

MEASUREMENT OF ISOTOPIC URANIUM IN TEXAS DRINKING WATER SUPPLIES BY LIQUID SCINTILLATION WITH ALPHA-BETA DISCRIMINATION

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ABSTRACT. We describe a simple, sensitive method for the measurement of uranium isotopes in water. We dispersed 20 ml of liquid scintillant suitable for both solvent extraction and alpha/beta discrimination in one liter of water at pH 1. Upon phase separation, U was nearly quantitatively extracted. (High yields of other actinides are also expected from theoretical considerations, but we have not confirmed this experimentally.) Pulse-shape-discrimination circuitry on the Beckman LS 6000 system permits α emissions from the extracted nuclides to be counted with near 100% efficiency against a background of 0.75 counts per minute (cpm). Alpha energy resolution is influenced by the concentration of U and other quenching agents, but is sufficient to permit the determination of $^{238}\text{U}/^{234}\text{U}$ ratios, and to distinguish between U and most other natural α emitters. The utility of this method is illustrated in a preliminary survey of Texas water systems that previously showed high levels of gross α activity.

INTRODUCTION

^{238}U and ^{234}U are often found in considerable radiological disequilibrium in potable waters (e.g., Kronfeld 1974). Conventional fluorometric methods are sensitive only to ^{238}U , and are subject to over- or underestimation of total U activity in proportion to the degree of disequilibrium. Gross alpha counting techniques respond to all U activity, but are unable to distinguish between U and other α emitters (an important consideration since maximum contaminant levels are based on nuclide-specific dosimetric properties). Alpha spectrometry with solid-state detectors easily resolves ^{238}U and ^{234}U (4.2 and 4.75 MeV average energies) as well as most other α emitters, but is more resource-intensive than fluorimetry or gross α counting. Prichard and Cox (1991) previously described modifications of extractive liquid scintillator techniques (McDowell 1986) for use with conventional liquid scintillation counting (LSC) systems. The advent of pulse-shape discrimination (PSD) circuitry on newer counting systems, such as the Beckman LS 6000, greatly extends the potential of solvent extraction techniques for measuring U and other actinides in water. A parameter, termed the R value, is assigned to each pulse on the basis of its decay time. In certain solvents, the difference in R values between typical alpha and beta pulses is sufficient to permit nearly complete separation of α and β pulses on this basis. The combination of large-volume solvent-extraction techniques with PSD abilities in conventional LS systems results in a simple analytical procedure that provides more spectral information than gross α counting and provides a much more accurate indication of total U activity than does fluorimetry.

METHODS

The difference in pulse duration upon which α/β discrimination rests is largely determined by the solvent. We have not encountered a solvent that exceeds the toluene-naphthalene solution described in McDowell (1986), but the pulse-shape resolution is a sensitive function of oxygen content. Diisopropylnaphthalene (DIN) and mixtures of DIN and phenylxylylene (PXE) produced adequate α/β separation, and their performance was not seriously degraded upon exposure to oxygen. Our initial work was conducted with Optiscint HiSafe™, a DIN-based commercial "environmentally safe" cocktail, to which we added 60 g liter⁻¹ of bis(2-ethylhexyl)phosphoric acid (HDEHP). (The

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addition of HDEHP seriously reduces the “environmentally safe” aspect of the solution.) Superior α/β resolution was noted subsequently with a prototype of the Excellent cocktail, which was used during the later phases of the project.

Maximum energy resolution was achieved by distributing emitted light as evenly as possible over the photomultiplier tubes. Translucent vials that diffuse light permit better energy resolution than transparent vials. Coating the bottom of the translucent vials with a reflective material also enhances α energy resolution. However, high concentrations of U tend to limit energy resolution, as discussed below.

Water samples were acidified with nitric acid to a pH between 1.0 and 2.0. At least ten volumes of nitrogen, aged air, or other radon-free and relatively non-reactive gas were bubbled through the sample to strip out any residual Rn. The sample was transferred to a 1-liter florence flask to which 20 ml of extractive scintillator was added. The phases were contacted by vigorous stirring with a magnetic bar for 30 min, after which the phases were allowed to separate. (DIN and PXE have specific gravities near one, and full phase separation requires several hours.) The organic phase was then pipetted from the neck of the florence flask and transferred to a tared plastic scintillation vial. We noted the weight of the transferred solution. Complete recovery of the scintillation solution is not necessary, provided that the fractional recovery is determined.

We identify pulses as either α or β/γ on the basis of “R value”, as described in the Beckman LS 6000 Operating Manual. Alpha and β/γ spectra are accumulated separately and, in principle, can be inspected for each sample. However, in most drinking-water screening programs, most samples probably do not contain sufficient activity to warrant full spectral analysis. These samples can be identified readily on the basis of integrated count rate in a region of interest set around the U α peaks. The minimum detection level for a 20-min count in this region is 0.01 Bq liter⁻¹ (0.3 pCi liter⁻¹), as described below. Samples showing significantly greater activity can then be recounted for longer periods to permit spectral analysis.

RESULTS

Alpha peak positions are influenced by the degree of quenching in the system. We observed the following relation between the H number (a measure of quench on Beckman systems) and the centroid of the ²³⁸U α peak in channel numbers (N)

$$N = 595 - 3.64(H) \quad . \quad (1)$$

Regressing α energy (E_α) against the centroid of the associated peaks (channel number, N) produced the following relation for a solution with an H number of 35

$$E_\alpha \text{ (MeV)} = 2.42 + 0.00384 N \quad . \quad (2)$$

The corresponding β -energy relation is

$$E_\beta \text{ (MeV)} = 0 + 0.000488 N \quad . \quad (3)$$

It is conventional in LSC to calibrate the energy scale for β energy. From the above equations, we see that the relation between α energy and α energy expressed in β energy units is approximately

$$E_\alpha \text{ (MeV)} = 2.42 + 7.85E_\beta \text{ (MeV)} \quad . \quad (4)$$

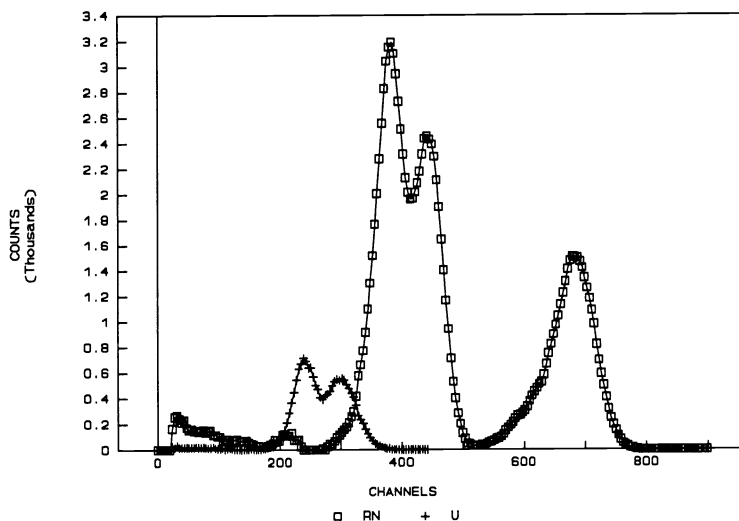


Fig. 1. α energy spectra of Rn and U in an extractive scintillator

Figure 1 shows the α spectrum of a solution containing both $^{238+234}\text{U}$ and ^{222}Rn with a β energy scale. The α peaks of ^{238}U , ^{234}U , ^{222}Rn , ^{218}Po , and ^{214}Po (4.2, 4.8, 5.5, 6.0, and 7.7 MeV, respectively) range from 200 to 800 keV on the β energy scale. (We note that the presence of U in the solution has degraded the energy resolution of both U and Rn spectra. Under similar conditions, but without appreciable quantities of U, the resolution of the 5.5 and 6.0 MeV features in the Rn spectrum is considerably more distinct.)

At a narrow window set around the U α feature, the α background count rate was 0.13 cpm. Without energy discrimination, the α background was 0.75 cpm. In this wider window, virtually 100% of α emissions in the solution are detected.

In a 20-min screening count, 15 counts are expected in the wide window, with a Poisson standard deviation of 3.9 counts. A minimum detection level of three standard deviations above the blank corresponds to 11.6 counts per 20 min, or .01 Bq (0.27 pCi). As the procedure assumes nearly complete extraction from 1 liter of water, the MDL corresponds to .01 Bq liter⁻¹ (0.27 pCi liter⁻¹). Lower limits can be achieved by narrowing the counting window and/or increasing the counting time.

We determined extraction efficiencies by adding known quantities of U acetate solution to liter quantities of distilled water and performing the extraction procedure described in the previous section. The fraction of scintillation solution recovered was determined by weight, and the α activity detected in the recovered scintillator was normalized to the weight of the scintillator initially added. We found U recovery to be virtually quantitative in the pH range of 1.0 to 2.0, as stated by McDowell (1986). Under the same conditions, ^{226}Ra was not detectably extracted.

SURVEY OF TEXAS WATER SUPPLIES

We conducted a field test of our method on 12 samples from Texas water systems with previously reported high ^{226}Ra or gross α levels. We analyzed three replicates of each sample for U and actinides. Table 1 presents the results. The three samples with gross α activities >0.5 Bq liter $^{-1}$ (2013, 2111 and 2103) were recounted for 500 min each to permit a detailed examination of the α spectra. Figures 2, 3 and 4, respectively, show these spectra. Only one (Sample 2013) displayed approximate equilibrium between ^{238}U and ^{234}U . Sample 2111 appears to be ^{234}U without detectable

TABLE 1. Texas Water Supply Survey Results (3 Replicates per Sample)

Sample ID	Mean (Bq liter $^{-1}$, gross α)	Standard deviation	Standard error of mean (%)
2108	0.02	0.005	13
2010	0.03	0.003	5
2112	0.01	0.004	23
2104	0.04	0.007	12
2105	0.10	0.008	5
2106	0.03	0.005	9
2013	2.50	0.007	0.2
2107	0.08	0.006	4
2102	0.16	0.016	6
2101	0.03	0.004	9
2111	1.30	0.029	1.3
2103	0.56	0.053	6

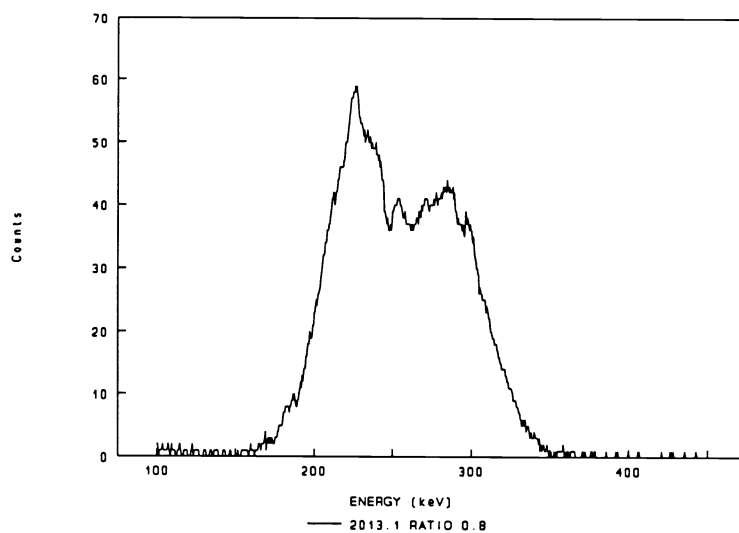


Fig. 2. U extraction from a Texas public drinking water supply displaying approximate ^{234}U - ^{238}U equilibrium

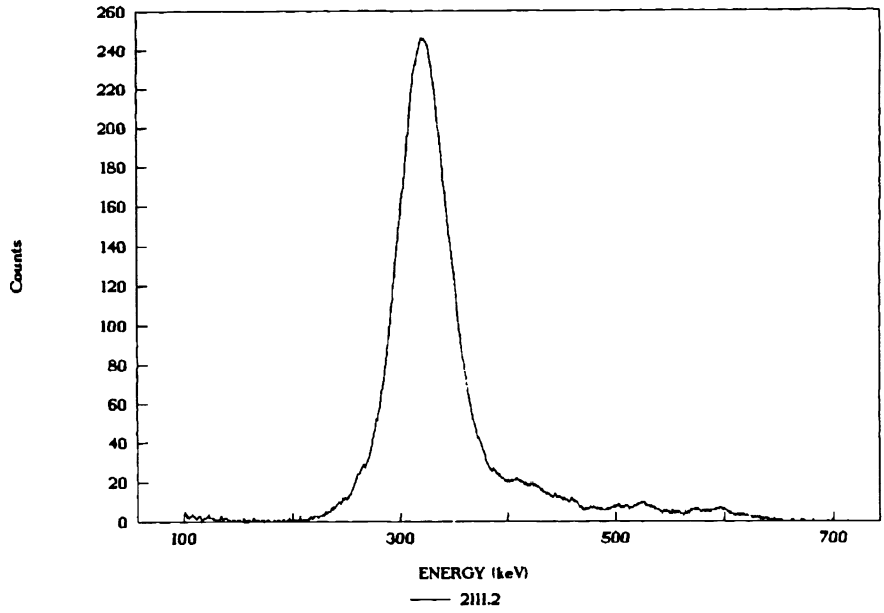


Fig. 3. U extraction from a Texas public drinking water supply showing ^{234}U with no detectable ^{238}U

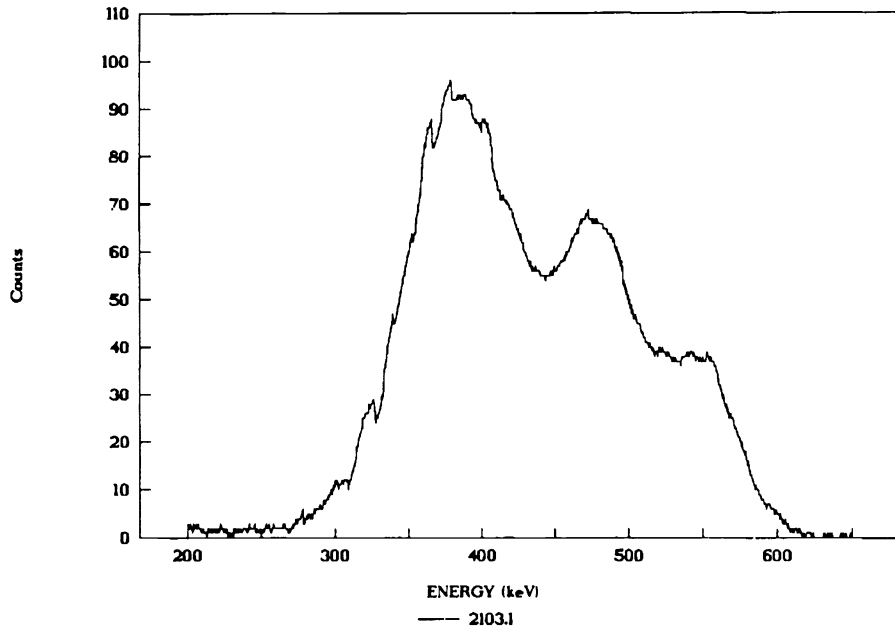


Fig. 4. Extraction from a Texas public drinking water supply of what appears to be the composite α spectrum of ^{228}Th and progeny

levels of ^{238}U in the same sort of marked disequilibrium noted by Kronfeld (1974). This activity would have gone unnoticed in a fluorometric U determination.

The spectrum of the third sample, 2103, did not appear to be due to U alphas. The energies were too high and the shape of the spectrum was wrong. The spectrum is consistent with the α -emitting daughters of ^{228}Ra , headed by ^{228}Th . However, one component of that series, the 8.8-MeV emission of ^{212}Po , was conspicuously absent. But the half-life of ^{212}Po is only 300 nsec, and its α emission is preceded by the 2.26-MeV β decay of ^{212}Bi . The LS 6000 circuitry would classify the dual decay as a single α event, but, because of the high relative light output of β particles, the assigned energy would be off-scale. In the prototype unit used in this project, such events are assigned to a high-end channel. These events normally comprise about 3% of the total α counts in a typical U spectrum and are not included in the analysis. In the case of Sample 2103, 18.9% of the total α counts were in this channel. The ~16% increase in this channel is consistent with the counts expected from the missing ^{212}Po peak. The total lack of 4.0 MeV alphas precludes the possibility that these counts were due to ^{232}Th contamination from reagents in our laboratory. Because of its insolubility, unsupported ^{228}Th is not likely to be found in natural waters. Sample 2103 had been stored at low pH for at least six months prior to analysis, allowing time for significant ingrowth from ^{228}Ra , which is considerably more soluble than thorium under natural conditions. At this writing, the aqueous phase is being analyzed for ^{228}Ra to test the hypothesis that the observed α spectrum is due to ^{228}Th and its progeny.

CONCLUSIONS

Solvent extraction combined with α/β discriminating LSC is a sensitive and informative alternative to conventional methods for screening water supplies for U and other actinide activity. The same simple preparation procedure produces a sample suitable for quick screening or for detailed spectral analysis. A preliminary survey of water supplies with known elevated gross α counts revealed several unanticipated nuclide mixtures that were first detected in a screening run and then investigated in a spectrographic run. Further research will determine other actinide recovery rates and extend the technique to include non-actinide nuclides of interest, primarily ^{226}Ra and ^{228}Ra .

ACKNOWLEDGMENTS

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