TOWARD A STANDARD METHOD FOR DETERMINING WATERBORNE RADON

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Abstract - Many details of the liquid scintillation method for the determination of waterborne Rn have underappreciated effects on the measurement. This paper quantifies effects arising from the type of cocktail, vial, standardization procedure, temperature control, and instrument parameters chosen in the procedure. Comments are made on sampling procedures, but further investigation regarding sampling techniques has been perfomed by Burkhart, Martin, & Gray (1991). Details are provided that allow an optimization of the technique so that concentrations approaching 8 Bq dm⁻³ (200 pCi/L) can be measured reliably with a precision (2σ) of 20% when counting times are only 20 minutes.

INTRODUCTION

Waterborne Rn has been determined most widely by the Lucas cell (Lucas 1964) and liquid scintillation methods (Prichard and Gesell 1977; Horton 1983), although gamma spectroscopy and many other methods have been employed. The liquid scintillation method is used by large majority of laboratories and has undergone the most extensive interlaboratory comparison studies (Whittaker et al. 1989; Hahn 1990), but the number of variables in both sampling and measurement is great. The goal of this paper is to provide data that support a measurement protocol appropriate for the regulatory maximum contaminant levels contemplated as part of the new Safe Drinking Water Act. Maximum contaminant levels (MCL) in the region of 7.4 - 74 Bq dm⁻³ (200 - 2,000 pCi/L) are under consideration. Very careful attention to methodological detail will be necessary to measure levels at the lower end of this range reliably.

Earlier risk assessments and surveys of waterborne Rn levels have perhaps led to more interest in revealing wells with exceptionally high (i.e.,>185 bq dm⁻³,or 5,000 pCi/L) levels rather than in refining methods to determine levels at or below 74 Bq dm⁻³. MCLs in the range of 37-740 Bq dm⁻³ (1,000-20,000 pCi/L) have been suggested (Cross et al. 1985), and some authors maintain that waterborne Rn levels of 14.8 kBq dm⁻³ (400,000 pCi/L) do not increase the risk of stomach or intestinal cancer by direct ingestion (Dundulis et al. 1984). Studies of both municipal water supplies (Hess et al. 1985) and private wells (Vitz 1988) suggest that waterborne Rn levels are probably lognormally distributed with geometric means in many state exceeding 37 Bq dm⁻³ (1,000 pCi/L), so that there are a

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relatively large number of wells having 74 - 111 bq dm^{-3} (2,000-3,000 pCi/L) of Rn but a relatively small number of wells with greatly elevated levels, although these levels can exceed 37kBq dm^{-3} (106 pCi/L).

New estimates of higher risk due to waterborne Rn, and impending requirements for risk reduction and widespread testing, necessitate specification of efficient methods capable of determining proportionately lower levels, and this report outlines some parameters that must be considered.

METHOD

Equipment

A Beckman 5000 TD liquid scintillation spectrometer[1] was used for all studies where spectra were presented, while a Packard Model 3255[2] was used where spectral analysis was not necessary.

Cocktails

The cocktails investigated were Beckman Ready Organic[1], Packard Optiflour-O[2], Dupont NEN Research Products NEF-957[3], and ICN Biomedicals BetaMax ES[4]. Another commercially available organic cocktail, Ecoscint[5], was not investigated.

Standards and Controls

Standard Ra solutions were obtained from the U.S. EPA Environmental Monitoring Systems Laboratory, Las Vegas, NV, and typically contained 185-555 kBq/kg (5-15 nCi/g) of Ra. The carrier content of some standards was not reported. Standard solutions were delivered with a Gilson Pipetman[6] and weighed with a Mettler AE163 balance (0.01 mg sensitivity) with an interfaced computer running Lotus 1-2-3[7] and National Instruments Measure[8], which simplified accurate recording of successive mass measurements. Cocktail was delivered in to scintillation vials with a Wheaton[9] 10-mL adjustable, self-refilling syringe. Carrier was prepared by dissolving Ba(NO$_3$)$_2$ (Merck S7497, Lot 12263) in 0.5 m HNO$_3$ to make a 15 to 150 ppm solution.

Other Supplies

Transfer syringes for water samples were made by forcing a 6 cm length of Tygon[10] R3603 (1/16" ID, 3/16" OD) tubing to the Luer tip of Becton Dickinson[11] 10 mL disposable syringes, #9604 (Fisher #14-823-2A). Plastic vials were Kimble #58515 20 mL polyethylene with polyethylene cone caps, while glass vials were obtained from Sun Brokers[12]. Glass vials were Kimble XB15288-65 (Fisher 03-337-05) with cork-backed, aluminum foil-lined white urea caps or Kimble XB15287-65 (Fisher 03-337-4 or 03-337-15)

with pulp-backed, polymer-faced, aluminum-lined white urea caps.

GENERAL CONSIDERATIONS

In our "standard" liquid scintillation method for the determination of waterborne Rn, 0.010 dm-³ aliquots of water are added in the field to duplicate scintillation vials containing an immiscible cocktail. In the lab, vials are placed in the spectrometer and time is allowed for distribution of Rn among the three phrases (or four phases if a plastic vial is used) and for the establishment of transient equilibrium. No temperature control was attempted. The samples were each measured for 20 min. sometimes with a selected window, excluding all but a few prominent alpha peaks to reduce background to a minimum. Standards were prepared by weighing Ra primary standards into scintillator vials with carrier and cocktail and allowing 30 d for equilibration. Measurement of the standard allows calculation of a conversion factor, which was/is used (with a decay factor) to calculate the concentration of Rn in the samples.

The relative solubilities of Rn in water, plastic, air, and cocktail solutions produce dramatic effects. For example, incorrectly installing a Teflon-faced, silicon rubber septum in vial cap invalidates results, as does uncontrolled variation in factors that affect chemical equilibrium, such as temperature, agitation, and volumes of each phase. Because Rn is nonpolar and hydrophobic (and parent and daughter nuclei are charged and hydrophilic), the effects of chemical equilibration are as important as radiologic equilibration in this system, and difficulties arise that are unique to this determination.

