

## CHAPTER 10

# Liquid Scintillation Alpha Spectrometry: A Method for Today and Tomorrow

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### ABSTRACT

Alpha spectrometry using liquid scintillation methods has matured into a technology showing great potential. The nonpenetrating properties shared by beta and alpha radiation make them both candidates for liquid scintillation counting/spectrometry. However, applying liquid scintillation to alpha spectrometry has been difficult, because inefficient light production by alpha particles led to poor alpha energy resolution and alpha-produced scintillation interference of beta- and gamma-produced scintillations. Recent developments in alpha liquid scintillation spectrometers and pulse-shape discrimination have removed the beta-gamma interference problem and greatly improved alpha energy resolution. In addition, selective solvent (liquid-liquid) extraction methods (phase-transfers), setting the nuclide of interest into the scintillator, simplifies sample preparation and provides important additional information for nuclide identification. Such rapid, selective procedures have been developed for radium, uranium, thorium, plutonium, polonium, and the trivalent transplutonium elements. Presently, available energy resolution (230 keV FWHM) allows identification of many of the isotopes of these nuclides. Chemical separations methods and typical alpha-spectral results are presented in this chapter. Promising methods of improving both energy resolution and chemical separations are suggested.

### INTRODUCTION

The maturing of alpha liquid scintillation spectrometry into a useful radiometric tool is a fascinating story. It has been known since 1950<sup>1,2</sup> that alpha particles could be counted by liquid scintillation methods, but little practical use has been made of this knowledge. The problems of poor alpha energy resolution, quenching and variable scintillator response, and beta and gamma radiation interference all combined to make useful applications of liquid scintillation to alpha assay extremely limited.

In 1964, D.L. Horrocks and co-workers<sup>3,4</sup> demonstrated that it was possible to obtain useful alpha energy resolution in liquid scintillation systems. They found it necessary to use a detector quite different from that used for beta liquid scintillation. It consisted of a single phototube facing a reflector, with

the sample between the phototube and reflector, and efficient optical coupling between the sample, reflector, and phototube. Both Horrocks and Hanschke<sup>5</sup> working independently, demonstrated that a highly-reflective, diffuse-white, hemispheric reflector cavity, oil-coupled to a single phototube provided the optimum alpha energy resolution in a liquid scintillation detector. Hanschke produced both an experimental and a mathematical demonstration of this. A cross section of such a detector may be seen in Figure 1.

Even though the detector described above was able to achieve useful alpha energy resolution in a liquid scintillation system, the problems of variable energy response/quenching and beta-gamma interference with the alpha spectra still prevented useful application of liquid scintillation to alpha counting and spectrometry.

The development of methods to overcome the latter two problems is the subject of this chapter.

## EXPERIMENTAL NARRATIVE

The experimental work reported here extended over 20 years. Some of it has never been reported, and none of it has been reported in this context, i.e., an overview of the development of Photon Electron Rejecting Alpha Liquid Scintillation (PERALS) spectrometry.

This development began in 1967 with a need to determine aqueous/organic phase distribution of the alpha-emitting trivalent actinides to an accuracy of  $\pm 1\%$  or better. It was found impossible to do this with plate-counting methods. Horrocks<sup>6</sup> suggested that liquid scintillation might be a possible answer to our problem. With well-characterized samples of trivalent actinides, we achieved the needed analytical accuracy using a commercial beta liquid scintillation counter. However, problems with this approach soon appeared. The two-phase distribution data for some nuclides did not fit the pattern we expected.

In order to determine that what we were counting was indeed the alpha from the trivalent actinide under investigation, we needed to see an energy spectrum of the sample. The 1960 model Packard Tricarb liquid scintillation counter was modified to allow the energy signal to be displayed on a multichannel analyzer (MCA). The pulses carrying the energy information did not exit through the window produced by the upper and lower discriminators but instead were converted to logic pulses that were sent to the scaler. In order to see a spectrum and to determine what portion was being counted, the scaler pulses were picked off, modified, and sent to the gate input of the MCA while the energy analog pulses were sent to the energy input. This allowed the discriminators effect on the energy spectrum to be viewed on the MCA. With this arrangement, we were able to observe that some nuclides had interfering beta/gamma-emitting daughters and/or beta-, gamma-, or alpha-emitting impurities, and in all cases the energy resolution was poor, on the order of 800

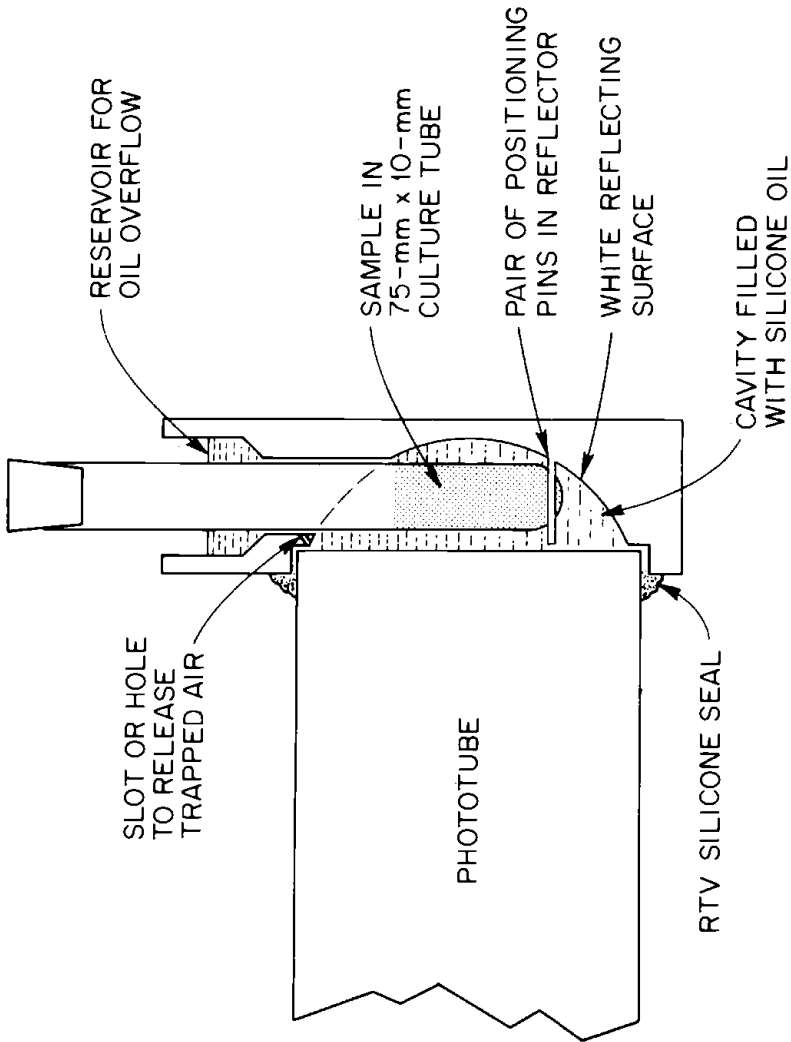


Figure 1. A cross section of a PERALS detector assembly.

to 900 keV full peak width at half maximum height (FWHM). In some cases the additional spectral information allowed a reasonably accurate determination of the test nuclide concentration, while in others it still did not yield the required analytical accuracy due to variations in the energy response of the scintillator, among other problems.

The next step taken was to build a detector that would give improved energy resolution following the work of Horrocks<sup>3,4</sup> and Hanschke.<sup>5</sup> An experimental enclosure (Figure 2) that would accommodate a variety of phototubes and reflectors was built for testing various detector optical arrangements. In true scientific manner, we tested somewhere in the neighborhood of 25 different optical arrangements of our own before we conceded that Horrocks and Hanschke were essentially correct. The contributions to detector construction that we have made are of the nature of refinements and compromises designed to enhance the practical usefulness of the detector. We added an improved reflecting surface, a light-coupling oil reservoir, and an insertion method for a small sample container (a 10×75 mm culture tube). The accurate positioning was an improvement suggested by Steve Musolino of Brookhaven National Laboratory.<sup>7</sup>

One of the crucial requirements uncovered by work on the detector was that the reflective surface must be highly reflective but nonspecular, i.e., diffusing. Magnesium oxide laid down in several layers and bonded by sodium silicate solution (water glass) was effective, but barium sulfate with a very small amount of binder was equally good and was commercially available (Eastman high reflectance coating). The need for a diffusing reflector appears to arise from the nonuniform response of the photocathodes in multiplier phototubes. Figure 3 illustrates typical sensitivity profiles of 2 in phototubes.

Spectra collected with the new detector gave much better energy resolution than those obtainable with the beta liquid scintillation spectrometer (see Figure 4), but we still had the problem of sample nonreproducibility and beta/gamma interference, either one of which alone could make alpha liquid scintillation of very limited practical use. Progress at this point in the development was reported in *Organic Scintillators and Liquid Scintillation Counting*.<sup>8</sup>

Variable energy response and variable quenching are problems associated with the scintillation cocktail. Most of those commonly used for beta assay were, and are, aqueous-phase accepting. These cocktails contain detergents and aqueous/organic coupling solvents. Usually an aqueous sample is added to the scintillation cocktail, where it is incorporated by the constituents of the cocktail into a reasonably clear and homogeneous solution. Variations in the matrix cause variable quenching, but because beta-emitting nuclides produce a continuous spectrum from zero to maximum, this quenching variation can usually be corrected by measuring the radiation produced in that sample by a known external or internal source. Quench corrections of this type cannot be used with alpha spectra. Initial small amounts of quenching do not reduce the counts under an alpha peak but simply shift the alpha peak to a lower voltage/energy scale position. More severe quenching can push the alpha peak out of



**Figure 2.** Experimental light-tight enclosure in which various reflector arrangements were tested.

the detectable region, but the reduction in count is not a simple function of the amount of quencher added. First the count reduction is small, then, with more quencher, large, and then, with still more quencher, small again, as the left edge, median and right edge of the bell-shaped curve pass below the detection threshold.

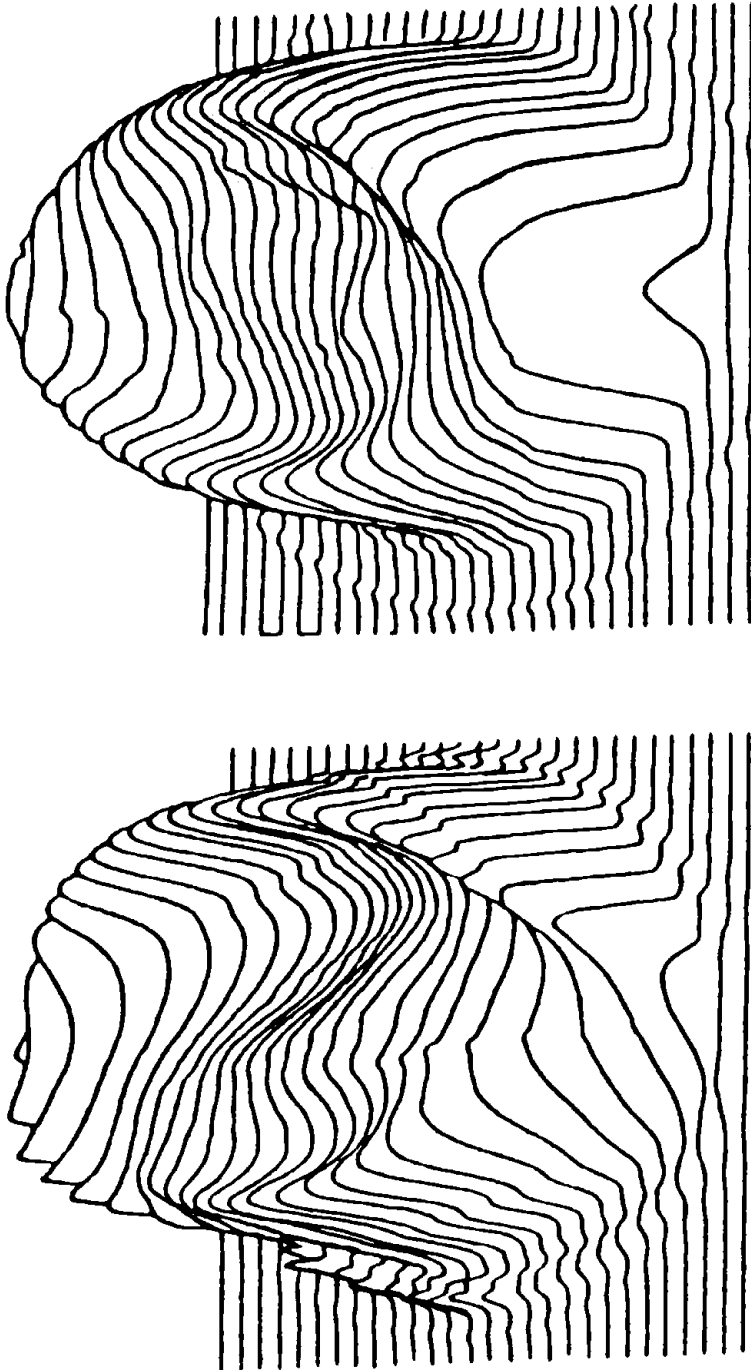
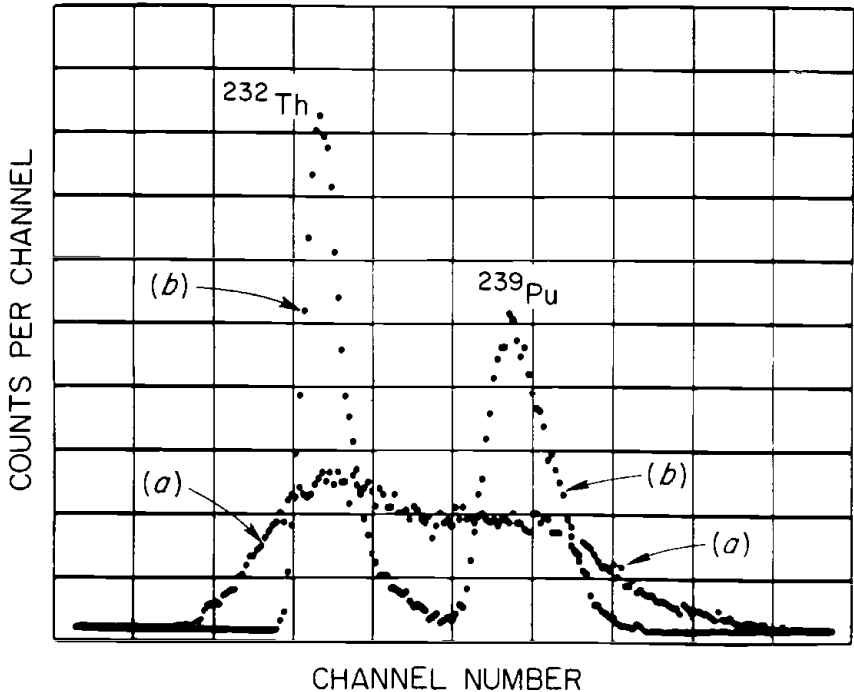


Figure 3. Typical sensitivity profiles of 2-in multiplier phototubes.



**Figure 4.** Comparison of the spectra of  $^{232}\text{Th}$ (4.01 MeV) and  $^{239}\text{Pu}$ (5.19 MeV) obtained on a beta liquid scintillation spectrometer (a) and on a PERALS spectrometer.

Thus, it became clear that a method of incorporating the alpha-emitting nuclide into the scintillation cocktail in some reproducible manner was necessary so that one could expect the peak for a given alpha energy to appear at the same position on the amplifier voltage output; thus at the same position on a spectrum as that displayed on a multichannel analyzer. Application of the extensive knowledge of liquid-liquid extraction existing in the Chemical Separations Research group at Oak Ridge National Laboratory<sup>9</sup> provided a solution to the cocktail reproducibility problem. Progress at this point was reported at the 1974 International Solvent Extraction Conference.<sup>10</sup>

Developing a method of placing the alpha-emitting nuclide into the scintillator so that each time the scintillator and its response to alpha energies would be the same required the production of an identical organic-phase-soluble compound for the nuclide in each sample. Variable quenching, either color quenching or chemical quenching, could not be tolerated. The first approach in many cases has been to transfer the nuclide into an organic phase by using liquid-liquid extraction or "solvent" extraction techniques and then add a portion of the organic phase to a scintillator. Our solution to this problem was to incorporate an extractant into the scintillator thereby producing an "extractive scintillator". There are several extractants one may choose for this purpose,

**Table 1. Properties of Selected Solvent Extraction Reagents Useful in Extractive Scintillators**

Type	Example	Metals Extracted
Cation Exchange	Bis (2-ethylhexyl) Phosphoric acid	Alkali and alkaline earths weakly extracted; pH 4-14. Lanthanides/actinides (III) strongly extracted; pH 3-5. Actinides (IV-VI) strongly extracted to pH 0.5.
	Neocarboxylic acids	Weak extractant for most ions pH 4-7. Strong Ext. for some ions in combination with appropriate crown ethers.
Ion Pair Coord-inators From sulfate systems <sup>a</sup>	Primary Alkyl Amines. MW > 250.	From Sulfate; Fe (III), Y, Zr, Nb(V), Tc(VII), Pd(II), In(III) Sn(II), Eu, Hf, Ta(V), Re(VII) Os(IV), Mo(VI), Pu(IV), U(IV) Th.
	Secondary alkyl amine, MW > 250 (extraction varies with structure.)	From Sulfate; Zr, Nb(V), Mo(VI) Tc(VII), Pd(II), Ta(V), Re(VII), Os(IV).
	Tertiary alkyl amine, MW > 250.	From Sulfate; U(VI).
	Quat. ammonium MW > 300.	From Sulfate; Mo(VI), Tc(VII) Ta(V), Re(VII), Os(VI), Pd(II).
Neutral Coord-inators	Trioctyl phosphine oxide.	From Nitrate; U(VI), Zr, Tc(VII) Au(III), Th, Np(IV)(VI), Pu(IV)(VI), Pa, Hf. From Chloride; Au(III), Zn, Zr, Sn(IV), Sb(III), Cr(IV), Mo(IV), Fe(III), Th, U(IV)(VI) Pu(IV)(VI), Ga(III), Nb, Bi.

<sup>a</sup>Extraction from nitrate and chloride systems are not listed because the amine salts of these ions are highly quenching and therefore not useful in scintillators.

*Note:* Amine perchlorates are not extractants. Perchloric acid can be used to strip metals from any of the ion-pair-coordinator extractants.

each having different metal-ion selectivities. Table 1 lists some extractants that are currently used and shows their selectivities from various aqueous systems. Figure 5 shows the quenching (peak shifting) effects of some organic phase compounds. The use of an extractive scintillator involves a simple two-phase equilibration of the scintillator with an appropriate aqueous phase. Then the scintillator is placed in a small culture tube, the tube placed in the PERALS detector, and the spectrum collected.

Thus, we found that in most cases the resolution of the sample nonreproducibility problem was to prepare a water-immiscible scintillator containing a liquid-liquid extraction reagent (in addition to the fluor and an energy transfer agent) and to extract (phase transfer) the nuclide-of-interest into such a scintil-

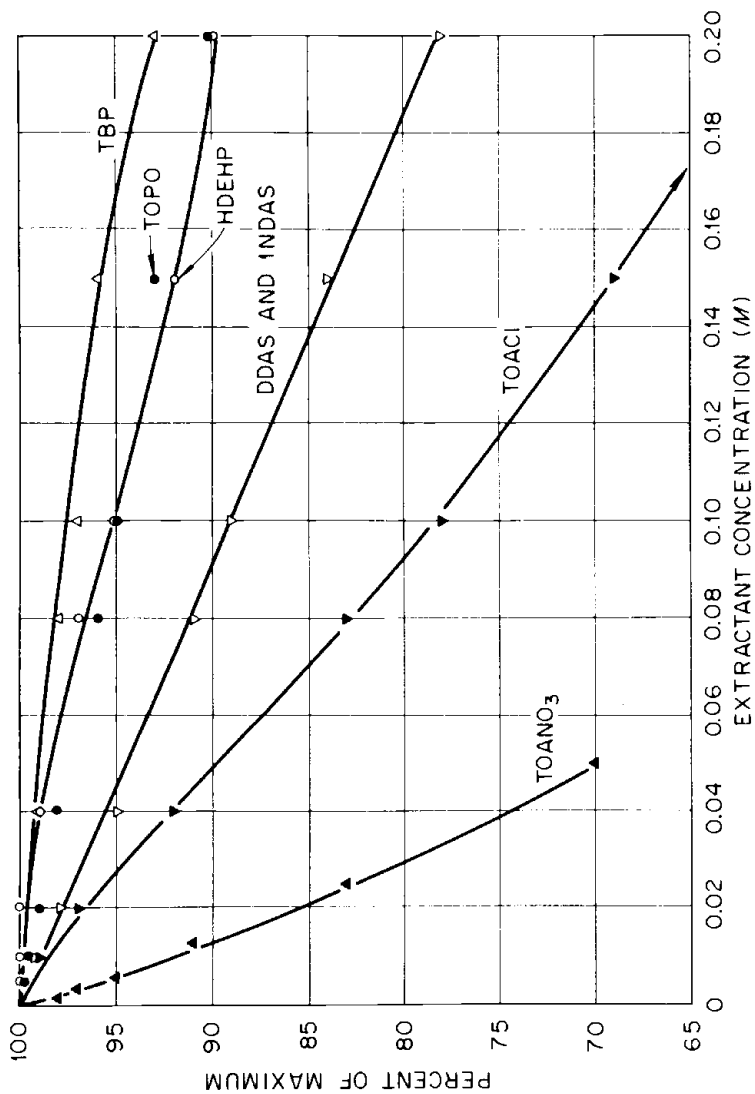


Figure 5. The quenching effects of various reagents.

lation cocktail. The material extracted into the scintillator solution had little or no effect on its energy response characteristics. This development resulted in a reproducible, calibratable system where the peak for 4.0 MeV  $^{232}\text{Th}$  or 5.15 MeV  $^{239}\text{Pu}$ , for example, would always appear at the same place on an energy scale. A number of applications of alpha liquid scintillation were made at this point and some were reported at the 1979 International Conference on Liquid Scintillation Counting.<sup>11,12</sup>

One additional, serious problem that impeded the use of liquid scintillation as a useful, practical method of alpha spectrometry, was the interference from beta and gamma radiation. Beta and gamma radiation are about 10 times more effective, keV for keV, in producing light in a liquid scintillator than alpha particles.<sup>13</sup> Thus, if a sample contains beta- and/or gamma-emitting nuclides, any alpha peak will be underlain with a beta/gamma continuum. This makes the alpha count background high, variable, and difficult to determine, and it sometimes even makes the alpha peak difficult to locate. In the following we describe how this problem was dramatically and elegantly solved.

The work we were doing with alpha liquid scintillation attracted numerous visitors to our laboratory. Among them was an electrical engineer named John Thorngate. We were explaining to him the terrible problem that the beta and gamma pulses presented when he said, "I can get rid of those pulses." The next day John returned with an armload of NIM modules and within an hour we were seeing liquid scintillation alpha spectra free of beta and gamma interference. By afternoon we had collected sufficient information to publish a paper.<sup>14</sup>

There is about a 40 nanosecond (nsec) difference in the length of beta- or gamma-produced and alpha-produced pulses in a liquid scintillation system.<sup>13</sup> It is possible to sort these pulses electronically and send only the longer, alpha-produced pulses to the multichannel analyzer. This technique is extensively used for separating gamma- and neutron-produced pulses. Similar electronic circuitry was adapted and improved for beta/gamma-alpha separation. In currently available alpha liquid scintillation detectors the rejection of beta/gamma pulses is >99.95% efficient,<sup>15,16</sup> thus it is possible to collect an alpha spectrum that is essentially free of beta/gamma interference.

At this point, we had the means of removing or minimizing the poor alpha energy resolution, the quenching and variable scintillator response, and the beta and gamma radiation interference. This provided the technology for the development of a practical method of producing liquid scintillation alpha spectra. We called this new development **Photon Electron Rejecting Alpha Liquid Scintillation (PERALS)** spectrometry. The development won an IR-100 award in 1981 and the PERALS spectrometer is now in commercial production.<sup>17</sup> A number of laboratories are having excellent success with the method. The special chemicals and extractive scintillators needed for the PERALS system are also commercially available.<sup>18</sup> Time will tell if the method is to fulfill its promise of a new and useful addition to the existing alpha assay methods.

## RESULTS

As in virtually all cases the advance in alpha liquid scintillation methods described above resulted from a search for a suitable radiometric method for our own work, which was primarily a study of the chemistry of solvent extraction separations of metal ions. There was very little separate funding for this work. However, the development of a useful radiometric method for alpha-emitting nuclides seems to fill a gap in the methods already available. Alpha energy resolution was not as good as surface-barrier or Frische-grid methods, but nuclide quantification was better and sample preparation was easier. Sample preparation steps for PERALS alpha spectrometry usually were selective for one ion or a group of ions, and this selectivity supplemented the identification of nuclides by peak position.

### Typical PERALS Analysis

Describing a typical analytical procedure may summarize the descriptive material above and bring it to focus on its end use: let us begin with a solid sample presented for thorium and uranium analysis that appears to be soil mixed with leaves and other organic material. One- to two-gram portions of the sample are weighed into crucibles and ignited at 600°C until all the organic material is destroyed. Then the material is placed in a solution of nitric, hydrochloric, and hydrofluoric acids; pressure vessels of organic fluoropolymers are best for this step.<sup>19-22</sup> Sulfuric acid is added and the other acids are boiled away (fusion methods can also be used).<sup>23</sup> Then the acidity of the sulfate system is adjusted to pH 1 to 2 in a 10 mL volume, and a two-phase equilibration extraction is made into a measured 1.2 to 1.5 mL water-immiscible extractive scintillator containing 0.3 *M* high-molecular-weight tertiary amine sulfate. This uranium in the sample now will have been quantitatively transferred to the scintillator phase. A 1 mL portion is pipetted into a small culture tube, and the spectrum is collected on a PERALS spectrometer. The remaining aqueous phase is contacted with a 1.2 to 1.5 mL portion of an extractive scintillator containing 0.3 *M* high-molecular-weight primary amine. Again 1 mL of the extract is counted. Multiplying the integral of the peak counts obtained in the first case by 1.2 or 1.5 and dividing by 0.9968 gives the disintegrations per minute (dpm) of uranium, and so calculating the integral of the peak obtained in the second instance gives the dpm of thorium. The accuracy of such a procedure depends on two factors: (1) how carefully the sample is prepared and (2) how many counts are accumulated. Standard mineral samples have been run giving consistent results within 0.1% of the given value.

### Solvent Extraction

This operation plays an important part in PERALS spectrometry in that it allows the radionuclide to be selectively and quantitatively transferred to the

(extractive) scintillator with little change in the scintillator composition. This makes it possible to obtain a reproducible calibration of the energy scale for a given extractive scintillator/aqueous phase composition. A solvent extraction system is composed of an organic extractant phase (one or more extraction reagents dissolved in an organic diluent) and an aqueous phase. These two phases are immiscible, but under proper conditions phase transfer of one or more species can occur across the organic/aqueous interface. Expansion of the interface by gentle agitation of the two phases allows phase equilibrium to be attained quickly, usually in one to two minutes.

In an aqueous/organic solvent extraction system, the distribution of a metal,  $M$ , between the two phases at equilibrium is defined by a distribution coefficient  $D_M$ .

$$D_M = (\text{Conc. } M)_{\text{org}} / (\text{Conc. } M)_{\text{aq}}$$

This is true at any phase ratio,  $V_{\text{org}}/V_{\text{aq}}$ . However, it should be remembered that  $D_M$  is a concentration ratio, and the amount of metal recovered depends also on the phase ratio. If we call the recovery factor,  $F_R$ , the relationship

$$F_R = D_M(V_{\text{org}}/V_{\text{aq}})$$

describes the total org/aq metal ratio. Thus if  $D_M$  is 1000 (not an unusual value) and  $V_{\text{org}}/V_{\text{aq}}$  is 1 then  $F_R$  is also 1000, but if  $V_{\text{org}}/V_{\text{aq}} = 1/100$  or  $1/1000$  the recovery is much less. The percent recovery in the first case (1:1 phase ratio) is  $100 \times 1000 / (1000 + 1) = 99.9\%$ ; while in the second case (phase ratio 1:100), the percent recovery is  $100 \times 10 / (10 + 1) = 90.9\%$ , and in a case where the phase ratio is 1:1000 the recovery will be only 50%. These simple calculations make obvious the importance of phase ratio in analytical applications of solvent extraction. It should also be emphasized that a distribution coefficient depends on the composition of both the organic and aqueous phases. If the composition of either phase is changed, the distribution coefficient can change. It is obvious that one should be aware of distribution coefficients and phase ratios in following, and more particularly in modifying, procedures for PERALS.

## OUTLINES OF PROCEDURES

Some procedures that have been tested in our laboratory and shown to work well are briefly described below. Certain requirements that apply to all samples should be noted. Samples to be counted should be optically clear and as colorless as possible. The objective is to get as much light as possible per alpha event to the phototube. All samples should be sparged with a dry, toluene-saturated oxygen-free gas. Dissolved oxygen in the sample impairs both energy and pulse-shape resolution. Any aqueous/organic system that transfers a

**Table 2. Quenching and Nonquenching Ions and Molecules**

<b>Species In Organic Phase</b>	<b>Relative Degree of Quenching</b>
Any yellow colored material.	Color quenching of varying severity depending on the intensity of the color.
Chloride salts of amines and most chlorine substituted organics and dissolved HCl.	Severe chemical quenching.
Nitrate salts of amines, nitrate substituted organics and dissolved HNO <sub>3</sub> .	Severe chemical quenching plus color quenching.
Alcohols and ketones.	Moderate quenching.
Ethers.	Slight quenching
Sulfate salts of amines.	Minimal quenching.
Phosphates, phosphate esters and phosphine oxides.	Minimal quenching.

quenching ion or molecule to the organic phase must be avoided for best results (see Figure 5 and Table 2).

### Counting on Glass-Fiber Filters<sup>24</sup>

For these two procedures to succeed the filter must be relatively clean, i.e., free of material of a dark color.

Place the filter (up to 2 in diam) in a 10 × 75 mm culture tube and add 1 mL of a PERALS aqueous-immiscible scintillator. Use either extractant-free or HDEHP [bis-(2-ethylhexyl)phosphoric acid]—containing scintillator. Momentarily evacuate the tube to water-aspirator pressures and release to argon. Do this twice to remove entrapped air and then count on a PERALS spectrometer. This allows separate determination of alpha and beta events. The spectrum of alpha energies is usually sufficiently resolved to allow identification of the alpha-active material.

### Uranium Activity on Cellulose Filters<sup>25</sup>

*Cellulose* air filters, clean or dirty, can be placed easily in solution and assayed as follows: the filter paper (up to 2 in diam) is placed in a 2 dram, screw-cap borosilicate glass vial and heated, open, in an oven or furnace at 500°C for 2 hr. After removing and cooling, add 2 to 5 drops of concentrated nitric acid, 3 drops of 30% hydrogen peroxide, and 1 drop of a saturated aluminum sulfate solution to the vial. The vial is then heated to 200°C to remove the nitric acid. The solids remaining are redissolved in a solution 1 M in Na<sub>2</sub>SO<sub>4</sub> and 0.01 M in H<sub>2</sub>SO<sub>4</sub>. A measured quantity of an extractive scintilla-

tor containing a high molecular weight tertiary amine sulfate is then added to the vial, and the two phases are equilibrated for 2 to 3 min. After the phases have separated, 1 mL of the organic phase is counted on a PERALS spectrometer. Alpha spectra thus obtained usually allow identification of the uranium isotopes present. The results are uniformly more accurate than direct counting of the air filter.

### Gross Alpha in Environmental Materials<sup>26</sup>

With the sample in solution in nitric or hydrochloric acid, add 0.5 g of  $\text{LiClO}_4$  and 1 to 1.5 mL of 0.1  $M$   $\text{HClO}_4$ . Evaporate under heat lamps or in an aluminum block at  $160^\circ\text{C}$  until boiling of the sample ceases and the first perchloric acid fumes appear. Cool the beaker and add 5 to 7 mL of water to dissolve the viscous residue. Measure the pH of the solution; it must be between 2 and 3.5. Transfer the solution to a small equilibration vessel and add a measured quantity, 1.2 to 1.5 mL, of an extractive scintillator that is  $\sim 0.2 M$  in HDEHP. Equilibration will transfer most of the alpha-emitting nuclides, with the exception of radium and radon, to the scintillator. Lanthanides are also extracted. Counting on a PERALS spectrometer will usually allow identification of the nuclides as well as an accurate quantification of them.

### Uranium and Thorium<sup>27</sup>

With the sample in solution as above, add sulfuric acid and sodium sulfate and convert to a sulfate system at pH 1 to 2. An initial extraction into a scintillator containing 0.3  $M$  high molecular weight tertiary amine sulfate such as trioctylamine sulfate will quantitatively remove uranium. A second extraction from the same aqueous using a scintillator containing a high molecular weight primary amine sulfate such as 1-nonyldecylamine sulfate will remove thorium. Each organic extractive scintillator solution is then sampled and counted on the PERALS spectrometer. Normal uranium in secular equilibrium will show the double peaks due to  $^{238}\text{U}$  and  $^{234}\text{U}$ . However, natural processes can concentrate  $^{234}\text{U}$  in water, and sediments and artificial processes have concentrated  $^{234-235}\text{U}$ ; thus, not all uranium now in the environment is "normal" uranium. If the uranium is highly enriched in  $^{235}\text{U}$ , the spectrum will show primarily  $^{234}\text{U}$ . Spectra of tailings from the enrichment processes will show a predominance of  $^{238}\text{U}$ .

### Uranium and Thorium in Phosphates<sup>28</sup>

These elements can be separated from a variety of phosphate-containing materials, e.g., fertilizers, bones, teeth, animal tissues, and wastes. The sample is dissolved and placed in a nitrate or nitrate perchlorate solution. Sufficient aluminum nitrate is added to this solution to complex the phosphate. The solution is then contacted with a toluene solution of trioctyl phosphine oxide

(TOPO). Both uranium and thorium are transferred to the organic phase. The organic phase is then stripped with an equal volume of 0.5 *M* ammonium carbonate solution, the ammonium carbonate is evaporated, the sample is converted to nitrate or nitrate/perchlorate, and any entrained organics are destroyed. The clear solution is then converted to a sulfate system and treated as above. In many nonphosphate samples uranium can be coprecipitated with magnesium hydroxide or otherwise concentrated and extracted from a sulfate system into a scintillator containing tertiary amine sulfate.

### Polonium<sup>29</sup>

The radioisotopes of polonium (usually <sup>210</sup>Po) have been difficult to analyze with accuracy using the conventional methods. Using PERALS, however, the procedure is simple, rapid, and accurate. With the sample in solution, add 3 to 5 mL of concentrated phosphoric acid and evaporate to remove other acids. Transfer this phosphoric acid solution to a small equilibration vessel using 3 to 5 mL of water. Add 1 mL of 0.1 *M* HCl. Add a measured volume, 1.2 to 1.5 mL, of an extractive scintillator that contains 0.1 *M* TOPO. Equilibrate and count 1 mL on a PERALS spectrometer. Because of the minimal chemical manipulations required, the accuracy of this determination easily can be better than  $\pm 1\%$ .

### Plutonium<sup>30</sup>

Plutonium can be chemically separated from all other elements except neptunium and counted quantitatively by this procedure, and the <sup>237</sup>Np peak can be resolved by its energy difference from <sup>239-240</sup>Pu. The initial extractant in this procedure is 0.3 *M* high-molecular-weight tertiary amine nitrate (TANO<sub>3</sub>) in toluene. The sample should be in solution in 3 to 4 *M* total NO<sub>3</sub><sup>-</sup> and 0.5 to 1 *M* HNO<sub>3</sub>. The plutonium is reduced with ferrous sulfate and reoxidized to Pu(IV) with sodium nitrite. This solution is contacted with not less than 1/4 its volume of TANO<sub>3</sub> solution. Equilibrate and separate the aqueous phase. Wash the organic phase with two 1/4-vol portions of 0.7 *M* HNO<sub>3</sub>. The aqueous from the first equilibration and the washes can be combined and analyzed for uranium, if desired. Plutonium can be stripped from the organic phase either with perchloric acid or, after diluting the organic phase with 2-ethylhexanol, with 1 *N* H<sub>2</sub>SO<sub>4</sub>. The plutonium is reextracted into a scintillator containing HDEHP in the first instance and into a scintillator containing 1-nonyldecylamine sulfate in the second instance.

### Radium<sup>31</sup>

A new extraction reagent allows radium to be separated from other alkaline earth elements and the following procedure allows separation from many, if not all, other cations. The sample solution is spiked first with <sup>133</sup>Ba, and 10 mg

of barium carrier is added. Then radium is precipitated from the sample solution as barium/radium sulfate. Next the precipitate is converted to the carbonate by heating it with a saturated potassium carbonate solution, and the separated barium/radium carbonate is dissolved in dilute acid. The pH of this solution is then adjusted to between 9 and 10, and the radium extracted selectively into an extractive scintillator containing a synergistic reagent mixture of a high-molecular-weight-branched carboxylic acid such as 2-methyl-2-heptylnonanoic acid (HMHN), 0.1 M, and dicyclohexano-21-crown-7 (DC21C7), 0.05 M. The extraction is quantitative, and any chemical losses in the coprecipitation and metathesis steps can be corrected by gamma counting the  $^{133}\text{Ba}$ . Radium is counted on a PERALS spectrometer, initially showing a single alpha peak each for both  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$ . All the alpha peaks from both radium daughters can be seen if one waits for their ingrowth. The percent relative error in this determination, with appropriate counting statistics, is usually less than  $\pm 5\%$  and can be much less.

## CONCLUSIONS

The basic steps leading to the development of the PERALS system of sample assaying for alpha-emitting nuclides have been presented. The many blind alleys and dead ends explored were not. This is not the end of the story, however. More selective and perhaps simpler procedures are certainly possible. Although pulse-shape resolution (the separation of beta-gamma pulses) hardly needs improvement, energy resolution does. We believe that this is possible. There seems to be no fundamental reason why resolution should be limited in such a system. We hope to be able to pursue this quest in the future.

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C.F. Coleman invented the name and acronym PERALS.

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