

CHAPTER 33

Liquid Scintillation Screening Method For Isotopic Uranium in Drinking Water

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ABSTRACT

The radiation dose resulting from the ingestion of uranium is determined by activity rather than mass; isotopes such as ^{234}U can contribute significantly to the total uranium activity, without being detected by mass-based fluorometric techniques. As $^{234}\text{U} / ^{238}\text{U}$ ratios significantly in excess of 1 are frequently noted in groundwater, the determination of uranium on a mass basis and the assumption of isotopic equilibrium can lead to serious dose underestimation. Techniques for specific uranium isotope determination are well developed, but involve considerably more effort than fluorimetry. The relative ease with which uranium can be extracted from water into a liquid scintillation compatible solution provides an alternative approach for screening drinking water supplies. A technique originally developed for PERALS (Photon, Electron Rejecting Alpha Liquid Scintillation) systems has been modified for use in conventional LS systems as a screening test for isotopic uranium and other actinides in drinking water. While lacking the degree of alpha/beta discrimination and energy resolution available with PERALS systems, conventional units offer the advantages of large sample volume, high throughput, and widespread availability. This chapter demonstrates that with appropriate sample preparation, the resolution and background attainable with conventional systems is more than adequate to provide a simple, effective screening technique for uranium concentrations of significance to public health.

INTRODUCTION

Because of its long half-life and correspondingly low specific activity, ^{238}U is by far the most abundant uranium isotope in water on a mass basis, but the radiation dose resulting from the consumption of the water is determined on an activity basis. Other uranium isotopes, notably ^{234}U , can contribute significantly to the total uranium activity without being detected by existing mass-based fluorometric techniques.^{1,2} The geochemical mobility of ^{234}U is often enhanced by the alpha recoil energy accompanying its formation, and $^{234}\text{U} / ^{238}\text{U}$ ratios significantly in excess of 1 are frequently noted in groundwater.^{1,2} The determination of uranium on a mass basis and the assumption of isotopic equilibrium can therefore lead to a serious underestimation of the radiation

dose from drinking water consumption. Techniques for specific uranium isotope determination are well-developed but involve considerably more effort than fluorimetry.

The high uranium extractability from aqueous solutions into organic solvents is well known and has long been exploited in uranium recovery processes. Uranium in natural waters is nearly always in the form of the uranyl ion (UO_2^{++}), and is often complexed with carbonate or OH ions.^{3,4} The complexes are destroyed below pH 4, leaving the simple uranyl ion in solution. At low pH, this ion is very readily extracted from water into toluene containing 60 g/L of HDEHP (bis[2-ethylhexyl] phosphoric acid), a scintillation compatible compound.⁵ Liquid scintillation is therefore an attractive option which offers the possibility of a single step process: directly concentrating uranium into the counting medium.

The procedure described in this chapter is derived from a solvent extraction, alpha liquid scintillation technique developed at Oak Ridge National Laboratory and published in "Alpha Counting and Spectrometry Using Liquid Scintillation Methods."⁵ The set of techniques outlined in that document rely on high resolution energy discrimination and pulse-shape discrimination available with the PERALS system, which uses small (ca. 1 mL) volumes of highly purified organic scintillators.

The high energy resolution and low backgrounds achievable with the PERALS system make this technology extremely attractive for many applications. However, the necessarily small liquid scintillator volumes and the amount of sample processing involved potentially limit the application of this approach to large scale, low specific activity drinking water screening programs. To meet this particular need, we have "scaled up" the extraction methods for use with conventional liquid scintillation systems, which have the advantages of large (20 mL) sample volume, automatic operation, and widespread distribution. The disadvantages of the commercial systems are low energy resolution, relatively high backgrounds, and less effective alpha/beta discrimination. However, in the restricted context of screening potable water for uranium, these disadvantages prove to be relatively unimportant. Furthermore, the energy resolution of commercial systems can be enhanced by a few simple steps to the extent that more definitive spectral analyses of positive samples can be performed.