From this brief description, it is clear that a standard method should specify a sample collection protocol, scintillation (and/or collection) vial and cap type, cocktail type, preparation of standards and samples, temperature control, and instrument parameters. These factors are interrelated, and all affect the measurement much more acutely than is generally appreciated. Each of the factors will be discussed below in turn.

PREPARATION OF STANDARDS AND CONTROLS

We differentiate *standards*, which contain ²²⁶Ra traceable to primary standards, from *controls*, which contain only Rn and its progeny.

Standards are made by adding 0.001 dm-³ of 15 ppm barium nitrate 0.5 M nitric acid carrier solution to a tared scintillation vial, adding the requisite quantity of radium solution by means of a microliter syringe, adding distilled water to give a total volume of cocktail. A 10-sample set of standards

using 0.005 dm³ of Packard cocktail in glass vials typically yields an average conversion factory of 187 cpm/Bq (6.92 cpm/pCi)with a 0.30% standard deviation, while a set of standards prepared with 0.010 dm³ cocktail yields a conversion factor of 215 cpm/Bq (7.97 cpm/pCi) with a 0.15% standard deviation.

The standards initially are in chemical disequilibrium because Rn daughters exist in the cocktail layer where they were formed. Figure 1 shows the effects of shaking the vial, which extracts progeny from the cocktail layer into the aqueous layer, where their volubility is much higher. This reduces the activity of the standard until transient equilibrium is restored in the cocktail in a minimum of 3 h. In practice, agitation of the standards is avoided after their initial preparation, and environmental samples are held at least 3 h in the dark (without agitation) so that they reach the same metastable state as the quiescent standards. This ensures that the conversion factor calculated for the standards can be applied to the samples. Laboratory-prepared samples should be shaken after preparation to hasten chemical equilibration, which, in the absence of agitation, takes longer than radiologic equilibration. Chemical equilibration involves diffusion of Rn among the headspace, water, cocktail, and plastic parts of the vial and cap.

Temperature Effects

Figure 2 shows the effect of changes in temperature on standards prepared in glass vials, and Figure 3 shows temperature effects on standards prepared in plastic vials. Standards were prepared as described above, then stored in a incubators at 37° C or in a refrigerator at 7° C and removed periodically for measurement. Temperature at time of measurement could not be controlled and leads to some of the scatter in the points. After equilibration for several weeks at the initial temperature, the vials were interchanged so that those originally stored at 37° C were store at 7° C, and vice versa, and the vials were again counted periodically to estimate the time required for reequilibration. The figures show that temperature equilibration takes on the order of weeks and leads to pronounced changes in activity of samples measured in plastic vials. There is virtually no hope of reaching the same state of metastable equilibrium in standards and environmental samples in plastic vials.

Carrier Effects

Addition of 1 mL of carrier solution during preparation of standards in plastic vials *reduces* the conversion factor. For example, Optiflour-O gave conversion factors (all channels counted) of 174 and 187 cpm/Bq (6.43 and 6.92 cpm/pCi) with and without carrier, respectively. This "counterintuitive" 2% - 10% reduction in count rate was observed for all cocktails studied and apparently arises at least in part because carrier saturates the cocktails (which have very little capacity for charged species like Ra) and precludes Ra from the cocktail. At later stages of

equilibration, the vial is involved in the processes that give rise to the observed carrier effect. Variability in the effect results from variability in the concentration of carrier in the primary standards. Addition of larger volumes of the barium nitrate/nitric acid carrier solution leads to no further reduction in count rate, and nitric acid alone does not exhibit the effect. Glass vials reduce the carrier effect drastically, and carrier may also fortuitously serve to reduce the accumulation of long-lived progeny on the glass. We did not (and do not) observe a gradual increase in the activity of standards as ^{210}Pb ($t_{1/2} = 21y$) and its progeny accumulate, presumably because it is extracted into the aqueous phase. Although ^{210}Pb is present in all standards supplied by EPA, it is not initially present in the cocktail phase (which extracts only Rn) of our Rn standards. Lead 210 will accumulate as standards age, but if the glass and cocktail phase are saturated with carrier, the ^{210}Pb may migrate principally to the aqueous phase, where it is not detectable. A large excess of carrier my affect quench levels and should be avoided, although no significant increase in quench was observed for the quantities of carrier described here.

Interference by Aqueous-layer Radionuclides

The contribution of aqueous-layer Ra was determined by boiling Ra solutions of 444–740 Bq dm^{-3} concentration for several minutes to remove Rn, cooling the solutions, and adding 0.009 dm^3 of this solution to a weighed plastic or glass scintillation vial. Then 0.001 dm^3 of carrier solution or distilled water and 0.005 dm^3 of Optifluor-O cocktail were added, that samples were shaken, and counting (over all channels) was begun within a few minutes. The samples were than allowed 30 d to reach secular equilibrium and counted again to determine their ultimate activity. In a typical standard containing 4.44 Bq (0.12 nCi) of Ra, the progeny alpha and beta activity through ^{214}Po should reach about 1,200 cpm in 30 d, and 0.17% of that in 30 minutes. Table 1 shows the percent of ultimate activity for each sample, prepared as above with and without carrier and in glass or plastic vials. The early activity exceeds that expected from initial in-growth of daughters at the time of measurement, but the activity is very low and some may arise from Rn not completely removed by boiling in addition to Ra in the aqueous layer. These data indicate that there is no significant interference from aqueous-phase radionuclides, especially in environmental samples where alpha activity is unlikely to exceed 3.7 Bq dm^{-3} (less than 1% of the concentration present in these samples). In samples at equilibrium, addition of carrier suppresses the sensitivity to aqueous radionuclides in plastic vials (here by about 2% in aged solutions because the Ra standard was not carrier-free), but not in glass vials. It does not appear that there can be significant interference from aqueous-layer radionuclides, even in aged samples, if glass vials are used with carrier solution. Plastic vials must provide some mechanism for interference that is not present in glass vials. There is no significant difference in quench level between the samples with and without carrier. Other cocktails may give

somewhat higher responses to aqueous-layer radionuclides.

Controls are made by immobilizing Ra, either on cation exchange resin (Hahn 1990) or on filter paper heat-sealed in a 3 mil polyethylene film (Whittaker et al, 1989). In a latter case, we applied a solution of cobalt chloride to the filter paper before drying and sealing it. If the color changes from blue [(CoCl$_4{}^{2-}$)] to pink [Co(H$_2$O)$_5$Cl$^+$] within a day or two, a leak is indicated and the control is discarded. Water diffuses through the polyethylene in several days, so all controls gradually change color toward pink. Glass beads or short lengths of glass rod should be added to the glass bottles (typically, 0.060 dm^3 with Teflon-lined plastic caps) containing the standard solutions to allow mixing before aliquots are removed, and their weight should be included in the tare before water is added to completely fill the vial.

Table 1. Effect of carrier and vial type on activity measured with Optifluor-O cocktail above boiled Ra solutions.

Container	Initial CPM/g solution	Ultimate CPM/g solution	Impact of aqueous radionuclides (%)
Plastic vial	1.42	95.4	1.5
Plastic vial w/carrier	1.06	93.4	1.1
Glass vial	2.3	105.0	2.2
Glass vial w/carrier	1.2	104.9	1.1

Only Rn and it progeny exist in the aqueous phase on controls, so these solutions are more similar to environmental samples than are the standards. Because the preponderance of activity of correctly prepared standards results from Rn alone, controls appear to have little advantage. A major disadvantage of the control samples is that they have a half-life of 3.8 d, that they are relatively difficult to prepare, and that Rn may be lost in transferring water to the scintillation vial. Controls are necessary for some of the experiments below and as a useful check on our procedures, however. Of course, if single-phase scintillation cocktail systems are used, control samples are necessary for standardization because the cocktail will respond to Ra in standards.

VIAL TYPE

Both polyethylene and glass scintillation vials are in wide use, and caps may have polyethylene cone (PC), cork-backed aluminum,

pulp-backed aluminum with polymer coating, and various other liners, or septa of various descriptions, but the most common septa are made of Teflon-coated silicon rubber (TR). Plastic vials are of course, resistant to breakage during handling, but they are permeable to some cocktails, suffer from occasional counting irregularities due to static electricity, and may have higher background activity than glass (in spite of the widespread notion the ^{40}K in glass always leads to a higher background). But, most important, since Rn is nonpolar, it diffuses through polyethylene quite readily. This leads to a variety of complications that are best avoided.

Absorption of Rn into Plastic Vials

Storage of Rn-rich water in plastic vials leads to significant loss of Rn in the water. If, for example, water with an initial Rn concentration of 1.96 kBq dm^{-3} (53,000 pCi/L control samples, prepared as described above) is added to both plastic (PC cap) and glass vials (TR septa) so that no air bubbles are visible, then stored for 4 d before aliquots are removed for measurement, the water from the plastic vial shows a 70% loss of Rn (after correction for decay). This loss has not always been explicitly mentioned (Hess and Beasley 1990). Table 2 shows data for water transferred from control samples prepared with resin-bound Ra (sample J-18 in Hahn 1990) and polyethylene-sealed Ra (sample C41 in Whittaker et al. 1989).

Table 2. Loss of Rn from water stored in different vial/cap combinations for 4 d.

Sample	Activity (kBq dm^{-3})	Measured activity (kBq dm^{-3})	Storage treatment (96h)
J-18	1.34	0.151	Glass vial, septum inverted
J-18	1.34	1.36	Glass vial, septum correct
C-41	2.45	0.343	Glass vial, septum inverted
C-41	2.45	2.35	Glass vial, septum correct
C-41	2.45	0.719	Plastic vial, poly cone cap
diluted	1.96	1.89	Glass vial, septum correct
C-41	1.96	0.734	Plastic vial, poly cone cap

Absorption into Septa

Table 2 also shows data for incorrectly installed sepa in caps of glass bottles. Remarkably, if Teflon-coated, silicone rubber septum caps are used on glass bottles, the Rn concentration of the

water will decrease by 85% - 90% in 4d if the septum is installed incorrectly, with the rubber side towards the water. There is no significant decrease in activity (after correction for radiologic decay) if the septum is correctly installed, with the TFE face of the septum towards the water. The interplay of cocktail type and vial type will be discussed later.

Clearly, only glass vials with Teflon or foil liners are suitable for sample containers if water samples are collected in the field in vials that contain no scintillation cocktail.

The dramatic absorbance of Rn into silicone rubber suggested that the two types of foil-lined white urea caps available for glass vials may cause different rate of Rn loss from water. Caps with cork-backed bare aluminum liners were compared to caps with pulp-backed aluminum that has been coated with polymer, by filling vials with control solutions and storing them for 5 d. No difference could be detected in the Rn concentration of water stored under the two types of aluminum-lined caps.

Effect of Headspace

One problem that remains when glass vials with either septum-or foil-lined caps are used for sampling is the presence of bubbles. Bubbles result from incomplete filling at time of sampling or from exsolution of dissolved gases in the water samples.

A spreadsheet model was used with reported distribution coefficient date (Nussbaum 1957) to predict the concentration of Rn that would remain in water in a 0.025 dm³. Figure 4 shows the calculated line assuming distribution coefficients of 0.34, 0.25, and 0.20 for 10°C, 20°C, and 30°C, respectively. The abscissa is the volume of gas entrapped in the vial, and the ordinate is the percentage of Rn initially present that remains in the water at equilibrium.

