

Measuring Low Radon Levels in Drinking Water Supplies

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Because a relatively low maximum contaminant level (approximately 300 pCi/L) is expected to be set for radon in the near future, research was conducted with liquid scintillation counting to determine whether this method of analysis could be used for low levels of radon. Counting with an optimized window and an optimized water-to-fluor ratio resulted in achievement of a lowest quantifiable level of 150 pCi radon/L. Lower levels can be quantified using a longer counting period.

Maximum contaminant levels (MCLs) for additional radionuclides are expected to be announced in the fall of 1991 by the US Environmental Protection Agency (USEPA). Radon (Rn) and uranium (U) will join radium (Ra-226 and Ra-228) as regulated radionuclides. The MCL for Rn is expected to be relatively low (approximately 300 pCi/L) compared with existing unofficial criteria and will have a significant impact on public groundwater supplies.¹ Because there is no separate method in *Standard Methods* for analyzing water for Rn, the USEPA's Las Vegas laboratory is currently engaged in evaluating two analytical methods: (1) liquid scintillation counting (LSC) and (2) Lucas cell counting. Earlier work published by the USEPA recommended that these two methods be considered validated and equivalent.² That research concluded that the LSC method is slightly more precise and accurate than the Lucas cell method, based on a collaborative assessment involving 18 laboratories. The USEPA is continuing its evaluation of the two methods, with a greater emphasis on LSC for Rn in drinking water.³ It is clear from that work and the large number of samples that will have to be analyzed that the LSC method is the more practical method. The LSC method is not as labor-intensive and is simple to perform.

Optimization of the LSC method for Rn has received little attention because most interest has been placed in waters having relatively high Rn (>1,000 pCi/L). In fact, until very recently a range of 10,000-40,000 pCi Rn/L in water was used by some states as an unofficial criterion for requiring treatment. For high Rn levels, the uncertainty of counting is low and optimization has not been an issue. The article most often cited by researchers employing LSC for Rn analysis is one by Prichard and Gesell.⁴ Kinner et al have investigated some of the details of sampling and analysis.⁵ In general, it appears that little effort has been made to optimize the LSC method for low Rn levels. The term optimization in this article means the process of establishing a standard protocol that will result in the minimum counting uncertainty. In

summary, there is a need to improve the existing method of analysis for Rn in drinking water supplies. Large numbers of Rn analyses will be dictated by the new regulation, and the current LSC method has not been optimized.

Recent research sponsored by the AWWA Research Foundation has significantly improved the existing LSC method for Rn and has introduced new methods for the analysis of U and Ra. This article summarizes the research involving LSC analysis of Rn.

Laboratory

All of the Rn analyses and experiments were conducted in a combined commercial and research laboratory* that routinely performs Rn and other radionuclide analyses for the water supply industry. More than 5,000 Rn samples have been analyzed by the laboratory, and analysis has progressively approached the optimized Rn protocol described in this article during the past two years (the final protocol was adopted for routine analysis in November 1990).

Experimental methods

Before explaining the methods used in this research, it is useful to provide some definitions of general terms used in the field of LSC. LSC cocktails are the solutions that contain the fluors that provide the link between atoms decaying and the

measurement of light energy by a photomultiplier tube. It is common to refer to the LSC cocktail as the fluor. The cocktail solvent and its solutes facilitate a transfer of kinetic energy into emitted photons. In the case of Rn, the fluor is immiscible and is also responsible for the extraction of Rn from the water. Progeny of Rn are not extracted but are produced by the ingrowth process from the extracted Rn. This process takes approximately 4 h, and at that point the LSC fluor contains Rn and its first four progeny, in secular equilibrium with Rn. Secular equilibrium means that Rn and all four progeny are at the same level of activity. All isotopes are counted by alpha or beta decay, and associated gamma radiation is also present.

In general, a typical commercial LSC used for Rn analysis does not represent the alpha energy of decay accurately on the spectral abscissa scale. For example, an alpha decay is detected at an energy approximately one tenth of the absolute energy value. These instruments represent the beta decay energy more closely, are approximately calibrated for 0-2,000 keV, and are commonly referred to as beta-counting instruments. Although the energy scale is not representative of the exact energy unit, meV or keV, the alpha-decaying isotopes in the fluor are counted with near 100 percent efficiency. The resulting spectrum contains counts of both alpha and beta decay, and channel numbers, rather than energy units, are used on the abscissa scale.

