

DETERMINATION OF ^{222}Rn IN DRINKING WATER USING AN ALPHA/BETA LIQUID SCINTILLATION COUNTER

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ABSTRACT. The U. S. Environmental Protection Agency's (EPA) proposed rule on the National Primary Drinking Water Regulations, as related to radionuclides in drinking water, will stimulate a new interest in analysis methods for ^{222}Rn . It is estimated that the EPA's proposed maximum contaminant level (MCL) of $11.1 \text{ Bq liter}^{-1}$ for ^{222}Rn will require the expenditure of \$1.6 billion in capital equipment for treating systems and an annual monitoring cost of \$5 million. Compliance with this new regulation will require a considerable increase in the number of measurements conducted on ^{222}Rn in water. In order to cope with this anticipated analytical demand, we evaluated alpha/beta liquid scintillation counting (LSC) vs. beta LSC counting. We also report comparative ^{222}Rn results for water from wells and from public water systems from northeast Georgia.

INTRODUCTION

In July 1991, the U. S. Environmental Protection Agency (EPA) issued proposed National Primary Drinking Water Regulations that set forth the maximum contaminant levels (MCLs) for several radionuclides. The proposed regulations will affect all public water systems that depend in whole or in part on a groundwater source, requiring, at a minimum, a program of regular monitoring for radionuclides. The proposed MCL for ^{222}Rn , at $11.1 \text{ Bq liter}^{-1}$ ($300 \text{ pCi liter}^{-1}$), is certain to have far-reaching consequences. The EPA estimates that some 26,000 public water systems in the United States will exceed this level, requiring capital expenditures of approximately \$1.6 billion for the construction of treatment facilities. Annual costs for monitoring requirements are expected to be an additional \$5 million (EPA 1991). The EPA anticipates that public health benefits will justify the investment in this major ^{222}Rn monitoring and treatment program.

During the past decade, much work has been reported on the health risks related to ^{222}Rn in air, and it is well established that inhalation of ^{222}Rn is the primary route of exposure to radiation (Prichard & Gesell 1981; Crawford-Brown 1987). Investigations related to ^{222}Rn in groundwater have been primarily concerned with the contribution to ^{222}Rn concentrations in air as a result of its volatilization from water used in the home. Much less attention has been given to the effects of the direct ingestion of ^{222}Rn in drinking water, but at least one recent study has indicated that it is more important than previously thought (Gosink, Baskaran & Holleman 1990).

As a result of both the proposed EPA regulations and the heightened awareness of the health risks posed by inhalation and direct ingestion of ^{222}Rn , the need for appropriate instrumentation for measuring ^{222}Rn concentrations in water will increase. Public compliance with EPA regulations will result inevitably in a demand for increased efficiency in analytical services, lower limits of detection and faster sample turnaround times, all at a minimum cost to the consumer.

Concentrations of ^{222}Rn in water are determined using either the Lucas (1964) cell method or by liquid scintillation counting (LSC). The Lucas cell method permits alpha counting against a low background for an overall high counting efficiency and a good detection limit. However, the large sample volumes required and the time needed for sample preparation and handling generally preclude the efficient use of this method in large-scale environmental programs. 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 limits on the order of $0.37 \text{ Bq liter}^{-1}$. Recent advances in LSC electronics have now

been incorporated into commercially available alpha/beta counters that use pulse-shape analysis for superior and rapid counting results for the determination of ^{222}Rn concentrations in water (Dazhu, Yongjun & Mobius 1991; Prichard, Venso & Dodson 1992).

The Center for Applied Isotope Studies (CAIS) has tested a new Packard Tri-Carb® 2550TR/AB α/β LS counter, using samples of water from wells and public water systems in northeast Georgia. Results from the α/β counter compared favorably to results from the same samples counted in a Tri-Carb® 2250LL β LS counter. Background was reduced significantly, from approximately 4 counts per min (cpm) to ~ 0.15 cpm. Sample counting times were reduced fivefold to reach the same detection limit, from 45 min to less than 10 min per sample.

METHODS

Water samples were collected using glass bottles with Teflon-lined rubber septa as described by Vitz (1991). Counting samples were prepared by injecting 10 ml of sample water under a 10-ml layer of organic scintillation cocktail in a glass LS vial, as described by Prichard and Gesell (1977). We investigated three high-flash-point organic cocktails for use in determining ^{222}Rn concentrations in the water samples: mineral oil (NEN Cat.# PSS-007H); di-isopropylnaphthalene (DIN) with 6 g liter $^{-1}$ PPO + 0.2 g liter $^{-1}$ POPOP; and a 50-50 mixture of phenyl-ortho-xylene (DIN/PXE) with 2.4 g liter $^{-1}$ PBBO. DIN was the most appropriate cocktail for this study. After the vials were capped and shaken vigorously to extract the Rn from the aqueous phase into the organic phase, they were allowed to sit for 4 h to allow the ^{222}Rn daughters to reach equilibrium. Samples were counted using the Tri-Carb® 2550TR/AB LS counter in the α/β counting mode. Water samples were also counted using mineral oil cocktail in a conventional LS counter for purposes of comparison.

The optimum pulse decay discriminator (PDD) setting for separating alphas from betas is dependent upon the cocktail, chemistry and sample load. To determine the optimum PDD setting, the manufacturer recommends counting a pure α emitter, such as ^{241}Am or ^{210}Po , and a pure β

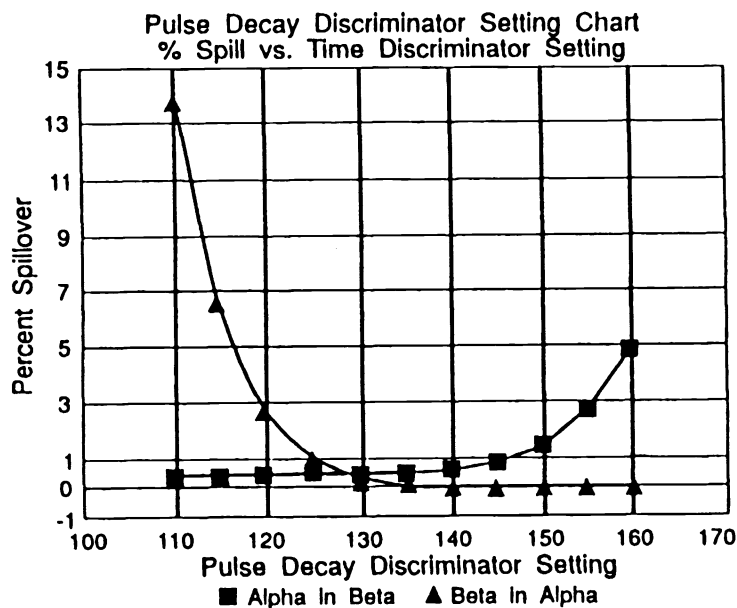


Fig. 1. Typical α/β crossover plot, ^{241}Am and ^{36}Cl . From Passo and Kessler (1992), reprinted with permission of the authors and Packard Instrument Co.