To verify the model, Rn solutions (control samples prepared as described above from resin-bound Ra samples J-18 and K-6 from Hahn 1990) were added to glass vials so that they filled the vial, or so that a 0.005 dm³ bubble existed. The vials were store for 4 d to simulate equilibration during shipping; then the aliquots of solution were removed and the Rn concentration was determined by standard methods. The experimental points were calculated by dividing the measured concentration of water in the vial containing a bubble by the measured concentration of Rn in the identically prepared vial without a bubble. The experimental points validate the experimental curve for the distribution coefficients given and show that reasonable care must be taken to fill glass vials completely when they are used as sample containers as described here.

Appearance of Activity in Vials

If the plastic and glass vials that were used as described above

to store Rn-enriched water (370 Bq dm^{-3}) for several days are emptied and rinsed several times with distilled water, then filled with 0.015 dm^3 of cocktail and capped, the measured activity of the vial changes as shown in Figure 5. The activity of the glass vial decreases as the adsorbed Rn progeny decay, but the activity of the plastic vial first increases as Rn diffuses into the cocktail, then begins to decay, with a rate that approaches exponential with a 3.8d half-life. As Figure 6 shows, the spectrum of the glass vial shows decay of the peak just above channel 800, with a rate determined by the decay first of ^{214}Pb (1.03 MeV beta with 26.8 min half-life) and then of ^{214}Bi (0.82-3.26 MeV beta with 19.7 min half-life). The beta peaks appear in channels 200-400, while the peak near channel 825 is an alpha peak due to the ^{214}Po (6.9 - 7.7 MeV, 1.6 X 10^{-4}s half-life in equilibrium with the 19.7 min ^{214}Bi). This peak grows in and decays as expected under control of the Pb and Bi precursors. We have observed a rapidly decaying peak attributable to ^{218}Po (6.0 MeV alpha 3.0 min half-life) below channel number 800 in some glass vials, but adsorbance is probably pH dependent and vials must be counted quickly.

The spectrum of the plastic vial initially shows extremely high activity in channels 200-400 and virtually none in the 700-900 region, as shown in Figure 7. The former broad peak decays with an initial half-life of less that 2 min, then with a much longer half-life (about 20h after 300 min). The 200-400 channel band must be due to activity of radionuclides still adsorbed on the vial surface, which are highly quenched. These species desorb rapidly to an environment where quenching is reduced, and new peaks appear at higher energies. These changes are due mostly to chemical, not radiologic, equilibration, since the vial was initially filled (to the exclusion of air) with Rn enriched water that had several days to reach transient equilibrium. The distribution coefficient (ration of the concentration of Rn in water to it equilibrium concentration in plastic) is small so that Rn migrates into the plastic from water. When the water was removed and a nonpolar cocktail added, the new distribution coefficient (ration of the concentration in cocktail to the equilibrium concentration in plastic) is large, favoring the diffusion of Rn into the cocktail. Thus, the Rn peak (5.5 MeV alpha) on the low side of the ^{218}Po peak below channel 800 grows in, and the overall measured activity actually increases as chemical equilibrium is established, even though the actual total activity of Rn present in the vial (and the progeny in equilibrium with it) must decrease. The increase in measured activity cannot be due entirely to the grow-in of progeny because the progeny are in radiologic (transient) equilibrium with the Rn, which was stored in the vial for 4 d. Eventually, the rate of migration of Rn into the cocktail becomes small, transient equilibrium of Rn in the cocktail with progeny in the cocktail is established, and the peaks around channel 800 begin to decay, with a half-life that is near 3.8 d after 60 h. Figure 7 also shows the spectrum of the plastic vial after 2 mo, with a prominent peak due to ^{210}Po (5.3 MeV alpha) and broad beta peaks due to ^{210}Pb and ^{210}Bi.

Low-intensity peaks suggest the presence of some Ra.

It is interesting that the glass vials with polar silanol groups adsorb Rn progeny, while plastic vials absorb Rn, so complementary spectra are obtained. The spectra of glass vials exposed to Rn-enriched water are variable and are dramatically affected by small concentrations of ions that compete for binding sites. These characteristics may be significance for both sample storage and standard preparation: *It is clear that plastic vials are not suitable for storage of water samples contain Rn, but adsorption of progeny by glass is of no consequence with regard to sample storage, and these vials retain Rn well, assuming that appropriate caps are used.*

It is possible to obtain the Rn peak alone by removing gaseous Rn, by means of a syringe, from the headspace of a vial containing a solution of Ra. If the gas is injected into a organic scintillator and measured repeatedly, the predictable changes occur in the peaks identified above.

Finally, if suitable cocktail is added to sampling vials before the water sample is added (in this case, water must be added with a syringe as described later), loss of Rn is reduced in plastic vials. Furthermore, glass vials with cocktail are less subject to breakage if the water is allowed to freeze and trapped air is inconsequential.

COCKTAIL TYPE

Most fluors are nonpolar species, so they are dissolved in nonpolar solvents like toluene, pseudocumene (1,2,4 - trimethylbenzene), long-chain alkylbenzenes, phenylxylylethane, and, to some extent, in mineral oil. Consequently, commercial scintillation cocktails based on all these solvents are available. Some cocktails are modified with surfactants and/or cosolvents so that single-phase systems are obtained when aqueous samples are mixed with the cocktail.

Most determinations of waterborne Rn have been done with cocktails that are immiscible with water. Chemical separation of Rn from other radionuclides is thus effected, and energy discrimination is not necessary to eliminate interfering activity. Narrow windows may, however, be used propitiously to reduce lower levels of detection, as described later. Two-phase cocktails are desirable because they allow the preparation of Ra standards that have a long useful lifetime but have activity due only to the Rn in the cocktail phase, which is in equilibrium (after 30 d or so) with Ra in the aqueous phase. If a cocktail is used that promotes dissolution of aqueous phases, it will respond to aqueous-phase radionuclides in all samples, and use of Ra standards will not be straightforward. We have, therefore, not investigated theses single-phase cocktail systems.

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There are some differences among the immiscible "organic" type cocktails, however, even though they have similar efficiencies and background levels under optimal conditions. For example, Figure 8 shows that if an aqueous solution of Ra is mixed with Beckman and Packard cocktails, the grow-in of Rn and its progeny to equilibrium depends on the vial type (cocktails manufactured by NEN and ICN show behavior similar to the Packard cocktail). In glass vials, Packard cocktail gave a slightly higher conversion factor of 187 cpm/Bq (6.93 cpm/pCi, or 3.13 cpm/dpm) compared to 172 cpm/Bq for Beckman cocktail. But in plastic vials, the Beckman cocktail gave a significantly lower conversion factor (measured over all channels). This is because the distribution constant (the ratio of the concentration of radon in the Ready Organic cocktail to the equilibrium concentration in plastic) for Ready Organic is smaller than the distribution constant (the ratio of the concentration of radon in cocktail to the equilibrium concentration in plastic) for Optifluor-O, so that the concentration of Rn in the Beckman cocktail is actually lower, due to the competing radiological processes for the two cocktails. The effect of added carrier that is apparent in the figure indicates that Beckman cocktail may be more sensitive to Ra in the aqueous phase, as discussed earlier.

It is interesting that while plastic vials allow the loss of Rn from water samples at a fairly rapid rate (on the order of 70% in 4 d as described previously), the rate of loss is drastically reduced by the addition of a suitable cocktail because of the large solubility of Rn in the nonpolar solvents of the cocktail. Where their resistance to breakage during shipping is important and utmost accuracy is not critical, plastic vials may be used as sample containers if they contain cocktail before the water sample is added. With 0.005 dm³ of Packard cocktail and 0.010 dm³ of Rn-containing water, for example, plastic vials lose Rn activity with a half-life of approximately 10 d due to diffusion through the plastic (after correction for radiologic decay). The rate of loss depends dramatically on temperature, agitation, and other factors. Since loss is not predictable for samples collected in the field, corrections cannot be made, and plastic vials are unacceptable for measurements of utmost accuracy. The sample actually has four phases ...cocktail, water, gas, and plastic... and is very difficult to model.

With any vial type, cocktail should be chosen for (1) the solubility of Rn, (2) insensitivity to aqueous radionuclides, and (3) the efficiency of the fluor. Plots like Figure 8 might be used for evaluation. There are only minor difference among the conversion factors for ICN, Packard, and NEN cocktails in plastic vials, indicating that they all compete favorable with plastic for Rn. The Beckman cocktail inhibits loss of Rn to plastic less efficiently, although it would probably perform as well as the other cocktails in glass vials. Beckman cocktail is based on pseudocumene, while the NEN Cocktail is based on mineral oil with a pseudocumene cosolvent, and the Packard cocktail is based on long-chain alkylbenzenes. A phenylxylylethane-based cocktail,

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Ecoscint, was not investigated.

SPECTRAL REGION AND QUENCH

As Rn and its progeny grow into equilibrium with the Ra in a standard, spectra like those in Figure 9 are obtained. A typical background spectrum (amplified by a factor of 50) is also shown in the figure, and, fortuitously, the minimum in the background is near the maximum of the best-defined alpha peaks in the standard spectrum. Counts due to beta and gamma decays are spread our over many channels. The sharpness of the alpha peaks in the spectra shown here is somewhat exaggerated by the logarithmic relationship between channel number and pulse height on our instrument. It is decidedly not fortuitous that the slope of the background spectrum is greater around the narrow sample peaks. If very high sensitivity is required, background subtraction can be complicated by variable quench in environmental samples, which shifts peaks as well as reducing their intensity. Typically, if standards are counted over the 0-1000 channel range, the conversion factor and background are 262 cpm/Bq and 48.2 cpm, while in the 700-900 channel range they are 165 cpm/Bq and 4.5 cpm, and in the 650-950 range they are 220 cpm/Bq and 7.06 cpm, respectively.

SAMPLE COLLECTION

We have accumulated data on duplicate samples collected by lay individuals (for the most part, homeowners) using several methods. The hose-and-funnel method originally proposed by the U.S. EPA (Partridge et al. 1979) was abandoned in favor of less cumbersome and equally effective methods wherein water is collected in a large beaker or pail. The beaker is held so that the end of the water spigot is below the surface of water, and the water is allowed to overflow from the beaker for 2 min. A hose may be attached to the spigot and immersed in the water. Samples are then taken from the collected water by either of the following methods:

(1) A disposable plastic syringe fitted with a 6 cm length of Tygon tubing is used to remove a 0.010 dm³ sample and inject the sample below the surface of the cocktail in glass or plastic counting vials. The Tygon tubing is chosen so that it can be forced over the Luer fitting of the syringe. Tubing with an inside diameter of 1mm or larger prevent cavitation and consequent exsolution of radon. The large negative pressures, agitation, and bubbling that can arise when a steel needle is used on a 10 mL syringe to take water samples for subsequent Rn determinations are avoided. The Tygon tubing is also safer for mailing and use by untrained personnel. The disadvantage of this method, where cocktail is supplied in the sampling vial, is that the laboratory cannot choose to change cocktails used in standard abruptly if sampling bottles have been stockpiled in the field. The advantages are that

laboratory work is minimized because the samples arrive at the laboratory ready to be placed into spectrometer, and that breakage due to freezing during shipment is eliminated.

A typical subset of our data base of several thousand duplicate measurements done by this method has an average difference between A and B samples of 10% and the absolute standard deviation of these percent differences is 22%. (In one-third of the pairs, A and B samples differed by more than 22%.) These samples were collected in poly cone-capped polyethylene vials by both homeowners and (not necessarily experienced) testing companies. The average LLD was 4.7 kBq dm³ (174 pCi/L), calculated as described below, but samples were counted over the entire energy spectrum. The large variance in results obtained by this method derives in part from physical leakage of poorly tightened caps in concert with other factors that are poorly controlled by lay personnel. Results would be improved by use of glass vials with foil-lined caps and the use of an optimized energy region.

(2) A glass vial and its septum cap are immersed in the water, and the vial is capped under water so that no gas is trapped. The water is transferred to counting vials in the laboratory with a syringe fitted with a double needle that allows air into the top of the vial as sample is removed from the bottom. Glass vials are susceptible to breakage by shock or by expansion of freezing water, although the septum cap reduces the latter problem. As mentioned previously, bubble formation in filled bottles, incorrect installation of the Teflon-coated rubber septa, as well as an occasional poorly sealing cap, all lead to loss of Rn from the water.

A typical subset of 180 tests from our data base of about 1000 duplicate measurements made by this method has an average difference between A and B samples of 24%, and the absolute standard deviation of these percent differences is 40%. Samples were collected in duplicate 0.016 dm³ septum-capped vials and transferred to duplicate poly cone-capped polyethylene vials for counting over the entire energy spectrum. The relatively large A/B difference arises predominantly from sampling errors (presence of headspace gas and inverted sepa) that occurred in spite of specific warnings. It is likely that samples collected in this manner by experienced personnel would show much lower variability.

The relatively high absolute standard deviation of the average differences indicates that there are a fairly small number of A/B pairs with a very large A/B difference. This bears out our suspicion that Rn is hard to contain and that duplicate testing is necessary to detect a relatively small number of catastrophic errors in sampling. Duplicate glass vials with aluminum foil-lined caps containing cocktail to which 0.010 dm³ samples are added by means of a syringe would minimize many sampling errors but would introduce some loss of Rn because these vials must be opened to remove water.

Sampling variability is not likely to arise from variability in the actual concentration of Rn in the well water, since all A/B pairs were taken within minutes of each other. The Rn concentration undoubtedly depends on volume of water used for many hours before the test and perhaps to a lesser extend, upon natural variation of the well water concentration. All results quoted in this section were obtained by measurements over all spectrometer channels.

RESULTS OBTAINED USING STANDARD METHOD

Table 3 shows typical results obtained for very-low-level control samples described in Hahn (1990), prepared with 0.005 dm³ of Optifluor-O cocktail glass vials, measured in duplicate. Samples were prepared in plastic vials for comparison. Five standard solutions were prepared in either glass vials with TFE/Silicone septa or plastic vials with poly cone caps. Matching blanks were prepared for background measurements. The samples and standards in glass vials were measured only over the 700-900 channel region, while the samples and standards in plastic vials were counted over all channels, so that the best available method can be compared with a common method. The same samples were measured repeatedly over several days to detect the loss of Rn by nonradiologic processes.

Our LLD depends, of course, mostly on the background level and is calculated very conservatively by using the formula:

LLD:

$$= \frac{(K_\alpha + K_\beta) \sqrt{\left[\frac{\sqrt{BCR \times BT}}{BT}\right]^2 + \left[\frac{\sqrt{SCR \times CT}}{CT}\right]^2} \times 100}{CF \times DF},$$

where K_{alpha} and K_{beta} are the normal curve ordinates corresponding to the confidence level desired for Type I and II errors, respectively, BCR and SCR are the background and sample count rates, respectively, BT and CT are the count times for the background and sample, CF is the conversion factor to Bq or pCi, and DF is the decay factor ($e^{-0.00769(t)}$) to adjust the LLD to the time of sampling (not measurement). We take $K_{alpha} = K_{beta} = 1.645$ (95% confidence level) and assume that the sample and background counts are close in samples that approach the LLD so the $\sigma_{s,t} = (2\sigma_b)^{1/2}$. The equation then reduces to:

LLD:

$$LLD = \frac{2\sqrt{2}(1.645) \sqrt{\left(\frac{\sqrt{BCR \times BT}}{BT}\right)^2} \times 100}{CF \times DF}. \quad (2)$$

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Table 3. Results of measurements of known samples by use of two liquid scintillation methods.

True value (Bq dm⁻³)	Delay (h)	Vial (window)	Measured level (LLD, 2σ% error) (Bq dm⁻³) [(Bq dm⁻³,%)]
3.7	8.5	Glass (700-900)	A: 3.5(1.2, 28%)
	21	Glass (700-900)	B: 2.7(1.2, 34%)
	80	Glass (700-900)	A: 2.7(1.3, 36%)
	103	Glass (700-900)	B: 3.5(1.3, 30%)
	146.5	Glass (700-900)	A: 3.1(2.0, 48%)
	205	Glass (700-900)	B: 2.8(2.0, 52%)
	18.5	Plastic (0-1000)	A: 3.3(2.5, 54%)
	76.5	Plastic (0-1000)	B: 2.4(2.5, 70%)
			A: 4.6(3.6, 54%)
			B: 4.5(3.6, 56%)
			A: Below LLD (5.4,-)
			B: Below LLD (5.4,-)
			Below LLD (3.6,-)
			Below LLD (5.7,-)
7.4	8	Glass (700-900)	A: 6.2(1.2, 18%)
	20.5	Glass (700-900)	B: 6.0(1.2, 18%)
	79.5	Glass (700-900)	A: 7.7(1.3, 16%)
	102	Glass (700-900)	B: 7.5(1.3, 17%)
	146	Glass (700-900)	A: 7.0(2.0, 24%)
	226	Glass (700-900)	B: 6.4(2.0, 26%)
	19	Plastic (0-1000)	A: 6.5(2.5, 30%)
	77	Plastic (0-1000)	B: 5.9(2.5, 33%)
			A: 5.9(3.6, 44%)
			B: 7.8(3.6, 35%)
			A: Below LLD(6.6,-)
			B: Below LLD(6.6,-)
			Below LLD(3.6,--)
			Below LLD(5.7,-)
18.1	9	Glass (700-900)	A:14.9(1.2, 10%)
	22	Glass (700-900)	B:16.5(1.2, 9%)
	80.5	Glass (700-900)	A:16.9(1.3, 10%)
	227.5	Glass (700-900)	B:18.1(1.3, 9%)
	18.5	Plastic (0-1000)	A:18.1(2.1, 12%)
	76	Plastic (0-1000)	B:17.4(2.1, 13%)
			A:17.1(6.7, 30%)
			B:13.9(6.7, 36%)
			13.3(3.7, 20%)
			11.5(5.7, 13%)

The background time was taken to be 20 min, although a cumulative background time for the five samples is justified and reduces the LLD. The factor "100" converts the 10 mL sample volume to liters. The conversion factor is calculated by dividing the net sample count rate by the absolute activity of Ra in the standard in Bq or pCi, and conversion factors for at least five standards are averaged to obtain the value used in calculating the Rn levels in samples. The LLD values reported are very conservative because we:

(1) use 95% confidence levels,
(2) include a decay term, and
(3) take background count time to be only 20 min,

not assuming invariance during the 12 h typically necessary to run a set of samples. Movement of equipment during our studies required the latter precaution.

The lever of Rn in the samples is calculated by using this formula:

$$C_{Rn} = \frac{(SCR - BCR) \times 100}{CF \times DF} \qquad (3)$$

The 2σ percentage error is calculated for the total number of counts obtained in 20 min. for each of the two samples, according to the following equation:

$$E_{2\sigma} = \frac{2 \times \sqrt{\left(\dfrac{SCR}{CT} + \dfrac{BCR}{BT}\right)} \times 100}{SCR - BCR} . \qquad (4)$$

The low bias in these very-low-level samples may be due to loss of Rn during removal of aliquots for measurement, or it may be due to absorption of Rn by the polymer beads or film used in preparation of the standards. This low bias also existed in the recent interlaboratory comparison (Hahn 1990). It is clear that very low levels of Rn can be measure even with a 20-minute count time if suitable precautions are taken.

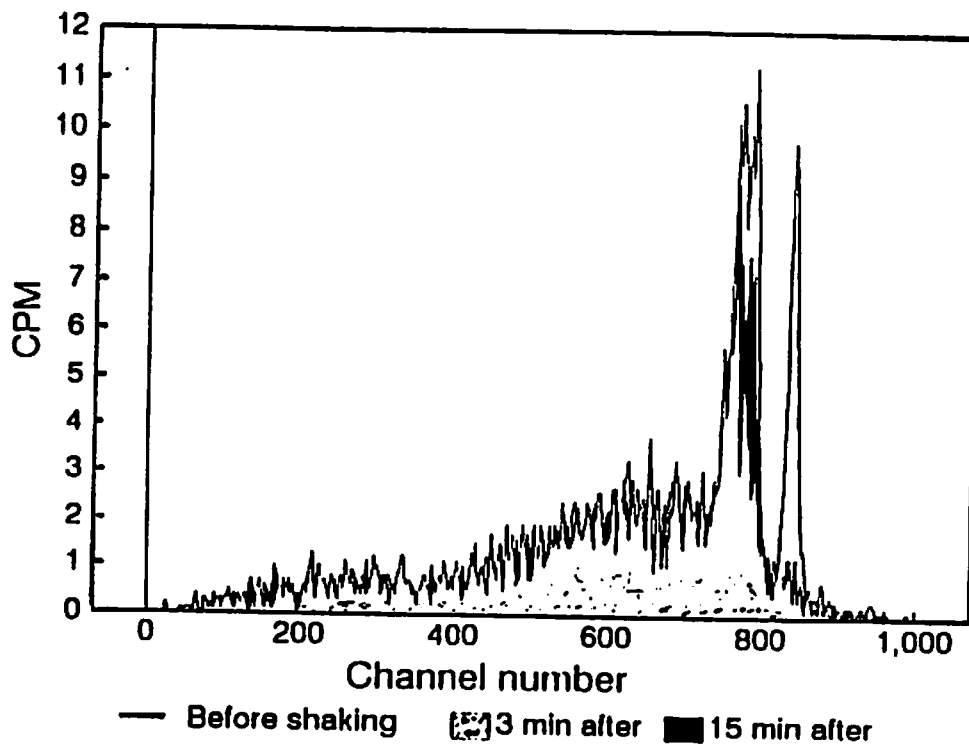Fig. 1. Typical standard solution before and after shaking. The peaks above channel 800 (^{214}Po α) and the upper part of the composite peak below channel 800 (^{218}Po α) disappear upon shaking, then grow in gradually to restore the original spectrum.
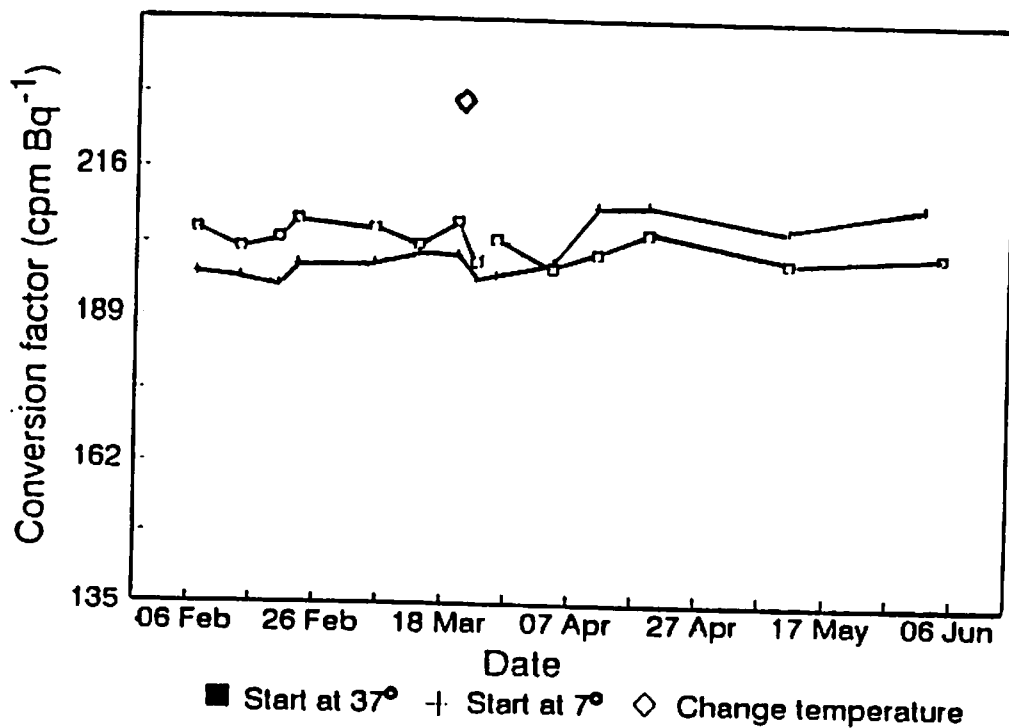
— Before shaking   [::]3 min after   ■15 min after

■ Start at 37°   + Start at 7°   ◇ Change temperature

Fig. 2. Effect of temperature changes on standards in glass vials.
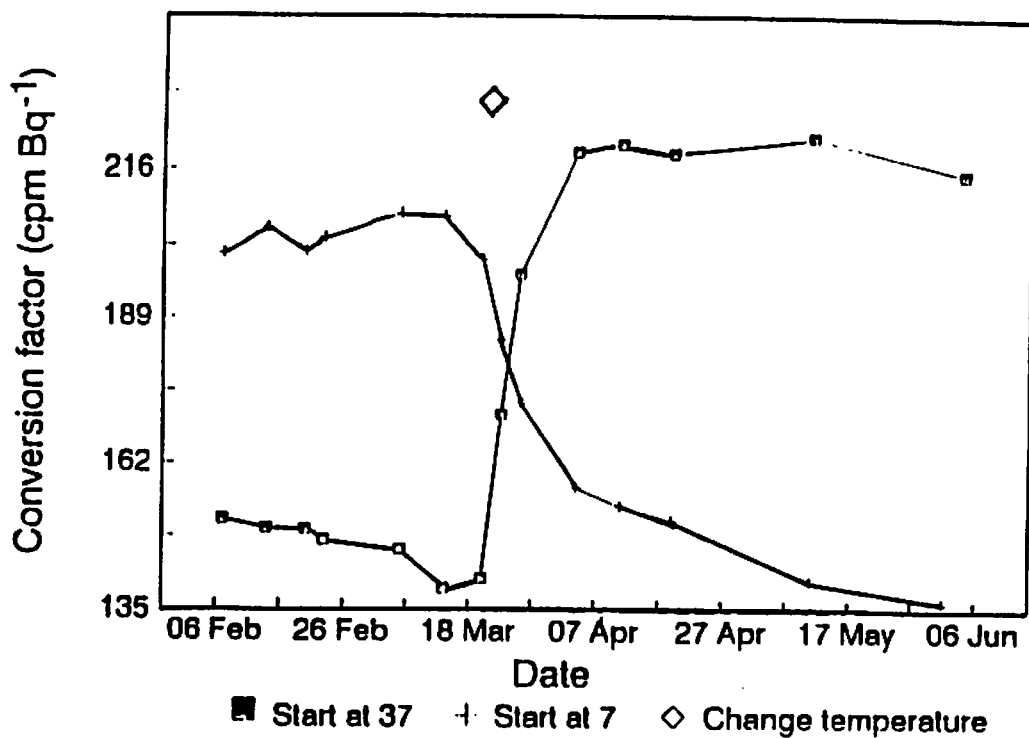
Fig. 3. Effect of temperature changes on standards in plastic vials.
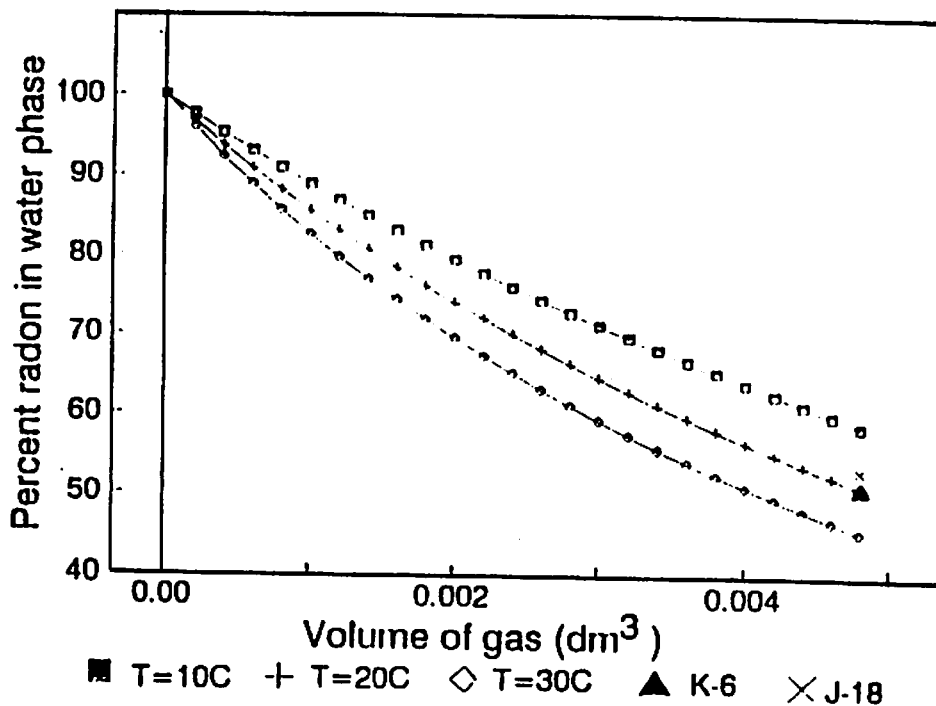
Fig. 4. