

ALPHA LIQUID SCINTILLATION ANALYSIS: SOME RECENT DEVELOPMENTS AND APPLICATIONS

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ABSTRACT. I review recent developments and applications in alpha liquid scintillation analysis. I examined a Packard Tri-Carb® 2200CA LS analyzer with pulse-shape discrimination (PSD) and found 99.7% counting efficiency for α emitters and 99.95% rejection of beta and gamma pulses. I tested a solid scintillator, LumaCap™, for α counting and observed high counting efficiency, low background, and satisfactory energy and PSD characters. I discuss recent applications of extractive scintillators and PSD for the determination of transuranium nuclides in intermediate-level radioactive sludges and high-level radioactive waste solutions.

INTRODUCTION

The accurate and sensitive measurement of alpha-emitting nuclides is essential in the nuclear fuel cycle, process control, radioactive waste management and environmental protection. However, the short ranges and self-absorption of α particles in matter make this task inherently difficult. Conventional techniques for α counting and spectrometry are based on the determination of thin uniform plating sources. They usually require long and complicated procedures of chemical separation and sample preparation, such as evaporation, electric deposition or vacuum sublimation. The counting efficiency and precision depend on many factors, such as the uniformity, thickness and geometry of the prepared sources.

In comparison with other methods, liquid scintillation counting (LSC) provides an alternative for α counting with the obvious advantages of high counting efficiency (nearly 100%), and easier sample preparation. During the last 20 years, many advances have been made in the development of α LSC. McDowell (1980) gave an excellent review at the international LSC conference in San Francisco. Since then, many new developments in instrumentation and methods as well as applications have been made. I discuss these below.

ADVANCED ALPHA/BETA DISCRIMINATION IN COMMERCIAL LS INSTRUMENTS

Ten years ago, commercial LS instruments were designed and produced exclusively for the determination of beta-emitting nuclides, such as ^3H and ^{14}C . However, such LS instruments, with high background, poor α -energy resolution, and possible interference from beta and gamma radiation, were not satisfactory for α counting. McDowell (1975, 1986), McDowell and Gase (1976, 1985, 1987), McDowell and Weiss (1977) and McKlveen and McDowell (1984) developed an α LS instrument, Photon/Electron-Rejecting Alpha Liquid Scintillation (PERALS®^V). Shaw (1989) and Cadieux (1990) reported remarkable results using the Oak Ridge PERALS® system, e.g., 99.7% counting efficiency for α emitters, 99.95% rejection of β and γ pulses, resolution of 5% (250 MeV) for α energies and an electronic background of 0.02 cpm.

During the 1980s, manufacturers began to study and install the pulse-shape discrimination (PSD) function in commercial LS instruments. Now, the major manufacturers of β LS instruments, (Packard, LKB, Beckman) market the LS instruments with PSD function as an option. I report results from a Packard Tri-Carb® 2200CA with PSD, which operates in our laboratory.

Figure 1 shows the spectra of a mixed sample of ^{241}Am and $^{144}\text{Ce/Pr}$ measured with and without the PSD function. The spectra of ^{241}Am and $^{144}\text{Ce/Pr}$ overlap if the PSD function is not used. With

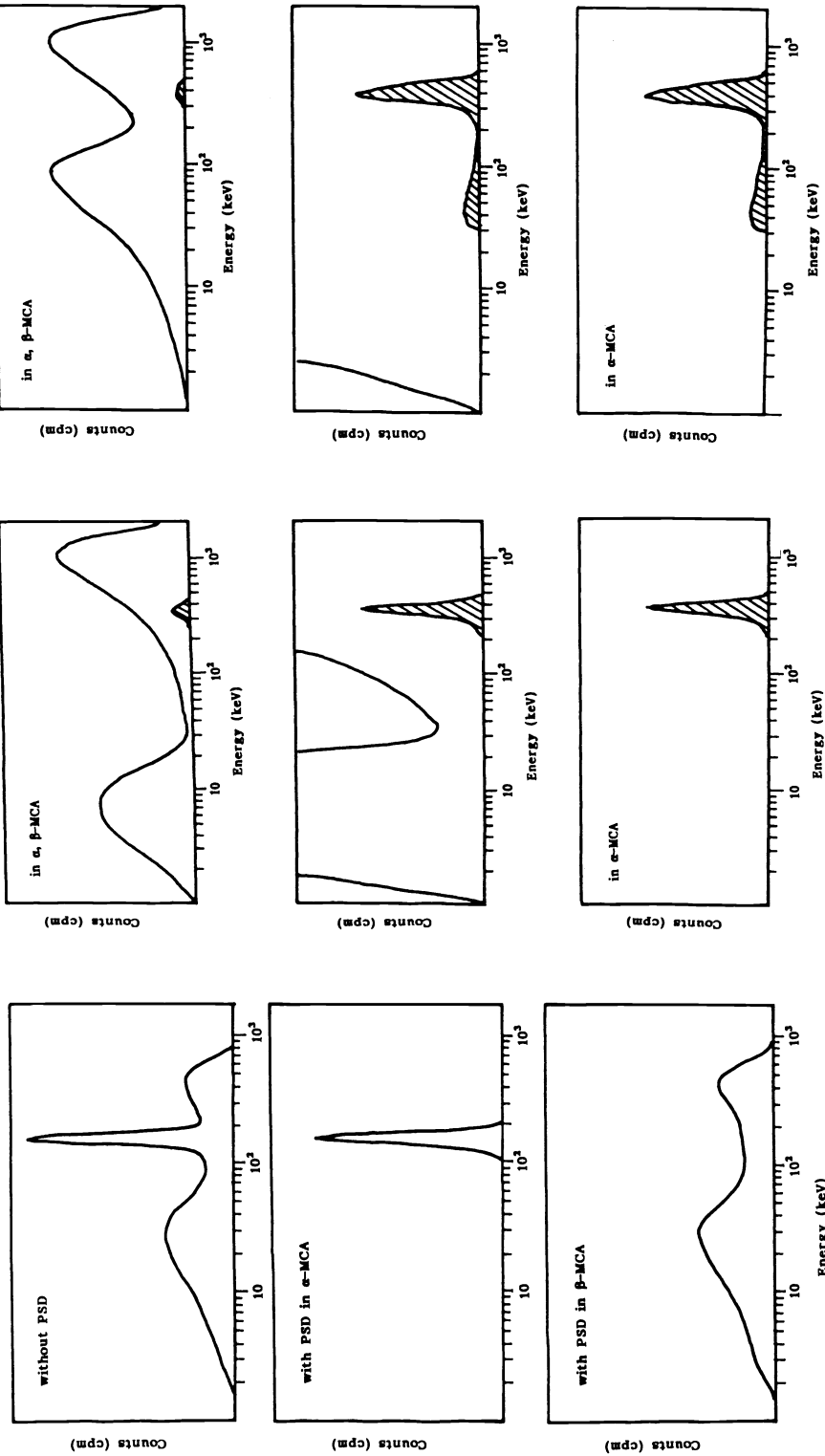


Fig. 1. Spectra of ^{241}Am and $^{144}\text{Ce/Pr}$ in a mixed sample measured with and without PSD function (10 ml 5 g liter $^{-1}$ PPO/0.5 g liter $^{-1}$ M $_2$ POPOP/50 g liter $^{-1}$ naphthalene-toluene)

Fig. 2. Spectra of $^{106}\text{Ru/Rh}$ and ^{241}Am in a mixed sample (10 ml 5 g liter $^{-1}$ PPO-0.5 g liter $^{-1}$ M $_2$ POP-OP/50 g liter $^{-1}$ naphthalene-toluene-Triton® X-100)

Fig. 3. Spectra of $^{144}\text{Ce/Pr}$ and ^{241}Am in a mixed sample (10 ml 5 g liter $^{-1}$ PPO - 0.5 g liter $^{-1}$ M $_2$ POPOP/50 g liter $^{-1}$ naphthalene-toluene-Triton® X-100)

PSD, α and β energy spectra can be separated and recorded in different multichannel analyzers (MCA), *i.e.*, ^{241}Am in the α MCA and $^{144}\text{Ce/Pr}$ in the β MCA. Tables 1A and 1B show the influence of the pulse-decay time discriminator (TD) on the α/β separation. With the optimum TD setting, the rejection of β activity is >99.98%, with >99.6% α counting efficiency. This technique can also be used to measure α -emitting nuclides, *e.g.*, actinides, in samples where β and γ radiation are very high. It is also useful in studies of the nuclear fuel cycle and radioactive waste management. Figures 2 and 3 show the spectra of synthesized samples with the large amount of β -emitting nuclides commonly found in the spent nuclear fuel, and a small amount of α -emitting nuclide, ^{241}Am . The interference of β counts in α counting could be ignored by using PSD, even if the β activity was 250 times higher than α activity. It is clear that the combination of PSD and LSC provides a useful method of α counting.

TABLE 1A. Influence of Pulse Decay Discrimination on α/β Separation

Pulse decay discriminator	^{241}Am (cpm)				Misclass. (%)
	α MCA 230–600 keV	α MCA 0–2000 keV	β MCA 230–600 keV	β MCA 0–2000 keV	
100	1322	1329	3	49	0.23
110	1350	1355	3	48	0.22
120	1343	1348	5	41	0.37
130	1330	1333	5	50	0.37
140	1320	1326	18	63	1.3
150	1231	1235	102	150	7.6
160	1108	1111	217	262	16.3

10 ml 5 g liter⁻¹ PPO-0.3 mol liter⁻¹ TOPO-100 g liter⁻¹ naphthalene-toluene, 20-ml glass vial

TABLE 1B. Influence of Pulse Decay Discrimination on α/β Separation

Pulse decay discriminator	$^{144}\text{Ce/Pr}$ (cpm)			Misclass. (%)
	α MCA 230–600 keV	α MCA 0–2000 keV	β MCA 0–2000 keV	
100	274	1384	25909	1.0
110	25	339	27054	0.09
120	4	49	27399	0.01
130	6	76	27302	0.02
140	5	46	27386	0.01
150	3	25	27615	0.01
160	2	21	27347	0.007

10 ml 5 g liter⁻¹ PPO-0.3 mol liter⁻¹ TOPO-100 g liter⁻¹ naphthalene-toluene, 20-ml glass vial

SOLID SCINTILLATOR FOR α COUNTING AND α/β SEPARATION

A major problem with LSC is the disposal of used cocktails that contain long-lived and high toxic α -emitting nuclides. By using solid scintillator caps, *e.g.*, LumaCap™ (Packard Instrument), waste can be greatly reduced. In our laboratory, we have studied the applicability of such a solid scintillator for α spectrometry. Results are given in Table 2 and Figures 4–6. Figure 4 shows the spectra of ^{239}Pu and ^{241}Pu in a solid scintillator (LumaCap™) and in the high-quality cocktail, Ultima Gold™ (Packard). The pulse height produced by the solid scintillator is much higher than that produced by the cocktail. Table 2 compares the efficiency and precision for α counting with the two scintillator types. The efficiency obtained by adding 20–100 μl of sample solution in the LumaCap™

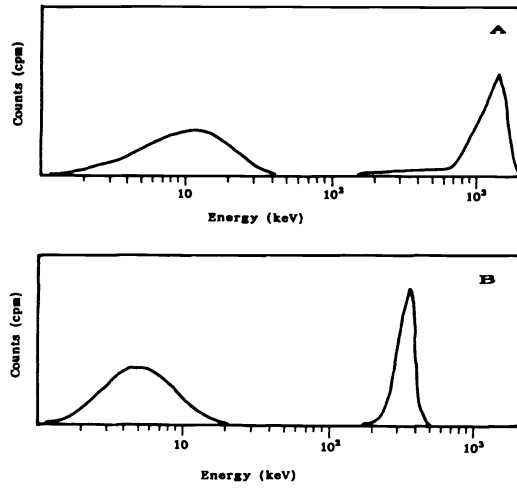


Fig. 4. Comparison between solid scintillator and cocktail. A. LumaCap™ + ²⁴¹Pu and ²³⁹Pu; B. 10 ml Ultima Gold™ + ²⁴¹Pu and ²³⁹Pu

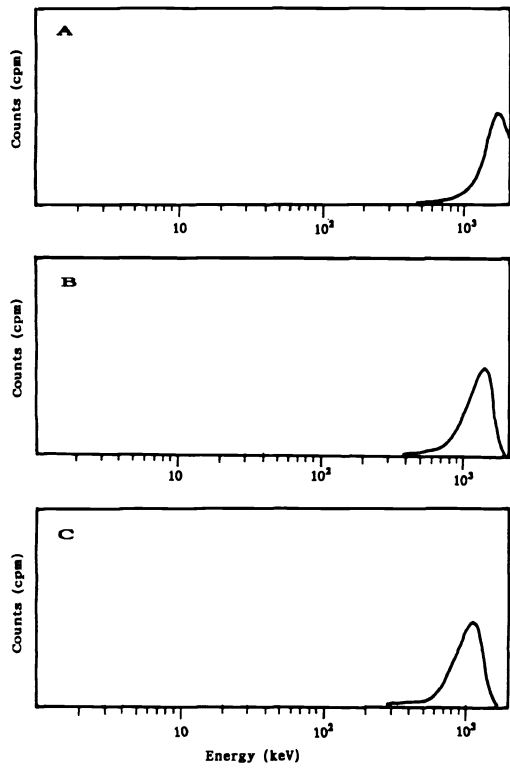


Fig. 5. Influence of PMT voltages on spectrum of ²⁴¹Am with LumaCap™ as scintillator. A. HVR 2749, HVL 2380 (normal voltages); B. HVR 2600, HVL 2200; C. HVR 2400, HVL 2000

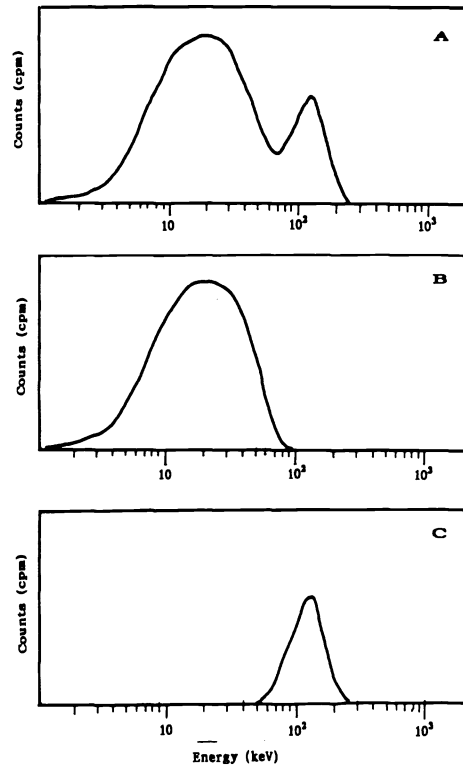


Fig. 6. Pulse-shape discrimination with LumaCap™ as scintillator. A. Without PSD; B. With PSD in β MCA; C. With PSD in α MCA

TABLE 2. Efficiency and Precision Comparison between Solid Scintillator and Ultima Gold™ Cocktail

Scintillator	Samples (μ l)	Counts (cpm)	Efficiency (%)
10 ml cocktail*	50	3672 \pm 22 (n=3)	100
	20	1396 \pm 19 (n=3)	95
		1538 \pm 19 (n=3)	or 107
LumaCap™	50	3279 \pm 33 (n=3)	89
		3586 \pm 36 (n=3)	or 98
	100	6975 \pm 143 (n=3)	95
		7304 \pm 142 (n=3)	or 99

*Ultima Gold™

scintillator caps is quite close to that with the cocktail. Figure 5 illustrates that the high photomultiplier tube voltages influence the spectrum of the α peak and counting efficiency. Normalized voltages for β spectrometry are not suitable for α counting and spectrometry. PSD can also be carried out with LumaCap™; Figure 6 shows the results of α/β separation using LumaCap™. The first spectrum was measured without PSD, and shows an overlap between α and β spectra. The second and third spectra were obtained with the PSD function; the separated spectra are observed in the α and β MCAs. The rejection of β activity is >99.4 % with <2 % loss of α -counting efficiency. Although these results are not as good as those using optimum cocktails for α/β discrimination, they do show the possibility of applying a solid scintillator for α/β separation. The change of the chemical constituent in solid scintillation would improve the α/β discrimination, and further study is in progress.

APPLICATIONS OF α LSC

Recently, many workers have applied selective extraction and PSD to α LSC. Table 3 shows some of these applications. Alpha LS analysis has been used or evaluated in the nuclear fuel cycle, waste management and environmental samples. In our laboratory, this method has been applied to the determination of transuranium (TRU) elements in high active waste (HAW) and in the sludge of medium active waste (MAW). The analytical procedures with di-(2-ethylhexyl)phosphoric acid (HDEHP) as extractant for the determination of Pu in MAW sludge is shown in Figure 7. MAW sludge was dissolved by a mixture of HCl, HNO₃ and HF. Cl⁻ and F⁻ were removed from the solution by heating and adding concentrated HNO₃. HDEHP was used to extract Pu(IV) from 3M HNO₃ solution after the adjustment of Pu to the +4 oxidation state. Figure 8A shows the spectrum of the sludge solution. Figures 8B,C show the spectra of the HDEHP solution after extraction. With the help of PSD, the α peak is discriminated in the α MCA. More experiments have indicated that the chemical separation was quantitative and PSD separation was complete. Similar methods with HDEHP, trialkylphosphine oxide (TRPO), thenoyltrifluoroacetone (TTA) and triisooctyl-amine (TiOA) as extractants were applied successfully for the determination of Pu, Am and Np in high active waste. Work is in progress in our laboratory to develop rapid and simple methods for process control and environmental samples.

TABLE 3. Some Recent Applications of α LSC

Applications	Reference
TRU elements in MAW sludges	Yang (1991)
TRU elements in HAW	Yang <i>et al.</i> (1991)
α -emitting nuclides in nuclear fuel cycle	Cadieux (1990)
^{226}Ra	Case & McDowell (1990)
Pu on filters and smear samples	Shaw (1989)
Total activity in groundwater	Killeen (1989)
^{239}Pu , ^{241}Am in tissue	Miglio & Willis (1988)
^{227}Ac	Shu-De, Forster and Lieser (1988)
Simultaneous α and β counting	Yang <i>et al.</i> (1990)
^{226}Ra , ^{222}Rn in water	Schönhofer (1987)
U on air filter	McDowell (1986)

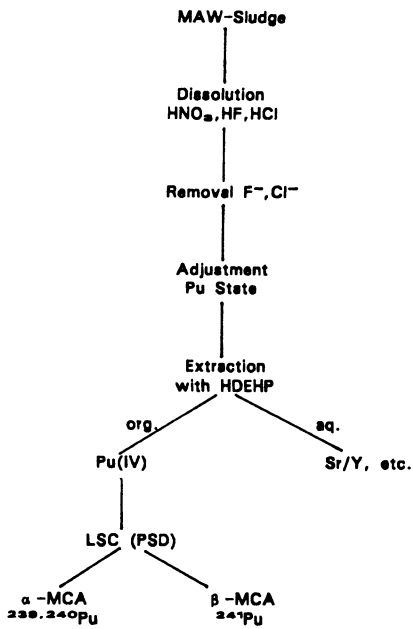


Fig. 7. Analytical procedure for Pu in MAW sludge

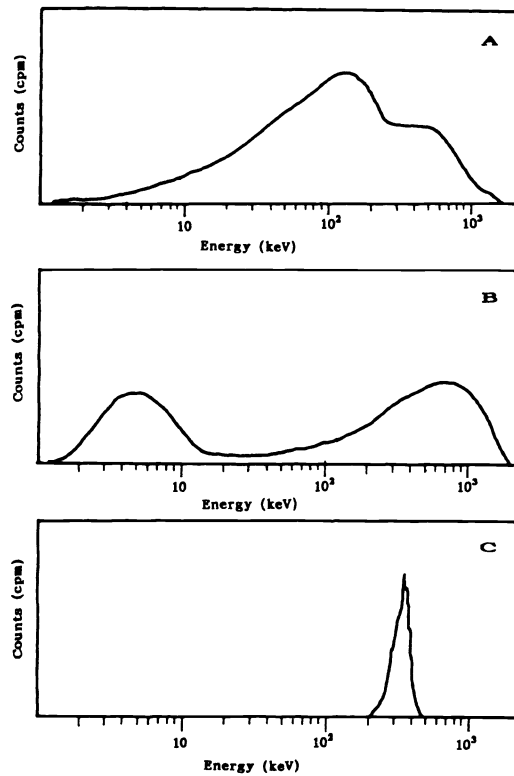


Fig. 8. Determination of Pu in MAW sludge. A. MAW sludge; B. Organic solution after extraction with HDEHP (in β MCA); C. Organic solution after extraction with HDEHP (in α MCA)

CONCLUSION

I suggest that further research in α LSC should entail investigation of the PSD quench correction. Our results from PSD depend on the quenching level of the sample; TD should be set properly for samples with different quenching levels to obtain α and β separation. The relation between the optimum TD and the quenching level of the samples should be studied for the PSD quench correction. Future work should also involve the improvement of the solid scintillator, as the solid scintillators now in use were developed for β counting. The change of the chemical constituent might improve the counting efficiency and/or the results of α/β separation.

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