A window is a term used to define the region of interest by channel numbers

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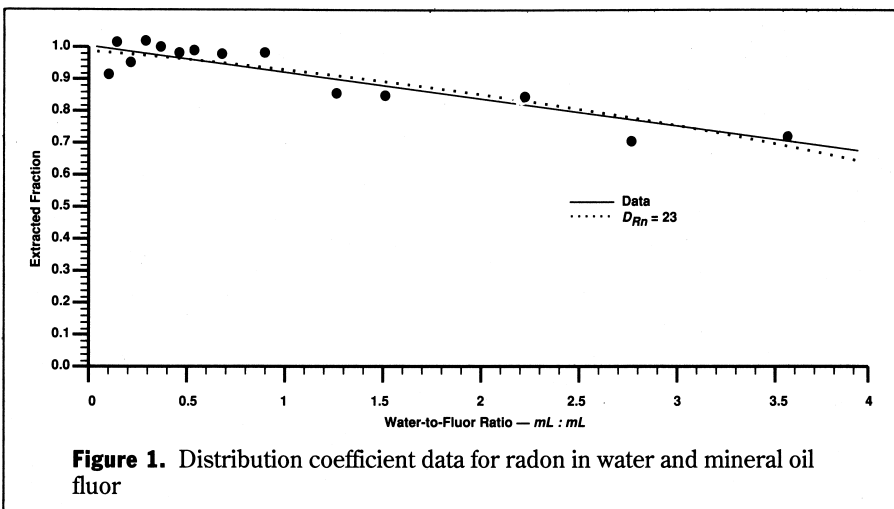


Figure 1. Distribution coefficient data for radon in water and mineral oil fluor

and can range from a one-channel width to a full window, which is 2,000 channels for the specific LSC used in this work. For any given window, there is an associated background count rate that results from a blank vial containing Rn-free water and the fluor. An important characteristic of any counting instrument detecting radioactive decay is the distribution of background counts along the energy scale (abscissa). For instruments that detect alpha, beta, and gamma activity, the distribution is generally weighted toward the low end of the scale, and is particularly high in the first 25 to 50 channels, because of cosmic activity, fallout, the scintillation vial, and terrestrial radiation. In addition to using heavy lead shielding to minimize background radiation, it is common practice to use a discriminator control to exclude the high background channels from the spectral data during the sample and the blank counts. Through discrimination of the counting window, the counting uncertainty can be minimized. Because the distribution of counts from Rn and its progeny along the energy scale is not the same as the background distribution, it is not a simple procedure to determine the optimum counting window. The optimum counting window is not constant as Rn increases from low to high levels; however, it is only at low levels of Rn that the absolute optimum window is important.

The LSC fluor used throughout the research is a high efficiency, mineral-oil-based scintillation cocktail.* Standards for Rn counting were made from dilutions of a USEPA (National Bureau of Standards-traceable) Ra-226 standard solution. Natural groundwater containing high levels of Rn was used in certain experiments for which there was a need for a short counting time and a low counting uncertainty. The LSC vials were standard 23-mL borosilicate glass with either polycone- or aluminum-faced caps. The LSC instrument† was interfaced to a personal computer and line printer. The LSC instrument gave 4,000 half-channel spectral information from its multichannel analyzer.

Although a specific LSC instrument and fluor were used throughout this research, the results are applicable generally. Some minor variations in the optimum window of discrimination and fine details of the protocol will probably occur with different LSC instruments and fluors, but the general concepts and process of optimization will remain unchanged. With any new setup of equipment and fluor, an optimization process, as described in this article, should be conducted.

Uncertainty

A Rn analysis has uncertainty associated with the sampling step, with

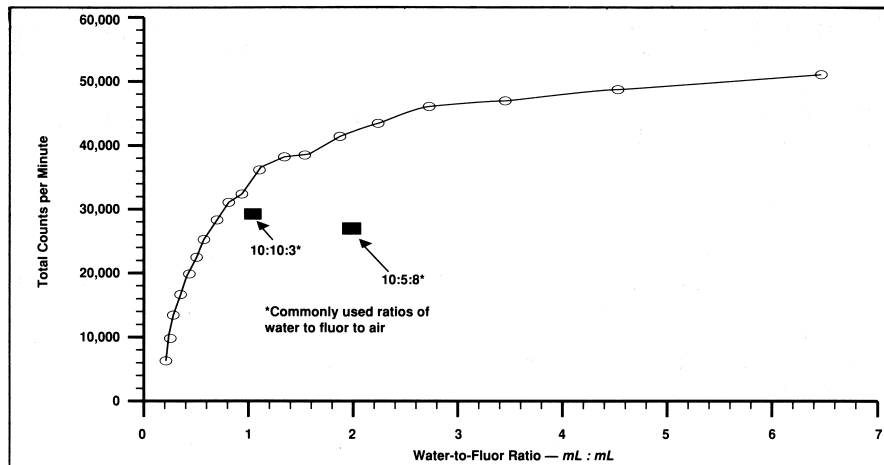


Figure 2. Extraction data for radon with variable water-to-fluor ratios

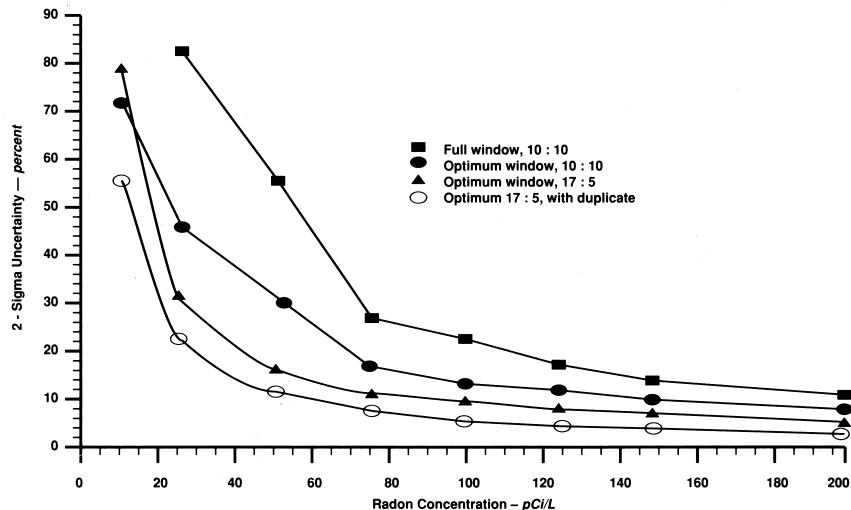


Figure 4. Two-sigma counting uncertainties for four LSC protocols for radon 60-minute counting period

sample setup in the laboratory, and with counting. An analysis of extensive field and laboratory data indicates that the sampling and laboratory handling steps have an associated combined uncertainty <3.0 percent (2-sigma). Earlier studies⁶ reported higher uncertainty for these sources, but hundreds of duplicate public water supply samples analyzed over the past two years have shown that the uncertainty from these sources is low.

For example, the most recent 108 independent duplicate samples (Rn > 500 pCi/L) taken by public water utility personnel across the United States have an average deviation of only 3.17 percent between duplicates compared with their average. These data reflect the total uncertainty associated with the entire process of sampling and analysis, as well as any real change in the Rn level during duplicate sampling. By taking a large number of samples with an Rn level of ≥ 500 pCi/L, the contribution of random counting uncertainty from the data set is virtually eliminated. Thus, the routine combined field sampling and laboratory sample setup uncertainty is <3.0 percent. It is difficult to discern from these data the actual true deviation of Rn between

vials that are sampled successively at a sample tap. It is clear, however, that for certain personnel at specific water utilities, the combined sampling and sample setup uncertainty is routinely <2.0 percent. In summary, deviations between replicate samples of significantly >3.0 percent, which cannot be explained by counting uncertainty, are almost certainly the result of poor sampling, poor setup, or actual temporal variation of the Rn level in the water at the time of sampling. If the samples are true splits, then the error would be from poor sampling or setup.

Ineffectively sealed sample vials have been suspected as a source of Rn loss while the sample is in transit to the laboratory. Because the vials are glass, the cap seal is the only possible route of escape. Silicon rubber septa faced with PTFE are commonly used to seal sample vials. Solid aluminum-lined caps are an alternative. Another alternative is to use direct injection into the LSC fluor vial in the field, without use of an intermediate sample vial for transit to the laboratory.

*NEF 957A, New England Nuclear/Dupont, Boston, Mass.
†Model 1500, Packard/Canberra, Downers Grove, Ill.