SCREENING WATER SAMPLES FOR TOTAL URANIUM ACTIVITY

The main purpose of a screening program is to show that water is suitable for consumption, in other words, to demonstrate the absence of uranium above a particular concentration. This approach greatly simplifies analytical requirements in the (presumably) great majority of cases where gross extractable radioactivity is in fact below an established level.

Method

To screen for total uranium activity, a 1 L sample of water is treated by aeration or boiling to remove radon, which is highly soluble in toluene. The sample is then brought to approximately pH 1.5 with HNO₃ and agitated with 20 mL toluene containing 60 g/L of HDEHP and an appropriate fluor concentration. After a few minutes of contact, the phases are allowed to separate and the extractant scintillator drawn off for counting. If the initial solution had not been purged of radon three or more hours prior to extraction, the extracts should be held at least 3 hr before counting to allow for radon daughter decay. A screening count is then taken in a region of interest empirically set around the uranium alpha peaks (4.2 and 4.8 MeV).

Extraction and Counting Efficiency

Figure 1 shows the spectra of a gels incorporating 2 mL aliquots of a spiked sample containing 412 Bq/L of natural uranium alpha activity (A) and a second aliquot taken after liquid-liquid extraction (B). The net alpha count rate in the second gel indicated an activity of 21 Bq/L in the aqueous phase, or a deficit of 391 Bq/L. The net alpha activity of the extract was 376 Bq, with another 6 Bq recovered after a secondary organic stripping of the aqueous phase. The recovered activity is in good agreement with the deficit, indicating that the alpha counting is virtually quantitative in the extract, as might be expected from general principles. The ratio of activities in the aqueous phases after and before extraction is 21:412, or 5.1%, indicating a 95% recovery.

Background and Detection Limits

In a narrow region of interest around the uranium alpha peaks, the blank counting rate was found to be 3.2 cpm on our system. While this is still higher than that of the PERALS unit, the twentyfold increase in sample volume available with conventional LS systems produces adequate statistical reliability at concentrations of regulatory interest. (Some users may prefer a wider window with higher background but more tolerance for quench variation.) Under these conditions, the minimum true detectable activity (MDTA),⁶ is given by:

$$\text{MDTA} = \frac{g(k_a + k_b)(C_B)^{0.5}}{g(K_a + K_b)C_B^{0.5}}$$

where g = calibration factor (Bq/count),

C_B = total measured background count,

and k_a

and k_b = number of normal standard deviations associated with the probabilities a and b of making Type I (false indication that activity is present) and Type II (false indication that activity is absent) errors.



Figure 1. Aliquots of natural uranium spike solution in gel prior to liquid-liquid extraction (A) and after extraction (B). Counting times, scales, and regions of interest are identical.

The approximation holds if the background is stable and the square root of the total observed background counts is much greater than k_a . For screening measurements, it is more important to avoid a Type II error than it is to avoid a Type I error, so we might choose to set $a = .05$ and $b = .025$, with $k_a = 1.645$ and $k_b = 1.960$. If the sample volume is 1 L and combined extraction and counting efficiency is 90%, then a 10 min screening count would be expected to produce $(10 \times 60 \times 0.9)$ or 540 counts per Bq/L, and $g = 1/540 = 0.00185$. The background count in 10 min, C_B , would on the average be $(3.2 \times 10) = 32$ counts, and $k_a + k_b = 3.605$. The minimum detectable true activity would then be:

$$\text{MDTA} = 0.00185 \times (3.605) \times (64)0.5 = 0.0377 \text{ Bq/L (1.02 pCi/L)}$$

SPECTROSCOPIC ANALYSIS OF POSITIVE SAMPLES

As noted above, the demonstration of the absence of activity poses less of an analytical challenge than the identification of the nuclide(s) producing an excess count rate. Several options are available for samples that exceed a predetermined screening level. One is to process the extract for high resolution alpha spectroscopy with either the PERALS system or solid state detectors. However, a relatively modest improvement in the energy resolution of conventional LS counting, combined with chemical and radiological considerations, is sufficient to identify and quantify the excess activity in many cases.

Resolution Enhancement

Because most liquid scintillation systems are multi-user devices, our efforts to further improve resolution have been directed to the vial and its contents, rather than on modifications to the instrument itself. As noted by McDowel,¹⁵ a number of simple modifications can be made to improve the energy resolution potential of a liquid scintillator. Sparging the organic scintillator with inert gas reduces oxygen quenching, thus increasing both absolute light output and energy resolution. Total light yield and energy resolution are also increased by adding of 200 g/L of naphthalene to the primary solvent and by using PBBO (2-(4'-biphenyl)-6-phenylbenzoxazole) instead of PPO as a fluor.

The substitution of a translucent for a transparent counting vial also has a marked effect on the alpha spectrum. (This was brought to my attention by Bernard Cohen⁷ in the context of our long-standing interest in detecting radon in air by activated carbon adsorption and subsequent liquid scintillator desorption. A similar effect is noted in Donald Horrocks's 1972 text on liquid scintillation.) The diffuse transmission of light through the translucent material decreases spectral degradation due to photocathode nonuniformity, thus improving resolution. Figures 2 and 3 show the spectra of ²³⁸U and ²³⁴U in

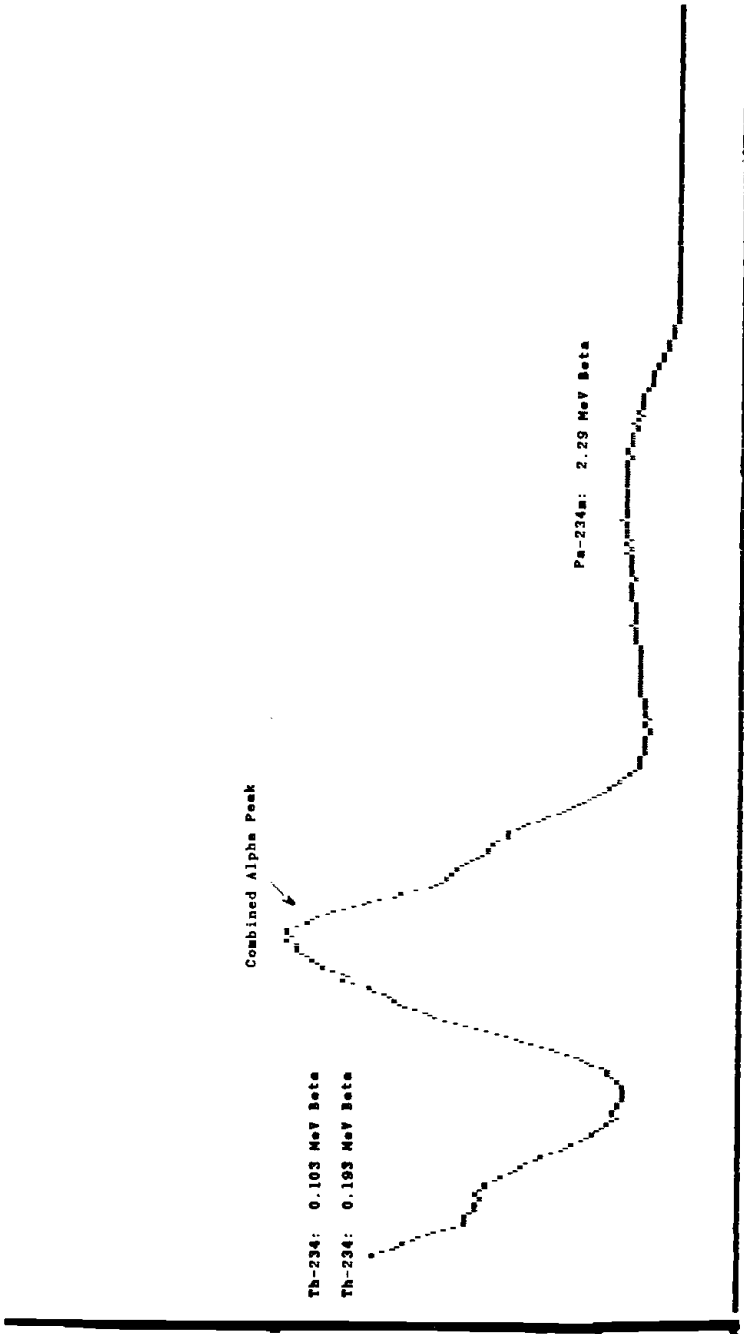


Figure 2. Alpha spectra of ^{238}U (4.2 MeV) and ^{234}U (4.7 MeV) obtained with conventional liquid scintillation (18 mL). The beta spectra of the short-lived intermediates are also shown.

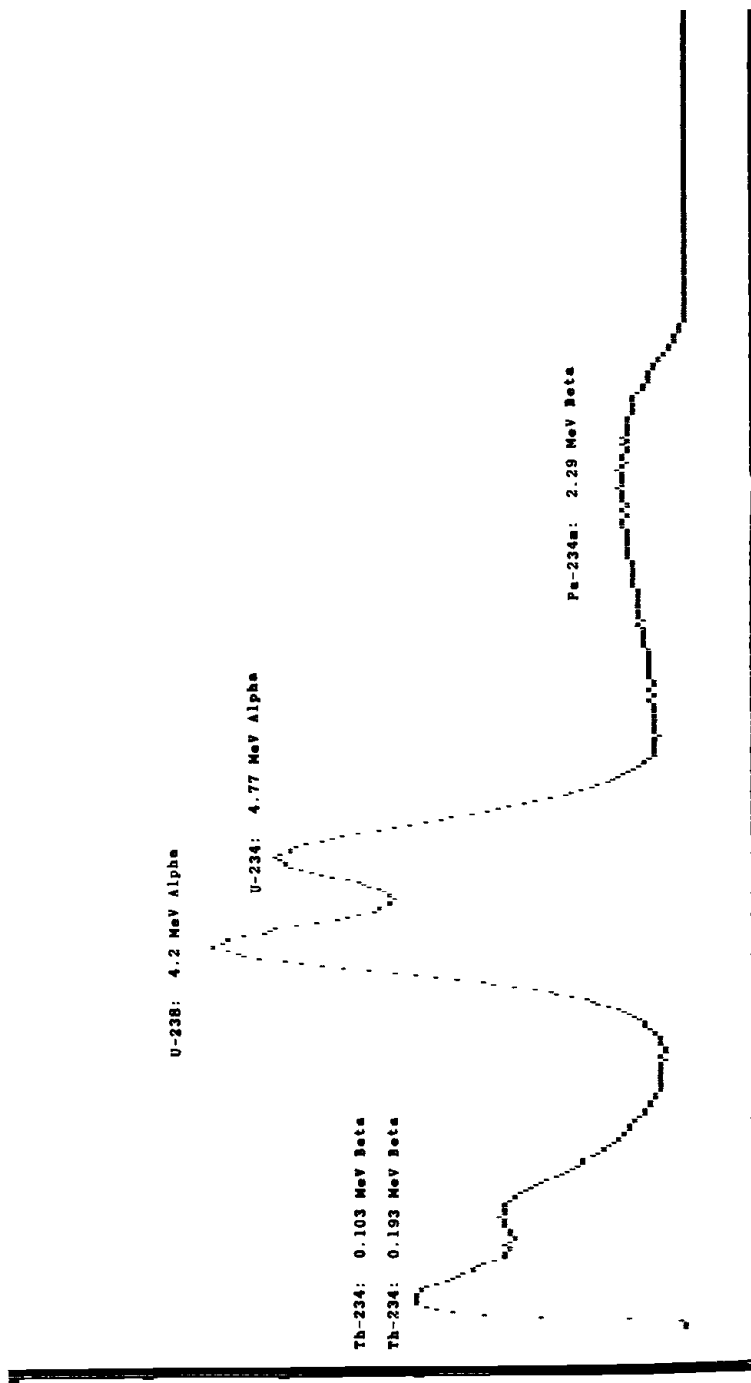


Figure 3. Spectrum of the solution shown in Figure 2 after transfer to resolution enhancing vial.

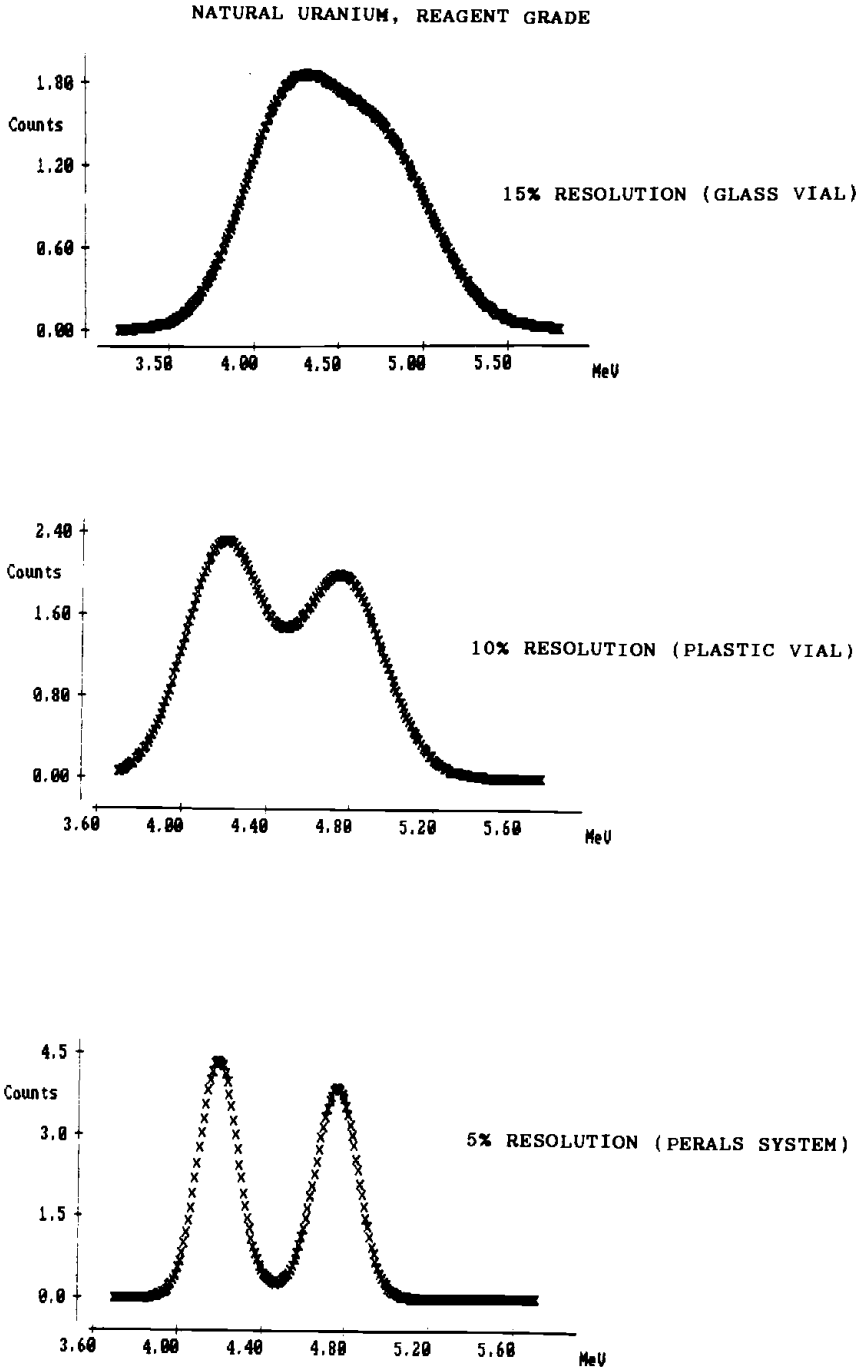


Figure 4. Simulated alpha spectra at three levels of resolution.

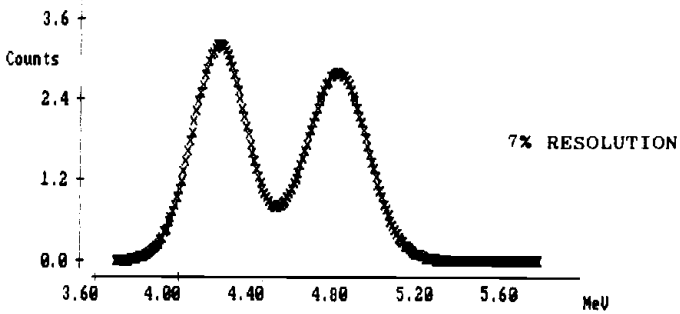
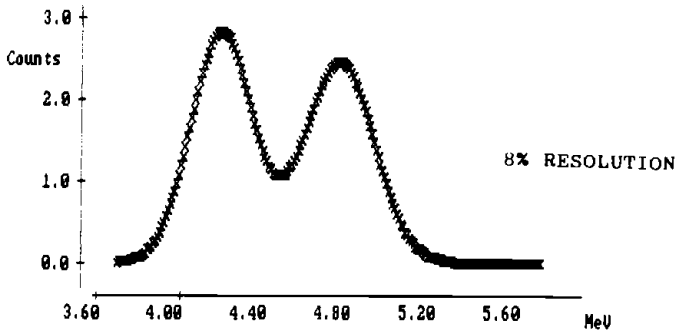
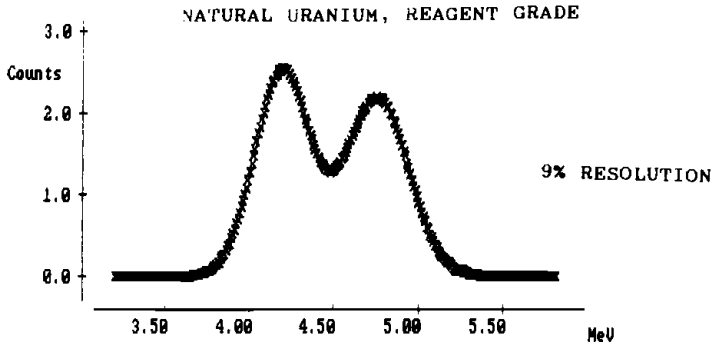


Figure 5. Simulated alpha spectra at three levels of resolution.

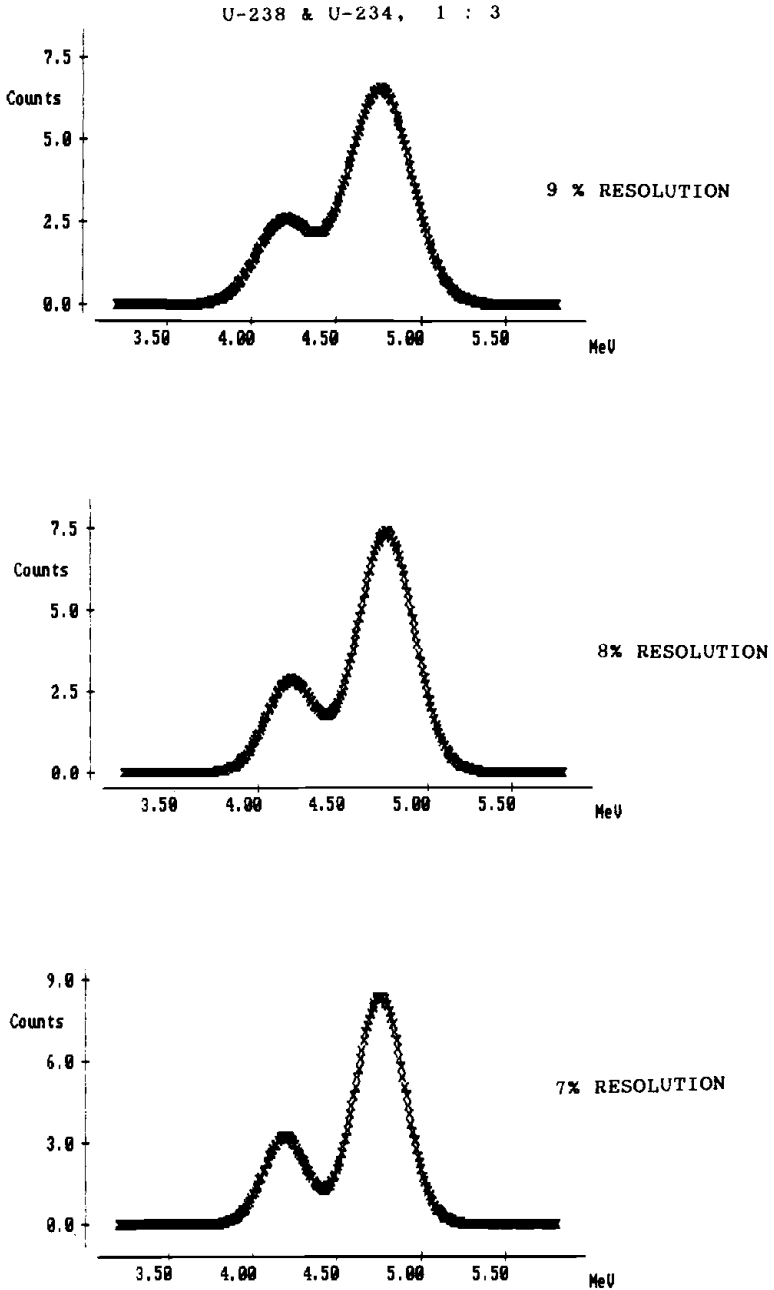


Figure 6. Simulated alpha spectra of ^{238}U and ^{234}U in disequilibrium at three levels of resolution.

argon-sparged extractant scintillator obtained in a glass and in a slightly modified polyethylene vial respectively. The beta spectra are largely unchanged, but the alpha resolution in the polyethylene vial is considerably improved. The alpha resolution is approximately 10% of the peak energy, just about midway between the resolution obtained in clear glass on a conventional system and the resolution available with a PERALS system, as shown in the simulated alpha spectra in Figure 4.

It is not yet known how much more resolution can be obtained on existing conventional LS systems by modifying the solvent and counting vial, but even if little additional resolution can be achieved, the level shown in Figure 3 is useful. While ^{238}U and ^{234}U are not completely resolved, the total alpha activity is obtained, and the degree of disequilibrium can be estimated from the relative peak areas. The importance of relatively small gains in energy resolution is illustrated in Figures 4 through 6. These figures depict synthetic alpha spectra generated by summing normal distributions with means corresponding to the ^{238}U , ^{235}U , and ^{234}U alpha peaks, full widths at half maximum at the stated percent of mean energy, and amplitude at the stated equilibrium ratios. ^{235}U is normalized to its natural abundance with respect to ^{238}U ; while not resolved at any level shown, the presence of its alpha emission between that of the other two isotopes diminishes the resolution to some extent. Figure 4 shows the two main uranium alpha peaks unresolved at 15% percent resolution, which may be compared with Figure 2, the actual alpha plus beta spectrum of our uranium extract in a glass vial. Also shown is a simulation of the 5% resolution spectrum obtainable with the PERALS system and the 10% resolution obtained with a slightly modified high density plastic vial in our conventional LS system.

Figure 5 shows the projected effects of improving resolution to 9, 8, and 7%. Each incremental gain is seen to produce noticeable effects. The importance of gains of this magnitude is further illustrated in Figure 6, in which uranium in a state of disequilibrium is viewed with 9, 8, and 7% resolution.

Nuclide Identification

The 10% resolution currently available permits discrimination between uranium isotopes and many of the other alpha emitters of interest. Table 1 lists the nuclides of the ^{238}U and the ^{232}Th decay series that emit alpha particles with energies between 3.75 and 5.25 MeV. These nuclides could not be readily distinguished from ^{238}U – ^{234}U at the present level of resolution. However, the screening extractant HDEHP does not extract radium from the aqueous phase. Furthermore, except in one unusual well, ^{232}Th and ^{230}Th concentrations over 0.1 pCi/L have not been found in potable water.² In short, natural alpha activity from 3.75 to 5.25 MeV extracted from drinking water with HDEHP is quite likely to be due to uranium.

Table 2 lists common naturally occurring nuclides with alpha energies greater than 5.25 MeV. These nuclides are thus readily distinguishable from

Table 1. Natural Radionuclides with Alpha Emissions Between 3.75 and 5.25 MeV

Nuclide	Half-Life	Alpha Energy (MeV)	Abundance (%)
²³² Th	1.4 × 10 ¹⁰ Y	3.95	24
		4.01	76
²³⁸ U ^a	4.5 × 10 ⁹ Y	4.15	25
		4.20	75
²³⁴ U ^a	2.5 × 10 ⁵ Y	4.72	28
		4.77	72
²³⁰ Th ^a	8.0 × 10 ⁴ Y	4.62	24
		4.68	76
²²⁶ Ra ^a	1.6 × 10 ³ Y	4.62	5
		4.78	95

^a²³⁸U series nuclide.

uranium at the 10% energy resolution currently available. ²²²Rn and its short-lived progeny can be easily excluded by appropriate sample handling. ²²⁴Ra would not be extracted into HDEHP, but would build up with a 3.6 day half-life into any ²²⁸Th extracted. A month after isolation, the ²²⁸Th alpha emissions will be accompanied by several high energy alphas from its progeny, including one at 8.78 MeV. As noted above, however, it is quite unlikely that significant levels of ²²⁸Th would be present in a drinking water sample, except through ingrowth (half-life = 1.9 years) into older samples containing ²²⁸Ra. The presence of significant amounts of ²²⁸Ra in even a fresh sample would cause a "false positive" in the initial screening test due to the rapid ingrowth of ²²⁸Ac, a complex beta emitter with a major portion of its beta emission overlapping the alpha window. Subsequent medium resolution spectrometry would clearly dis-

Table 2. Natural Radionuclides with Alpha Emissions Above 5.25 MeV

Nuclide	Half-Life	Alpha Energy	Abundance (%)
²¹⁰ Po ^a	138.4 D	5.30	100
²²⁸ Th	1.9 Y	5.34	28
		5.43	71
²²⁴ Ra ^b	3.6 D	5.45	6
		5.68	94
		6.05	25
		6.09	10
		6.29	100
		6.78	100
²²² Rn ^{a,b}	3.8 D	8.78	36
		5.49	100
		6.00	100
		7.69	100

^a²³⁸U series member.

^bIncludes radiations from short-lived daughters.

Table 3. Important Artificial or Enriched Alpha Emitters

Nuclide	Half-Life	Alpha Energy	Abundance (%)
²³⁵ U	7.1×10^8 Y	4.37	18
		4.40	57
		4.42	5
		4.56	5
²³⁷ Np	2.1×10^6 Y	4.8c ^a	86
²⁴² Pu	3.8×10^5 Y	4.86	24
		4.90	76
²³⁹ Pu	2.4×10^4 Y	5.10	12
		5.14	15
		5.16	73
²⁴¹ Am	458 Y	5.44	13
		5.49	86

^aComplex peaks near 4.8 MeV.

tinguish between uranium isotopes and actinium. This, in effect, leaves ²¹⁰Po as the only common natural alpha emitter in this energy range likely to be present in a timely HDEHP extraction from potable water.

If artificial transuranic nuclides might be present in a sample, the situation becomes more complicated, as illustrated in Table 3. ²⁴¹Am alphas are energetic enough to be distinguished from ²³⁴U at 10% resolution, but ²³⁹Pu is only marginally distinguishable. ²⁴²Pu and ²³⁷Np would be interpreted as uranium unless higher resolution spectroscopic techniques or chemical separations are employed.

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