficiencies were low. However, the many improvements in liquid scintillation technology have greatly increased the popularity of this technique. These improvements include: the production of plastic counting vials which have the effect of reducing background (as discussed below) principally because they have no ^{40}K and much lower alpha contamination than glass vials; the development of new scintillation cocktails which are based on solvents which diffuse much more slowly into plastic (pseudocumene and di-isopropylnaphthalene) and have a much greater aqueous accepting capability; improvements in PMT and electronic designs; and the entire concept of producing low background instrumentation for environmental applications.

Essentially, there are three methods of sample preparation prior to low level environmental ^{3}H water analysis by liquid scintillation counting.

Direct Addition of Water With or Without Distillation

Direct addition without distillation is most appropriate when the sample has been effectively filtered to remove particulate matter and the dissolved organic content (with potential ^{3}H contamination) is low. The water is simply added to one of the aqueous accepting cocktails described below. A maximum of approximately 12 mL of water can be accommodated in a standard vial. Distillation may be required to lower the ionic strength of the sample, remove dissolved organic carbon or contaminating radionuclides, and generally improve the sample quality. This does increase the preparation time but can result in increased volumes being accepted by the cocktail. Liquid scintillation counters designed specifically for tritium analysis are available. Such LSC's can accommodate larger sample vials (100 mL). The efficiency of such instruments is somewhat lower than for a standard LSC but lower limits of detection are possible.

Table 4-2 illustrates typical limits of detection for ^3H analysis for a 1000 minute counting period and optimum regions using the Packard Tri-Carb 2250CA LSC, calculated according to Currie (1968). The data are from Cook and Anderson (1993) and indicate that limits of detection of about 1.6 Bq L^{-1} (13 TU approximately) are achievable.

Cocktail	BCC*	Vial Type	Limit of Detn. (Bq L^{-1})
Pico-Fluor LLT	Off	Glass	2.88
Pico-Fluor LLT	On	Glass	1.97
Pico-Fluor LLT	Off	Plastic	1.78
Pico-Fluor LLT	On	Plastic	1.59
Ultima Gold XR	Off	Glass	2.65
Ultima Gold XR	On	Glass	2.03
Ultima Gold XR	Off	Plastic	1.80
Ultima Gold XR	On	Plastic	1.73

*Burst counting circuitry = Low level count mode

Table 4-2.

Limits of detection for the Packard 2250CA under a range of counting conditions using Pico-Fluor LLT and Ultima Gold XR (1000 minute counting period).

In biological samples there are two basic forms of tritium: tissue free water tritium (TFWT) and tissue bound tritium (TBT). The former is defined as tritium associated with the water fraction of tissue and this can be obtained by freeze-drying fresh samples. The latter is obtained by combustion of the freeze-dried samples and subsequent collection of the water of combustion. Most often, the measurement of biological samples will be in association with environmental survey work around nuclear power plants or in tracer studies. In either case, direct addition of liquid samples, solubilization, or combustion of tissue samples are the most common techniques. Production of water samples via combustion has been fully automated in the Packard System 387 automatic sample oxidizer. The System 387 uncaps vials, combusts the samples, deposits them into vials with cocktail, recaps the vials, and loads them into cassettes ready for counting. The Model 307 oxidizer is the basic oxidizer unit without the robotic sample handling ability.

Electrolytic Enrichment

This procedure is based on the principle of selective isotopic enrichment using electrolysis. Because of slightly elevated binding energies, molecules of THO are not decomposed to form H_2 and O_2 as readily as H_2O or DHO (T = tritium, D = deuterium). Each phase transition (water to vapor and water to gas, etc.) produces isotopic fractionation and enrichment of tritium in the water. Electrolytic decomposition of a water sample down to about 5% of its initial volume will conserve approximately 80% of the ^3H in the initial water volume. This procedure typically takes several days to bring about the 95% reduction in volume and so multicell designs are most common. Modern systems with electronic control will stop the electrolysis procedure after a preset number of ampere-hours, control the temperature, and prevent current flow when the temperature is either too high (causing increased evaporative losses) or too low (electrolyte frozen) which may occur after interruption to the main electricity supply. A typical multicell system could have 20 - 40 cells. The enrichment factor in each run is determined by adding a known tritium activity to a small number of the cells. The mean of these can then be assumed to be valid for the cells containing samples. Each time an electrolysis run is carried out, different cells are spiked with the known tritium concentration. In this way, enrichment efficiency values can be determined for each cell and the reproducibility of each cell can be monitored. Following distillation of the remaining electrolyte, the same cocktails as described for direct addition are used and limits of detection of approximately 1 TU are achievable from a 1000 minute count. However, Morgenstern et al., (1993) state that in general, these systems have a reproducibility error of about 3-6% which limits the accuracy of the total measurement process and should be taken into account in any calculations, although there are methods of reducing this error term.

Benzene Synthesis

The third method of preparation is the synthesis of high purity benzene from water samples. The apparatus required is identical to that used in benzene synthesis for radiocarbon dating (see ^{14}C analysis). In this instance, the sample water is added to calcium carbide in an evacuated reaction vessel and acetylene (C_2H_2) is generated. The acetylene is then cyclotrimerised to high purity benzene using a chromium or vanadium based catalyst. For benzene counting, there is no requirement for a scintillation cocktail. The fluors can be added in solid form directly to the vial; a standard vial will accommodate about 22 mL of benzene. The synthesis of this volume can be time consuming and generally volumes between 8 and 15 mL are more typical. One sample per vacuum apparatus per day would be optimal. Noakes and De Filippis (1988) achieved a counting efficiency of 45.4% and a background of 3.6 CPM for 15 mL benzene counted in a modified Packard 2050 CA/LL. Table 4-3 compares limits of detection calculated from Cook and Anderson (1993) and Noakes and De Filippis (1988).

Method	Optimum Efficiency (%)	Optimum Background (CPM)	MDA (Bq)	MDA (TU)
Direct counting (10 mL) using Pico-Fluor LLT	22.6	2.1	1.59	13.5
Benzene synthesis (15 mL) + PPO/POPOP	45.4	3.6	0.99	8.4
Enrichment (assuming x 20 enrichment) 10 mL + Pico-Fluor LLT	22.6	2.1	0.08	0.7

Table 4-3.

Comparison of limits of detection for ^3H by three techniques: direct H_2O addition, benzene synthesis from H_2O and electrolytic enrichment of H_2O.

Summary

These results demonstrate that for environmental monitoring, direct counting of water will give acceptable limits of detection for most radiological purposes. Conversion of water to benzene will lower the detection limit but sample preparation is much more time consuming. Electrolytic enrichment followed by liquid scintillation counting will give much lower limits of detection than the other two techniques and is the preferred method for many hydrological studies.

References

Addison, R. F. 1983. PCB replacements in dielectric fluids. *Environmental Science and Technology*. 17: 486A-494A.

Amano, H. 1992. Environmental monitoring of tritium around radioactive waste disposal area - analysis of tritium movement in a forest. *Fifth International Seminar for Liquid Scintillation Analysis*. 55-76, Tokyo, Japan.

Begemann, F. and Libby, W. F. 1957. Continental water balance, ground water inventory and storage times, surface ocean water mixing rates and worldwide water circulation patterns from cosmic-ray and bomb tritium. *Geochimica et Cosmochimica Acta*. 12: 277-296.

Cook, G. T. and Anderson, R. 1993. An evaluation and comparison of traditional and DIN-based cocktails for ^3H analysis by time-resolved liquid scintillation counting. *Radioactivity & Radiochemistry*. 4: 8- 13.

Currie, L. A. 1968. Limits of quantitative and qualitative detection. *Analytical Chemistry*. 40: 586-593.

Geyh, M. A. and Schleicher, H. 1990. *Absolute Age Determination*. Springer-Verlag, Berlin.

Grosse, A. V., Johnston, W. H., Wolfgang, R. L. and Libby, W. F. 1951. Tritium in nature. *Science*. 113: 1-2.

Hofstetter, K. J. and Wilson, H. T. 1993. Continuous tritium effluent water monitor at the Savannah River site. In *Advances in Liquid Scintillation Spectrometry 1992*, ed. Noakes, J. E., Schönhofer, F. and Polach, H. A. 335-342, Radiocarbon Publishers.

Kaufman, S. and Libby, W. F. 1954. Natural distribution of tritium. *Physical Review*, 93: 1337-1344.

Libby, W. F. 1946. Atmospheric helium three and radiocarbon from cosmic radiation. *Physical Review*. 69: 671-672.

Libby, W. F. 1963. Moratorium tritium geophysics. *Journal of Geophysical Research*. 68: 4485-4494.

Momoshima, N., Takashima, Y. and Okai, T. 1990. Tritium in the environment. *Fourth International Seminar for Liquid Scintillation Analysis*, 108-125. Tokyo, Japan.

Morgenstern, U., Hebert, D. and Stolz, W. 1993. Electrolytic tritium enrichment of natural water samples for tritium analysis. In *Advances in Liquid Scintillation Spectrometry 1992*, ed. Noakes, J. E., Schönhofer, F. and Polach, H. A., 355-360. Radiocarbon Publishers.

Noakes, J. E. and De Filippis, S. 1988. Tritium monitoring of nuclear power plants by liquid scintillation counting. *Second International Seminar for Liquid Scintillation Analysis*, 123-138. Tokyo, Japan.

Roether, W., Münnich, K. O. and Schoch, H. 1980. On the ^{14}C to tritium relationship in the North Atlantic ocean. *Radiocarbon*. 22: 636-646.

Thomson, J. 1989. Di-Isopropylnaphthalene - a new solvent for liquid scintillation counting. In *Liquid Scintillation Counting and Organic Scintillators*, ed. Ross, H., Noakes, J. E. and Spaulding, J. D., 19-34. Lewis Publishers.

Yoshida, T. and Kojima, H. 1978. Studies on environmental safety of di-isopropylnaphthalene (DIPN). Part II. Biodegradation of ^{14}C-DIPN with activated sludge, *Chemosphere*. 6: 497-501.

Chapter 5: Radiocarbon

^{14}C in the Environment

^{14}C has a half-life of 5730 years and decays by beta emission (E_{max} = 156 keV) to the stable nuclide ^{14}N. Since ^{14}C is ubiquitous in our environment it is also one of the most common radionuclides measured by LSC. It occurs naturally as a result of production via the interaction of cosmically produced neutrons with atmospheric nitrogen in the upper atmosphere. It is also produced artificially from a number of sources including atmospheric nuclear weapons testing (principally during the 1950's and 60's); discharges from facilities associated with the nuclear fuel cycle; discharges from facilities which synthesize radiolabeled compounds for biomedical, biological and agricultural tracer studies; and discharges from hospitals, universities, research centers, etc., of the labeled materials used in tracer studies.

^{14}C Measurement Applications

The environmental applications for ^{14}C measurements can be divided into three main categories as follows:

Radiocarbon Dating

The constant natural production of ^{14}C in the upper atmosphere and its uniform uptake as $^{14}CO_2$ in living plant material and subsequent transfer through the food chain, is the basis of the radiocarbon dating technique. The end result of the food chain transfer is almost uniform labeling of all living organisms. ^{14}C dating is used in a wide range of scientific disciplines including archaeology, geology (particularly of the Quaternary Period), soil science, climatic reconstruction and oceanography. LSC is now the most commonly used measurement technique.

Environmental Measurements

Typically, these measurements are performed on samples from the environment around facilities which produce labeled compounds and facilities associated with the nuclear fuel cycle. Although ^{14}C is not among the most abundant of the anthropogenic radionuclides, its long half-life and high environmental mobility mean that it delivers one of the highest collective effective dose equivalents to the global population. This is the reason for the interest in its measurement in the environment.

Food Adulteration Studies

Petroleum derivatives are occasionally used to adulterate natural food and drink products without the buyers knowledge. Because petroleum based products are sufficiently old that they contain no ^{14}C, depletions in the natural ^{14}C content are normally indicative of adulteration. Examples of this include the adulteration of wines, spirits, wine or cider vinegars, and other natural products.

Sample Preparation

Regardless of the source of ^{14}C or of the scientific discipline involved in its measurement, sample preparation for LSC is performed by either CO_2 absorption or benzene synthesis.

CO_2 Absorption

Direct absorption of CO_2 using quaternary amines is a widely used technique, particularly where the activities are enriched relative to natural production. Carbo-Sorb® is a high capacity carbon dioxide absorber which is compatible with LSC cocktails. Direct absorption into inorganic bases is another means of absorbing the CO_2. Aqueous solutions of up to one molar sodium or potassium hydroxide, or methanolic solutions of two molar potassium hydroxide, have been routinely used. However, these have three distinct disadvantages: (1) they are strong quenching agents; (2) they have low trapping capacities compared to the amines; and (3) they produce severe chemiluminescence.

Benzene Synthesis

This technique is the one used almost exclusively by practitioners of the radiocarbon dating technique and involves the following steps. Sample carbon is converted to CO_2 by combustion in a pure oxygen atmosphere for organic carbon samples. Occasionally, wet oxidation with chromic acid is used for low organic carbon samples while acid hydrolysis is used for inorganic carbon samples such as shell material and carbonate deep ocean sediments. The CO_2 is subsequently converted to lithium carbide by absorption onto molten lithium. On cooling, the addition of water causes the production of acetylene (Barker, 1953). The acetylene is then cyclotrimerised to benzene using a chromium or vanadium based catalyst (Noakes et al., 1963).

Benzene is an ideal counting medium for the following reasons:

1. It is a clear organic solvent capable of dissolving sufficient fluor concentrations.
2. It has excellent energy transmission properties.
3. It has a high carbon content (92.3%).
4. It is relatively easy to synthesize.
5. It has reasonable resistance to quenching.

Measurement and Cocktail Considerations

CO_2

Typically, Permafluor E+ cocktails would be recommended for use with Carbo-Sorb. All of these products are produced by Packard Instrument Company. For CO_2 samples absorbed into base solutions, a cocktail such as Hionic-Fluor™, which can accept high ionic strength solutions, is added. For low accuracy measurements the advantages of the absorption technique are that sample preparation is less time consuming than for benzene synthesis and the sample preparation apparatus is relatively simple. Where improved accuracy is required, as for example in the small number of laboratories performing ^{14}C dating, the advantages are somewhat lessened. The major disadvantage of this technique is the amount of carbon that can be absorbed: 10 mL of Carbo-Sorb is approximately the maximum quantity that would be miscible with Permafluor E in a 20 mL vial. This is capable of absorbing 58 millimoles of CO_2 which is equivalent to 0.7 g of carbon. In comparison, it is possible to add approximately 19 g of carbon into a vial via benzene synthesis, although 3-7 g is more typical. Detailed information on the absorption technique may be obtained from Qureshi et al. (1989).

Benzene

The trend in the radiocarbon dating discipline has been to use only a primary fluor and to use it at relatively high concentrations (12-15 mg per gram of benzene). This is now possible since the wider wavelength response of modern PMT's has negated the requirement for a secondary fluor (wavelength shifter). However, it should be noted that non-programmable TR-LSC, as discussed in chapter two, was designed for primary and secondary fluor use and, in order to optimize performance, it is vitally important that the correct type and concentration of fluors be chosen. The Tri-Carb 2000 and 2200 series of instruments have the fixed delay of 75 nsec between the onset of the prompt pulse and the measurement of afterpulses. Therefore, any cocktail which generates significant afterpulsing beyond the 75 nsec delay will reduce counting efficiency, since the events will be indistinguishable from background. The principal example of this is the use of a primary fluor only (particularly *butyl*-PBD). Which leads to a significant reduction in counting efficiency when the low level option is enabled. Table 5-1 indicates the changes in counting efficiency observed as a function of either *butyl*-PBD or PPO primary scintillator concentration. Table 5-1 shows that with the BCC option enabled (low level on), efficiency is much more variable as a function of fluor concentration, and there are considerable reductions in efficiency as compared to when the BCC is switched off, particularly at the higher fluor concentrations. The addition of a secondary fluor does not always enhance efficiency. Tables 5-2 and 5-3 indicate that of the secondary fluors which have been tested (*bis*-MSB, POPOP and dimethyl-POPOP), only *bis*-MSB substantially enhances efficiency. In addition, the concentration of *bis*-MSB required to maximize this enhancement is greater than would normally be expected if it were acting solely as a wavelength shifter. This enhancement in efficiency is brought about by *bis*-MSB reducing the delayed component of the pulse.

Fluor Concentration (mg/g C-6 H-6)	**%Efficiency *LL on**	**t-SIE LL on**	**%Efficiency LL off**	**t-SIE LL off**	**Difference in % Efficiency**
(a) butyl-PBD					
2	84.1	557	91.8	557	7.7
4	80.7	683	93.5	681	12.8
6	78.9	730	92.8	732	13.9
8	76.6	749	93.5	751	16.9
10	75.7	757	93.2	755	17.5
12	75.2	761	93.6	762	18.4
14	74.8	761	93.1	760	18.3
16	73.9	760	93.4	759	19.5
18	73.5	758	93.0	759	19.5
20	73.7	755	93.8	755	20.1
(b) PPO					
2.2	85.4	582	92.5	579	7.1
3.3	84.8	620	91.7	614	6.9
4.4	84.0	635	92.8	629	8.8
5.6	83.6	639	93.5	635	9.9
7.8	82.8	638	92.6	634	9.8
10.0	82.3	634	92.6	629	10.3

*LL=Low level option (i.e., BCC).

Table 5-1.

Variation in ^{14}C counting efficiency (0-156 keV) in Packard Tri-Carb 2000CA/LL as a function of *butyl*-PBD or PPO concentration.

Fluor Concentration (mg/g C-6 H-6)	%Efficiency *LL on	t-SIE LL on	% Efficiency LL off	t-SIE LL off	Difference in % Efficiency
(a) POPOP					
0	83.6	639	93.5	635	9.9
0.1	83.9	652	93.5	651	9.6
0.2	82.9	661	93.8	659	10.0
0.7	81.9	696	93.8	696	11.9
1.1	82.0	694	93.4	688	11.4
(b) dimethyl POPOP					
0.1	83.2	615	92.8	613	9.6
0.2	82.3	632	93.4	630	11.1
0.7	82.6	653	93.6	652	11.0
1.1	82.4	671	92.7	663	10.3
(c) bis-MSB					
0.2	85.4	661	93.0	659	7.6
0.7	87.5	682	93.1	682	5.6
1.3	88.0	695	93.8	696	5.8
2.7	89.6	702	93.7	699	4.1
5.3	89.1	672	93.7	678	4.6

*LL=Low level option (i.e., BCC).

Table 5-2.

Effect of incorporating varying concentrations of secondary scintillants (POPOP, dimethyl POPOP and *bis*-MSB) into a fixed concentration of PPO (5.6 mg g^{-1} of C_6H_6) (0-156 keV counting window). Carried out using a Packard 2000CA/LL.

Considerable research has been carried out into the optimization of a cocktail for use with these instruments (Cook, et al., 1990a, 1990b; Anderson and Cook, 1991; Cook and Anderson, 1992) and the recommended concentrations on the basis of this work are 2.8 mg of *butyl*-PBD and 3.0 mg of *bis*-MSB per gram of sample benzene.

The main reason why other researchers use high concentrations of a primary fluor and no secondary fluor is that it can be weighed as a solid into the vial, which minimizes volume addition and consequently minimizes any background increases associated with volume increase. To overcome the difficulties involved in weighing such small quantities of two fluors into vials, a technique has been developed for dispensing them in solution and then removing the solvent. The technique is as follows: 2.8 grams of *butyl*-PBD and 3 grams of *bis*-MSB are accurately weighed and dissolved in scintillation grade benzene, the total weight being made up to 1 kg. Sufficient cocktail can then be accurately dispensed or weighed in order to yield the optimum concentrations of fluors. The benzene can then be removed by freeze-drying. This can simply be a large vacuum desiccator to hold the vials, a cold finger surrounded by liquid nitrogen to freeze out the benzene vapor, and a small rotary pump to create a vacuum. The cocktail must be frozen in the vials prior to commencement of benzene removal. This technique consistently gives total benzene removal with no loss of fluors, which are confined almost totally to the base of the vials. This technique also has the additional advantage that the vials can be screened for variations in tSIE and background prior to freeze-drying, thus enabling selection of vials of uniform specification. Also, the precision of fluor addition to the vials is much better and more uniform than can be achieved by weighing the solid material. When carried out in a batch mode, the process is no more time consuming.

Fluor Concentration (mg/g C-6 H-6)	%Efficiency *LL on	t-SIE LL on	% Efficiency LL off	t-SIE LL off	Difference in % Efficiency
(a) POPOP					
0	74.6	760	94.0	762	19.4
0.1	76.6	767	94.5	768	17.9
0.2	76.3	770	93.7	770	17.4
0.7	78.7	767	93.2	766	14.5
1.1	78.8	759	94.0	759	15.2
(b) dimethyl POPOP					
0	75.1	755	93.5	755	18.4
0.2	75.6	732	93.6	734	17.0
0.7	77.2	726	93.5	726	16.3
1.3	78.1	726	94.0	725	15.9
2.7	78.8	715	93.5	717	14.7
(c) bis-MSB					
0	74.7	757	93.3	754	18.9
0.2	81.1	752	93.5	755	12.4
0.7	83.9	752	93.9	750	10.0
1.3	86.6	743	93.6	740	7.0
2.0	87.4	734	93.5	732	6.1
2.7	87.4	722	93.2	718	5.8
3.3	88.0	708	93.3	707	5.3
4.0	88.5	696	93.1	695	4.6
4.7	87.2	680	92.7	681	5.5
5.3	88.0	679	93.6	683	4.6

*LL=Low level option (i.e., BCC).

Table 5-3.

Effect of incorporating varying concentrations of secondary scintillants (POPOP, dimethyl POPOP and *bis*-MSB) into a fixed concentration of *butyl*-PBD (12 mg g^{-1} of C_6H_6) (0-156 keV counting window). Carried out in Packard Tri-Carb 2000CA/LL.

The Tri-Carb 2500 and 2700 series of instruments have the variable delay-before-burst feature (programmable TR-LSC) which allows user modifications to the instrument setting rather than modifications to the cocktail. Figure 5-1 demonstrates no improvement in the optimum E^2/B term as the burst delay is increased for the cocktail which was optimized for non-programmable TR-LSC.

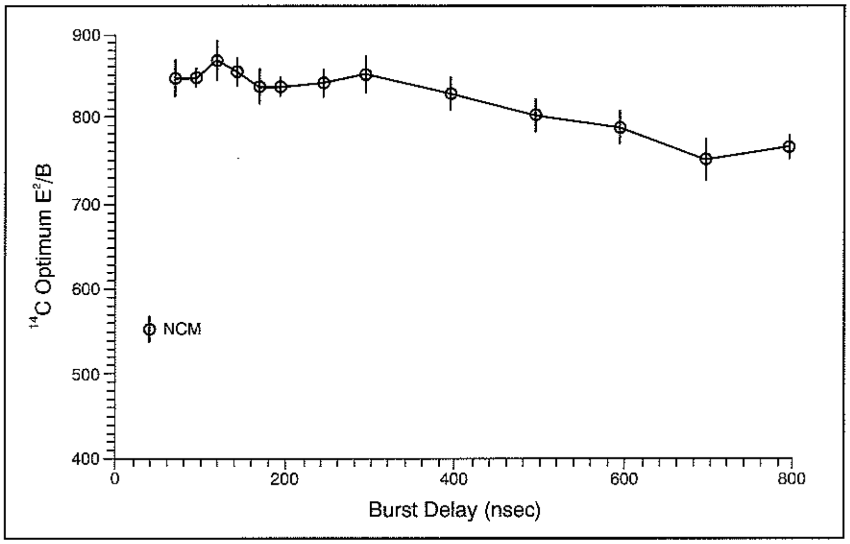


Figure 5-1.
Effect of increasing delay-before-burst on optimum E^2/B using
butyl-PBD/bis-MSB cocktail (15 g benzene geometry) (Cook and Anderson, 1993).

Figure 5-2 demonstrates a significant increase in the optimum E^2/B term for a cocktail which gave a poor response in a non-programmable instrument.

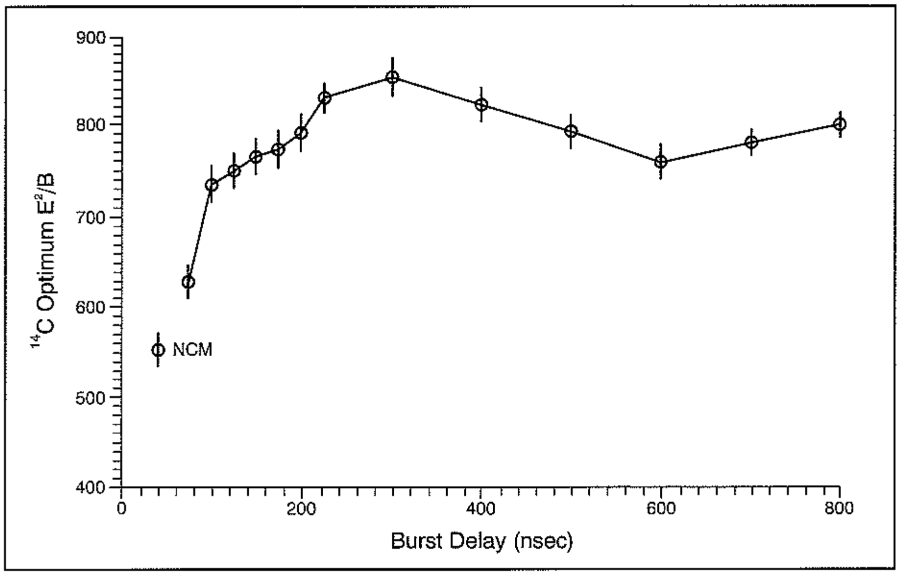


Figure 5-2.
Effect of increasing delay-before-burst on optimum E^2/B
using butyl-PBD cocktail (15 g benzene geometry) (Cook and Anderson, 1993).

No advantage in terms of background reduction is obtained from the use of Teflon vials. Table 5-4 indicates the background count rates and efficiencies obtained when comparing 15 mL Teflon vials with 20 mL standard low potassium glass vials. Background count rates in an open window are significantly greater for Teflon. In an optimum window (for the glass vial) the background for Teflon is greater by more than a factor of two.

Vial Type	**% Efficiency (0-156 keV)**	**Background (CPM)**	**% Efficiency (8.5-75 keV)**	**Background (CPM)**
Glass	89.9	5.40	72.0	1.68
Teflon	89.6	8.55	73.1	3.56

Table 5-4.

Comparison of efficiencies and backgrounds between 15 mL Teflon vial and 20 mL glass vial in Packard Tri-Carb 2260XL (4.5 g geometry and optimum fluor concentrations and ratios), LL on.

Table 5-5 compares the use of these 20 mL glass vials with the equivalent 7 mL size. The results indicate an immense reduction in background with the low level option (LL) on (combined with substantial increases in E^2/B) and that there is no significant difference in background between the two vial sizes. Note that with the low level off, vial size is important. Similar studies with the Tri-Carb 2260XL indicate further improvements in performance and, with this instrument, the small vial is significantly better (see Table 5-6). Results for efficiencies using the same geometries suggest a marginal increase for the 2 g geometry using the 7 mL vial compared with the 20 mL vial.

Vial Size	**2 g Geometry** (0-156 keV)	(11-90 keV) (opt. window)	**4 g Geometry** (0-156 keV)	(11-90 keV) (opt. window)
(a) Background				
7 mL (*LL on)	5.2	1.3	6.5	2.1
7 mL (LL off)	18.3	6.2	18	6.3
20 mL (LL on)	5.6	1.4	6.6	2.1
20 mL (LL off)	23.5	7.6	24.5	8.3
(b) Efficiency				
7 mL (LL on)	89.6	71.7	89.6	71.6
7 mL (LL off)	94.4	75.7	94.0	75.2
20 mL (LL on)	89.1	70.1	89.4	71.2
20 mL (LL off)	94.0	74.0	94.4	75.2
(c) E^2/B				
7 mL (LL on)	1540	3840	1250	2410
7 mL (LL off)	490	930	490	910
20 mL (LL on)	1430	3490	1210	2370
20 mL (LL off)	380	720	360	680

*LL=Low level option (i.e., BCC).

Table 5-5.

Comparison of background count rates and efficiencies between 7 and 20 mL Packard low potassium glass vials in a Packard Tri-Carb 2250CA (2 g and 4 g geometries, optimum fluor concentrations and ratios).

Table 5-6 charts the progressive improvements in performance that can be achieved with different models and special vial holders (Pico-XL vial holders) manufactured from slow scintillating plastic material which serves as an additional detector guard to further reduce background. For information on performance using the BGO detector guard and vial holders, refer to Table 1-5.

Counting Conditions	Open Window % Efficiency	Optimum Window % Efficiency	Optimum Window Background (CPM)	E^2/B
Tri-Carb 2000CA *LL off	92.1	57.8	2.87	1170
Tri-Carb 2000CA LL on	88.1	65.0	1.31	3230
Tri-Carb 2000CA LL on + vial holders	87.5	66.0	0.85	5130
Tri-Carb 2260XL LL on	86.9	70.2	0.94	5270
Tri-Carb 2260XL LL on + vial holders	88.6	71.4	0.69	7380

*Low level option (i.e., BCC).

Table 5-6.
Progressive optimization of the Packard low level counting system (2.4 g benzene geometry).

The advantages of the benzene synthesis technique are the achievement of much higher accuracy and precision analyses and the great improvement in MDA.

Age Determinations

The following procedure is typical of how many ^{14}C laboratories would carry out the measurement procedure and age calculation:

Sample counting in many laboratories follows the quasi-simultaneous batch counting procedure. For example, each batch might consist of approximately 20 vials which includes four backgrounds (both commercially purchased scintillation grade benzene and benzene which has been synthesized from “infinite age” material); four modern reference standards (benzene synthesized from NBS Oxalic Acid II - SRM-4990C); and approximately 12 samples. Finally, a single high activity standard is used to monitor stability of efficiency (from count rate) and quenching (from tSIE). The high activity standard would normally be vialed in a sealable ampoule since it is used on a long term basis. Any effects of the sealing process on efficiency are of no consequence since its use is purely comparative. Each sample is counted for 50 minutes but with a 2s of 1%. Only the high activity standard is limited by this (if the time to reach the preset error is constant, then efficiency will be constant). After 40 cycles (2000 minutes), the following procedures are carried out:

1. Mean gross count rates ± standard error are calculated on each vial.
2. A mean background count rate is calculated from the four individual vials.
3. Net count rates are calculated for all modern standards and samples.
4. A mean modern count rate is calculated from the four individual vials.

Although the benzene production procedure yields a relatively uniform product, small variations in the degree of quenching do occur. To compensate for this, a quench curve is set up using about 16 vials containing known ^{14}C activities (as far as possible identical) in an identical counting geometry to samples and quenched over a tSIE range of about 100 units using acetone. Count rate or counting efficiency is plotted and regressed against tSIE thus producing the quench curve from which counting efficiency can be determined for all samples. Rather than calculating DPM, sample count rates are normalized to the efficiency of the least quenched standard in the quench curve by applying a quench factor (QF); samples and the least quenched standard are normally within ±0.5%. Fractionation factors (FF) are calculated from $\delta^{13}C$ values measured by mass spectrometry, according to the following equation:

$$FF = 1-[2(\delta^{13}C+25)/1000]$$

$\delta^{13}C$ = $^{13}C/^{12}C$ fractionation of samples and Oxalic Acid II (measured by mass spectrometry) with respect to *Belemnita americana* from the Peedee formation in South Carolina, commonly referred to as PDB.

Sample age is calculated from the first order decay equation:

$$A_t = A_o e^{-\lambda t}$$

Where: A_t = sample activity at some time, t
A_o = initial sample activity
λ = decay constant, equivalent to $\ln 2/t_{1/2}$

This rearranges to:

$$t = 8033.\ln[A_{ON}/A_{SN}]$$

using the Libby half-life of 5568 years and where A_{ON}(A_0) = normalized Oxalic Acid II activity, *i.e.,* net CPM/g benzene x 0.7459 (normalization factor for Oxalic Acid II) x QF x FF (mean A_{ON} is derived from the four individuals).

A_{SN}(A_t) = normalized sample activity, *i.e.,* net CPM/g benzene x QF x FF.

The uncertainty on the age measurement is calculated from the errors on background count rate, modern count rate, sample count rate, quench factor, fractionation factor, and replicate analyses on a homogeneous bulk sample. A sample calculation follows:

Mean gross sample count rate = 31,103 CPM
Number of background samples = 4

B-223	1.451 CPM
B-226	1.493 CPM
B-244	1.463 CPM
B-248	1.438 CPM

Average background = 1.461 CPM
Standard deviation = 0.024 CPM

Number of modern reference standards = 4

Net count rates corrected for fractionation and quenching, and with the 0.7459 normalization factor applied:

M-59	8.704 CPM	S.D. = 0.032 CPM
M-60	8.700 CPM	S.D. = 0.033 CPM
M-61	8.667 CPM	S.D. = 0.034 CPM
M-62	8.719 CPM	S.D. = 0.036 CPM

Weighted mean modern activity = 8.697 CPM = A_{ON}
Error on modern activity = 0.017 CPM

Using the background, the mean sample gross count rate, and applying QF (0.9991) and FF (1.0074) factors, the corrected net sample count rate is calculated.

(Mean sample gross CPM - mean background CPM) * QF * FF =
(31.103 - 1.461) * 0.9991 * 1.0074 =
Corrected net CPM = 29.834

Then, correcting per gram of benzene:

29.834 CPM/4.003g = 7.453 CPM (A_{SN})

Finally, substituting values for A_{SN} and A_{ON} (weighted mean modern activity):

$t = 8033 \ln(A_{ON}/A_{SN})$
$t = 8033 \ln(8.697/7.453)$
$t = 1240$ years

The above ^{14}C date is quoted in conventional years BP (before 1950 AD) and is uncalibrated with respect to dendrochronological age.

The error on this age measurement is calculated using the following equation:

$$\sigma(t) = 8033\left[\frac{\sigma A_{SN}^{2}}{A_{SN}^{2}} + \frac{\sigma A_{ON}^{2}}{A_{ON}^{2}}\right]^{\frac{1}{2}}$$

This calculation incorporates all the counting errors except those associated with the quench factor, fractionation factor, and replicates. For a more comprehensive review of the calculations refer to Gupta and Polach, 1985.

Summary

A quaternary amine will give greater CO_2 absorption than inorganic bases. Carbo-Sorb in combination with the Permafluor E cocktail is a suitable combination. However, the amount of carbon which can be retained in a vial is much reduced compared to the benzene synthesis technique. Glass vials are recommended unless the measurement is carried out soon after cocktail addition, in which case, the use of plastic vials is possible.

For benzene measurement, a cocktail comprising 2.8 mg of *butyl*-PBD and 3.0 mg of *bis*-MSB per gram of sample benzene is recommended. For instruments equipped with programmable TR-LSC (see chapter one), the use of a primary fluor only is possible but the delay-before-burst setting will have to be optimized. If the total volume is 7 mL or less, the 7 mL mini vials are more suitable. Teflon vials produce poorer E^2/B factors because of higher background and plastic vials are totally unsuitable for benzene. Instruments incorporating the slow fluorescence lifetime guard (Tri-Carb 2260 and 2560 models) and/or the vial holders made from the same material will improve performance further. However, the use of *butyl*-PBD alone is not recommended as the plastic absorbs the light output and re-emits it as slow pulses which are indistinguishable from background. This brings about extremely low efficiency.

References

Anderson, R. and Cook, G. T. 1991. Scintillation cocktail optimization for ^{14}C dating using the Packard 2000 CA/LL and 2260 XL. *Radiocarbon*. 33: 1-7.

Barker, H. 1953. Radiocarbon dating: Large scale production of acetylene from organic material. *Nature*. 172: 631-632.

Cook, G. T. and Anderson, R. 1992. A radiocarbon dating protocol for use with Packard scintillation counters employing burst-counting circuitry. *Radiocarbon*. 34: 381-388.

Cook, G. T., Hold, A. G., Naysmith, P. and Anderson, R. 1990b. Applicability of 'new technology' scintillation counters (Packard 2000 CA/LL and 2260 XL) for ^{14}C dating. *Radiocarbon*. 32: 233-234.

Cook, G. T., Naysmith, P., Anderson, R. and Harkness, D. D. 1990a. Performance optimization of the Packard 2000 CA/LL liquid scintillation counter for ^{14}C dating. *Nuclear Geophysics*. 4: 241-245.

Gupta, S. F. and Polach, H. A. 1985. *Radiocarbon dating practices at ANU*. Australia: ANU printing services.

Noakes, J. E., Isbell, A. F., Stipp, J. J., and Hood, D. W. 1963. Benzene synthesis by low temperature catalysis for radiocarbon dating. *Geochimica et Cosmochimica Acta*. 27: 797-804.

Qureshi, R. M., Aravena, R., Fritz, P. and Drimmie, R. 1989. The CO_2 absorption method as an alternative to benzene synthesis method for ^{14}C dating. *Applied Geochemistry*. 4: 625-633.

Section III.

Environmental Radionuclide Analysis - Natural Series Radionuclides

Chapter 6: Uranium

Uranium in the Environment

Isotopes of the uranium and thorium series are naturally occurring radioisotopes. Several isotopes of uranium and thorium are to be found in the three natural decay series, either as the parents (*i.e.*, ^{238}U, ^{235}U, or ^{232}Th) or as the daughters (*e.g.*, ^{234}U, ^{234}Th, ^{228}Th, etc.). Natural decay series radionuclides occur in rocks, soil, and often in water. Together with ^{40}K, they contribute to most natural radioactivity. The general distribution patterns vary in each matrix. The National Council on Radiation Protection and Measurements publication (NCRP) report no. 50 provides more details on the occurrence and the concentrations of individual uranium and thorium series radionuclides.

Uranium Monitoring Applications

Although fluorimetry, ICP-MS, and colorimetry are important techniques for low level uranium measurement, liquid scintillation methods have been used to monitor for uranium in a variety of matrices including water, urine, phosphate containing materials, and air (Bouwer et al., 1979; Bower, 1993; Hinton et al., 1990; Horrocks, 1974; Miller, 1991; Prichard and Cox, 1991; Venso et al., 1993).

Cocktail Choices

Many of the reported analysis of uranium involves extractive scintillator techniques. Prichard and Cox (1991) and Venso et al. (1993) combined an extractive agent, Bis(2-ethylhexyl) phosphoric acid (HDEHP), with either a toluene based or a di-isopropylnaphthalene (DIN) based cocktail. If alpha/beta discrimination techniques are used, cocktails containing mixtures of phenyl-ortho-xylylethane (PXE) and DIN or DIN alone give good alpha/beta separation without purging the sample of oxygen.

Sample Preparation

Prichard has studied the uranium content of water using both a conventional LSC and one capable of alpha/beta discrimination. In both studies, extractive scintillators were used to isolate the uranium with 95% recovery of activity. The simple extraction procedure used by Prichard (1993) is shown in Figure 6-1. The weight of the organic phase (scintillation cocktail) is recorded by weighing the volume in a tared scintillation vial to correct for recovery of scintillation solution. A preliminary survey of 12 samples from Texas water systems with known elevated alpha activity were screened for activity and radionuclide composition.

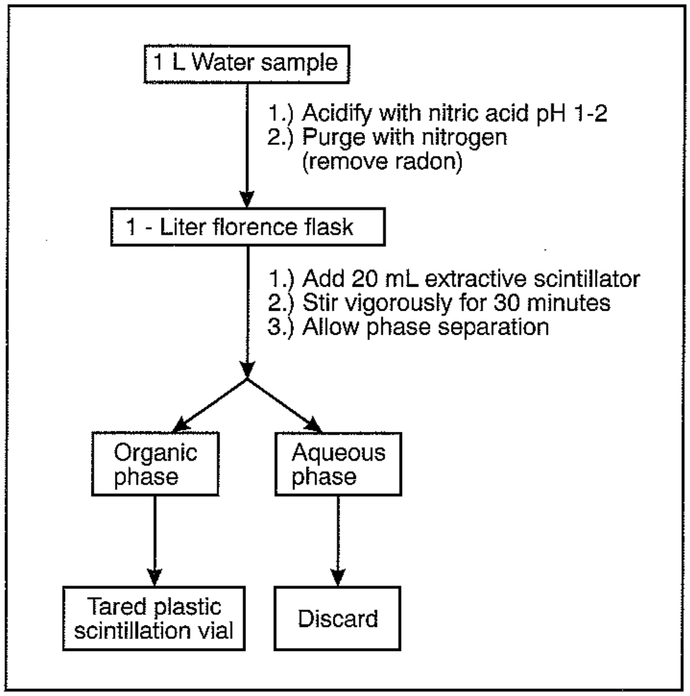


Figure 6-1.
Extraction of uranium from water.

Coating the bottom of translucent vials with a reflective material improved energy resolution to the degree that some nuclide identification among ^{234}U, ^{238}U, and other alphas was possible.

Ion exchange chromatography (Bio-Rad AG® 1-X8, 50-100 mesh) has been used by Miller (1991) to isolate excreted uranium in urine as the complex anion $UO_2Cl_4^{2-}$. The complex anion is formed by mixing equal volumes of the urine sample with an equal or excess volume of concentrated hydrochloric acid (HCl). Most interferences, including thorium, do not form complex anions at high molar HCl and are not adsorbed on the resin. After separation, the samples were analyzed by alpha spectrometry, but the author mentions that it is possible to use an extractive scintillant for measurement by LSC methods. Although the author mentions photon electron rejecting alpha liquid scintillation spectrometry (PERALS®, Ordela, Inc., Oak Ridge, Tennessee) as an alternative, it is likely that alpha/beta discriminating LSC may also provide adequate resolution information.

Detection Limits by LSC

Prichard (1991) reported a minimum detection limit of 0.0377 Bq L^{-1} (1.02 pCi L^{-1}) for the HDEHP extraction method and counting with a conventional LSC, assuming 90% combined counting efficiency and recovery, an average background of 3.2 CPM with a counting time of ten minutes.

A minimum detectable limit for alpha/beta discriminating LSC has been reported as 0.01 Bq L^{-1} (0.27 pCi L^{-1}) because of the lower alpha background (Venso et al., 1993) for a one liter sample counted for 20 minutes. Lower detection limits are possible by narrowing the counting window or increasing the count time. For urine samples, the extraction method and measurement by alpha/beta LSC may be a time saving screening alternative to routine analysis by traditional alpha spectrometry. Detectable limits are very near 0.1 pCi L^{-1}, which is the ANSI N13.30 specified limit for uranium in urine. Department of Energy facilities (DOE Order 5480.11) suggests utilization of the ANSI N13.30 detection limits.

Summary

Extraction of uranium and ion exchange of uranyl anion complexes are popular separation schemes that can be applied to a variety of sample matrices. Initial sample pretreatment/preparation may be necessary to obtain a suitable form for subsequent purification. Alpha/beta discriminating LSC shows great promise as an analytical tool to measure uranium samples because of easy sample preparation and low detectable limits. The 0.27 pCi L^{-1} detectable limit achievable with alpha/beta LSC in 20 minutes is slightly above the detection limits specified in ANSI N13.30.

References

American National Standards Institute, ANSI N13.30, 1989. *Draft American National Standard for Performance Criteria for Radiobioassay.*

Bouwer, E. J., Mckleeven, J. W. and McDowell, W. J. 1979. A solvent extraction scintillation, method for assay of uranium and thorium in phosphate-containing materials. *Nucl. Technol.* 42: 102.

Bower, K. 1993. Alpha-beta discrimination liquid scintillation counting for uranium and its daughters. Paper presented at the Canberra Instruments/Nuclear Data User's Group Meeting. April 28-30, San Diego, California.

Hinton, Jr. E. R., Adams, T. T., and Burchfield, L. A. 1990. Gross alpha counting of air filters using a pulse-shape discriminating alpha liquid scintillation counter. Paper presented at *36th Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry.* Oak Ridge, Tennessee.

Horrocks, D. L. 1974. Measurement of low levels of normal uranium in water and urine by liquid scintillation alpha counting. *Nucl. Instrum. Methods.* 117: 589-595.

Miller, T. J. 1991. Development of a rapid, economical and sensitive method for the routine determination of excreted uranium in urine. *Analytical Letters.* 24(4): 657-664.

Prichard, H. M. and Cox, A. 1991. Liquid scintillation screening method for isotopic uranium in drinking water, In *Liquid Scintillation Counting and Organic Scintillators.* ed. Ross, H., Noakes, J. E., and Spaulding, J. D., Lewis Publishers, 385-397.

NCRP Report No. 50. 1976. Environmental Radiation Measurements. *National Council on Radiation Protection and Measurements.* Washington, D.C.

Venso, E. A., Prichard, H. M., and Dodson, C. L. 1993. Measurement of isotopic uranium in Texas drinking water supplies by liquid scintillation with alpha-beta discrimination. In *Advances in Liquid Scintillation Spectrometry 1992*, ed. Noakes, J. E., Schoenhofer, F. and Polach, H., *Radiocarbon.* 425-430.

Chapter 7: ^{234}Thorium

^{234}Th in the Environment

^{234}Th ($t_{1/2}$ = 24.1 days) is the immediate daughter of ^{238}U ($t_{1/2}$ = 4.5 x 10^9 years), which is the parent radionuclide in one of the three natural decay series depicted in Figure 7-1. ^{238}U is found almost ubiquitously in soils, rocks, sea water and fresh water. In many instances, ^{238}U is found at extremely low concentrations and consequently because of its daughter's short half-life, ^{234}Th tends to have a similar distribution pattern.

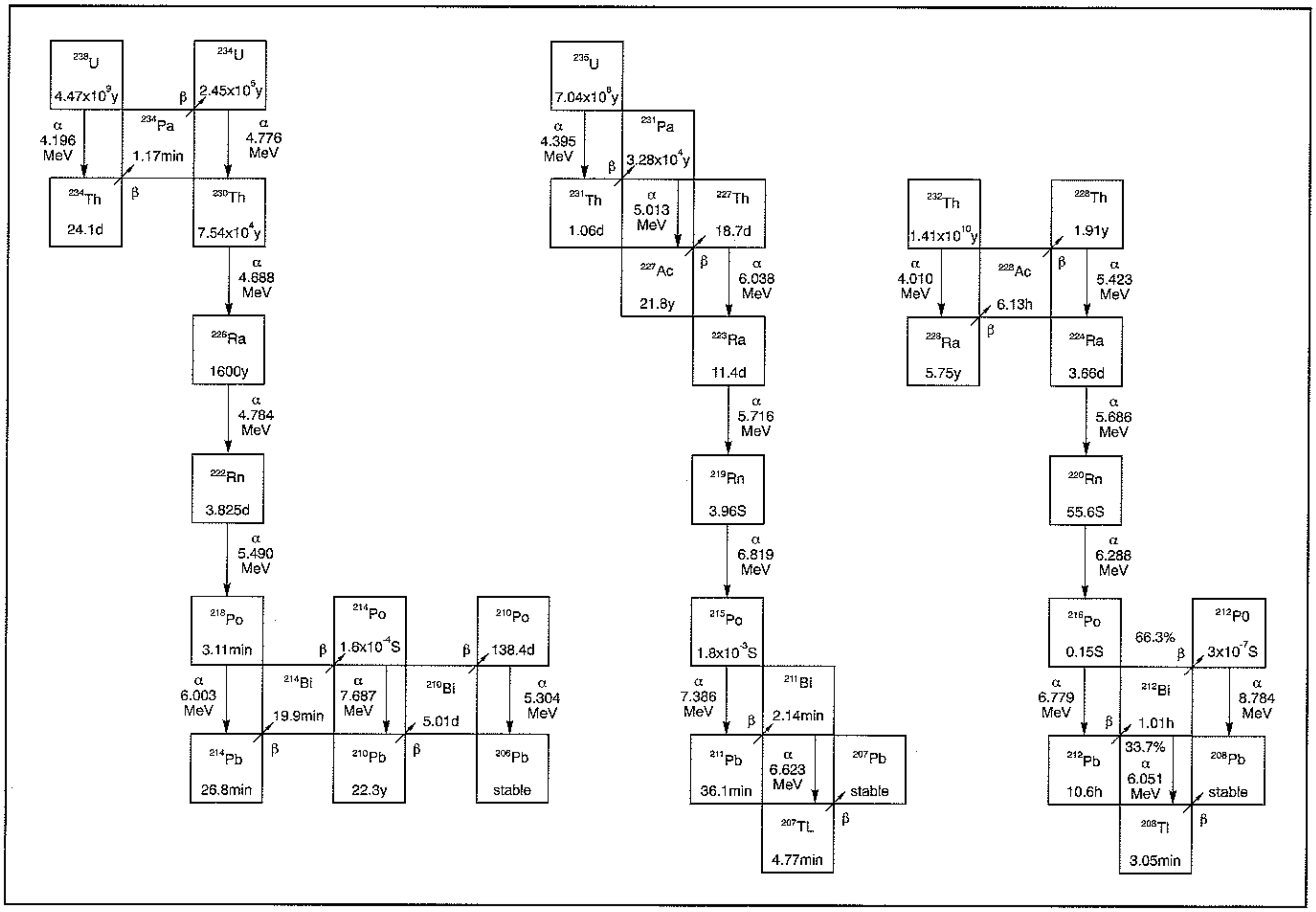


Figure 7-1.

^{238}U, ^{235}U, and ^{233}Th natural decay series (Pates et al. 1993).

^{234}Th Monitoring Applications

To date, ^{234}Th has been used principally to study processes occurring in the marine environment. Uranium and thorium have markedly differing solubilities in sea water under oxidizing conditions. Uranium is soluble, existing as an anionic carbonate complex of the uranyl ion $(UO_2(CO_3)_3^{4-})$ and is relatively unreactive with respect to particle sorption processes (Hodge et al., 1979). As a result, uranium is conservative in sea water, so that its concentration varies as a function of salinity. For open ocean water (salinity = 35), the ^{238}U content is 2.5 DPM L^{-1} and its decay gives rise to a constant rate of production of its thorium daughter in the water column. In contrast to uranium, thorium is insoluble because the hydrolysis product, $Th(OH)_n^{(4-n)+}$, is a highly particle reactive species which can be removed from solution by sorption (Turner et al., 1981). In mid-depth ocean water where particle fluxes are low, ^{234}Th is normally in secular equilibrium with ^{238}U in solution. However, in situations where there is a higher concentration of particulate matter, ^{234}Th rapidly becomes associated with solid phase material and is therefore depleted relative to ^{238}U because of particle settling. This partitioning between the solid and aqueous phases can provide a powerful tracer for investigating a range of oceanographic processes including particle fluxes to, and re-working at, the deep sea floor, stratification within the euphotic zone, euphotic zone production rates and near shore scavenging processes (Coale and Bruland, 1987; De Master et al., 1985; Aller and De Master, 1984; Tanaka et al., 1983; Murray et al., 1989).

Sample Preparation and Measurement

There are significant difficulties associated with ^{234}Th analyses: ^{234}Th is a weak emitter [E_{max} = 190 and 96 keV (72.5 and 18.5% probabilities per decay, respectively)] which decays to ^{234m}Pa which in turn has a half-life of 1.17 minutes and emits energetic alpha or beta particles (E_{max} = 2.33 MeV). ^{234m}Pa has no significant gamma photon emissions, while the principal emission from ^{234}Th is at 63 keV but with only a 3.8% probability. Thus, ^{234m}Pa is generally present in secular equilibrium during the ^{234}Th analysis. The two conventional approaches to ^{234}Th analysis in sea water have been as follow:

1. Collect and filter samples of 30-40 liter volume. For analysis of the dissolved fraction, the sea water is then spiked with a ^{230}Th (alpha-emitter) yield tracer, equilibrated and co-precipitated with $Fe(OH)_3$. The precipitate is then collected, dissolved in HCl and the thorium isotopes are separated by anion exchange. This is followed by electrodeposition of the nearly weightless source onto a stainless steel or platinum planchet. The ^{230}Th activity is determined using a calibrated silicon surface barrier or passivated implanted planar silicon detector while the ^{234}Th/^{234m}Pa activity is determined by calibrated gas flow proportional counting. Major limitations in this methodology are that both counting systems are 2 π geometries and require separate calibrations and intercalibration.

2. Pump large volumes (1000-4000 liters) of sea water via *in situ* pumps, firstly through a fine pore size polypropylene cartridge filter (0.45 μm) to remove particle associated ^{234}Th and then through two manganese oxide impregnated adsorbers to remove the ^{234}Th which is in solution. The ^{234}Th on the filters and adsorbers is then measured by gamma spectrometric determination of the low intensity 63 keV gamma photons using an intrinsic germanium detector (Buesseler et al., 1992a, 1992b; Baskaran et al., 1993). The advantage of this method is that it can be carried out totally on board a ship. The disadvantage is that even with the most sophisticated pumping apparatus, the pumping of 1000-4000 liters would require between 30 minutes and two hours under optimum working conditions.

A third approach to the analysis of ^{234}Th is to use liquid scintillation spectrometry. LSC has several advantages including much higher detection efficiencies. Approximately 100% efficiency for the ^{230}Th yield tracer and approximately 200% efficiency for the ^{234}Th since it is in equilibrium with ^{234m}Pa. However, these efficiencies would be subject to reductions if optimum counting windows are selected. The provision of a spectroscopic capability allows the simultaneous analysis of ^{230}Th and ^{234}Th/^{234m}Pa as well as simpler separation and source preparation techniques.

Low Level Counting Method Using the Packard Tri-Carb 2000CA/LL

Initial research into this technique was confined to method development and verification of activities in the aqueous phase of replicate estuarine samples (Anderson et al., 1991) using a Packard Tri-Carb 2000CA/LL. Although there is a reasonable degree of spectral separation of the ^{230}Th from the ^{234}Th/^{234m}Pa, it is not complete. Because the energy to light conversion efficiency for alpha particles is approximately one tenth of that for betas, the ^{230}Th spectrum overlaps the ^{234m}Pa continuum. However, if the degree of quenching in samples remains constant, the percentage spectral interference will remain constant and enable correction factors to be calculated. Through careful control of sample chemistry, Anderson et al. (1991) were able to achieve this. In this study, they used counting windows of 0-80 keV for the ^{234}Th/^{234m}Pa (137% counting efficiency relative to ^{234}Th for combined ^{234}Th/^{234m}Pa) and 100-220 keV for the ^{230}Th (approximately 100% counting efficiency). Under constant quench conditions, the percentage interference of the ^{234}Th/^{234m}Pa in the 100-220 keV ^{230}Th window will be a constant percentage of the count rate in the 0-80 keV counting window and this value can easily be determined using pure ^{234}Th/^{234m}Pa. Using the low level count mode gave only a marginal improvement in precision. This was accompanied by an approximate 10% loss in ^{234}Th/^{234m}Pa efficiency within the 0-80 keV window and a 45% loss in ^{230}Th efficiency. The cause of this is the broad pulse widths produced by alpha particles (and energetic betas) which are often indistinguishable from the non-quenchable background pulses which the low level feature rejects.

The technique employed for separation of the thorium from sea water is as follows:

Twenty liter sea water samples are immediately filtered through 0.45 m millipore cellulose nitrate membrane filters and the filters are retained for subsequent analysis. Immediately following filtration, the water samples are acidified to pH 2 with hydrochloric acid (HCl) to maintain the thorium solubility. At this point, the ^{230}Th spike (50 DPM total activity) is added and the samples are thoroughly mixed. Thereafter, 500 mg of $FeCl_3{\bullet}6H_2O$ and 50 mg $Al(NO_3)_3{\bullet}9H_2O$ are added to scavenge out the Th/U etc. by pH adjustment to nine. Following stirring and then overnight settling, the precipitate is removed by filtering through GF/A paper after decanting the bulk of the solution. The precipitate is then redissolved in 9M HCl and the solution is passed through a 1 x 6 cm column of Bio-Rad® (Hercules, California) AG 1-X8 (100-200 mesh) chloride form resin to retain the iron and uranium. The eluate containing the thorium and aluminium is then reduced in volume to 20-30 mL and transferred to a 50 mL conical centrifuge tube. The pH is raised to approximately nine by the addition of ammonia to precipitate the aluminium and thorium. The solution is centrifuged for a maximum of two minutes at 4500 rpm and decanted. The precipitate is washed with distilled water and the process is repeated. The precipitate is then redissolved in a minimum volume of HNO_3, the pH again raised to nine, and the centrifugation and washing procedures are repeated to remove the last traces of chloride. The precipitate is then dissolved in 30 mL of 8M HNO_3 and the solution is passed through a 1 x 6 cm column of Bio-Rad AG 1-X8 (100-200 mesh) nitrate form resin to retain the thorium which is eluted using 9 M HCl. The solution is heated just to dryness in a 7 mL scintillation vial and a fixed volume (0.5 mL) of dilute HCl is added. Typically, 0.1 or 1 M have been used. Five grams of Hionic-Fluor scintillation cocktail (Packard Instrument Company) are added and the resultant mixture is counted in the liquid scintillation spectrometer. Hionic-Fluor is used because of its ability to retain a suitable counting emulsion in the presence of significant concentrations of acid.

For analysis of the particulate material, ^{230}Th spike is added to the moist filter papers which are then combusted at 400 °C. After the ash is dissolved using HNO_3/HCl, 50 mg $Al(NO)_3{\bullet}9H_2O$ are added, and thereafter, the procedure is as outlined above.

With a 200 minute sample counting time, the one sigma propagated errors are typically in the 5-10% range.

Alpha/Beta Discrimination Technique Using the Packard Tri-Carb 2550TR/AB
A more refined approach is to use liquid scintillation spectrometry with alpha/beta separation capabilities (Pates et al., 1993). In theory, the ^{230}Th alpha events should be sent to one MCA and the ^{234}Th/^{234m}Pa beta events to a second, negating the requirement for spectral overlap calculations. The alpha events will be detected at near 100% counting efficiency and the beta counting efficiency will again approach 200% in an open window. Initial development of this alpha/beta method was carried out using a Packard Tri-Carb 2250CA with alpha/beta discrimination and was later continued using a Packard 2550TR/AB. Again, replicate 20 liter estuarine water samples were used for method development. The ^{238}U content of the samples was measured by inductively coupled plasma mass spectrometry and found to be 2.27 DPM L^{-1}. This is the maximum ^{234}Th activity which can be supported. The thorium separation procedure is identical to that outlined previously in the method for the Tri-Carb 2050CA/LL. In this instance, however, five grams of Ultima Gold AB scintillation cocktail are added to the 0.5 mL fixed volume of HCl. Ultima Gold AB was designed specifically for the separation of alpha from beta events while it also has excellent acid holding qualities.

Additional features incorporated into the Tri-Carb 2550TR/AB instrument simplify and enhance the technique, namely: (1) the optimum pulse decay discrimination (PDD) time setting can be calculated automatically; (2) the low level option can be used on the events classed as being beta; and (3) on the Tri-Carb 2000 and 2200 series instruments, the low level has a fixed burst count delay of 75 nsec after initiation of the prompt pulse while the 2500 and 2700 series instruments have a selectable delay. This selectable delay enables background count rate reductions to be made when measuring a high energy beta emitter. Thus, the possibility exists that the limits of detection for ^{234}Th/^{234m}Pa can be improved after alpha/beta separation through TR-LSC on the events classed as beta, without significantly reducing the beta counting efficiency. The optimum misclassification for the Tri-Carb 2550TR/AB as developed by Pates et al. (1993) is depicted in Figure 7-2 and shows a 3.57% spillover of alpha events into the beta MCA and 3.92% of beta events into the alpha MCA.

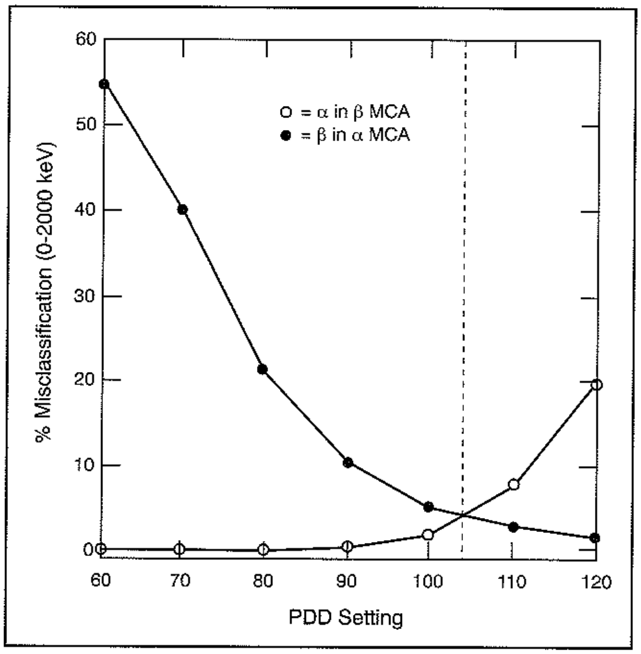


Figure 7-2.
Misclassification curve for ^{230}Th and ^{234}Th using a Packard Tri-Carb 2550TR/AB (Pates et al. 1993).

These misclassification values are higher than had been anticipated on the basis of their earlier work carried out on the Tri-Carb 2250CA/AB using ^{238}Pu and ^{90}Sr/^{90}Y which have similar energy distributions. This is possibly in part due to protactinium following the uranium chemistry and differences in the two instruments which were used. However, these misclassification values are for 0-2000 keV counting windows. The counting windows which were selected for the analyses are 10-140 keV in the beta MCA for the ^{234}Th/^{234m}Pa and 140-300 keV in the alpha MCA for the ^{230}Th. For ^{230}Th in the selected alpha window, only 0.9% of the alpha events are misclassified which has an almost negligible effect on alpha counting efficiency, and appear in a part of the beta MCA which is not used in the analysis. There are no ^{230}Th counts in the 10-140 keV region (beta window used in the analysis). For ^{234}Th in the 10-140 keV window, 5.4% of the total number of events are misclassified into the alpha MCA. Thus, the beta counting efficiency will be reduced by this amount. Again, the misclassified events are in a part of the alpha MCA which is not used in the ^{230}Th determination. However, 11.3% of the beta events in the 140-300 keV window are also misclassified into the alpha MCA. In this case, the misclassification is highly relevant as these events are included with those from the ^{230}Th yield tracer and will give an inaccurate yield determination. However, this misclassification represents only 1.4% of the total beta activity in the 0-2000 keV window of the beta MCA. The practice of adding 50 DPM of ^{230}Th yield tracer to 20 liters of sea water with a maximum 2.5 DPM L^{-1} of ^{234}Th (*i.e.,* 50 DPM total activity) means that 1.4% will be the maximum error introduced and of course the error will be smaller in samples where ^{234}Th scavenging has occurred.

The results presented in Figure 7-3 demonstrate the relationship between the measured ^{234}Th activities and the theoretical ingrowth. The dashed line indicates the theoretical ingrowth (with the assumption of zero ^{234}Th at t_0). The solid line indicates the best fit through the results. Note that this line is tending towards the dashed line and should intercept it at 2.27 which is the maximum ^{234}Th activity in DPM L^{-1} that can be supported by the ^{238}U. In fact, using the equation of the best fit line through the data, a value of 2.19 DPM L^{-1} is calculated at the theoretical maximum of 2.27 DPM L^{-1}. The intercept on the x-axis is approximately 0.2 DPM L^{-1} indicating approximately 90% removal of ^{234}Th from sea water in the estuary.

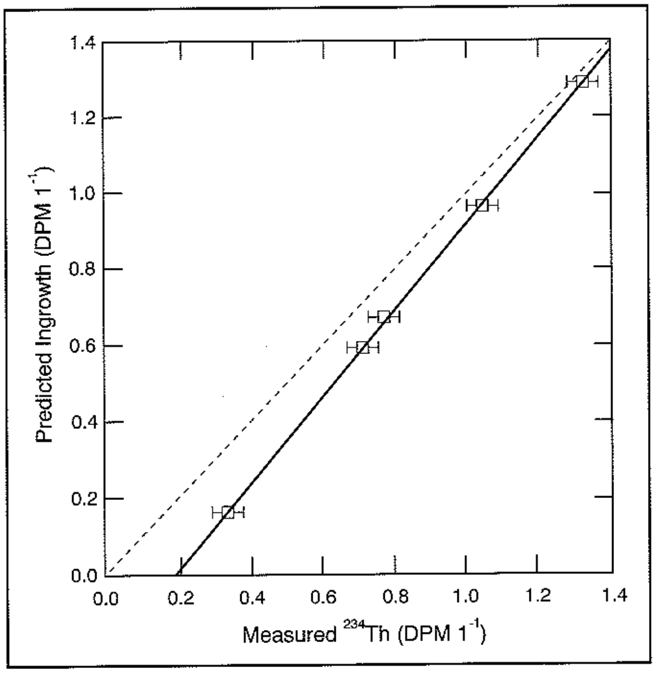


Figure 7-3.
Measured vs. predicted ingrowth of ^{234}Th (Pates et al. 1993).

The effect on ^{234}Th counting efficiency with programmable TR-LSC is shown in Table 7-1. By introducing the low level mode with the normal burst counting delay of 75 nsec, the relative counting efficiency in the 0-140 keV window is greatly reduced. Despite a greater than three fold reduction in background, the relative E^2/B factor is significantly reduced. However, relative efficiency is more than doubled by applying a delay of 400 nsec. Through programmable TR-LSC, this has the effect, despite a slight increase in background, of increasing the relative E^2/B factor to a significantly greater value than normal count mode (NCM) or when low level and the factory set 75 nsec delay are invoked. Increasing the delay beyond 400 nsec brings about no further increase in E^2/B.

Low Level	**Burst Count Delay (nsec)**	**Fraction of CPM in 0-140 keV window, BCC off**	**Background**	**Relative E^2/B (CPM) $\pm 2\sigma$**
Off (NCM)	N/A	1	21.23	471 ± 20
On	Factory set	0.148	6.07	288 ± 16
On	400	0.875	9.61	797 ± 36
On	600	0.923	10.73	794 ± 34
On	800	0.938	11.11	792 ± 34

Table 7-1.
Effect of increasing the burst count delay on ^{234}Th efficiency and background following alpha/beta separation.

Summary

These results demonstrate the potential of alpha/beta separation liquid scintillation spectrometry for the measurement of ^{234}Th in oceanic water column studies. The advantages of this over traditional methods are: (1) simpler preparative chemistry compared with the gas counting technique; (2) both the ^{234}Th and its yield tracer (^{230}Th) can be measured in a single count on equipment employing automatic sample changing; and (3) counting efficiencies are much higher, thus introducing the possibility of carrying out the determinations on much smaller samples. ^{234}Th measurements are entirely possible on five liter samples by this method. The advantages of the alpha/beta separation technique using the Packard Tri-Carb 2550TR/AB over the standard LSC method are: (1) no spectral overlap calculations are required — the results can simply be calculated from a 10-140 keV window in the beta MCA and a 140-300 keV window in the alpha MCA; and (2) the use of the delay-before-burst feature enables a two fold reduction in background with the loss of only about 10% of the relative efficiency. This has the overall effect of lowering the limit of detection for a 200 minute count from 0.63 DPM to 0.49 DPM total ^{234}Th activity.

References

Aller R. C. and De Master, D. J. 1984. Estimates of particle flux and reworking at the deep-sea floor using ^{234}Th/^{238}U disequilibrium. *Earth and Planetary Science Letters*. 67: 308-318.

Anderson R., Cook, G. T., MacKenzie, A. B. and Harkness, D. D. 1991. The determination of ^{234}Th in water column studies by liquid scintillation counting. In *Liquid Scintillation Counting and Organic Scintillators*, ed. Ross, H., Noakes, J. E., Spaulding, J. D., Chelsea, Michigan, Lewis Publishers: 461-470.

Baskaran, M., Murphy, D. J., Santschi, P. H., Orr, J. C. and Schink, D. R. 1993. A method for rapid *in situ* extraction and laboratory determination of Th, Pb, and Ra isotopes from large volumes of seawater. *Deep-Sea Research*. 40: 849-865.

Buesseler, K. O., Bacon, M. P., Cochran, J. K. and Livingston, H. D. 1992a. Carbon and nitrogen export during the JGOFS North Atlantic bloom experiment estimated from ^{234}Th:^{238}U disequilibria. *Deep-Sea Research*. 39: 1115-1137.

Buesseler, K. O., Cochran, J. K., Bacon, M. P., Livingston, H. D., Casso, S. A., Hirschberg, D., Hartman, M. C. and Fleer, A.P. 1992b. Determination of thorium isotopes in seawater by nondestructive and radiochemical procedures. *Deep-Sea Research*. 39: 1103-1114.

Coale K. H. and Bruland, K. W. 1987. Oceanic stratified euphotic zone as elucidated by ^{234}Th:^{238}U disequilibria. *Limnology and Oceanography*. 32: 189-200.

De Master, D. J., McKee, B. A., Nittrouer, C. A., Brewster, D. C. and Biscaye, P. E. 1985. Rates of sediment reworking at the HEBBLE site based on measurements of Th-234, Cs-137 and Pb-210. *Marine Geology*. 66: 133-148.

Hodge, V. F., Koide, M. and Goldberg, E. D. 1979. Particulate uranium, plutonium and polonium in the biogeochemistries of the coastal zone. *Nature*. 277: 206-209.

Murray, J. W., Downs, J. N., Strom, S., Wei, C-L. and Jannasch, H. W. 1989 Nutrient assimilation, export production and ^{234}Th scavenging in the eastern equatorial Pacific. *Deep-Sea Research*. 36: 1471-1489.

Pates J. M., Anderson, R., Cook, G. T. and MacKenzie, A. B. 1993. The determination of ^{234}Th in oceanic tracer studies by liquid scintillation spectrometry employing / separation techniques. In *International Conference on Advances in Liquid Scintillation Spectrometry*, ed. Noakes, J. E., Schoenhofer, F. and Polach, H. A., Radiocarbon Publishers, University of Arizona. 417-423.

Tanaka, N., Takeda, Y. and Tsunogai, S. 1983. Biological effect on removal of Th-234, Po-210 and Pb-210 from surface water in Funka Bay, Japan. *Geochimica et Cosmochimica Acta*. 47: 1783-1790.

Turner, D. R., Whitfield, M. and Dickson, A. G. 1981. The equilibrium speciation of dissolved components in freshwater and seawater at 25 °C and 1 atm pressure. *Geochimica et Cosmochimica Acta*. 45: 855-881.

Chapter 8: ^{226}Radium, ^{228}Radium, and ^{222}Radon

^{226}Ra and ^{228}Ra in the Environment

^{226}Ra ($t_{1/2}$ = 1602 years) is a naturally occurring radioisotope of the ^{238}U decay series. The principle emissions are two alpha particles [4.602(5.5%) and 4.785 (94.5%) MeV] with a small probability of associated conversion electron and gamma activity.

^{228}Ra ($t_{1/2}$ = 5.75 years) is a low energy pure beta emitter (E_{max} = 55 keV) and a naturally occurring radionuclide in the ^{232}Th decay series. It is produced by the decay of the ^{232}Th parent which is primarily an alpha emitter.

Earth, marine, and environmental scientists often require analysis of radium isotopes in natural waters because of both public health concerns and the fact that ^{226}Ra, ^{228}Ra and ^{224}Ra have proved fruitful as tracers of geochemical processes in estuaries, coastal regions, and the open sea (Burnett and Tai, 1992). The measurement of radium in public water supplies has become a matter of interest because radium is one of the most hazardous elements with respect to internal exposure (Higuchi et al., 1984). In fact, regulations have made the analysis of ^{226}Ra and ^{228}Ra very common in U.S. ground water. Title 40 of the U.S. Code of Federal Regulations (CFR) of July 1, 1992 part 141.15 requires that the combined ^{226}Ra and ^{228}Ra maximum contaminant level is 5 pCi L^{-1} (0.18 Bq L^{-1}) in community water systems. Parts 141.25 further require that the ^{226}Ra and ^{228}Ra minimal detection limits do not exceed 1 pCi L^{-1} and 3 pCi L^{-1}, respectively, in order to insure compliance. The maximum contaminant level for gross alpha including ^{226}Ra but excluding radon and uranium is 15 pCi L^{-1} (0.55 Bq L^{-1}).

^{226}Ra and ^{228}Ra Monitoring Applications

Natural waters and drinking water are by far the most common sample matrices assayed for radium by liquid scintillation methods. However, the ^{226}Ra content of tissue, soil, sediment, and rock samples has also been determined by liquid scintillation methods (Higuchi, 1981; Blackburn and Al-Masri, 1992; Saarinen and Suksi, 1992).

Cocktail Choices

Many procedures for determining ^{226}Ra activity in water involve liquid scintillation counting of the daughter product, ^{222}Rn, alone or radon plus daughters. Typical liquid scintillation cocktails that are used in these procedures are toluene, xylene, or mineral oil-based since ^{222}Rn is more soluble in these organic solvents than in water. However, a linear alkylbenzene-based product, Opti-Fluor® O, a less volatile, less toxic, biodegradable cocktail from Packard Instrument Company has been used successfully.

^{226}Ra/^{228}Ra Sample Preparation and Measurement

No special sample collection procedures have been published other than concentration of natural water or other liquid samples by either liquid-liquid extraction, cation exchange chromatography, and/or barium sulfate precipitation. Manganese oxide impregnated acrylic fiber, known for its strong adsorption affinity for radium, has been used to concentrate radium from sea water (Moore, 1976; Orr, 1988). Many radionuclides, and particularly radium, have been concentrated by ion exchange techniques from water samples in the field for a number of years (Harley, 1976).

Water Analysis for ^{226}Ra - Traditional Methods

The analysis of water samples for ^{226}Ra often involves measuring the ingrown daughter, ^{222}Rn, from the water sample and inferring the radium activity from the radon activity (Parks and Tsuboi, 1978; Gesell et al., 1978; Prichard et al., 1980; Cooper and Wilks, 1981; Horiuchi and Murakami, 1981; Nobrega et al., 1987; Chu and Khalique, 1990; Schoenhofer et al., 1991). Therefore, any measurement of radium will have significance for radon measurements as well.

The common method for the analysis of ^{226}Ra in water involves a volume reduction of at least a factor of ten down to a 20 mL sample that is sealed in a radon bubbler for ingrowth. The radon is then transferred to a scintillation flask (Lucas cell) for alpha counting of ^{222}Radon and its short-lived daughters (Prichard et al., 1980). This de-emanation approach after barium sulfate precipitation of radium is the radiochemical method for water samples published in the Eastern Environmental Radiation Facility Radiochemistry Procedures Manual and is the basis of EPA method 903.1. The method is both sensitive and reliable, but it is time consuming and requires complicated operations for handling radon gas which excludes it in environmental surveillance programs where large numbers of samples need to be assayed (Higuchi et al., 1984; Prichard et al., 1980). EPA method 903.0, which involves counting alphas in the barium sulfate precipitate by gas flow proportional counting, is a simple alternative to method 903.1 but does not have equivalent sensitivity. Problems of complexity have been responsible for the popularity of liquid scintillation methods for analysis after radium separation. Measurement of separated ^{226}Ra by liquid scintillation methods is frequently performed because of the high solubility of ^{222}Rn, the immediate daughter of ^{226}Ra, in organic solvents and the simplicity of the method.

Liquid-liquid extraction, ion exchange chromatography, barium sulfate or barium carbonate precipitation are the most common separation techniques used for radium. Specific extractants for radium have been developed, especially for use with alpha liquid scintillation counting (McDowell and McDowell, 1994). Refer to the section later in this chapter entitled, *Water Analysis - ^{226}Ra by Alpha Liquid Scintillation*, for additional details. In some of the early work with ion exchange techniques, Prichard, Higuchi, and others reported a method which involved placing a small amount of water-saturated ion exchange resin containing concentrated radium in a vial with scintillation fluid and counting the ingrowth of the trapped radon into the organic cocktail. Higuchi (1991) refined the method by further investigating the conditions for purifying the radium on the column and removing interfering metal ions from the resin by complexation with ethylene diamine tetraacetic acid (EDTA). The direct batch counting of the resin was an improvement over removing either the radium or ingrown radon from the resin prior to counting.

In other methods, radium is separated and concentrated from an environmental water sample by barium sulfate precipitation. The barium sulfate precipitate is solubilized with EDTA; the radon daughters are allowed to ingrow in an organic scintillator, and is counted by LSC using a mineral oil scintillator or equivalent. The barium sulfate precipitation separation method of Chu and Khalique (1990) is an example of this approach and is shown in Figure 8-1.

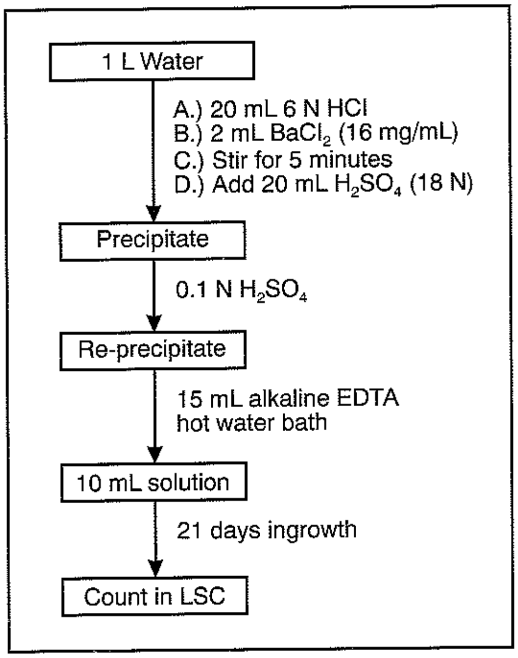


Figure 8-1.
^{226}Ra barium sulfate precipitation method.

Recoveries for the method ranged from 90-99.5% with good precision and accuracy. Reliability of the method was tested by determining the ^{226}Ra content in five EPA performance evaluation and cross-check water samples. Values for the method ranged from 96-114% of the EPA target values. In addition, results from 12 groundwater samples from various locations in Illinois, U.S.A. were in agreement with the results obtained from the de-emanation method.

Water Analysis for ^{226}Ra by Alpha Liquid Scintillation

There have been some attempts at applying pulse shape analysis to the determination of ^{226}Ra alpha particles (Cross and McBeth, 1976; Coombs, 1980; Noguchi et al., 1984; Burnett and Tai, 1992; Blackburn and Al-Masri, 1992; Saarinen and Suksi, 1992). The advantage of using pulse shape analysis is that any potential beta interferences that remain after separation can be removed, including the often used ^{133}Ba yield tracer. Simultaneous measurement of ^{226}Ra alpha and/or alpha daughters and the gamma emitting ^{133}Ba tracer ensures the reliability of the yield determination. Furthermore, alpha backgrounds are reduced by pulse shape discrimination which will increase sensitivity.

Extractive scintillators (a combination of an extractive agent and liquid scintillator) have been used to isolate radium from natural water samples prior to alpha liquid scintillation counting with a PERALS spectrometer (Burnett and Tai, 1992). The extractive scintillator used in this application has been described by Case and McDowell (1990). The organic extractant solution consists of a toluene, xylene, or mesitylene solution of a high molecular weight neo-carboxylic acid (HNA) together with the crown ether, dicyclohexano-21-crown-7 (DC21C7), used in a mole ratio 2:1 HNA:crown ether. An extractive scintillator is created by combining the extractant solution with a fluor, PBBO, and an energy transfer agent, naphthalene. This extraction system separates radium from barium, strontium, and calcium by factors of 9.3, 12, and 58 respectively (McDowell and McDowell, 1994). Besides removing potential interferences by elements chemically similar to radium, the use of extractive scintillators offers the advantages of transferring the alpha emitter to a water-immiscible scintillator of constant composition, which eliminates variable quenching that can interfere with alpha discrimination and resolution.

Commercially available liquid scintillation analyzers capable of alpha/beta discrimination such as the Packard Tri-Carb 2500 and 2700 series are currently being used to develop ^{226}Ra methods (Blackwell, 1993; Momohara, 1994; Lilly, 1994). In fact, Blackwell is refining the method to determine ^{226}Ra/^{228}Ra simultaneously in water samples. Encouraging results were obtained with control samples spiked with known amounts of ^{226}Ra and with EPA ^{226}Ra and ^{228}Ra cross-check samples.

Water Analysis for ^{228}Ra

Various liquid scintillation techniques have been described for the measurement of ^{228}Ra. These include alpha liquid scintillation spectrometry of the ^{228}Th alpha emitting daughter, liquid scintillation beta-gamma coincidence spectrometry, and ^{220}Rn (thoron) emanation (Orr, 1988). The emanation method is similar to the ^{222}Rn emanation technique used for ^{226}Ra including the possibility of using organic liquid scintillators to trap the ^{220}Rn daughter of ^{224}Ra, a decay product of ^{228}Ra. However, the limiting factor of this approach is the slow ingrowth of the ^{228}Th ($t_{1/2}$ = 1.9 years) daughter of ^{228}Ra and parent to ^{224}Ra.

An additional method for ^{228}Ra determination based on counting ^{228}Ac, the immediate daughter has been reported by Petrow et al. (1964). This approach has potential for using alpha/beta LSC as a method for measurement since the beta emitting ^{228}Ra and its ^{228}Ac daughter can be separated from ^{226}Ra by pulse decay or pulse shape analysis.

Detection Limits by LSC

Detection limits reported for ^{226}Ra with concentration and analysis by the radon ingrowth method range from 0.1 pCi mL^{-1} (0.004Bq mL^{-1}) for biological samples to 0.5 pCi L^{-1} (0.02 Bq L^{-1}) for environmental samples. Lower detection limits have been reported for methods where pulse shape analysis was used to isolate the alpha activity from interfering beta or gamma activity (Blackburn and Al-Masri, 1992; Saarinen and Suksi, 1992; Blackwell, 1993; Momohara, 1994). Information on detection limits for ^{228}Ra by liquid scintillation methods is scant. However, Orr (1988) reported achievable detection limits for various methods of analysis including liquid scintillation methods that give acceptable precision for the analysis of ^{228}Ra in sea water samples which contain an average of 0.5 DPM/100 kg. Blackwell reported a detectable limit of 2.98 pCi L^{-1} for ^{228}Ra (0.5 L processed sample; 30 minute count time) in water with a method being developed for the direct simultaneous analysis of ^{226}Ra and ^{228}Ra on a Packard Tri-Carb 2550TR/AB LSC capable of alpha/beta discrimination.

^{222}Rn in the Environment

^{222}Rn ($t_{1/2}$= 3.8 days) is an inert noble gas and a radioactive decay product of ^{226}Ra, which is a daughter product of the ^{238}U natural decay series. Natural radiation accounts for the majority of human exposure to radiation with radon decay products being the largest contributor in spite of the increased use of manmade radiations in industry, medicine, and scientific research (Tso and Li, 1987).

The earth's crust contains trace amounts of ^{238}U and ^{232}Th which decay to ^{222}Rn (radon) and ^{220}Rn (thoron gas), respectively (Tso and Li, 1987). ^{222}Rn and two of its daughters, ^{218}Po (Radium A) and ^{214}Po (Radium C'), are alpha emitters, while ^{214}Pb (Radium B) and ^{214}Bi (Radium C) are beta/gamma emitters. Inhalation of radon and thoron alpha daughters pose a radiation health hazard to the lungs. However, thoron is often ignored in these studies because of its short half life ($t_{1/2}$ = 55.3 seconds) and the fact that it is generally lower in concentration than ^{222}Rn in geological material. However, in areas where soil concentrations are high in ^{232}Th, the thoron parent, thoron measurements are also important. ^{222}Rn measurements in air and water are discussed in this section although the methods that apply for radon measurement will also apply to thoron.

^{222}Rn Monitoring Applications

Radon Measurements in Air

Radon has long been identified as a serious health hazard in uranium mines. It has recently been cited as a hazard in indoor air, especially in poorly ventilated areas. Radon gas emanates from the soil into homes from cracks in flooring or through basement floors by molecular diffusion or pressure driven flow (Tso and Li, 1987). In addition, ^{238}U and ^{232}Th present in building materials can also be a source of radon gas.

Because of the radon health concern, several methods have been developed to monitor for radon and its daughters in air. These include alpha track, activated charcoal adsorption, continuous radon monitoring, grab radon sampling, and radon progeny integrated sampling (Passo and Floeckher, 1991). All of these methods are recognized by the U.S. Environmental Protection Agency as approved methods for radon screening. Specific information on screening protocols and radon action levels is contained in the U.S. EPA publication number EPA 520/1-86-014-1. As a screening method, the charcoal adsorption technique is popular because it is inexpensive and easy to use. Typically, radon gas is trapped by activated charcoal contained in a circular canister, approximately 10 x 3 cm in dimension and the trapped radon daughters detected by gamma spectrometry (George, 1984). An attractive alternative to the gamma spectrometry method of detection has been to use liquid scintillation counting to measure the radon and daughters passively trapped by activated charcoal (Prichard et al., 1980; Prichard and Marien, 1985). The liquid scintillation charcoal technique offers greater sensitivity, simplicity, and the ability to automate the counting of large numbers of samples. This has made the LSC method of detection ideal for radon screening. Commercially, Packard Instrument Company was the only manufacturer of liquid scintillation equipment to offer a radon gas collection device which was the size of a standard plastic LSC vial and contained several grams of activated charcoal and desiccant. Currently, no instrument manufacturer is offering this type of product. However, the Pico-Rad™ (Niton Corporation, Bedford, Massachusetts) collection system, originally marketed by Packard Instrument Company, is still available through Niton Corporation (P.O. Box 368, Bedford, Massachusetts, 01730-0004 U.S.A.). Refer to the section entitled *Pico-Rad* for a brief description of the Pico-Rad system.

Radon Measurements in Water

The ^{222}Rn concentration in water is due to the decay of ^{226}Ra associated with the rock and soil. Apparently, the radon gas percolates through the soil and rock, and dissolves in the water. Therefore, the concentration of radon in water is higher than one would expect if the activity were due only to supporting dissolved ^{226}Ra in the water. Even so, since radon is the immediate daughter of ^{226}Ra, radon measurements have significance for determining the amount of ^{226}Ra in water as well. Refer to the section of this manual entitled *^{226}Radium* for specific information on radium analysis. To date, no maximum permissible concentration levels (MCL's) exist for radon in drinking water although radon is expected to join radium (^{226}Ra and ^{228}Ra) on the U.S. EPA list of regulated radionuclides. The maximum concentration level (MCL) for radon is expected to be relatively low (300 pCi L^{-1}). Although the regulation was to appear at the end of 1993, the EPA delayed the regulation for at least a year because of the heated debate over the cost of compliance.

Although ^{222}Rn in large volume water samples has been measured by the gamma spectrometry of its daughter products, the most prevalent methods for measuring radon concentrations is by the Lucas cell and liquid scintillation methods (Lucas, 1957; Lucas, 1964; Prichard and Gesell, 1977; Prichard et al., 1980). The popularity of using liquid scintillation for radon analysis is due to the high solubility of radon in organic solvents such as toluene and xylene, which are used in LSC cocktails. Properly collected water samples can be added directly to the scintillation cocktail and form a two phase aqueous/organic system. The radon will be partitioned between the water/scintillation cocktail and the air space in the vial, and will be available for measurement by LSC methods.

Cocktail Choices

Since the common LSC approach to radon measurement is first to trap the radon gas in an organic solvent that is a component of the liquid scintillation cocktail, organic accepting cocktails are candidates for radon measurement by conventional LS methods. Since radon is soluble in solvents such as toluene and xylene, cocktails containing those solvents are desirable for radon analysis. However, Insta-Fluor™, a lipophilic xylene based cocktail, is available from Packard Instrument Company and is used for radon in air applications with Pico-Rad detectors and is also applicable for water measurements. Opti-Fluor O, a lipophilic environmental cocktail, is a desirable choice for direct measurement of radon in water and an alternative to mineral oil scintillators. Salonen (1993) measured radon in water with alpha/beta LSC and reported the use of aqueous accepting di-isopropylnaphthalene (DIN) based cocktails where water forms a homogeneous liquid with the cocktail. The authors picked two cocktails, OptiPhase Hi-safe 3 (EG&G/Wallac) and Ultima Gold XR (Packard Instrument Company). These DIN based cocktails were used since they provide good alpha/beta separation.

^{222}Rn Sample Preparation and Measurement

Air Sample Collection by Filtration

Various filtration methods to collect radon-laden air have been reported (Amano et al., 1985; Tso and Li, 1987). The method used will depend on the type of detection system. A typical procedure is that described by Amano et al., who used liquid scintillation to detect radon by bubbling cave air through a toluene-based liquid scintillator after elimination of radon progeny by pre-filtering the air with suction through a glass fiber filter. The air was bubbled for 15 minutes at a flow rate of 0.7 L per minute until the radon concentration in the scintillator reached equilibrium. 100 mL of the bubbled liquid scintillator was sealed in a Teflon vial for the measurement of radioactivity.

Air Sample Collection - Pico-Rad System

The use of activated charcoal to create a passive radon trapping device is a common collection technique for screening radon in air.

Such a device has been marketed under the name Pico-Rad by Packard Instrument Company and is now manufactured and distributed by Niton Corporation of Bedford, Massachusetts, U.S.A. A Pico-Rad detector is a specially designed plastic scintillation vial which contains a porous canister held securely near the top of the vial (Passo and Floeckher, 1991). The porous canister contains a bed of a controlled weight of activated charcoal (1.3 gram) and silica desiccant (0.9 gram). The vial has a removable cap to prevent moisture or radon from entering the vial during storage or after exposure. A Pico-Rad detector is shown in Figure 8-2. Pico-Rad detectors are passive collection devices requiring no power.

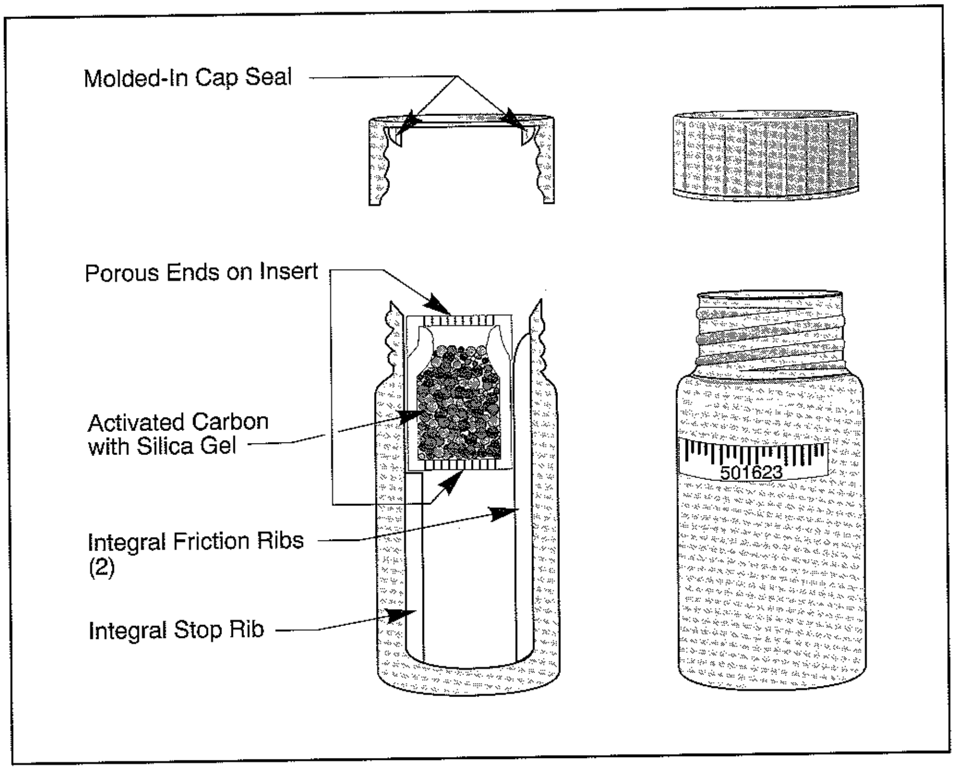


Figure 8-2.
Pico-Rad detector.

Exposure is initiated by removing the cap to allow radon laden air to passively diffuse into the charcoal. The typical exposure time is 48 hours, at which point the radon accumulation has reached 95% of saturation. High humidity problems require a shorter exposure time of 24 hours to prevent loss of maximum activity. The radon accumulation reaches 80% of its saturation value in 24 hours. The exposure period is ended by replacing the cap on the detector.

Eluting the radon from the charcoal is accomplished by adding 10 mL of a xylene based cocktail, such as Insta-Fluor, to the bottom of the vial. The desorption of radon takes place through the vapor phase since the cocktail is not in direct contact with the charcoal. Desorption is about 80% complete after three hours which is the time for full equilibrium of the decay products. The maximum count rate is achieved in eight hours (see Figure 8-3). This curve is in agreement with the elution curve determined by Schroeder et al. (1989), using a detector of their own design.

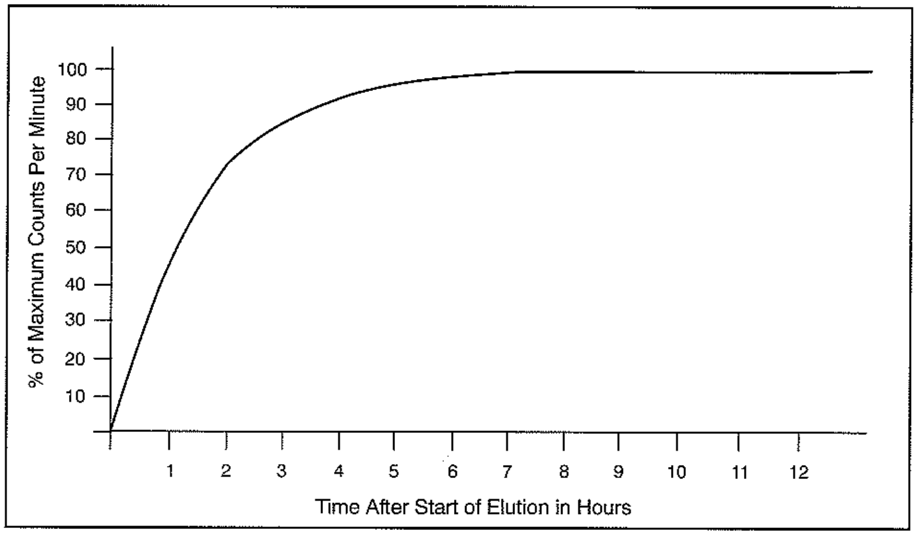


Figure 8-3.
Elution curve for Pico-Rad detector.

Radon in Air Sample Measurements
Final radon concentrations are calculated with the Pico-Rad detectors by taking the observed CPM due to radon and daughters counted in a 25-900 keV region of interest and applying an empirically determined calibration factor, as well as factors to correct for the decay of radon, adsorption time, and elution time. A database computer program that contains calculation routines based on the factors for Pico-Rad detectors is available through Niton Corporation of Bedford, Massachusetts.

A study of radon values obtained with the Pico-Rad LSC system were compared with those obtained by gamma spectrometry of the radon trapped with 150-200 grams of activated charcoal in the standard 10 x 3 cm cannister. The study consisted of exposing both types of collection devices at the same location in the basement of eight private homes. The mean results of two to six individual determinations for each location are shown in Figure 8-4.

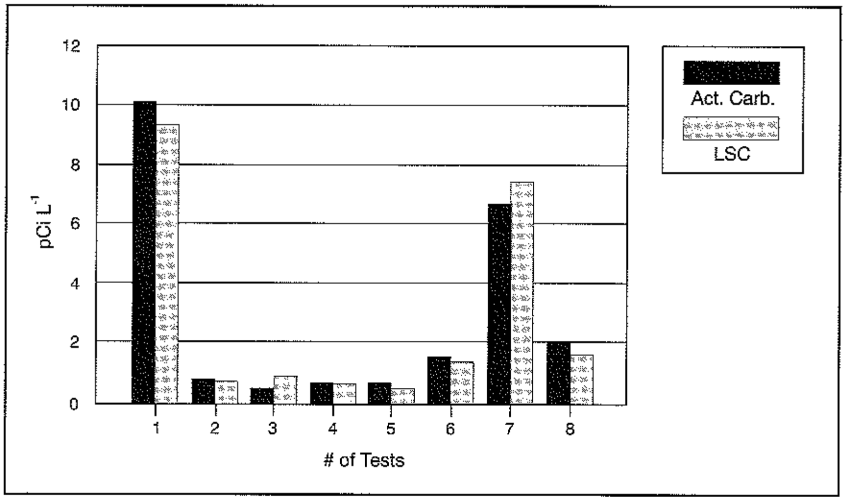


Figure 8-4.
Radon analysis cannister vs. LSC method (Passo and Floeckher, 1991).

The correlation of the two methods is shown in Figure 8-5.

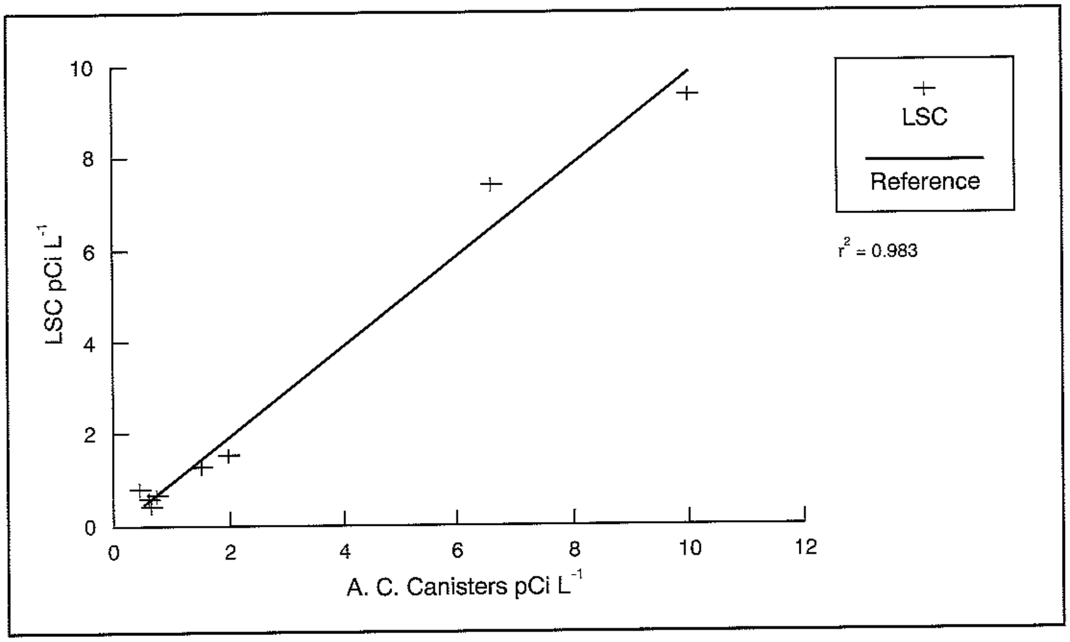


Figure 8-5.

Radon analysis correlation-cannister vs. LSC method (Passo and Floeckher, 1991).

As shown in Figure 8-5, the results for the two methods used in this study correlate well. Although it may be argued that a more accurate reference method of detection may be used, this study shows that results comparable to traditional screening methods can be obtained for the LSC method.

Sample Collection - Radon in Water

Much information has been published concerning the proper method to sample water for radon measurement. The U.S. EPA Eastern Radiation Facility describes a procedure for sampling potable water from a home faucet in the published document (EPA/EERF-Manual-78-1) entitled “Radon in Water Sampling Program.” Most other collection methods are based on this procedure.

The basic steps include:

1. Attach a sampling funnel and tubing to the faucet.
2. Turn on the water and allow a steady flow for two minutes.
3. Slow the water flow and invert the funnel (mouth up). Adjust the flow so that the pool water in the funnel cavity is not turbulent.
4. Insert the needle of a 20 mL hypodermic syringe below the water surface and withdraw several mL of water and discard. Repeat this rinse several times.
5. Withdraw 12-15 mL of water slowly to minimize air bubbles. Invert syringe to eject any air bubbles and retain 10 mL of water.
6. Place the syringe needle under the surface of 10 mL of an appropriate organic accepting liquid scintillation cocktail contained in a glass scintillation vial and slowly eject the water from the syringe into the cocktail.
7. Slowly withdraw the syringe and tightly cap the vial.
8. Measure the sample by LSC.

Obviously, steps 1, 2, and 3 can be modified if collection is not from a faucet. If taking water from a lake or stream, a direct sample can be taken into a standard EPA type water collection bottle with a volume of at least 20 mL. These bottles have rubber-Teflon septa and prevent radon leakage from the bottle.

The high solubility of radon in organic solvents is exploited for making radon measurements in water. The injected water sample forms a separate phase when mixed with organic accepting cocktails, such as Insta-Fluor and Opti-Fluor O, or a high efficiency mineral oil scintillator such as NEF-957A, available from E.I. du Pont de Nemours & Co., NEN Products, Boston, Massachusetts. The radon contained in the water sample fully partitions into the organic cocktail phase in about three hours. The radon content can then be quantitated by a conventional LSC using a wide window.

Radon Sample Measurements in Water

The reference method for radon in water measurements has employed a radon bubbler and the Lucas cell. Prichard and Gesell (1977) determined a calibration factor for the LSC method by comparing the CPM results of sixteen determinations with those obtained with the Lucas cell. Ideally, 11 particles/minute/pCi should be detected by LSC for every decay of radon and its first three daughters. A predicted calibration factor of 9.75 CPM pCi^{-1} was obtained by considering the solubility of radon in the 5 mL of cocktail, 10 mL of water, and 8 cc of air that made up the total volumes of the 20 mL vials used. Empirically, a calibration factor of 9.34 CPM pCi^{-1} was determined, which is in agreement with the predicted value.

Studies such as the one performed by Prichard have led to the general acceptance of the LSC method for analysis of radon in water. The United States EPA has recognized LSC as an approved method for radon in water analysis.

Radon Measurements with Alpha/Beta LSC

Instruments capable of alpha/beta discrimination are currently being used in the determination of radon and its daughters. Most often these measurements are performed with ground water and drinking water (Chalupnik and Lebecka, 1993; Irlweck and Wallner, 1993; Mobius et al., 1993; Spaulding and Noakes, 1993; Zelensky et al., 1993; Prichard et al., 1991). Although ground water is the most common matrix assayed for radon, alpha/beta LSC has been used to detect radon in surface waters and radon interference in radiocarbon dating (Salonen, 1993; Polach and Kaihola, 1988).

The advantage of using alpha/beta LSC vs. typical beta LS counting for radon in water measurements is the low alpha background which makes it possible to achieve lower detection limits. This lower detection limit makes it possible to measure radon concentrations in surface water where the radon concentration may be several orders of magnitude lower than ground water. Hydrological studies are then possible with the more sensitive alpha/beta LSC method.

Alpha/beta LSC methods for radon counting have taken two approaches. The approach used by Salonen was homogeneous counting of samples and standards with a safe cocktail. Optimization of alpha/beta discrimination was performed with ^{241}Am and ^{36}Cl prepared aqueous standards which were mixed in an aqueous accepting di-isopropylnaphthalene based cocktail. Efficiency and background calibrations were performed with a ^{226}Ra aqueous standard homogeneously mixed in the cocktail. Since this method involves direct mixing of the water sample and cocktail, interferences from other radionuclides in surface and ground waters must be considered. However, the author points out that typically, the concentration of interfering radionuclides in surface and ground waters is on the average two to three orders of magnitude lower than the radon concentration. The author reported better reproducibility with this homogeneous counting approach than with the most common two phase counting approach. In this latter method, the radon-laden water exists as a separate phase under an immiscible organic cocktail and radon partitions over several hours into the organic phase. This two phase approach requires manual optimization of alpha/beta discriminator settings because radon and its daughters emit both alpha and beta particles; therefore, it is not possible to optimize with a pure alpha and a pure beta standard. A known amount of a ^{226}Ra water standard can be mixed with an appropriate organic accepting cocktail to allow radon partitioning into the organic phase. Once the radon has equilibrated into the cocktail, the alpha/beta discriminator can be adjusted to allow for the expected number of alpha counts to appear in the alpha MCA. Because ^{222}Rn and its short-lived progeny emit three alphas and two betas in their decay, approximately 60% of the total activity in a wide energy window is due to alpha decay. A plot of alpha MCA count rate vs. discriminator setting can be used to determine the optimum discriminator setting (Figure 8-6). Such an approach was used by Spaulding and Noakes (1993) to optimize the pulse decay discriminator (PDD) with a Packard Tri-Carb 2550TR/AB alpha/beta LSC. An organic accepting di-isopropylnaphthalene (DIN) based cocktail was found to be the most effective of several cocktail formulations in providing good alpha/beta separation and low alpha backgrounds. The plateau region of the curve in Figure 8-6 represents the setting at which approximately 60% of the total counts appear in the alpha MCA. A comparison of radon determinations from private wells made with the alpha/beta LSC method versus the conventional beta LSC method is shown in Table 8-1. A good correlation exists between the two counting methods (Figure 8-7).

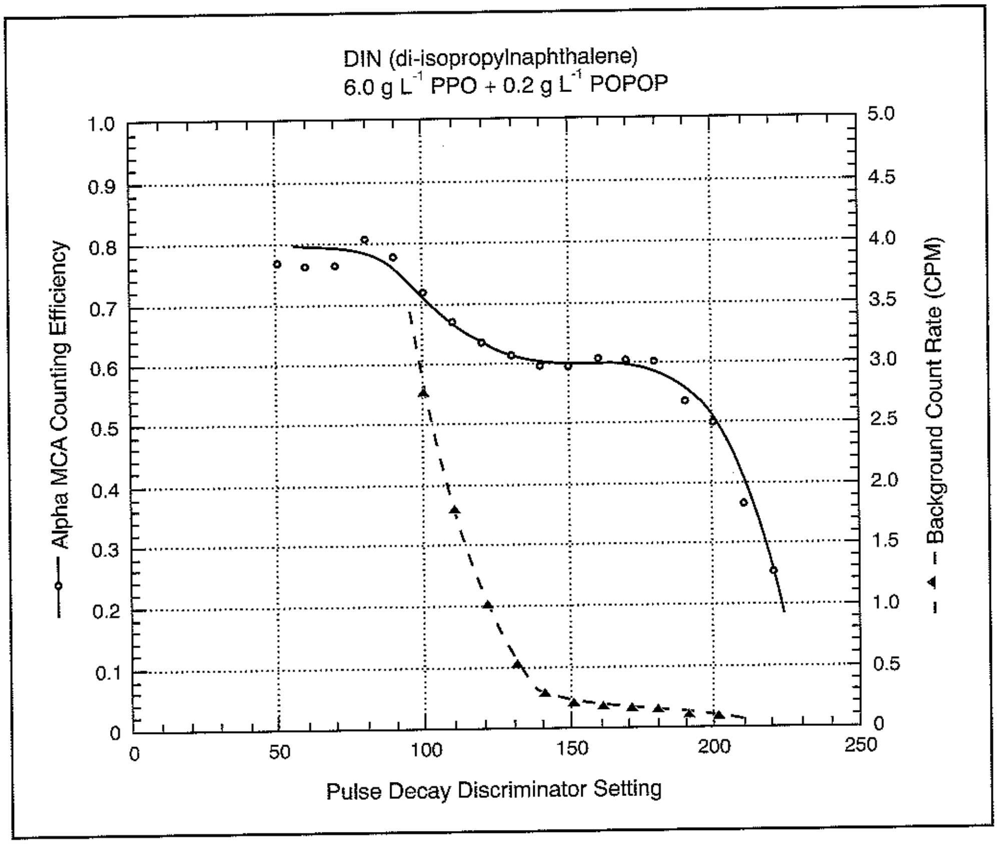


Figure 8-6.
Relative counting efficiency for alpha MCA vs. PDD setting for DIN cocktail (Spaulding and Noakes, 1993).

Well	Depth (m)	Beta LSC activity (Bq/liter)	tSIE	Alpha/beta LSC activity (Bq/liter)	tSIE
1	15	5.8 ± 0.7	546	6.0 ± 0.8	745
2	61	20.5 ± 1.6	579	20.3 ± 1.6	740
3	52	48.1 ± 2.4	551	47.2 ± 2.4	714
4	91	49.3 ± 2.5	516	54.0 ± 2.6	724
5	122	77.5 ± 3.2	520	81.5 ± 3.1	711
6	137	223.9 ± 5.5	553	223.2 ± 5.8	742
7	84	281.4 ± 6.0	548	269.8 ± 7.0	753

Table 8-1.
Radon determinations from private wells,
alpha/beta LSC vs. conventional LSC (Spaulding and Noakes, 1993).

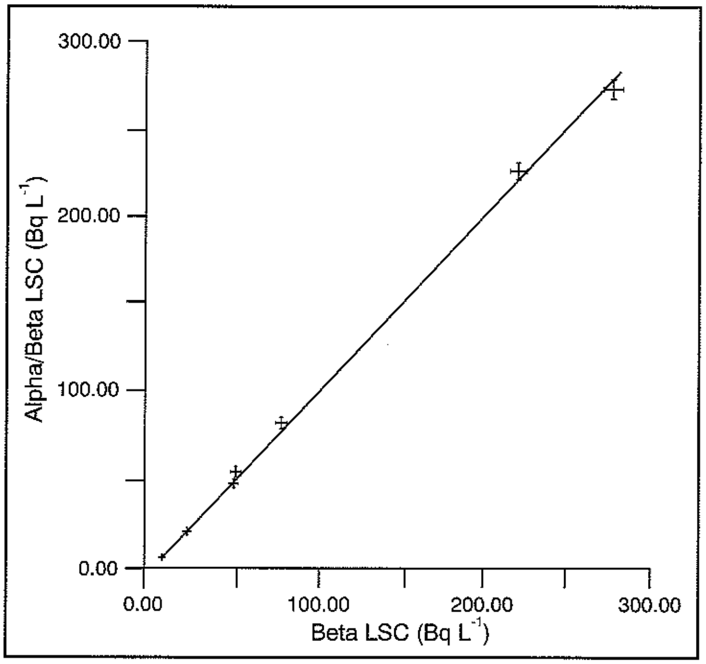


Figure 8-7.
^{222}Rn activities from alpha/beta vs. beta LSC methods (Spaulding and Noakes, 1993).

Detection Limits by LSC

Minimal detection limits for radon measurements in air by the Pico-Rad/LSC system are reported in the order of 2 mBq L^{-1} (Morishima et al., 1992).

10min/sample BKG ~0.15CPM

Liquid scintillation techniques for measuring ^{222}Rn in water, first described by Prichard and Gesell (1977), have the advantages of minimal sample preparation time, small sample sizes and automatic sample changing, with detection limit in the order of 0.37 Bq L^{-1} (Spaulding and Noakes, 1993). Certainly, the desired counting time and the acceptable degree of uncertainty will dictate the achievable detectable limit. For example, Lowry (1991) reported an actual detection limit of 1.65 Bq L^{-1} with a 60 minute count time and with a two sigma total sampling and analytical uncertainty of 15%.

Tri Carb α/β LSC

Tri Carb 1550

Lower limits are achievable for radon water analysis through the use of alpha/beta LSC in a shorter time. A comparison of the minimum detectable activity vs. count time at 95% confidence between alpha/beta LSC and conventional LSC has been made by Spaulding and Noakes (1993) and is shown in Figure 8-8. The figure shows that alpha/beta LSC is able to achieve a detectable limit in one fifth the time of conventional beta LS counting.

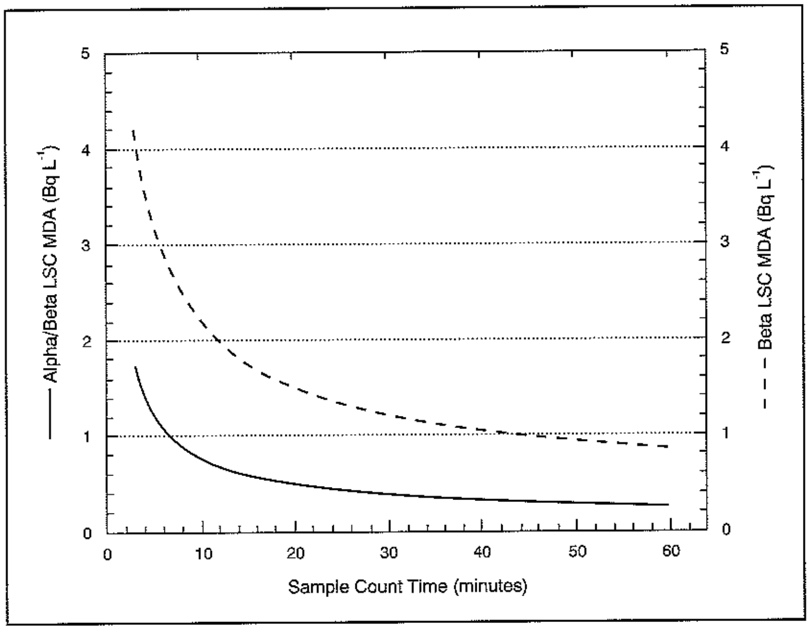


Figure 8-8.
Minimal detectable activity at 95% confidence for alpha/beta LSC and beta LSC (Spaulding and Noakes, 1993).

Summary

^{226}Ra methods, which measure the ^{222}Rn daughter, remain popular alternatives to the radon bubbler and Lucas cell approach primarily because of the simplicity of the technique and the ability to automatically count large numbers of samples with good sensitivity. The prospect exists for increasing the sensitivity and performing simultaneous ^{226}Ra/^{228}Ra analysis with modern instrumentation capable of alpha/beta discrimination. As this instrumentation becomes widespread, new methods should appear which take advantage of this capability.

LSC methods for radon measurements have many advantages over other methods. LSC sample collection techniques are well documented and LSC methods provide low limits of detection, minimal sample preparation, and high unattended sample counting. Both air and water analyses are possible with LSC methods making it a versatile tool for radon analysis.

The use of alpha/beta LSC is even more attractive for radon analysis since lower limits of detection are possible in shorter time periods because of low alpha backgrounds.

References

Amano, H., Kasal, A. and Matsunaga, T. 1985. Simultaneous measurement of Radon and its progeny in cave air by liquid scintillation techniques and alpha ray spectrometry. *Health Physics.* 49(3): 509-511.

Blackwell, A. E. 1993. Simultaneous determination and quantification of radium-226 and radium-228 via liquid scintillation counting. Paper presented at the *39th Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry.* Colorado Springs, CO.

Blackburn, R. and Al-Masri, M. S. 1992. Determination of radium-226 in aqueous samples using liquid scintillation counting. *Analyst.* London, 117(12): 1949-1951.

Burnett, W. C. and Tai, Wei-Chei 1992. Determination of radium in natural waters by alpha liquid scintillation. *Anal. Chem.* 64: 1691-1697.

Case, G. N., and McDowell, W. J. 1990. *J. Radioact. Radiochem.* 1: 4.

Chalupnick, S. and Lebecka, J. M. 1993. Determination of ^{226}Ra, ^{228}Ra and ^{224}Ra in water and aqueous solutions by means of liquid scintillation counting. In *Advances in Liquid Scintillation Spectrometry,* ed. Noakes, J. E., Schoenhofer, F. and Polach, H. 1992. *Radiocarbon.* 397-403.

Chu, L. and Khalique, A. 1990. Determination of ^{226}Ra in water by liquid scintillation counting. *Trans. Am. Nucl. Soc.* 61: 5-6.

Coombs, E. G. 1980. High resolution alpha spectroscopy by liquid scintillation techniques. University of Maine Orono, master's thesis.

Cooper, M. B. and Wilks, M. J. 1981. *Analytical method for radium (^{226}Ra) in environmental samples by the use of liquid scintillation counting.* Report number ARLTR-040 Australian Radiation Lab, Melbourne.

Cross, P. and McBeth, G. W. 1976. Liquid scintillation alpha particle assay with energy and pulse shape discrimination. *Health Physics.* 30: 303-306.

George, A. C. 1984. Passive integrated measurement of indoor radon using activated carbon. *Health Physics.* 46(4): 867-872.

Gesell, T. F., Prichard, H. M. and Haygood, J. R. 1978. Applications of commercial liquid scintillation counters to radon-222 and radium-226. Paper presented at the *11th Symposium on Radiation Instrumentation,* San Diego, California. 258-271.

Harley, J. 1976. *EML Procedures Manual* (HASL-300).

Higuchi, H. 1981. Analytical methods for the radium in environmental samples. *Radioisotopes* (Tokyo). 30(11): 618-627.

Higuchi, H., Uesugi, M., Satoh, K., and Ohashi, N. 1984. Determination of radium in water by liquid scintillation counting after preconcentration with ion exchange resin. *Anal. Chem.* 56: 761-763.

Horiuchi, K. and Murakami, Y. 1981. New determination of ^{226}Ra, ^{224}Ra, and ^{228}Ra in water. Extraction of radon and thoron and integral counting with a liquid scintillation counter. Nippon Kagaku Kaishi. 1: 116-121.

Irlweck, K. and Wallner, G. 1993. Determination of ^{226}Ra in Lake Sediments by liquid scintillation counting of cocktail extracted ^{222}Rn. In *Advances in Liquid Scintillation Spectrometry 1992, ed.* Noakes, J. E., Schoenhofer, F. and Polach, H. *Radiocarbon.* 391-395.

Lilly, J. 1994. Fermco. Fernald, Ohio. Personal communication.

Lowry, J. D. 1991. Measuring low radon levels in drinking water supplies. *J. Amer. Water Works Assoc.* April 1991.

Lucas, H. F. 1957. Improved low level alpha scintillation counter for radon. *Rev. Scient. Instrum.* 28: 680.

Lucas, H. F. 1964. A fast and accurate survey technique for both radon-222 and radium-226. In *The Natural Radiation Environment*, ed. Adams, J. A. S. and Lowder, W. M., University of Chicago Press.

McDowell, W. J. and McDowell, B. L. 1994. *Liquid Scintillation Alpha Spectrometry.* Boca Raton, Florida, CRC Press, Inc.

Mobius, S, Kamolchote, P., Ramamonjisoa, T. L., and Yang, M. 1993. Rapid determination of Ra, Rn, Pb, and Po in water using extractive scintillation. In *Advances in Liquid Scintillation Spectrometry 1992*, ed. Noakes, J.E., Schoenhofer, F. and Polach, H. Radiocarbon. 413-416.

Momohara, D. 1994 Analytical Resources, Inc. Personal communication.

Morishima, H., Koga, T., Kawai, H., Kondo, S., Mifune, M., Konishi, Y., and Shirai, C. 1992. Radon measurement using a liquid scintillation spectrometer. Proceedings of the third low level counting conference using liquid scintillation analysis proceedings, Tokyo, Japan. 179-184.

Nobrega, A. W., Sachett, I. A. and Hespanhol, E. C. B. 1987. Determination of ^{226}Ra by alpha spectrometry of liquid scintillation. *Quim Nova.* 10(3): 175-179.

Noguchi, M., Satoh, K., and Higuchi, H. 1984. Low level alpha activity measurements with pulse shape discrimination. Measurement system and the characteristics. *Radioisotopes* (Tokyo). 33(12): 835-840.

Orr, J. C. 1988. Evaluation of counting methods for oceanic radium-228 J. Geophys. Res. 93(C7): 8265-8278.

Parks, N. J. and Tsuboi, K. K. 1978. Emulsion counting of radium and radon. *Int. J. Appl. Radiat. Isot.* 29(2): 77-80.

Passo, C. J. Jr. and Floeckher, J. M. 1991. The LSC approach to radon counting in air and water. In *Liquid Scintillation Counting and Organic Scintillators*, ed. Ross, H., Noakes, J., and Spaulding, J. D. Lewis Publishers. 375-384.

Petrow, H. G., Cover, A., Schiessle, W., and Parsons, E. 1964. Radiochemical determination of radium-228 and thorium-228 in biological and mineral samples. *Anal. Chem.* 36: 1600.

Polach, H. and Kaihola, L. 1988. Determination of radon by liquid scintillation alpha/beta particle spectrometry: Towards the resolution of a ^{14}C dating problem. *Radiocarbon.* 30: (1).

Prichard, H. M., Gesell, T. F., and Meyer, C. P. 1980. Liquid scintillation analyses for Radium-226 and Radon-222 in potable waters. In *Liquid Scintillation Counting Recent Applications and Development.* Volume 1, Physical Aspects, ed. Peng, C., Horrocks, D. L. and Alpen, E. L. Academic Press. 347- 355.

Prichard, H. M., Gesell, T. F., and Meyer, C. R. 1980. Liquid scintillation analyses for radium-226 and radon-222 in potable waters. In *Liquid Scintillation Counting Recent Applications and Development*, Vol. II Sample Preparation and Applications, ed. Peng, C., Horrocks, D. L., and Alpen, E. L. London, Academic Press.

Prichard, H. M. and Gesell, T. F. 1977. Rapid measurements of ^{222}Rn concentrations in water with a commercial liquid scintillation counter. *Health Physics.* 33: 577-581.

Prichard, H. M. and Marien. K. 1985. A passive diffusion ^{222}Rn sampler based on activated carbon adsorption. *Health Physics.* 48(6): 797-803.

Prichard, H. M., Venso, E. A., and Dodson, C. L. 1991. Liquid scintillation analysis of ^{222}Rn in water by alpha/beta discrimination. *Radioactivity and Radiochemistry.* 3(10): 28-36.

Saarinen, L. and Suksi, J. 1992. Determination of uranium series radionuclides Pa-231 and Ra-226 using liquid scintillation counting (LSC). *Report of the Nuclear Waste Commission of Finnish Power Companies.*

Salonen, L. 1993. Measurement of low levels of ^{222}Rn in water with different commercial liquid scintillation counters and pulse-shape analysis. In *Advances in Liquid Scintillation Spectrometry 1992*, ed. Noakes, J. E., Schoenhofer, F. and Polach, H. . Radiocarbon. 361-371.

Schoenhofer, F. Barnet, J. M., and McKleevev, J. 1991. Determination of 222Rn and 226Ra in drinking water by low level liquid scintillation counting - Surveys in Austria and Arizona. In *Liquid Scintillation and Organic Scintillators*, ed. Ross. H., Noakes, J. and Spaulding, J. D. Lewis Publishers. 537-545.

Schroeder, M. C., Vanags, U., and Hess, C. T. 1989. An activated charcoal-based, liquid scintillation analyzed airborne Rn detector. *Health Physics.* 57(1): 43-49.

Spaulding, J. D. and Noakes, J. E. 1993. Determination of ^{222}Rn in drinking water using an alpha/beta liquid scintillation counter. In *Advances in Liquid Scintillation Spectrometry 1992*, ed. Noakes, J. E., Schoenhofer, F. and Polach, H. Radiocarbon. 373-381.

Tso, M. W. and Li, C. 1987. Indoor and outdoor ^{222}Rn daughters in Hong Kong. *Health Physics.* 53(2): 175-180.

U.S. EPA 520/5-84-006. *Radiochemistry Procedures Manual.* Eastern Environmental Radiation Facility. Montgomery, Alabama.

U.S. EPA 520/1-86-014-1. February 1987. *Interim protocols for screening and follow up radon and radon decay product measurements.* U.S. Environmental Protection Agency, Office of Radiation Protection Programs, Washington, D.C. February 1987.

Zelensky, A. V., Buzinny, M. G., and Los' I. P. 1993 Measurement of ^{226}Ra, ^{222}Rn, and Uranium in Ukrainian groundwater using ultra-low level liquid scintillation counting. In *Advances in Liquid Scintillation Spectrometry 1992*, ed. Noakes, J. E., Schoenhofer, F. and Polach, H. Radiocarbon. 405-411.

Section IV.

Environmental Radionuclide Analysis - Manmade Beta Emitting Radionuclides

Chapter 9: ^{89}Strontium and ^{90}Strontium/^{90}Yttrium

^{89}Sr and ^{90}Sr/^{90}Y in the Environment

^{89}Sr and ^{90}Sr/^{90}Y are fission products that are created in nuclear explosions and nuclear fuel consumption. Therefore, the main source of these radionuclides is nuclear weapons testing in the atmosphere and releases from the nuclear fuel cycle. Fallout from nuclear weapons testing is primarily responsible for the ^{89}Sr and ^{90}Sr/^{90}Y concentrations found in soil. The geographic and depth distribution pattern (typically located in the upper 15 cm) varies due to changes in the deposition rates over time and gradual depletion by decay, erosion, and leaching (NCRP report no. 50). Releases from the nuclear fuel cycle occur primarily in the form of effluent discharges from nuclear facilities.

^{90}Sr is an important fission product (FP) because of its long physical and biological half-life. ^{89}Sr shares the same biological significance, but has a much shorter physical half-life and thus will not have a long term environmental impact. However, the presence of both radioisotopes in environmental samples is of great interest. Water, milk, soil, vegetation, and urine are the typical sample matrices that are assayed for radiostrontium.

Sample Preparation and Measurement

General Analytical Scheme for Radiostrontium (^{89}Sr; ^{90}Sr/^{90}Y)

The quantitation of radiostrontium is based on three major considerations: sample pre-treatment (to bring the sample into a suitable matrix), isolation of radiostrontium by chemical treatment, and nuclear counting (Wilken and Joshi, 1992).

Sample pre-treatment includes sample collection or preservation techniques (mostly for water) as well as any ashing (organic material) or concentration procedures that are required. Sampling procedures for environmental water samples are described in "Environmental Radioactivity Surveillance Guide," published by the U.S. Environmental Protection Agency (EPA) as report ORP/SID 72-2. In this document, the EPA recommends the following for water collection: Preserve the sample by adding 50 mL of 8 N nitric acid (final concentration 0.1 M) containing 80 mg each of strontium and barium carriers per 4 liters (1 gallon) of sample. However, if determination is to be made for ^{89}Sr and ^{90}Sr content in the separate dissolved and suspended fractions of the sample, then those fractions must be separated before the preservative is added, since the preservative may change the radiostrontium distribution in the sample. Samples brought to the laboratory for filtration without preservative must be carefully evaluated since container wall effects and temperature could change the radiostrontium distribution in the two sample fractions.

Much of the emphasis for assay of radiostrontium has been focused on separation chemistry. Chemically, strontium mimics calcium which makes separation difficult in environmental samples where, inevitably, calcium is abundant. The fuming nitric acid procedure (Gregory, 1972) has been commonly used for ^{90}Sr assay since the early 1970's. The EPA reference method (EPA-600/4-76-011) for measuring ^{89}Sr and ^{90}Sr is a version based on this procedure. The procedure was developed to assay environmental water, but could be adapted to matrices containing organic matter, if steps are taken to destroy the organic material. In this method, strontium nitrate carrier is added to the sample and both the carrier and radioisotopes are precipitated as strontium nitrate from fuming nitric acid. The radioisotopes and carrier are then precipitated as strontium carbonate, dried, and weighed for recovery of carrier, and the radioactivity determined and normalized to 100% based on the recovery factor. The activity of ^{90}Sr is determined by separating and counting its daughter ^{90}Y since ^{89}Sr cannot be separated from ^{90}Sr by chemical procedures. At equilibrium, the activity of ^{90}Y is equal to ^{90}Sr. The ^{89}Sr activity is then determined by difference. The original method proposed a counting system with a low background proportional or Geiger-Muller type counter. Although liquid scintillation counting is not mentioned as an analytical tool, the method is applicable for LSC. A more recent version (Wilken and Diehl, 1990) involves the use of ^{85}Sr (gamma) as a tracer (to evaluate the chemical yield) and thus is dedicated to counting with a proportional counter since ^{85}Sr would interfere with the ^{89}Sr and ^{90}Sr measurement by LSC.

Early ^{90}Sr Methods by LSC

Several methods of measuring strontium using a liquid scintillation counter have been reported. (Carmon, 1979; Piltingsrud and Stencel, 1972; Uyesgi and Greenberg, 1965; Reynold and Eldridge, 1980; Shimizu et al., 1985; and Martin, 1987). These are categorized as either liquid scintillation and/or Cerenkov counting methods.

The measurement of ^{90}Sr alone by LSC is complicated because ^{89}Sr may also be present and will interfere with ^{90}Sr measurement. In addition, environmental ^{3}H, present in water samples, may further complicate the analysis. Typically, pre-concentration, and chemical separation by extraction and chromatographic techniques have been applied because of the complexity of the sample matrix and the low levels of ^{89}Sr and ^{90}Sr and other environmental radionuclides in the sample matrix. The exact separation scheme will depend on the sample matrix and whether individual activities of ^{89}Sr and ^{90}Sr are required.

Cerenkov measurements usually require two or more measurements for ^{89}Sr and ^{90}Sr in the presence of ^{90}Y (Carmon, 1979; Reynold and Eldridge, 1980).

Early attempts at strontium assay by LSC involved precipitation of strontium as insoluble salts and suspension in a suitable cocktail solvent containing a gelling agent such as silicon dioxide or Cab-O-Sil (Cab-O-Sil is a thixotropic sample dispersant-suspending agent manufactured by Eastman Kodak Co., Rochester, New York) (Helf et al., 1960; Von Erdtmann and Herrmann, 1960; Myers and Brush, 1962; Piltingsrud and Stencl, 1972). Others report a method of concentrating inorganic ions from large aqueous samples with a scintillating ion exchange resin (Heimbuck et al., 1963). All of these early methods suffered from several limitations, such as failure to correct for yield recovery, quenching, and non-uniformity of samples. In addition, the methods required that strontium and yttrium be in secular equilibrium (except for Piltingsrud and Stencel, 1972). This requirement added considerably to the time needed to complete an assay.

Methods were then attempted to assay for ^{90}Sr in non-equilibrium conditions. One such method also employed the use of Cab-O-Sil gelling agent to suspend an insoluble strontium precipitate of a sample containing ^{90}Y, ^{90}Sr, and ^{89}Sr, and a spectrum unfolding computer program to determine the quantity of each of the three isotopes (Piltingsrud and Stencel, 1972). Another method describes precipitation as strontium carbonate, dissolving in glacial acetic acid and adding 2-ethylhexanoic acid to form strontium and yttrium 2-hexanoates that are then soluble in a toluene based cocktail (Uyesgi and Greenberg, 1965). The authors point out that the method has several advantages over conventional beta counting (proportional counting) including the immediate assay of ^{90}Sr after separation thus eliminating the usual two week ingrowth period for ^{90}Y. Other advantages of the method include high counting efficiencies for ^{90}Sr (81%) and ^{90}Y (98%), and avoidance of the counting problems of self-absorption, poor geometry, and non-uniformity of sample mounting.

Currently, the most popular separation methods for radiostrontium involve the use of ion exchange chromatography (Amano and Yanase, 1990), liquid-liquid (solvent) extraction (Tait and Wiechen, 1993; Dietz and Horowitz, 1993) and extraction chromatography (Dietz et al., 1991; Vajda et al., 1992).

The analytical method of Amano and Yanase was used to assay air concentrations of ^{90}Sr by collecting dust samples on a Toyo type HE40-T cellulose (80%) glass fiber (20%) filter. The analytical scheme is shown in Figure 9-1.

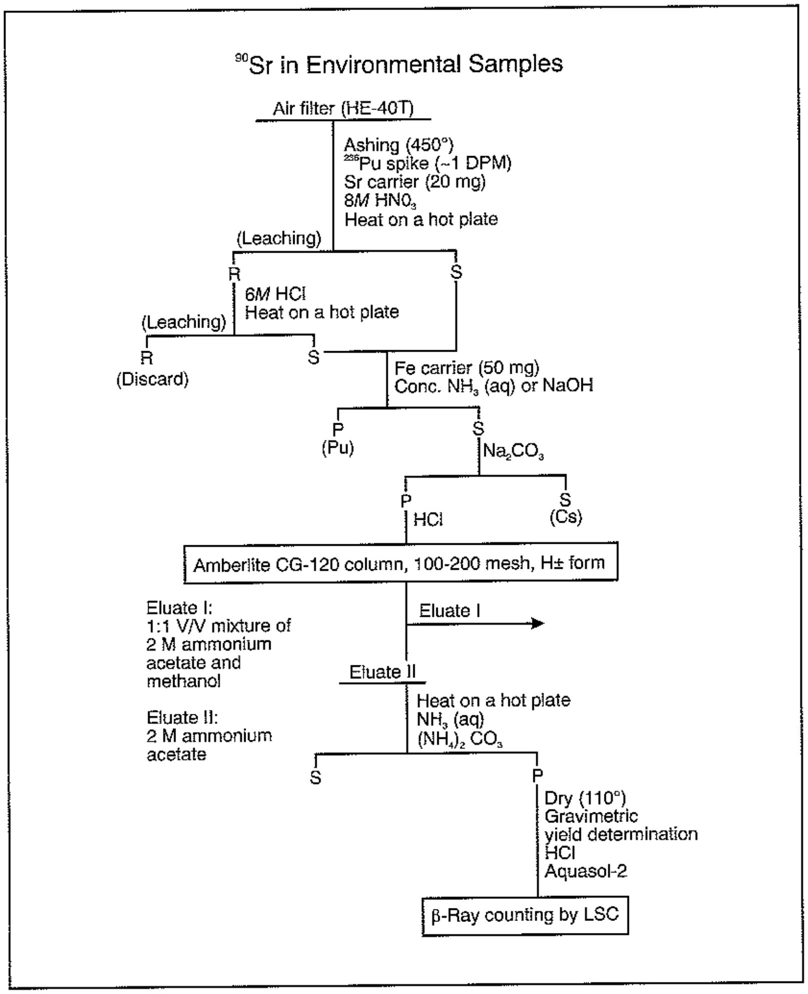


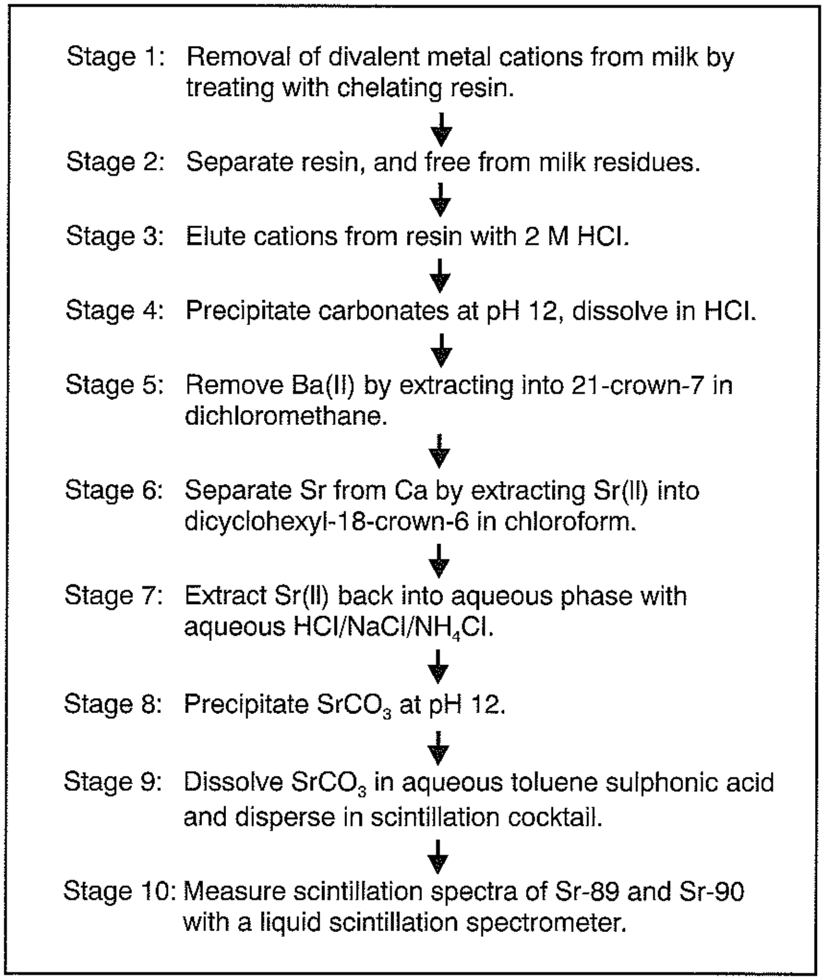
Figure 9-1.
Analytical scheme for ^{90}Sr and ^{89}Sr in a dust sample (Amano and Yanase, 1990).

Two channels of the counter were used to determine ^{90}Sr, ^{90}Y, and ^{89}Sr free from the effects of environmental ^{3}H. Calculations were performed to determine the activity of ^{89}Sr and gross activity of ^{90}Sr and ^{90}Y. After chemical separation of strontium, the ^{90}Sr activity is determined by subtracting the amount of ^{90}Y that has grown in at the time of measurement.

Recent Separation Techniques and LSC Measurement

Liquid-liquid (solvent) extraction has been used for process-scale separation and pre-concentration of radionuclides. Recent research has focused on the development of a workable acid-side extraction process for the removal and recovery of ^{90}Sr from nuclear waste streams (Dietz and Horowitz, 1993). Macrocyclic polyethers ("crown ethers") have been proposed to overcome the unique problems of low charge and large ionic radius of Sr(II). This low charge density made it difficult to strip away associated water molecules that must accompany the strontium into the organic phase to maintain electrical neutrality. The net result was poor extraction efficiency. An improvement was developed by Dietz and Horowitz when they combined a crown ether (bis-4,4'(5')-tert-butylcyclohexano-18-crown-6) in 1-octanol. This improved extraction specificity and the ability to accommodate a substantial amount of water. This crown ether is the basis of the new strontium extraction and recovery (SREX) process. Liquid-liquid extraction methods using crown ethers have been applied to analytical work. However, liquid-liquid extraction is time consuming and may generate a substantial amount of radioactive waste. A recent more manageable approach has been to coat a small portion of extractant solution onto an inert solid polymeric support such as Amberlite XAD-7 or its small particle analog, Amberchrom CG (Rohm and Haas, Philadelphia, Pennsylvania). Sr-Spec (strontium specific) is such a chromatographic material that has become commercially available (Eichrom Industries, Darien, Illinois). The combination of an extraction agent on an inert support is known as extraction chromatography.

Liquid-liquid extraction was used by Tait and Weichen (1993) to determine ^{89}Sr and ^{90}Sr in milk. This method used a chelating resin to isolate strontium and other divalent cations followed by two crown ether extractions to isolate the strontium. $SrCO_3$ was then precipitated and dissolved in toluene sulfonic acid for LSC measurement. The analytical scheme is reproduced in Figure 9-2.



Stage 1: Removal of divalent metal cations from milk by treating with chelating resin.

Stage 2: Separate resin, and free from milk residues.

Stage 3: Elute cations from resin with 2 M HCl.

Stage 4: Precipitate carbonates at pH 12, dissolve in HCl.

Stage 5: Remove Ba(II) by extracting into 21-crown-7 in dichloromethane.

Stage 6: Separate Sr from Ca by extracting Sr(II) into dicyclohexyl-18-crown-6 in chloroform.

Stage 7: Extract Sr(II) back into aqueous phase with aqueous $HCl/NaCl/NH_4Cl$.

Stage 8: Precipitate $SrCO_3$ at pH 12.

Stage 9: Dissolve $SrCO_3$ in aqueous toluene sulphonic acid and disperse in scintillation cocktail.

Stage 10: Measure scintillation spectra of Sr-89 and Sr-90 with a liquid scintillation spectrometer.

Figure 9-2.
Analytical scheme for extraction of radiostrontium from milk.

A simple spectrum stripping technique was applied to calculate activities from the spectra of real samples. The authors report recoveries of 87.7% ±3.5% for ^{89}Sr and 90.4% ±3% (± 1 S.D.) for five, two liter milk samples with a detection limit of 0.014 Bq for ^{90}Sr samples free of ^{89}Sr. The predicted detection limit of ^{90}Sr will increase with the presence of increasing activities of ^{89}Sr and ^{90}Y.

Separation methods using extraction chromatography appear to be very popular for assaying radiostrontium. This technique has been applied to bioassay as well as environmental samples. Dietz et al., 1991, employed extraction chromatography to determine ^{89}Sr and ^{90}Sr in urine. The separation scheme involved acid digestion of the urine sample (600 mL) to remove organics and precipitation of basic calcium phosphate. The residue was redissolved in nitric acid and loaded onto a Sr-Spec column to isolate radiostrontium. The separation scheme is shown in Figure 9-3.

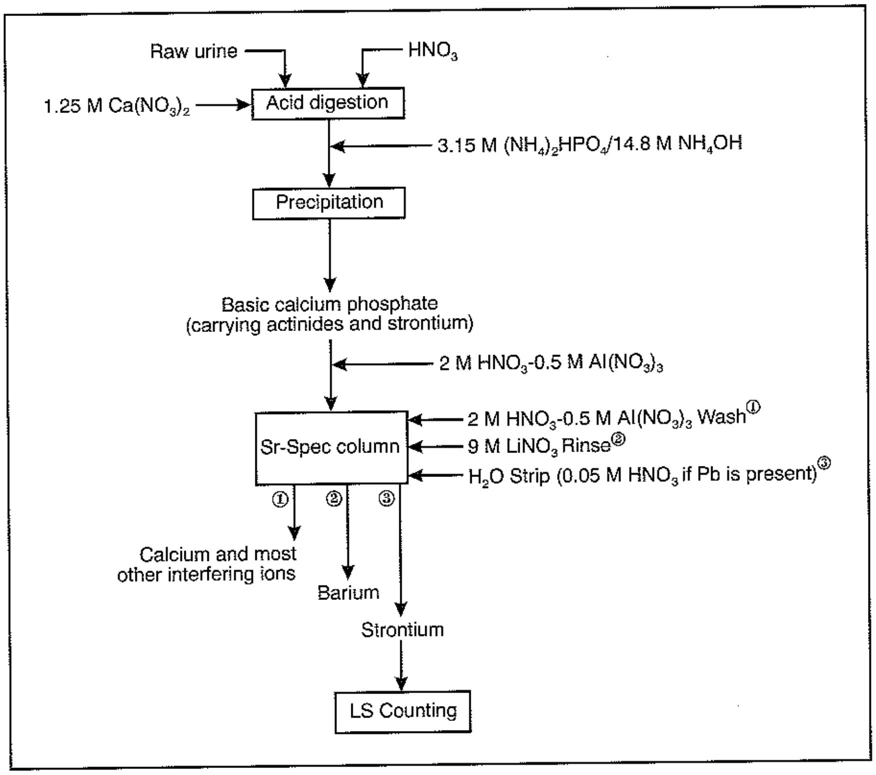


Figure 9-3.

Proposed scheme for the isolation of radiostrontium in urine (Dietz et al., 1991).

The strontium containing sample was ultimately eluted from the column with 5 mL of water and mixed with 17 mL of scintillation cocktail. Two energy windows, 20-500 and 500-1400 keV, were defined on a Packard Tri-Carb 2200CA liquid scintillation analyzer (Figure 9-4). The samples were counted three times for 30 minutes each. Standards containing pure ^{90}Sr, pure ^{90}Y, and pure ^{89}Sr were counted under the same windows to determine coefficients in a set of simultaneous equations describing the counts expected in each window at any time after strontium isolation. The observed count rate of samples was then used to determine the contribution of each isotope to the expected count. The authors report that the advantage of this method is that samples can be counted immediately after strontium separation. Yield determination from the co-precipitation step and column recoveries were reported to be around 95% ± 5% overall. The limit of detection was reported as *ca.* 1.5 DPM L^{-1}; 0.025Bq L^{-1}. This is approximately six times lower than the value specified as acceptable (7 DPM L^{-1}; 0.117 Bq L^{-1}) for either ^{89}Sr or ^{90}Sr by the American National Standards Institute (ANSI) in ANSI N13.30, 1989.

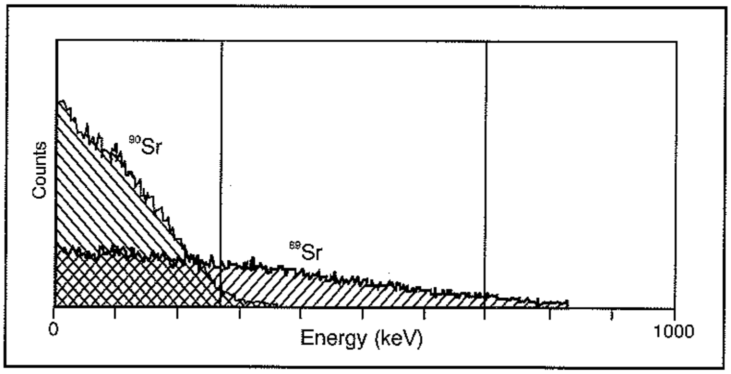


Figure 9-4.
Spectra of ^{89}Sr and ^{90}Sr from a Packard Tri-Carb 2200CA (Dietz et al., 1991).

Extraction chromatography and liquid scintillation counting with a Packard Tri-Carb 2250CA has also been used to determine total radiostrontium in soil samples (Vajda et al., 1992). The method consisted of three basic steps: (1) oxalate precipitation after ashing to precipitate the alkaline earth metals such as potassium and calcium which are major soil components; (2) chromatographic separation utilizing a Sr-Spec (Eichrom Industries, Darien, Illinois) column; (3) oxalate precipitation of strontium to evaluate chemical yield. The separation scheme proposed is shown in Figure 9-5. Radiostrontium is then determined via liquid scintillation analysis by counting 1-2 mL of the dissolved precipitate in 15 mL of Packard Insta-Gel cocktail. As in the study performed by Dietz et al. (1991), two windows were used. In this study, a "^{90}Sr" window (15-250 keV) and "^{90}Y" (250-1000 keV) window were used. The authors point out that if ^{89}Sr determination is necessary, then appropriate windows can be selected on the basis of ^{90}Sr and ^{89}Sr energies as performed by Dietz et al. The chemical yield was about 80%. The sensitivity for 10 g soil samples is reported as 10 Bq kg^{-1}.

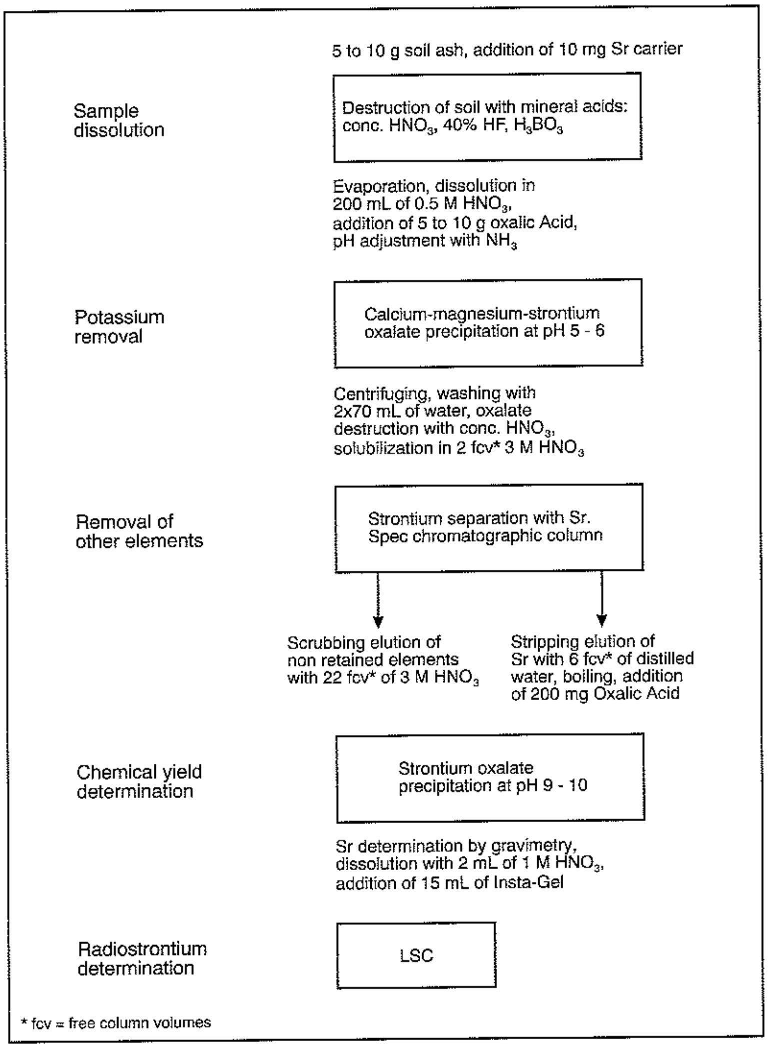


Figure 9-5.
Separation scheme of strontium from soil samples (Vajda et al., 1992).

Cerenkov Counting

Several attempts have been made to determine radiostrontium by Cerenkov counting (Randolph, 1975; Buchtela and Tschurlovits, 1975; Carmon, 1979; Reynolds and Eldridge, 1980; Martin, 1987; and Rucker, 1992). These methods are based on the fact that both ^{89}Sr and ^{90}Y can be detected with high counting efficiency (greater than 40%) by Cerenkov counting in aqueous solution. Interference from ^{90}Sr is at a minimum because of its low Cerenkov counting efficiency (less than 1.4%). This fact has been the reason of the appeal for Cerenkov counting because it allows immediate determination of ^{89}Sr in a fresh mixture of ^{89}Sr-^{90}Sr.

In all of the above references, conventional separation techniques, including precipitation, ion exchange or liquid extraction, were used to isolate radiostrontium. After separation, the ^{90}Y component is used to quantitate the ^{90}Sr activity. Martin (1987) radiochemically separated the ^{90}Y component while Carmon (1979) mathematically calculated the amount of ^{90}Y ingrown within two hours after the separation. Reynolds and Eldridge (1980) waited for ^{90}Y ingrowth (^{89}Sr levels were found to be insignificant). Rucker (1992) used a combination of Cerenkov counting for ^{89}Sr and then added scintillation cocktail to determine the total ^{89}Sr and ^{90}Sr activity with a mathematical correction for ^{90}Y ingrowth. Banavali et al., 1992 proposed a method which involves the use of carbonate precipitation and extraction chromatography to isolate total radiostrontium which is counted via Cerenkov (primarily ^{89}Sr). The sample is counted via Cerenkov again two to three days after sufficient ^{90}Y ingrowth to determine the amount the activity of ^{90}Sr via ^{90}Y.

Cerenkov counting techniques allow the use of ^{85}Sr as a yield tracer since this isotope is not detected by Cerenkov counting. This can make the process simpler because evaporative steps and desiccation steps to determine a gravimetric yield can be avoided.

Calculated detection limits of 9.4 pCi L^{-1} (0.35 Bq L^{-1}) for ^{89}Sr and 7.9 pCi L^{-1} (0.29 Bq L^{-1}) for ^{90}Sr were reported by Rucker (1992) for a 1 liter sample, 20 minute count time, and 80% chemical recovery. In an unpublished report, Gordon Cook reported similar calculated detection limits for ^{90}Y (^{90}Sr) of 0.5 and 0.54 Bq L^{-1} for plastic and glass vials, respectively, with a Packard Tri-Carb 2250CA in low level count mode.

Some typical Cerenkov ^{90}Sr/^{90}Y counting performance data acquired on a Packard low level LSC are shown in Table 9-1. The data were acquired in both the normal count mode (NCM) and low level count mode (LLCM) using polyethylene plastic and standard low potassium glass scintillation vials. Sample volume was 20 mL. Standards were counted for 100 minutes while backgrounds were counted for 500 minutes.

		0-30 keV Window		**Optimized Window**	
Vial Type	**Count Mode**	**% Efficiency**	**Background (CPM)**	**% Efficiency**	**Background (CPM)**
Plastic	NCM	71.7	15.8	68.8	13.1
Plastic	LLCM	67.2	11.1	65.6	9.7
Glass	NCM	62.7	24	61.5	21.2
Glass	LLCM	53.8	8	49.8	6.6

Table 9-1.
^{90}Sr/^{90}Y Cerenkov counting performance.

A typical ^{90}Y (^{90}Sr) spectrum and background is shown in Figure 9-6.

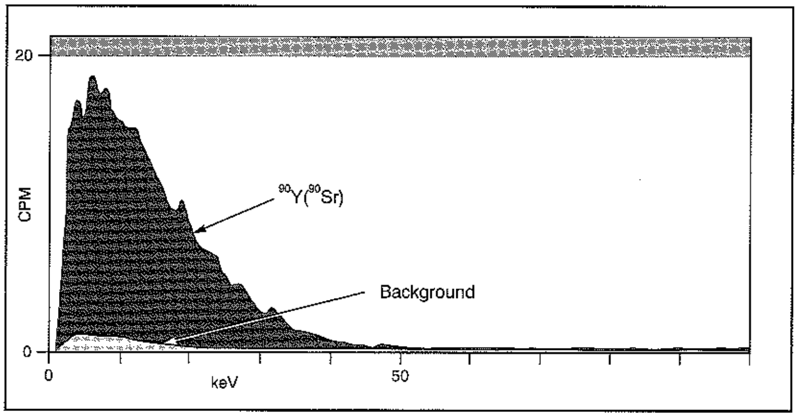


Figure 9-6.
^{90}Y(^{90}Sr) Cerenkov spectrum in low level count mode using a Tri-Carb 2250CA.

Summary

Much of the emphasis on the assay of radiostrontium has been on separation chemistry. Recently, extraction chromatography methods of separation have gained in popularity. The analytical techniques for the determination of ^{89}Sr, ^{90}Sr and ^{90}Y are dependent on the decay characteristics of the three radionuclides and the desired detection limits. LSC offers the ability to count radiostrontium at very high counting efficiencies after separation. Cerenkov counting of the ^{90}Y daughter can be combined with cocktail counting of radiostrontium to determine the radiostrontium component of a sample. LSC detection limits are reported to be less than 1 Bq L^{-1}.

References

Amano, H. and Yanase, N. 1990. *Measurement of ^{90}Sr in environmental samples by cation-exchange and liquid scintillation counting*. Talanta. 37(6): 585-590.

American National Standards Institute, ANSI N13.30, 1989. *Draft American National Standard for Performance Criteria for Radiobioassay.*

Banavali, A. D., Moreno, E. M., and McCurdy. 1992. Strontium-89, 90 analysis by Eichrom column chemistry and Cerenkov counting. Abstract in *Proceedings of the 38th Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry*. Santa Fe, New Mexico.

Buchtela, K. and Tschurlovits, M. 1975. A new method for determination of Sr-89, Sr-90, and Y-90 in Aqueous solution with the aid of liquid scintillation counting. *Int. J. Appl. Rad. Isot.* 26: 333-338.

Carmon, B. 1979. The use of Cerenkov radiation for the assay of radiostrontium in aqueous solutions. *Int. J. Appl. Radiat. Isot.* 30: 97.

Dietz, M. L. and Horowitz, E. P. 1993. Novel chromatographic materials based on nuclear waste processing chemistry. *LC-GC*. 11(6): 424-436.

Dietz, M. L., Horowitz, E. P., Nelson, D. M. and Wahlgren, N. 1991. An improved method for determining ^{89}Sr and ^{90}Sr in urine. *Health Physics*. 61(6): 871-877.

Gregory, L. P. 1972. A simplified separation of strontium, radium, and lead from environmental media by precipitation followed by fractional elution. *Anal. Chem.* 44: 2113-2115.

Heimbuck, A. H., Gee, H., Bould, H., and Schwarz, W. J. 1963. USAEC Report, NYO-10405.

Helf, S., White, C. G. and Schelley, R. N. 1960. *Analyt. Chem.* 32: 238.

Martin, J. E. 1987. *J. Appl. Radiat. Isot.* 38: 953.

Myers, L. S. and Brush A. H. 1962. *Analy. Chem.* 34: 342.

NCRP report No. 50. 1976. *Environmental Radiation Measurements*. International Council on Radiation Protection and Measurements.

Piltingsrud, H. V. & Stencel, J. R. 1972. Determination of ^{90}Y, ^{90}Sr, and ^{89}Sr in samples by use of liquid scintillation beta spectroscopy. *Health Physics.* 23: 121-122.

Randolph, R. B. 1975. Determination of strontium-90 and strontium-89 by Cerenkov and liquid scintillation counting. *Int. J. Appl. Radiat. Iso.* 26: 9-16.

Reynold, S. A. and Eldridge, J. S. 1980. In Liquid Scintillation Counting-Recent Applications and Development. Peng, T., Horrocks, D. L., and Alpen, E. L. 397-405. Academic Press, New York.

Rucker, T. L. 1992. Calculational method for the resolution of ^{90}Sr and ^{89}Sr counts from Cerenkov and liquid scintillation counting. In *Liquid Scintillation Counting and Organic Scintillators*, ed. Ross, H., Noakes, J., and Spaulding, J, 529-535. Lewis Publishers.

Shimizu, N., Hayashi, K., Akutsu, T., Nomura, T., Yamato, A., and Iwai, M. 1985. Hoken Butseri. 20:139.

Tait, D. and Weichen, A. 1993. Use of liquid scintillation for fast determination of ^{89}Sr and ^{90}Sr in milk. *Sci. Total Environ.* 130/131: 447-457.

U.S. EPA ORP/SID 72-2 *Environmental Radioactivity Surveillance Guide.* U.S. Environmental Protection Agency.

Uyesgi, G. S., and Greenberg, A. E. 1965. Simultaneous assay of Strontium-90 and Yttrium-90 by liquid scintillation spectrometry. *Intl. J. Appl. Rad. Isot.* 16: 581-587.

Vajda, N., Ghods-Esphahani, A., Cooper, E., and Danesi, P. R. 1992. Determination of radiostrontium in soil samples using a crown ether. *J. Radioanal. Nucl. Chem.* 162: 307.

Von Erdtmann, G. & Hermann, G. Z. 1960. Electrokem. 64: 1092.

Wilken, R. D. and Diehl, R. 1990. Strontium-90 in environmental from northern Germany before and after the Chernobyl accident. *Radiochim. Acta.* 51: 195-198.

Wilken, R. & Joshi, S. R. 1991. Rapid methods for determining ^{90}S, ^{89}Sr, and ^{90}Y in environmental samples: a survey. *Radioactivity & Radiochemistry.* 2(3): 14-27.

Chapter 10: ^{63}Nickel

^{63}Ni in the Environment

^{63}Ni is a long-lived ($t_{1/2}$ = 9.2 years) weak beta emitting radionuclide (E_{max} = 0.067 MeV) and one of the major radioactive corrosion products existing in the water coolant of nuclear power reactors (Lo et al., 1993). The product is formed from the neutron capture of nickel released from the steel piping due to corrosion. ^{63}Ni is included in the list of low level, long-lived radioactive wastes from nuclear power reactors specified in the Nuclear Regulatory Commission (NRC) Regulation 10CFR Part 61 published by the NRC in 1982.

Since December 1993, utilities and other generators of radioactive waste in the U.S. have been required to identify and quantify the radionuclides in the waste sent to burial sites for disposal. Releases of ^{63}Ni from leaks in the water coolant system, such as from a condenser, are possible and will have a radiological impact on the environment (Lo et al., 1993).

^{63}Ni Monitoring Applications

The measurement of ^{63}Ni in environmental samples by liquid scintillation requires separation and purification from the original sample matrices because of its weak beta radiation and interference from coexisting radionuclides.

Procedures for measuring ^{63}Ni have been reported for various sample matrices including liquid effluents, water, sea water, vegetation, urine, sludge and resins, and metals (Harvey and Sutton, 1970; Yu, 1988; Kojima and Furakawa, 1985; Lo et al., 1993; Kramer, 1981; Russow and Dermietzel, 1990; NUREG/CR- 4101/Part 1; Radwan et al., 1981).

Water Analysis

Since ^{63}Ni is a major radioactive corrosion product existing in the water coolant of nuclear power reactors, water or liquid effluent is the most common sample matrix assayed. Chemical separation of nickel by precipitation with dimethylgloxime (DMG) followed by quantitation by LSC is the common method used for assay. Precipitation as the dipyridine nickel dithiocyanate complex $[Ni(C_2H_4N)_4](CNS)_2$ and solubilization in dioxane-based liquid scintillation cocktail has also been reported (Harvey and Sutton, 1970). Often, prior to DMG treatment, the liquid sample must be concentrated and/or chemically separated from radionuclides that would interfere with liquid scintillation counting. This is especially true for an environmental sample such as sea water or soil.

Cocktail Choices

Historically, toluene and dioxane-based scintillation cocktails have been used to assay the nickel complex. Recently, procedures based on DMG complexation have used both Insta-Gel and the latest generation of safer, biodegradable, less toxic cocktails such as Ultima Gold or Ultima Gold XR from Packard Instrument Company. Ultima Gold, or an equivalent, is the cocktail cited in the U.S. Department of Energy (DOE) compendium methods manual (DOE/EM-0089T, Rev. 1 1993) for ^{63}Ni.

Sample Preparation

The sample matrix will dictate if any specific sample collection or preservation procedure is required. Although the literature does not emphasize specific collection procedures, the addition of HCL or HNO_3 acid (pH <2), stable nickel carrier, and/or complexing agent has been documented (DOE Methods Compendium, RP300 1993; Harvey and Sutton, 1970; Terlikowska-Drozdziel and Radoszewski, 1992). In addition, filtering of water samples such as sea water is commonly performed (Lo et al., 1993). Samples such a sludges, resins or organic material require wet ashing with strong acids to dissolve the matrix (NUREG/CR-4101/Part 1; Russow and Dermietzel, 1990).

Sample processing includes chemical separation methods which are required to isolate ^{63}Ni for LSC measurement. A $Fe(OH)_3$ scavenger has been used and is necessary to remove organic complexing agents such as ethylene diamine tetraacetic acid (EDTA) and other contaminants in order to quantitatively precipitate the nickel as nickel dimethylgloxime. Nickel will remain in the precipitate at a pH of 6-8, while at higher pH, $Ni(OH)_2$ will start to dissolve. Anion exchange has also been used to pretreat the effluent samples from nuclear reactors to remove heavy metals which are likely to interfere with the precipitation of nickel (Harvey and Sutton, 1970). A preconcentration procedure for enrichment of ^{63}Ni from sea water by adsorption on hydrous magnesium oxide is also described (Lo et al., 1993).

A representative chemical separation method involving DMG has recently been published in the DOE Methods Compendium manual. The method is used to determine the activity of ^{59}Ni and ^{63}Ni in a solution. The method was developed to assay drainable liquids and acid dissolved sludges. In this method, a nickel sample solution is loaded onto a column of DMG which is prepared by mixing an ethanol slurry of DMG with Microthene™ (Quantum, Inc., Tuscola, Illinois), a 50 mesh polyethylene powder. The LSC was calibrated for efficiency by counting the standards and blanks that were prepared with the analytical batch. Quench correction was not performed in this procedure since chemical quench was assumed to be relatively constant between the standards and samples, as the standards were identically processed. Chemical recoveries for the method were greater than 90% while the percent bias was between -6% and -9% for ^{63}Ni. Details of the method and possible interferences are published as radiochemistry procedure RP300 in the March 1993 addendum of the DOE Methods Compendium manual. A summary of the method is shown in Figure 10-1.

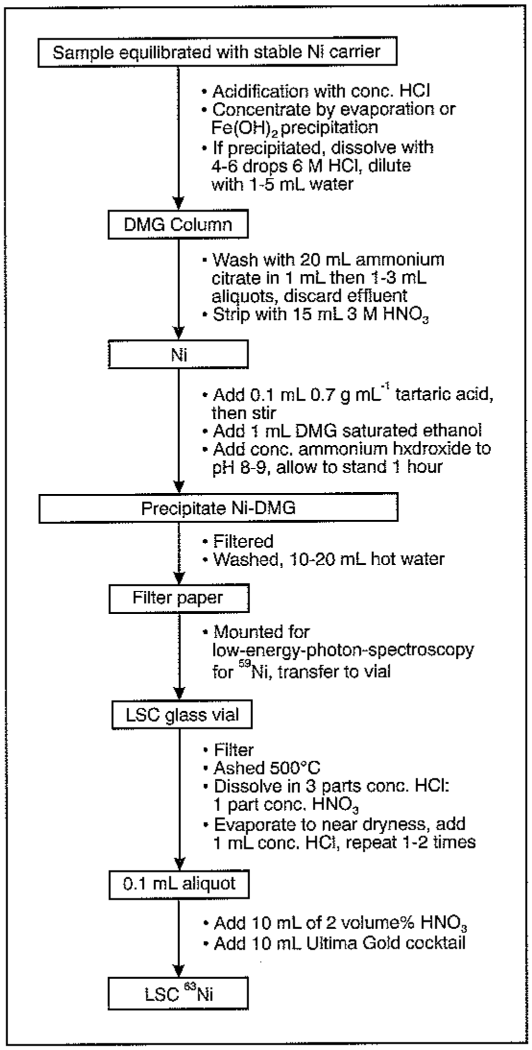


Figure 10-1.
^{63}Ni separation scheme with DMG column.

Detection Limits by LSC

No detectable limit was reported for the DOE procedure discussed earlier. However, various detectable limits have been reported by other investigators. Russow and Dermetzel (1990) reported a minimum detectable limit for ^{63}Ni in plant tissue of 80 Bq g^{-1} dry matter assuming a count time of ten minutes and a standard deviation of ± 3% at the 95% confidence level. Harvey and Sutton (1970) spiked samples with varying known amounts of ^{63}Ni and stable nickel carrier and could detect as little as 0.099 Bq (2.7 pCi) per sample with counting efficiencies in excess of 60% and a background of 20-25 CPM using an older Packard Model 3320 LSC. Kojima and Furakawa (1985) reported a limit detection of 0.06 Bq g^{-1} Ni (1.6 pCi g^{-1}) at 95% confidence assuming a counting time of 1000 minutes in their method, while Kramer reported a limit of .055 Bq (1.5 pCi) per sample in urine.

None of the above measurements were made with instruments capable of low level performance since most of the reported backgrounds were in the range of 20-25 CPM. Modern instrumentation equipped with electronic background pulse discrimination will produce even lower detection limits since backgrounds will be substantially reduced. The background for an optimum ^{63}Ni window on a Packard Model 2550TR low level instrument could be an order of magnitude less than that obtained with older instruments.

Summary

Liquid scintillation is the most suitable method for quantitating ^{63}Ni. Methods utilizing DMG precipitation are most common and have been improved. Lower detection limits are achievable by utilizing the low level feature on modern instruments.

References

DOE/EM-0089T, Rev 1. 1993. *DOE methods for evaluating environmental and waste management samples.* National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia.

Harvey, B. R. and Sutton, G. A. 1970. Liquid scintillation counting of nickel-63. *Intl. J. Appl. Rad. Isot.* 21: 519-523.

Kramer, G. 1981. Optimization of the analysis of nickel-63 in urine. Internal report AECL-7248 Atomic Energy of Canada Ltd., Chalk River, Ontario.

Kojima, S. and Furukawa, M. 1985. Liquid scintillation counting of low activity ^{63}Ni. *J. Radioanal. Nucl. Chem.* 95(5): 323-329.

Lo, J. M., Cheng, B. J., Tseng, C. L., and Lee, J. D. 1993. Preconcentration of nickel-63 in sea water for liquid scintillation counting. *Anal. Chim. Acta.* 281: 429-433.

NUREG/CR-4101/Part 1. 1985. *Assay of long-lived radionuclides in low level wastes from power reactors.* Nuclear Regulatory Commission, Washington, DC.

Radwan, M., Przybylska, A., Mykowska, E., and Gibas, K. 1981. Measurement of nickel-63 low activity in samples of metals and alloys with the help of liquid scintillators. *Int. J. Appl. Radiat. Isot.* 32(2): 97-99.

Russow, R., and Dermietzel, J. 1990. Determination of ^{63}Ni-activity in plant materials. *Isotopenpraxis.* 26(10): 502-504.

Terlikowska-Drozdziel, T., and Radoszewski, T., 1992. Investigation of radioactive counting of selected radionuclides in various liquid scintillators. *Nucl. Instr. Meth. Phys. Res.* A312: 100-103.

Yu, Y. (1988) Determination of ^{63}Ni contents in water. *Fushe Fanghu.* 8(2): 146-151.

Chapter 11: ^{99}Technetium

^{99}Tc in the Environment

^{99}Tc, a pure beta emitter (E_{max} = 292 keV 292 MeV) with a half-life of 2.12 x 10^5 years, is a ^{235}U and ^{239}Pu fission by-product with a fission yield of 6%. Analysis of environmental samples is required around nuclear facilities to assess the impact of releases to the environment due to ^{99}Tc's long half-life and mobility of the pertechnetate ion (TcO_4^{-1}), the oxidized form of technetium, in the environment (Beals, 1992). Substantial amounts have been produced from the operation of nuclear reactors of which some 150-200 TBq is thought to have been released to the environment (Beasley and Lorz, 1986). Weapons fallout has contributed to a soil concentration of 6.2 mBq kg^{-1} (Rouston and Cataldo, 1978). Direct measurements in rainfall range from 1.8 to 36 fCi/L (Ehrhardt and Attrep, 1978). Environmental measurements of technetium have gained in interest because of the high mobility and solubility of technetium (as pertechnetate TcO_4^{-1}) in ground water and its high transfer rate from soil to edible vegetation.

^{99}Tc Monitoring Applications

Several methods have been used to measure ^{99}Tc in the environment. Separation techniques include anion exchange, organic extraction, and/or selective precipitation (Boyd and Larsen, 1960; Cattarin et al., 1985; Golchert and Sedlet, 1969; Holm et al., 1984; Paviet et al., 1991; Luxemburger and Schuttelkopf, 1984; Silva et al., 1988; Walker et al., 1979). Quantitation has typically been by liquid scintillation or beta proportional counting. Recently, methods using a TEVA-Spec resin (Eichrom Industries, Darien, Illinois) and liquid scintillation counting or inductively coupled plasma mass spectrometry (ICP-MS) have been reported for measurement of the technetium concentration in environmental samples (Beals, 1992; Scarpitta, 1993; Sullivan et al., 1991).

Water Analysis

Ground water is a typical sample matrix for ^{99}Tc. Sampling is usually performed in the vicinity of nuclear facilities since ^{99}Tc is found in spent nuclear fuel and nuclear test debris. Technetium in the pertechnetate form (TcO_4^{-1}) is known to be soluble in ground water and not associated to any extent with particulate materials like rock. Thus, one would expect technetium to be very mobile in the environment and follow ^{3}H in its migration pattern (Silva et al., 1988).

Cocktail Choices

For obvious reasons, cocktails capable of handling a large amount of water are desirable for the measurement of ^{99}Tc. Classical cocktails such as Insta-Gel XF and environmentally safer cocktails such as Ultima Gold AB, and Ultima Gold XR, are good choices for counting technetium in water. All of these cocktails are capable of holding up to 50% water.

Sample Preparation and Measurement

Sample volumes of up to one liter are typically collected for ^{99}Tc analysis. Information on the proper collection container is scant; however, there seem to be few adsorption effects by glass or polypropylene for samples stored up to three months when stored as TcO_4^{-1}(Pacer, 1980). The sample may be acidified to approximately 0.1 M with a small amount of concentrated hydrochloric acid or nitric acid, but acidification is not absolutely necessary. 30% hydrogen peroxide is added to the sample in an amount to 1% of the volume to ensure that technetium exists in the TcO_4^{-1} form.

Ion Exchange

A representative ion exchange separation method (adapted from Luxenburger and Schuttelkopf, 1978) was performed by Silva et al., 1988. The method involved separating ^{99}Tc from samples of archived Nevada Test Site (NTS) ground water using AG 1-X8 (100-200 mesh) anion exchange resin. ^{95m}Tc was used for chemical yield determination and a spectral stripping technique was used to determine concentrations of ^{99}Tc and ^{95m}Tc. ^{99}Tc and ^{95m}Tc were finally identified by their characteristic spectra and column elution when compared to known isotope standards. The separation method is summarized in Figure 11-1 and the column elution pattern is shown in Figure 11-2. The 2 mL column fractions were ultimately counted 1000-2000 minutes. The detection limit was reported to be less than 0.5-2.0 DPM L^{-1}.

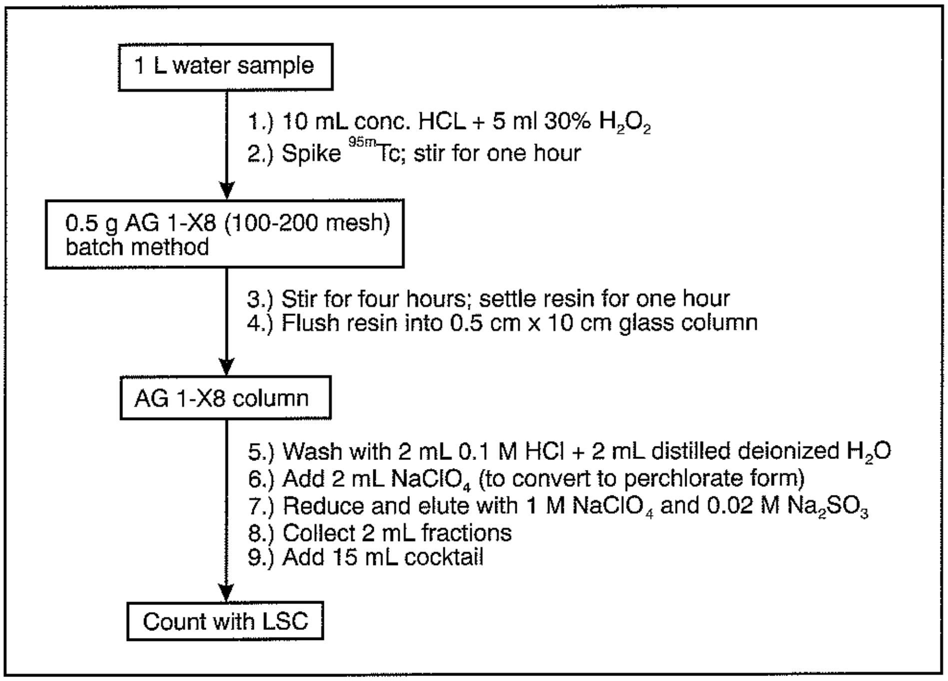


Figure 11-1.
Separation of ^{99}Tc with AG 1-X8 resin.

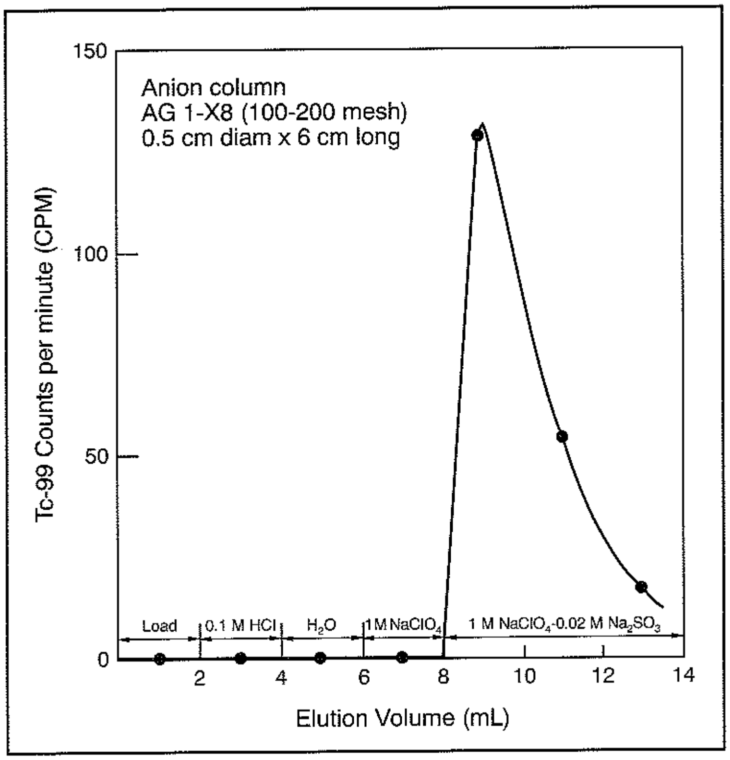


Figure 11-2.
^{99}Tc elution from AG 1-X8 (Silva et al., 1988).

Other Separation Methods

Liquid-Liquid Extraction

Procedures based on liquid-liquid extraction or a combination of liquid-liquid extraction and ion exchange have been proposed for isolation of ^{99}Tc (Paviet et al., 1991; Luxemburger and Schuttelkopf, 1984; Walker et al., 1979; Verrezen and Hurtgen, 1992). Various extractants have been used including DB18-C6 crown-ether (dibenzo-18-crown-6), carbon tetrachloride and an aqueous solution of sodium thiosulfate, tetraphenyl arsenium chloride followed by tri-n-butyl phosphate.

Extraction Chromatography

Recently, extraction chromatography has been used to separate ^{99}Tc from various sample matrices including water and vegetation for quantification by liquid scintillation (Scarpitta, 1993; Sullivan et al., 1991). A consolidation of the extraction chromatography method for water analysis has recently been included in the U.S. Department of Energy (DOE) Methods Compendium manual (DOE/EM 0089T, Rev. 1, 1993). The method proposes analyses by either ICP-MS or liquid scintillation. Quantitation by liquid scintillation is viewed as a very practical approach since access to an LSC is more universal than ICP-MS. A summary of the method is shown in Figure 11-3.

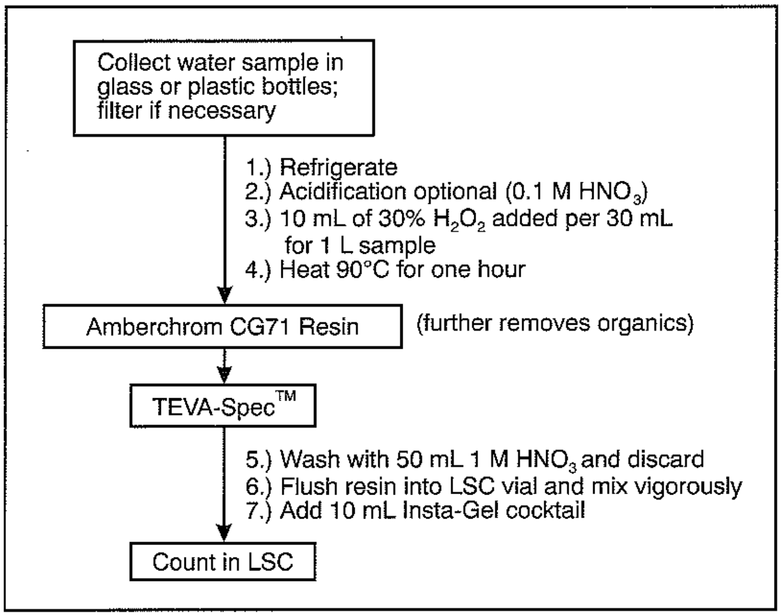


Figure 11-3.
^{99}Tc separation with TEVA-Spec.

The LSC counting efficiency is determined from a known ^{99}Tc standard prepared with an equivalent amount of resin, water, and cocktail. Blanks are prepared similarly but without the ^{99}Tc. Quench curves may be needed prepared if the samples vary in quench. However, the sample preparation technique predicts constant quenched samples. A ^{99}Tc spiked duplicate sample was used for chemical recovery.

Alternatively, instead of flushing the resin into the LSC vial, the ^{99}Tc can be eluted with 7-9 M HNO_3 and an aliquot submitted for LSC. In addition, ^{97}Tc or ^{99m}Tc could be used as a yield tracer using dual label isotope analysis. The LSC detection limit for a one liter sample is reported to be 1 pCi L^{-1} (0.037 Bq L^{-1}).

As mentioned the TEVA-Spec resin was also used to separate ^{99}Tc from water and vegetation samples by Scarpitta at the EPA Environmental Measurements Laboratory (EML). The radiochemical separation procedure is essentially the same as the DOE method except for the extra steps of adding Ca, Ba, and Fe carriers; precipitating an alkaline solution with Na_2CO_3 to remove alkaline earth, transition metals, and rare earth elements; and co-precipitating technetium (IV) with ferric hydroxide. The precipitate is dissolved in concentrated HNO_3 to oxidize Tc(IV) to Tc(VII) and re-precipitated to remove the Fe as the hydroxide. The alkaline supernatant is pH adjusted with nitric acid to 0.1 M HNO_3 and applied to a properly prepared TEVA-Spec column. The resin is extruded into a low K borosilicate glass LSC vial and Packard Insta-Gel cocktail is added. A 1-500 keV window is used for counting.

The vegetation samples are wet ashed with nitric and hydrochloric acids with the addition of 30% H_2O_2. Water is added and the solution is filtered through glass fiber filter paper. At this point, the procedure is the same as for water samples.

The revised chemical separation procedure is shown in Figure 11-4.

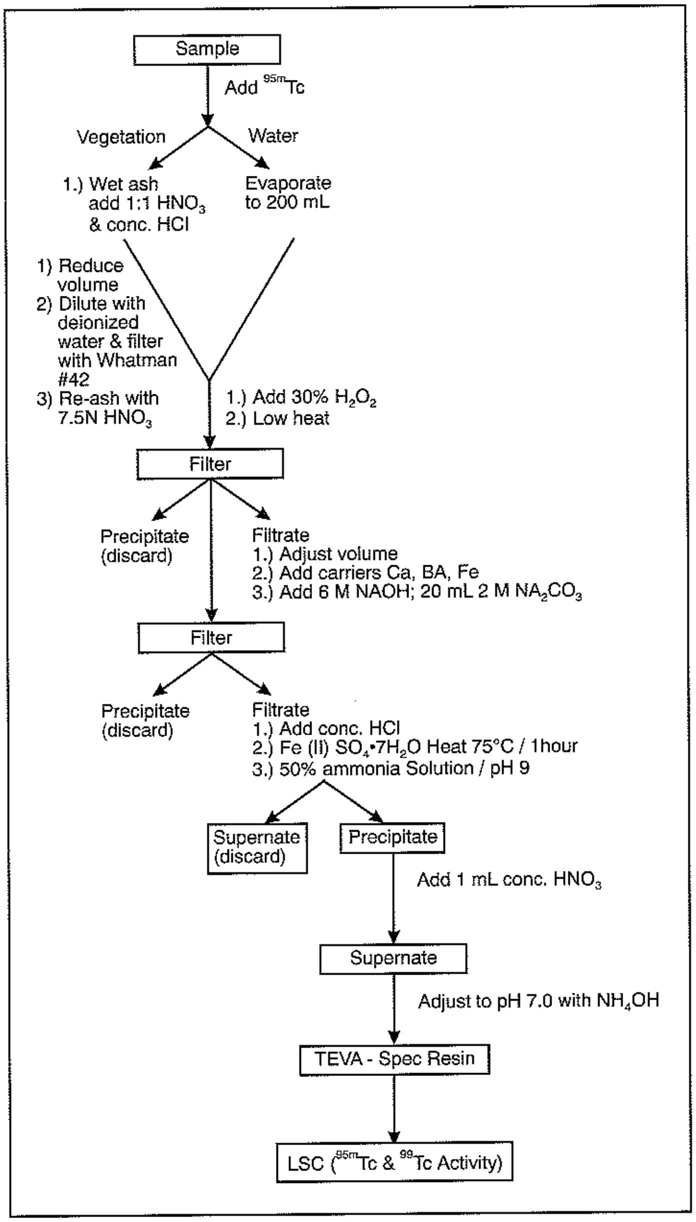


Figure 11-4.

Environmental measurements laboratory ^{99}Tc chemical separations procedure.

The chemical separation method was validated using (1) an artificially spiked water sample containing mixed alpha, beta and gamma radionuclides; (2) environmental water samples measured by ICP-MS; and (3) a NIST (National Institute of Standards and Technology) standard reference material measured radiochemically. The extraction chromatography step removes interfering Ruthenium (97%), which is carried through the pre-chemistry.

The method was reported as accurate to within 10% for ^{95m}Tc:^{99}Tc ratios ranging from 15:1 to 0.5:1. The ^{95m}Tc activity is held constant at 252 DPM while the ^{99}Tc is increased. The method is shown to be accurate for samples well within the range of environmental levels. Although conventional dual label counting techniques were not used in this study, it is conceivable that the accuracy range could be extended, if necessary. However, the advantage of full spectrum analysis, as opposed to a window method is that the highest possible counting efficiency is maintained for low activity samples. The reported detection limit for the method was 0.28 Bq/sample for a one hour count.

Detection Limits by LSC

Detection limits for ^{99}Tc are in the range of 0.008-0.037 Bq L^{-1} after chemical separation. Lower detection limits are possible if samples are quantitated using the low level count mode feature available on modern LSC's equipped with additional background pulse discrimination. Programmable TR-LSC, a feature on the Packard Tri-Carb 2500 series low level LSC's, is especially suited to counting higher energy beta emitters such as ^{99}Tc. Sensitivity with programmable TR-LSC can increase by a factor of two to three over conventional techniques.

Summary

The advantages of using dual label liquid scintillation counting for technetium is that the technique allows simultaneous quantitation of both the ^{95m}Tc gamma yield tracer and the ^{99}Tc in quenched samples. There is no need to split the sample or pre-count the sample with conventional gamma counting. In addition, ^{99}Tc counting efficiency is generally greater than 90% and ^{95m}Tc is generally greater than 80% with Insta-Gel cocktail for samples with acid loads less than 2 M and water loads up to 50%.

References

Beals, D. 1992. Measuring technetium-99 in aqueous samples by ICP-MS. *Proceedings of the Third International Conference on Nuclear and Radiochemistry*. Vienna, Austria.

Beasley, T. and Lorz, H. 1986. A review of the biological and geochemical behavior of technetium in the marine environment. *J. Environ. Radioact.* 3: 1-22.

Boyd, G. E. and Larson, Q. V. 1960. Solvent extraction of heptavalent technetium. *J. Phys. Chem.* 64: 988-996.

Cattarin, S., Doretti, L., and Mazzi, U. 1985. Determination of ^{99}Tc in urine by liquid scintillation counting to evaluate internal contamination. *Health Physics*. 11(5): 795-804.

Ehrhardt, K. C. and Attrep, M. 1978. Technetium in the atmosphere. *Am. Chem. Soc.* 12: 55.

Golchert, N. W. and Sedlet, J. 1969. Radiochemical determination of technetium-99 in environmental water samples. *Anal. Chem.* 41: 669-671.

Holm, E., Rioseco, J., and Garcia-Leon, M. 1984. Determination of Tc-99 in environmental samples. *Nucl. Instrum. Phys. Res.* 23: 204-207.

Luxenburger, H. J., and Schuttelkopf, H. 1984. *Proceedings of the 5th International Conference on Nuclear Methods in Environmental and Energy Research*. CONF/TIC-840408, NTIS, Springfield, Virginia. 376.

Pacer, R. A. 1980. Evaluation of counting efficiency, possible container sorption and quenching characteristics in the liquid scintillation counting of ^{99}Tc. *Int. J. Appl. Radiat. Isot.* 31(12): 731-736.

Paviet, P. Raymond, A. and Metcalf, R. 1991. A rapid method for the analysis of technetium-99. In *Liquid radioactive wastes*. Monograph Second International Conference on Methods and Applications of Radioanalytical Chemistry. American Nuclear Society, Washington, DC, p. 44.

Rouston, R. C. and Cataldo, D. A. 1978. Accumulation of ^{99}Tc by tumbleweed and cheatgrass grown on arid soils. *Health Physics*. 34: 685-690.

Scarpitta, S. 1993. Technetium-99 in water and vegetation by liquid scintillation analysis. Presented at the *39th Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry*, Colorado Springs, Colorado.

Silva, R. J., Evans, R., Rego, J. H., and Buddemeier, R. W. 1988. Methods and results of Tc-99 analysis of Nevada test site ground waters. *J. Radioanal. Nucl. Chem.* 124(2): 397-405.

Sullivan, T., Nelson, D., and Thompson, E. 1991. Determination of ^{99}Tc in borehole waters using extraction chromatographic resin. Presented at the *37th Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry*, Ottawa, Canada.

Verrezen, F., and Hurtgen, C., 1992. The measurement of technetium-99 and iodine-129 in waste water from pressurized nuclear-power reactors. *Appl. Radiat. Isot.* 43(1-2): 61-68.

Walker, C. R.; Short, B. W. and Spring, H. S. 1979. Determination of technetium-99 by liquid scintillation counting. Radioelem. *Anal: Prog. and Probl., Proc. of the Conf. on Anal. Chem. in Energy Technol.* 23rd, Gatlinburg, Tenn. Ann Arbor Sci. Publ. Inc, Michigan, 1980, p. 101-110.

Chapter 12: ^{241}Plutonium

^{241}Pu in the Environment

^{241}Pu is a pure low energy (E_{max} = 21 keV; $t_{1/2}$ = 14.4 years) beta emitter which decays to ^{241}Am. The fallout from past nuclear weapons testing and small releases from nuclear facilities as gaseous or liquid effluents are the two predominate sources of environmental contamination for this radionuclide (Pimpl, 1992). In nuclear power facilities, the production of ^{241}Pu begins by neutron capture in ^{238}U, the most abundant constituent in reactor fuel, followed by a succession of beta decays and neutron captures to yield ^{240}Pu and ^{241}Pu (Martin, 1986). In fact, ^{241}Pu is the only significant beta emitting transuranic (TRU) nuclide in low level radioactive waste (LLW) from nuclear power plants. Because of their toxicity and long half-lives, TRU radionuclides (especially ^{241}Am) have received particular attention relative to their disposal by shallow land burial (Martin, 1986). These radionuclides as well as others must meet certain classification and accounting requirements before burial at commercial sites. In the United States, the regulations are promulgated by the U.S. Nuclear Regulatory Commission (NRC) and published in Title 10 part 61 of the Code of Federal Regulations. In order to satisfy the requirements for shallow land burial, ^{241}Pu must be measured in LLW in addition to environmental assays. Since ^{241}Pu beta particles are of low energy, liquid scintillation analysis of radiochemically separated Pu is the logical and preferred method.

^{241}Pu Monitoring Applications

^{241}Pu is the largest constituent of TRU activity. Quantitation of ^{241}Pu in LLW and environmental samples is of real significance because it is a precursor to other TRU's that have longer half-lives, greater environmental mobility, and greater toxicity. Thus, it may have a greater impact on future environmental and health concerns after disposal or release. Some typical samples from nuclear power plants that are assayed for this important radionuclide are smears, clear and dirty liquid effluents, environmental samples, filters, and demineralizer resins (Hands and Conway, 1977; Martin, 1986). ^{241}Pu has also been measured in tissue subjected to an accidental exposure (Miglio and Willis, 1988). Organic extraction has recently been the method of choice for purifying plutonium isotopes.

Cocktail Choices

Since extractive agents dissolved in toluene or xylene are often employed in the purification scheme, a liquid scintillation cocktail designed for non-polar samples is a good choice. Three specific lipophilic cocktails offered by Packard Instrument Company are candidates for this application - Insta-Fluor (xylene base), Opti-Fluor O (alkylbenzene base), and Ultima Gold F (di-isopropylnaphthalene base). For those procedures in which the plutonium is in the acid or aqueous phase, universal cocktails such as Insta-Gel XF (pseudocumene base), Ultima Gold XR or Ultima Gold AB (both di-isopropylnaphthalene based) are appropriate. Both Opti-Fluor O and the Ultima Gold family of cocktails are considered biodegradable type cocktails. Additional information on the performance of commercial cocktails for ^{241}Pu measurements have been made by Cook and Anderson (1991) using a Packard low level LSC. Measurements were made by direct LSC counting of electroplated plutonium.

Sample Preparation and Measurement

The diversity of sample matrices collected for ^{241}Pu analysis makes it impossible to make general statements on sample collection. However, pretreatment and processing procedures adapted from the U.S. Environmental Protection Agency for analyzing low activity environmental samples are often used and were referred to by Martin (1986) for determining ^{241}Pu in low level reactor waste. These procedures typically involve ashing at 500 °C or evaporation to a smaller volume, leaching with strong acids, followed by extraction techniques, and alpha spectroscopy to measure the alpha plutonium activity. Until recently, measurement of ^{241}Pu in low level radioactive wastes involved radiochemical separation followed by alpha spectroscopy of the ^{241}Am daughter and back calculation of ^{241}Pu (Martin, 1986; Cline and Hertzer, 1978). This method was necessary when the basic approach was to use alpha spectroscopy. The major drawback to this method was the slow ingrowth of the ^{241}Am daughter which greatly extended analysis time. The alpha spectroscopy approach has largely been replaced by liquid scintillation analysis since a quick, direct analysis of ^{241}Pu after separation is possible. However, alpha spectroscopy is still required if measurement of all plutonium isotopes is necessary. Pimpl used such an approach for plutonium measurements in various samples. In this method, ^{241}Pu was measured in the electrodeposited Pu fraction after alpha spectroscopy. The analytical separation procedure used by Pimpl (1992) is shown in Figure 12-1 with reported 70-95% yield recoveries. After electrodeposition, deposited material is recovered by twice boiling with 8 M HNO_3 and extracting once more with TOPO/cyclohexane. Direct measurement of the electrodeposited ^{241}Pu was also attempted but the method lacked precision and sensitivity. The organic phase is washed with 0.5 M CH_3COONH_4 and a 5 mL portion of the organic phase mixed with scintillator and counted by LSC. Simpler versions of the method have been reported where a combination of ion exchange and/or extraction techniques have been used (Hands and Conway, 1977; Martin, 1986; Hakanen et al., 1978; Raymond et al., 1990; Yufu et al., 1992; Fliss and Enge, 1993). A typical ^{241}Pu (beta) spectrum with an associated alpha plutonium peak is shown in Figure 12-2, which was the result of a TOPO/heptane extraction from nitric acid solution (Fliss and Enge, 1993).

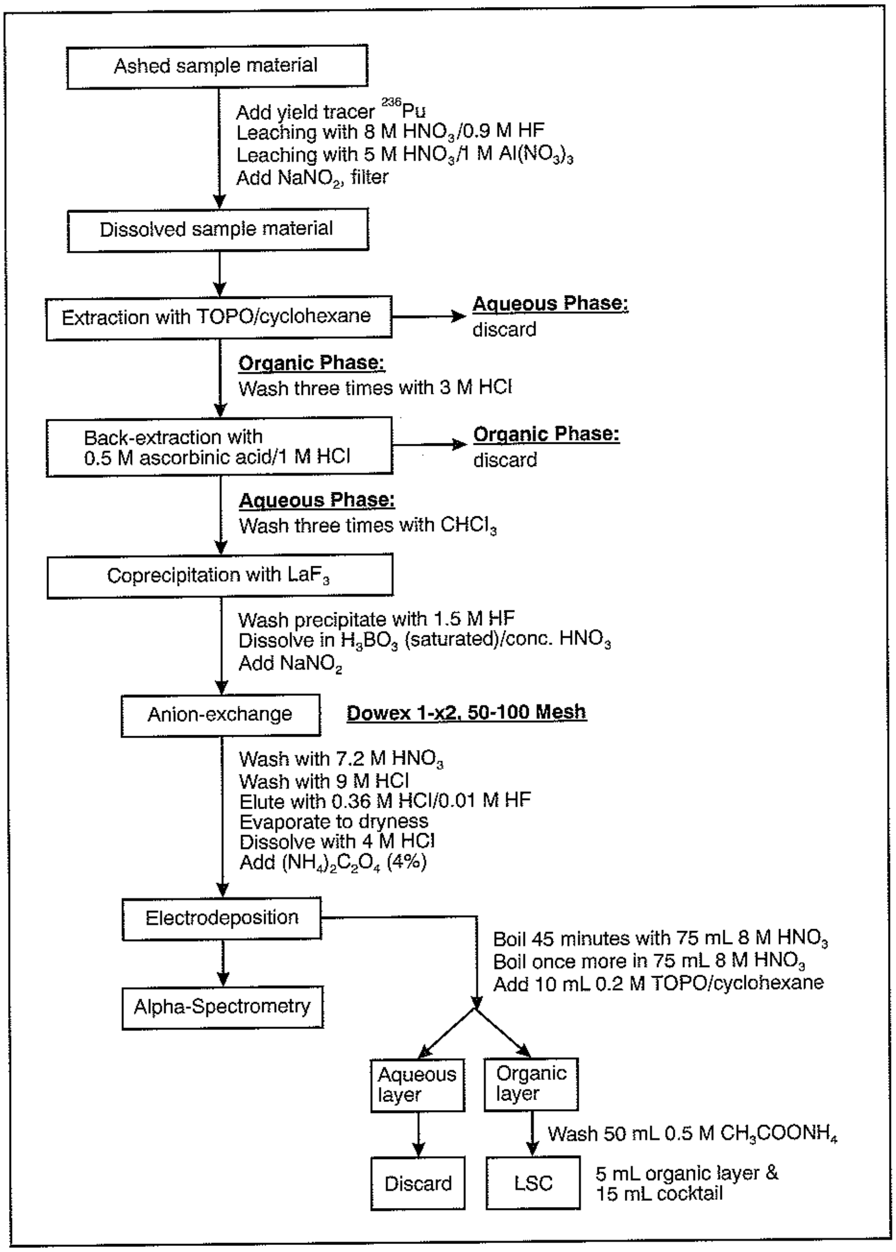


Figure 12-1.

Schematic representation of the procedure used for Pu separation from sample matrices (Pimpl, 1992).

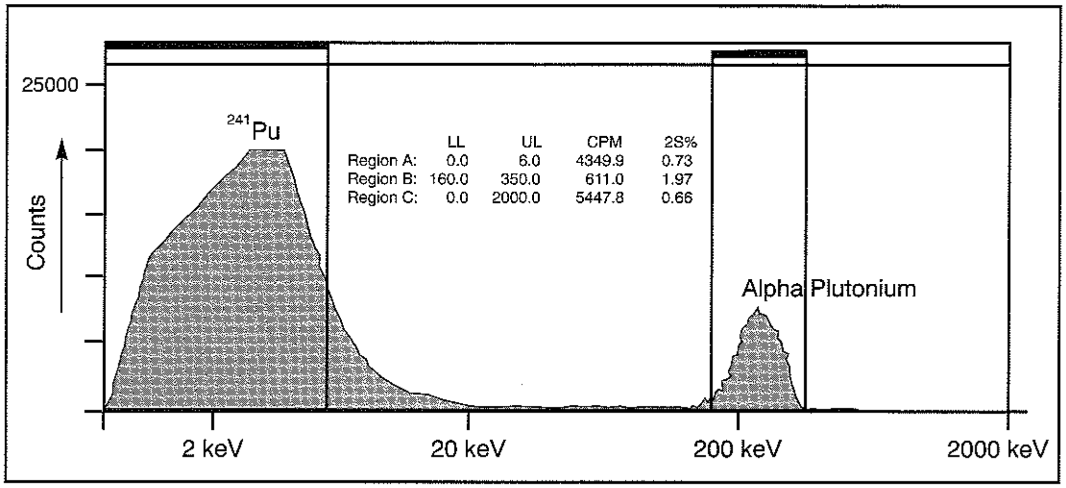


Figure 12-2.
LSC spectra of betas (^{241}Pu; counting efficiency approximately 33%) and alphas (counting efficiency approximately 100%) extracted with TOPO (Fliss and Enge, 1993).

If alpha spectroscopy of plutonium is not required, then extracted ^{241}Pu may be measured by utilizing either conventional beta counting or the alpha/beta separation feature of Packard Tri-Carb 2500 or 2700 series LSC's equipped with Pulse Decay Analysis (PDA). Usually, the organic extraction agent is dissolved in xylene or toluene, and is compatible with LSC cocktails.

Detection Limits by LSC

Cook and Anderson (1991) in their study of cocktails reported a minimum detection limit of 44 mBq per sample based on $2*2^{1/2}*B^{1/2}$ (where B is total background counts) error on 100 minute count for samples counted with the low level count mode feature enabled on a Packard Tri-Carb 2250CA. Pimpl (1992) reported a detectable limit of 50 mBq for 100 minute count using a formula based on 3.29 (95% confidence) times the background error. Hands and Conway (1977) reported a detection limit of 63 mBq per sample based on their procedure for a 100 minute count time and a significance of three times the background error.

Summary

^{241}Pu determinations by LSC are typically performed one of two ways:

a. In solution producing a 4 π counting geometry. A common method is to solubilize the electroplated plutonium that has been measured by alpha spectroscopy.

b. Direct counting of electroplated plutonium by placing the stainless steel planchet in the LSC vial and adding cocktail.

Because of the low energy, a tritium window is typically used for ^{241}Pu.

^{241}Pu determinations with an instrument capable of alpha/beta discrimination has not yet been documented. However, the possibility exists that such determination is possible for organically extracted samples, although alpha/beta separation is not required for LSC analysis. Background in a 0-20 keV window can be reduced by a factor greater than two with TR-LSC background reduction.

References

Cline, J. E. and Hertzer, D. C. 1978. *Study of transuranic concentration levels in solid radioactive waste from commercial power reactors*. Electric Power Research Institute. Palo Alto, Ca, EPRI NP-4037.

Cook, G. T. and Anderson, R. 1991. The determination of ^{241}Pu by liquid scintillation spectrometry using the Packard 2250CA. *J. Radioanal. Nucl. Chem.*, Letters. 154(5): 319-330.

Fliss, P. and Enge, R. 1993. Detection of alpha emitters in solidified radioactive waste. *Nuclear Engineering and Design*. 147: 111-114.

Hakanen, M. Korpela, H. Jaakkola, T. and Kiirikki, E. 1978. *Determination of ^{241}Pu in environmental samples by liquid scintillation counting*: preliminary report. University of Helsinki (Finland), report no. COO—3011-10.

Hands, G. C. and Conway, B.O.B. 1977. Simultaneous determinations of plutonium alpha and beta activity in liquid effluents and environmental samples. *Analyst*. 102: 934-937.

Lieberman, R. EPA/5-84-006. 1984. *Eastern Environmental Radiation Facility Radiochemical Procedures Manual.* U.S. Environmental Protection Agency, Montgomery, Alabama.

Martin, J. E., 1986. Determination of ^{241}Pu in low level radioactive wastes from reactors. *Health Physics*. 51(5): 621-631.

Miglio, J. J. and Willis, L. C. 1988. Simultaneous liquid scintillation determination of ^{239}Pu and ^{241}Am in tissue. J. *Radioan. Nucl. Chem. Articles*. 123(2): 517-528.

Pimpl, M. 1992. Increasing the sensitivity of ^{241}Pu determination for emission and immission control of nuclear installations by aid of liquid scintillation counting. *J. Radioan. Nucl. Chem.* 161(2): 429-436.

Raymond, A., Pochitaloff, P. Bilcot, J. B. and Poletiko, C. 1990. Determination of Pu-241 in radioactive wastes. In *International seminar on quality control of radioactive waste packaged for removal*, ed. Warnecke, E., Odoj, R., and Simon, R., 1st Proc. 741 p. Juelich, Germany.

Yufu, Wu., Bjoernstad, H. E., Salbu, B. 1992. Determination of plutonium-239 + plutonium-240 and plutonium-241 in environmental samples using liquid scintillation spectrometry. *Analyst*. 117(3): 439-442.

Section V.

Environmental Radionuclide Analysis - Manmade Alpha Emitting Radionuclides

Chapter 13: Transuranium Elements (Np, Pu, Am, Cm)

Transuranium Elements in the Environment

The transuranic radionuclides of neptunium (Np), plutonium (Pu), americium (Am), and curium (Cm) are products of the nuclear industry and are found in spent nuclear fuel along with fission products. These elements are of importance in the nuclear fuel cycle and in radioactive waste management. For example, the recovery of ^{239}Pu, is economically attractive since it can be used as nuclear fuel in fast breeder reactors. At the same time, disposal of transuranics is a concern because most are long-lived radionuclides with high toxicity.

Because of their toxicity, strict restrictions govern the limits allowed for transuranium elements in the environment. Therefore, the determination of these elements in high level radioactive waste is important since it will influence the method of disposal. However, the measurement of transuranics in high activity waste is not trivial since concentrations are low, while activities of beta and gamma radionuclides and salt concentrations are high (Yang, 1990).

Transuranium Applications

The measurement of transuranium elements in high activity waste and the nuclear fuel reprocessing cycles are common. Direct measurement of radionuclides in these sample matrices is not possible because of the number of radionuclides present and the complexity of the matrix. Separation and concentration are important to reduce the volume and radioactive identity of material to dispose, which will lower waste handling costs and treatment. Similarly, the determination of radionuclides in biological and environmental samples often requires separation and concentration since the radionuclides are present in low concentrations in a potentially complex sample matrix.

Liquid-liquid extraction (also called solvent extraction) is usually the method of choice for process-scale separation and concentration of radionuclides (Dietz and Horowitz, 1993). Extractive agents coated onto an inert solid support provide the basis for extraction chromatography, which is more appropriate for analytical-scale separation procedures.

Cocktail Choices

Since extractive techniques are commonly employed in transuranic separation schemes, the cocktail chosen must be compatible with the separation method. For process scale separation where the radionuclide of interest is separated by solvent extraction, lipophilic cocktails constitute the best choice, such as Packard Insta-Fluor or the safer Opti-Fluor O or Ultima Gold F. When extraction chromatography is used as the separation method, samples are aqueous acid solutions and will require an aqueous accepting cocktail with acid holding capability such as Ultima Gold AB.

Sample Preparation and Measurement

Sample matrices containing transuranium elements are typically aqueous based materials although organic materials such as resins are possible. Nuclear fuel reprocessing and waste management streams are responsible for the generation of these samples. The composition of these waste or reprocessing samples varies with their sources. Solvent extraction chemistry or extraction chromatography are the most popular separation and concentration methods.

Transuranic-element solvent extraction by the TRUEX process is now being tested at nuclear facilities around the world (Dietz and Horowitz, 1993). This process involves the use of the organophosphorus extractant octyl(phenyl)-N,N-di-isobutylcarbamoylmethylphosphine oxide (CMPO) in a paraffinic hydrocarbon containing a moderate amount of tri-n-butyl phosphate (TBP) as a second extractant. A schematic of the TRUEX process is shown in Figure 13-1.

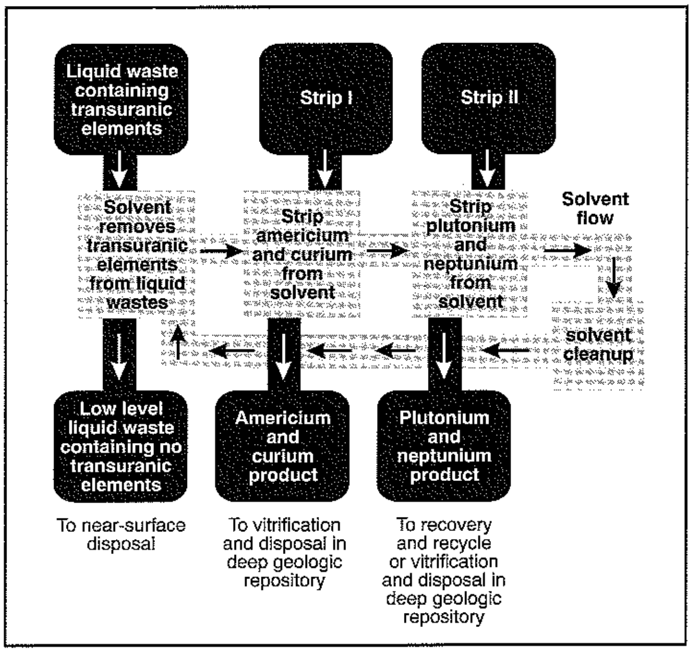


Figure 13-1.
Schematic of the TRUEX process (Dietz and Horowitz, 1993).

Yang (1990) proposed two extraction schemes for the isolation of various transuranic elements in high activity waste streams. One such method shown in Figure 13-2 is proposed for Np, Pu, and Am. This scheme involves the use of two extractants, di-(2-ethylhexyl)phosphoric acid (HDEHP) and trialkyl phosphine oxide (TRPO). The other scheme shown in Figure 13-3 was developed for the assay of Np in the presence of relatively high Pu and Am content. After extraction, the samples were analyzed using a Packard Tri-Carb 2550TR/AB alpha/beta liquid scintillation analyzer to eliminate any beta interferences that may have been co-extracted. By using a combination of solvent extraction and alpha/beta discrimination, Yang observed that alpha activity can be quantitated in the presence of 10^5 excess of beta activity in high activity waste.

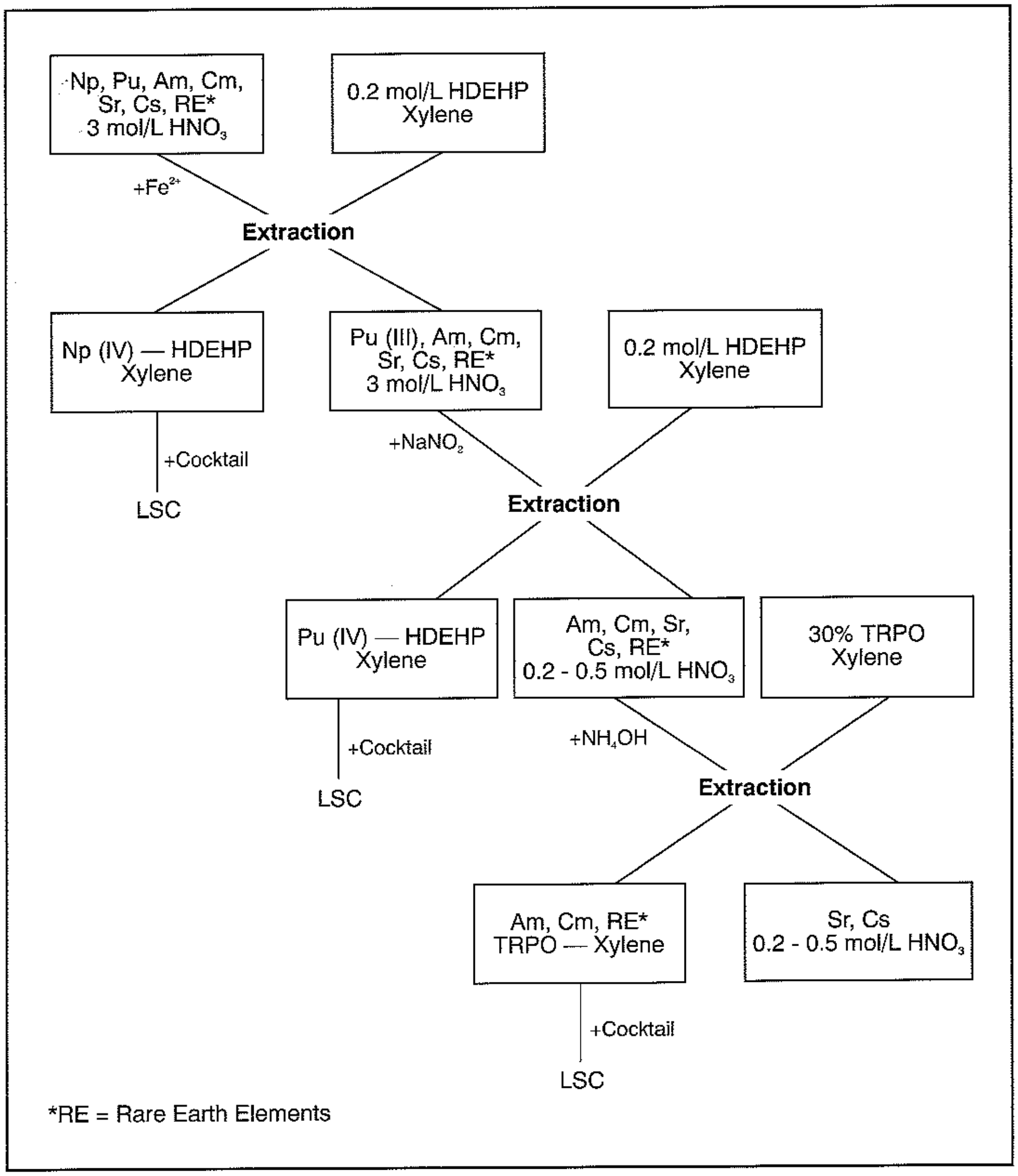


Figure 13-2.
Extraction scheme for Np, Pu, and Am.

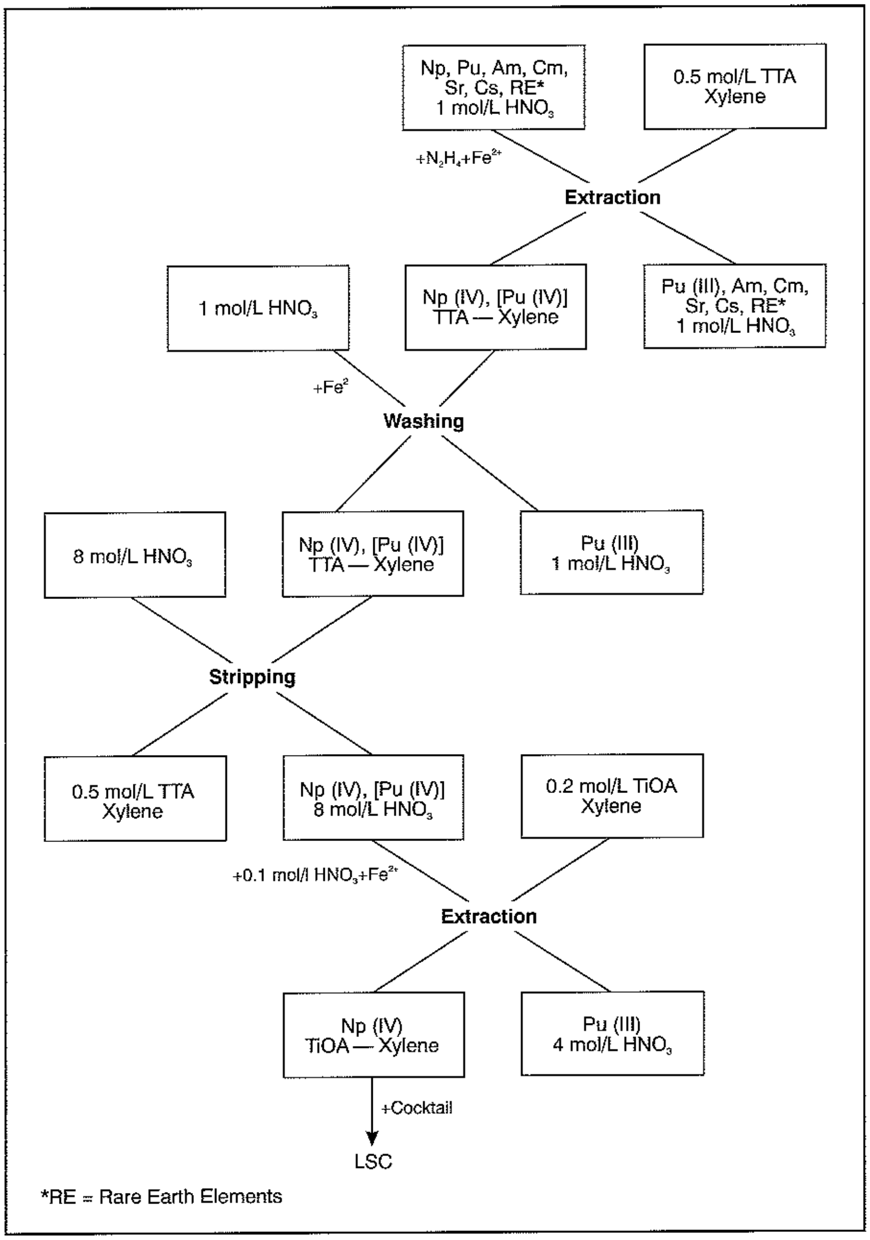


Figure 13-3.
Extraction Scheme for Np.

Extractive scintillators combine an organophilic metal-ion complexing agent (extraction agent) in an aromatic diluent that contains a scintillating fluor. The solution is then both an extractant and a scintillator (McDowell and McDowell, 1993). Much of the pioneer work in the area of alpha liquid scintillation counting and the development of extractive scintillator technology is the result of the work of McDowell, McKleeven and others at Oak Ridge National Laboratories (ORNL).

There are several commercially available extractive scintillators. Table 13-1 lists the properties of the extractive scintillators available through ETRAC® (East Tennessee Radiometric/Analytical Chemicals, Inc., Oak Ridge, Tennessee). An in-depth discussion of separation methods using extractive scintillators can be found in the book *Liquid Scintillation Alpha Spectrometry* by Jack McDowell, CRC Press, Boca Raton, Florida, USA.

Extractive Scintillator	Elements Extracted	Applications
ALPHAEX$_\alpha$™	Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No	Any original matrix after conversion to: 1 M HNO$_3$ for Th, U(IV, VI); pH 2-3, 1 M nitrate for others
URAEX$_\alpha$™	Uranium selectivity	From 1 M sulfate at pH 2
THOREX$_\alpha$™	Thorium and uranium	From 1 M sulfate at pH 2
POLEX$_\alpha$™	Polonium selectively	From 7.5 M H$_3$PO$_4$, 0.01 M HCL
RADAEX$_\alpha$™	Radium selectively	From 0.3-0.5 M NaNO$_3$ at pH 11-12
RADONS$_\alpha$™	Radon selectively	Radon from water or aqueous solution
STRONEX$_\alpha$™	Strontium selectively	From 0.3-1.0 M NaNO$_3$ at pH 9-11

Table 13-1.

Properties of extractive scintillators (McDowell and McDowell, 1993).

Extraction chromatography was first proposed by Siekierski and Kotlinska (1959). Since then, many extraction chromatographic materials have been prepared and a variety of analytical and preparative-scale schemes have been proposed (Dietz and Horowitz, 1993). Extraction chromatography resins are commercially available from Eichrom Industries (Darien, Illinois) which are specific for transuranic, uranium, and tetravalent actinides. Although the general separation principle is to strongly absorb the element(s) of interest in high acid concentration and elute the element of interest in a lower acid concentration, this scheme must be modified when the elements cannot be adequately separated by elution with different acid concentrations. For example, separation schemes with TRU•Spec® (Eichrom Industries, Darien, Illinois), a transuranic specific resin, involves both the isolation of the elements of interest, *i.e.*, actinides, from the sample matrix as well as the separation of the actinides from one another on the resin. For example, Figure 13-4 shows the adsorptivity of selected actinide ions on TRU•Spec resin. The k' factor (y-axis) is actually the number of free column volumes of eluent required to reach the peak maximum in the elution curve. One can see from Figure 13-4 that loading the sample in high acid concentration and eluting with a lower concentration will not effectively separate the actinides listed, other than americium(III). However, a selective elution scheme can be developed by taking advantage of the ability of these ions to form aqueous complexes with different complexing agents or by changing their oxidation states. In addition, the separation schemes used for a specific resin can sometimes be modified to separate other elements by observing their elution behavior under specific conditions.

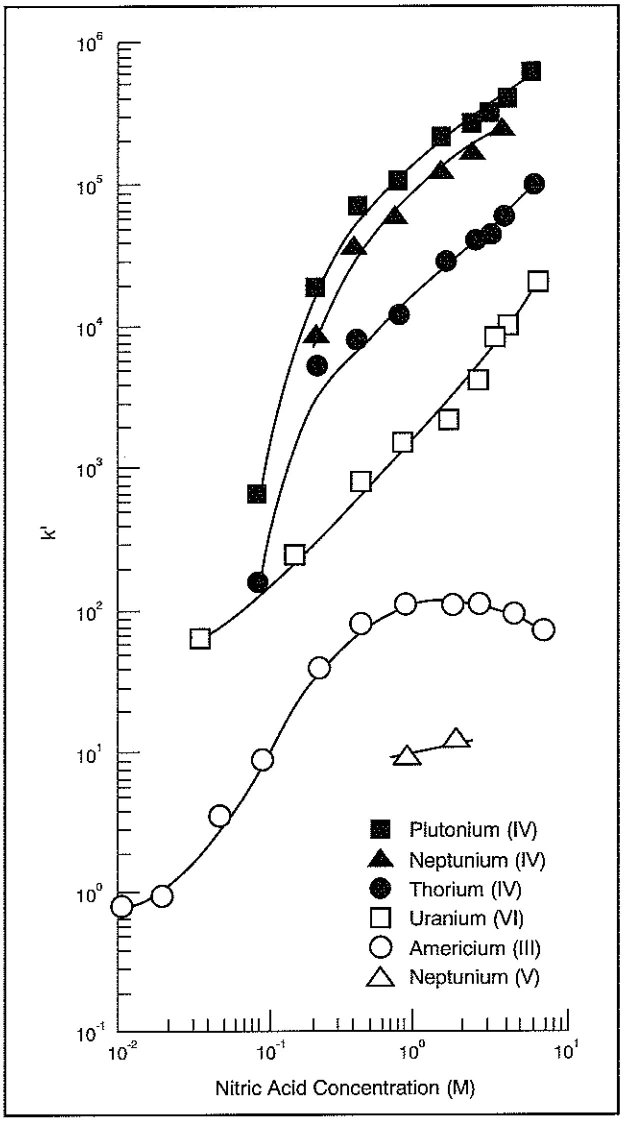


Figure 13-4.
Nitric acid dependencies of the capacity factors of selected ions
on the transuranic-element specific resin (Dietz and Horowitz, 1993).

Detection Limits by LSC

Detection limits will depend on the degree of concentration achieved in the separation scheme and the amount of beta interference that is present. Instruments capable of alpha/beta discrimination can reduce the beta interference and thus lower the alpha detection limit. McDowell reports a conservative estimate of 0.016 Bq L^{-1} for alpha with the PERALS (Photon Electron Rejecting Alpha Liquid Scintillation) system. Detectable limits for alpha with conventional LSC's equipped with alpha/beta discrimination are in the order of 0.2 - 0.5 Bq L^{-1} for a 60 minute count time without concentration of the sample. Concentration of the sample will result in a lower limit.

Summary

Solvent extraction is a common separation technique for transuranic elements on a process-scale. Alpha/beta LSC can often be used as an analytical tool to quantitate the extracted transuranics in a simple reproducible manner. Nuclear fuel recycling and waste management are two applications where the use of alpha/beta LSC is being investigated. For analytical work, extraction chromatography coupled with alpha/beta LSC offers a simple, time saving, and more reproducible alternative to traditional separation techniques and quantitation by gas flow proportional counting. In some screening applications, alpha/beta LSC may be a viable alternative to alpha spectrometry. Additional work is still needed to determine the full potential of quantitation of transuranics by LSC methods.

References

Dietz, M. L. and Horowitz, P. 1993. Novel chromatographic materials based on nuclear waste processing chemistry. *LC•GC*. 11(6).

McDowell, J. and McDowell, B. L. 1993. The Growth of a radioanalytical method: alpha liquid scintillation spectrometry. In *Liquid Scintillation Spectrometry 1992,* ed. Noakes, J. E., Schoenhofer, F. and Polach, H. A. Radiocarbon. 193-200.

McDowell, W. J. and McDowell, B. L. 1994. *Liquid Scintillation Alpha Spectrometry*. Boca Raton, Florida. CRC Press, Inc.

Siekierski, S. and Kotlinska, B. 1959. *At. Energiya* 7: 160.

Yang, D. 1990. *Study on determination of Np, Pu, and Am with extraction-liquid scintillation counting and its application to assay of transuranium elements in high-level radioactive waste*. Ph.D. thesis. Tsinghua University, Beijing, P.R. China.

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