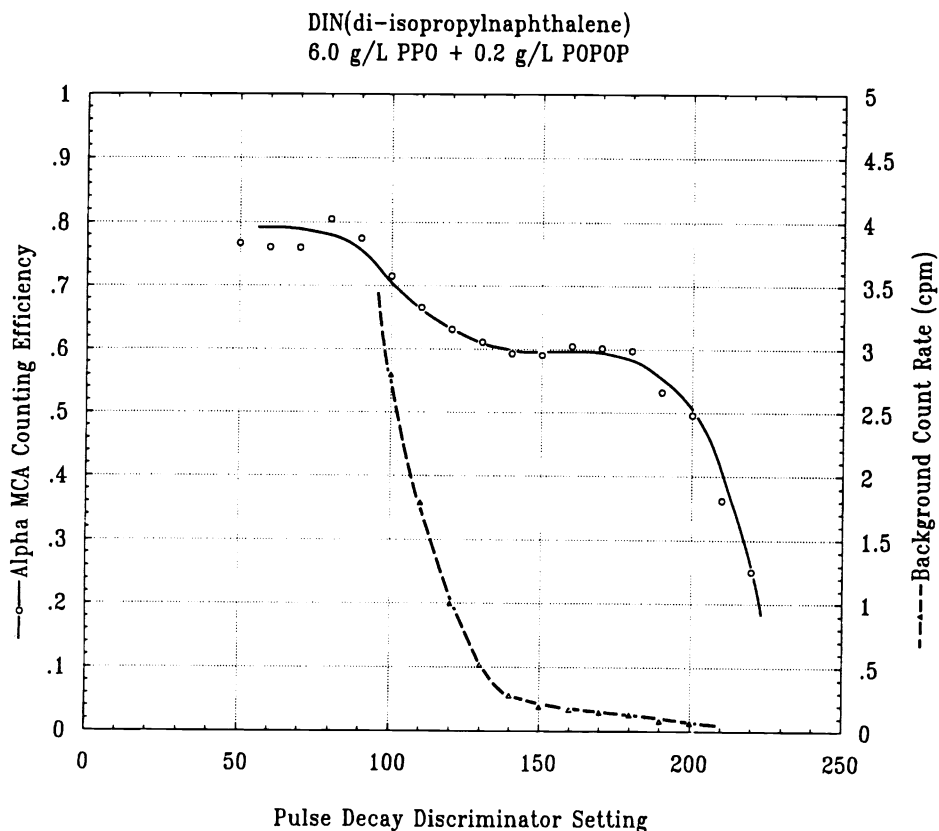


Fig. 2. Relative counting efficiency for α MCA vs. PDD setting for DIN cocktail

emitter, such as ^{36}Cl , to produce a crossover chart, shown in Figure 1. This figure shows the spillover of α counts into the β multichannel analyzer (MCA) and the β counts into the α MCA.

Another way to determine the optimum PDD setting with a mixed α/β sample, such as ^{222}Rn , is to plot α MCA count rate vs. PDD setting (Fig. 2). At low PDD settings, betas are counted in the α MCA, and with a wide-open energy window, the counts should approach five times the disintegration rate of ^{222}Rn , as 3 alphas and 2 betas are in the decay of ^{222}Rn and its short-lived progeny. Adding energy discrimination by setting a pulse-height window around the α peaks (Fig. 3A) lowers the count rate in the α MCA to approximately four times the disintegration rate of ^{222}Rn , as this rejects about one-half of the betas.

As the PDD setting is increased, fewer betas are counted in the α MCA until a point is reached where essentially all betas are excluded and a plateau appears in the midregion. At this point, the α MCA count rate should be three times the disintegration rate of ^{222}Rn . Figures 3A and B show the α MCA spectra and β MCA spectra, respectively, using a PDD setting in this plateau region. Continued increases in the PDD setting lead to a point where alphas begin to be counted in the β MCA. If the background count rate in the α MCA is also plotted on this graph, as shown in Figure 2, an optimum PDD setting can be chosen where the slope of both the counting efficiency and background are zero. This PDD setting yields a very stable setup for counting alphas with this cocktail and chemistry.

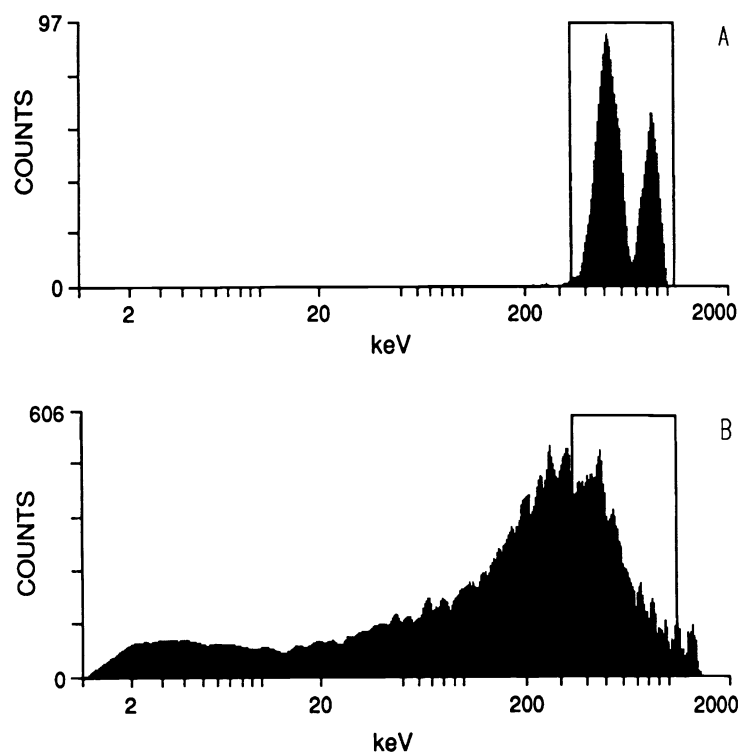


Fig. 3. A. α MCA spectrum and B. β MCA spectrum

RESULTS

Figures 2 and 4 show the relative counting efficiency for the α MCA vs. the PDD settings for DIN and DIN/PXE cocktails, respectively. Background count rate is also shown vs. PDD settings for each cocktail. Each plot has an expected shape, with the highest count rate occurring at low PDD settings, as both alphas and betas in the energy window are counted in the α MCA (Table 1). As the PDD setting is increased, a point is reached where only alphas are counted. Continued increases in the PDD setting eventually reach a point where alphas begin to be counted in the β MCA. The optimum operating point would be somewhere in the central plateau region where the background changes very slowly with changes in PDD.

Figure 5 shows the α MCA count rate for two samples vs. PDD settings for the mineral oil cocktail. One sample was a standard made by using ^{226}Ra water, allowing it to come to secular equilibrium, and the other was well water known to have significant amounts of ^{222}Rn . The responses from these samples are not as expected, as they show no central plateau region, and as the PDD is increased the counting efficiency of the well-water sample drops off much more rapidly than for the ^{226}Ra standard. Each sample had a different quench as indicated by the transformed spectral index of external standard (tSIE). The well-water sample had a tSIE of 535 compared to 597 for the ^{226}Ra standard sample. Further studies will be carried out to determine the cause of this difference.

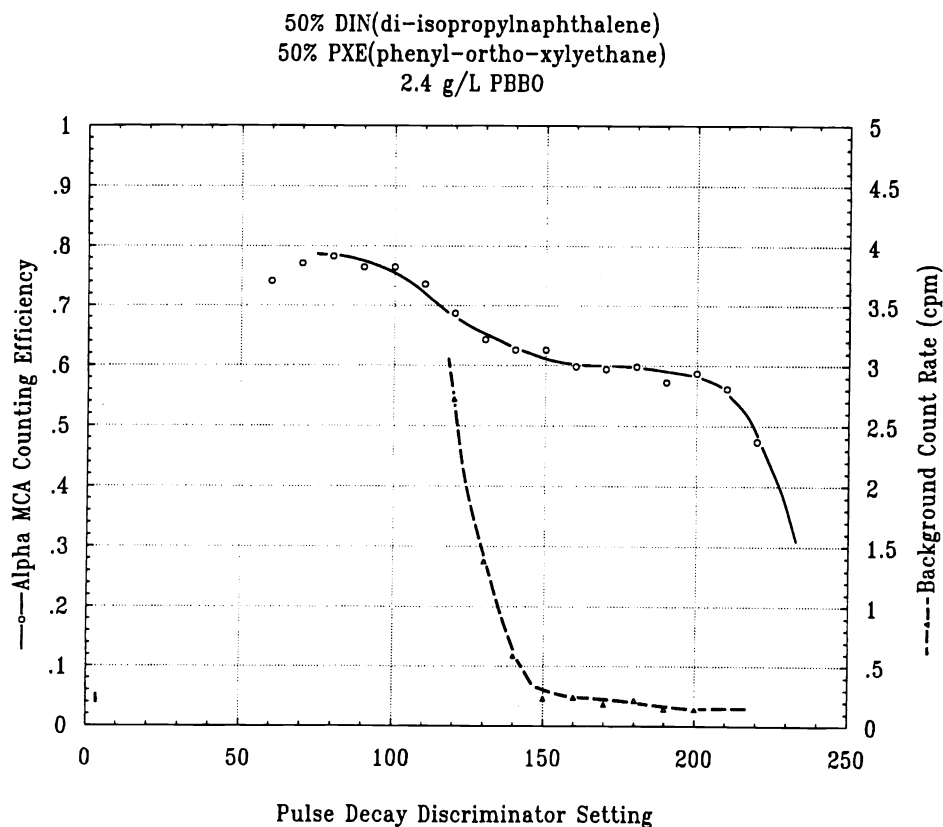


Fig. 4. Relative counting efficiency for α MCA vs. PDD setting for DIN/PXE cocktail

TABLE 1. Minimum Detectable Activity at 95% Confidence

LS counter	Cocktail 10 ml	Sample volume (ml)	tSIE	PDD	Energy window (keV)	Bkg (cpm)	Count time (min)	MDA Bq liter ⁻¹
Tri-Carb® 2550TR/AB	DIN	10	756	170	350–1100	0.15	7	0.976
Tri-Carb® 2550TR,AB	DIN/PXE	10	693	170	300–1000	0.18	7	1.04
Tri-Carb® 2250LL	Mineral oil	10	580	--	200–700	3.89	45	0.985

Table 1 lists the chosen counting conditions and the corresponding calculated minimum detectable activity (MDA) using the method outlined by Currie (1968), discussed by Passo and Kessler (1992), and based on the following equations

$$MDA (95\%) = \frac{4.65S_b + 2.71}{K\varepsilon VT} \tag{1}$$

If we assume that $S_b = (C_b T)^{1/2}$, then

$$\text{MDA (95\%)} = \frac{4.65 \left(\frac{C_b}{T}\right)^{1/2} + \frac{2.71}{T}}{K\varepsilon V} \quad (2)$$

where MDA (95%) = minimum detectable activity at 95% confidence interval (Bq liter⁻¹)
 C_b = background count rate (cpm)
 T = sample count time (min)
 ε = counting efficiency
 V = sample volume (liter)
 K = 60

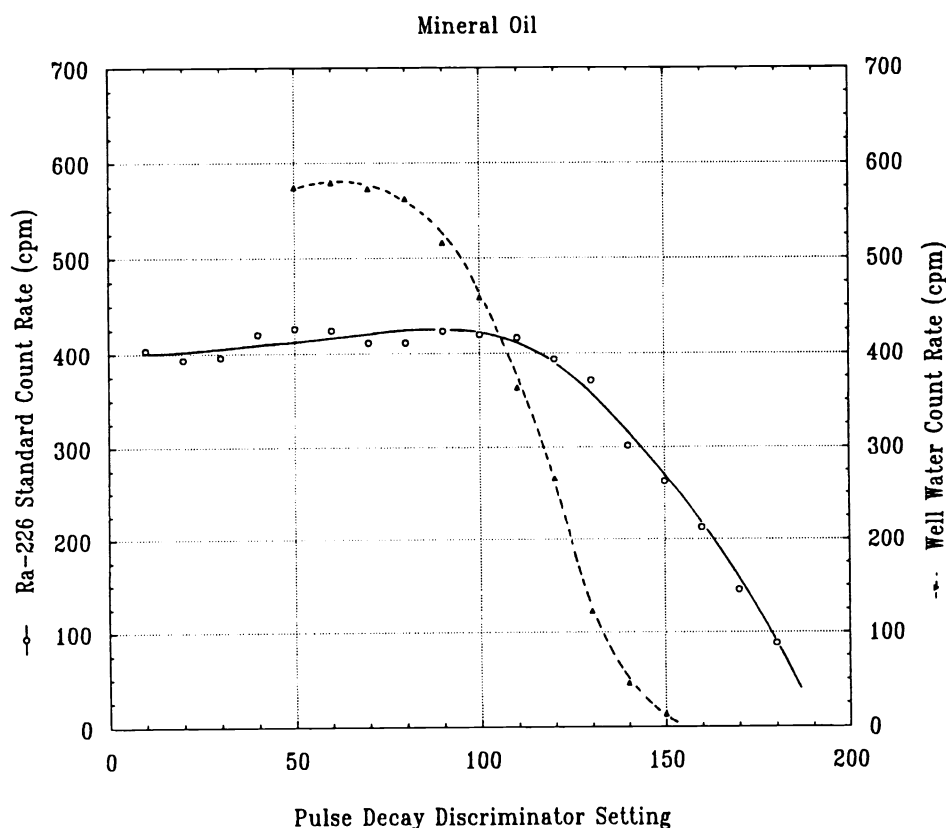


Fig. 5. Count rate for α MCA vs. PDD setting

Figure 6 shows the MDA for both types of LS counters as a function of sample count time. For an MDA of 1 Bq liter⁻¹, the count time of the α/β counter is reduced by at least a factor of five over the count time of the β counter.

Due to the problems encountered with the mineral oil cocktail, it was not used for determining ²²²Rn concentrations in the water samples on the Tri-Carb® 2550TR/AB counter. The DIN cocktail

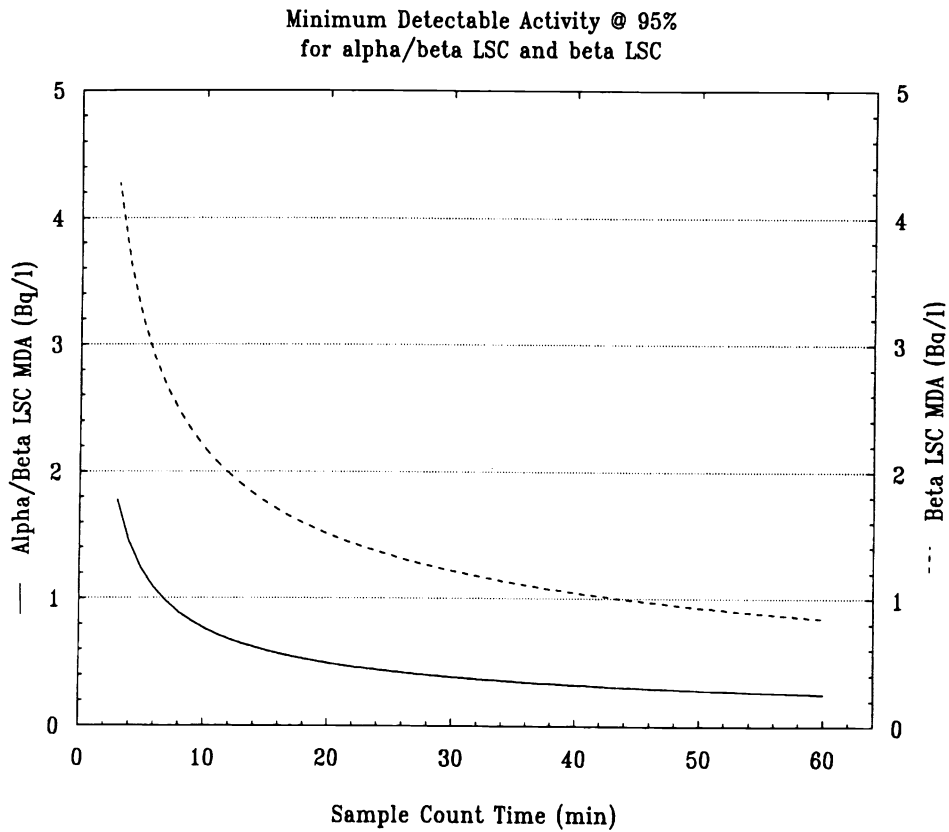


Fig. 6. Minimum detectable activity (95%) for α/β and β LS counters

TABLE 2. Public Water Systems

City	tSIE	Bq liter ⁻¹
Athens, GA	742	0.32 ± 0.11
Commerce, GA	726	0.73 ± 0.19
Ila, GA	754	56.7 ± 1.85

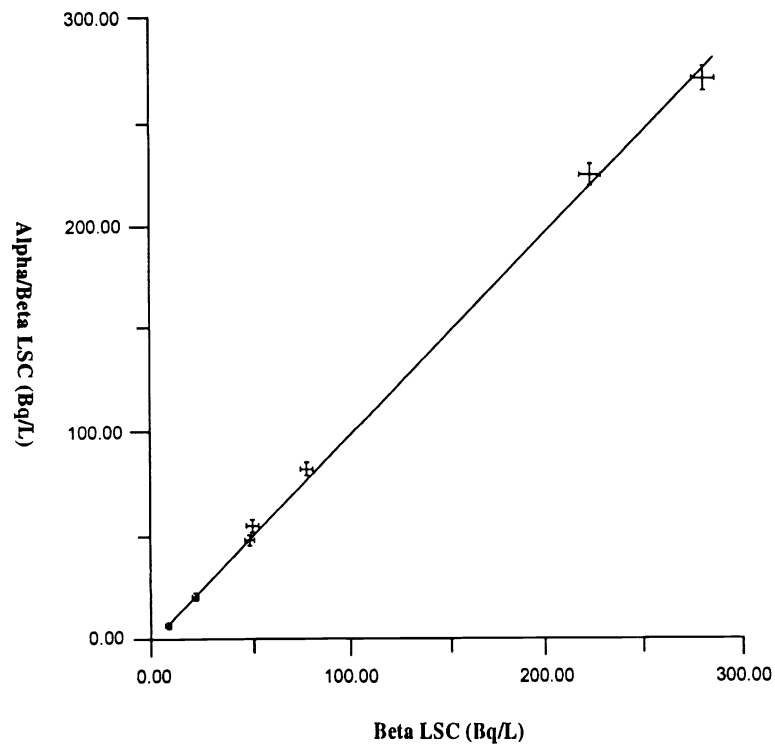
was chosen for use over the DIN/PXE cocktail because of its slightly lower background and the flatter central plateau region on the curve. Other cocktails will be examined for future use.

Table 2 lists the results of sampling some public water systems in a 40-km radius of Athens, Georgia. The cities of Athens and Commerce obtain their water from rivers, and as expected, the ^{222}Rn concentrations are quite low. On the other hand, Ila is a small town that derives all of its water from wells ~200 m deep. This water exceeds the proposed EPA MCL for ^{222}Rn by a factor of five, and will require remediation.

Table 3 details the ^{222}Rn activities obtained when well-water samples were counted in a conventional LS counter using a mineral oil cocktail and in the Tri-Carb® 2250TR/AB using a DIN-based cocktail. These samples are taken from wells that are located within 15 km of Athens, Geor-

TABLE 3. Private Wells

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

Fig. 7. ²²²Rn activities from α/β vs. β LS counters (error bars are $\pm 2 \sigma$)

gia. As expected, the samples from deeper wells had the higher concentrations of ²²²Rn, with the exception of well #7. The results are typical of ²²²Rn concentrations found in northeast Georgia, with exceptions that are dependent on the underlying geology. Figure 7 shows the data from the β LS counter plotted against the data from the α/β counter and demonstrates a good correlation between these two counting methods.

CONCLUSIONS

The concentrations of ^{222}Rn in drinking water using an α/β LS counter reported here compare favorably to results from samples counted using a β LS counter. Background was reduced significantly, from about 4 cpm to 0.15 cpm. The count time was reduced to 1/5 of that required for standard LS counters, so that sample throughput is increased by a factor of five. This increase will gain importance as the EPA compliance deadline of January 1996 approaches and the number of water samples requiring ^{222}Rn testing rises dramatically.

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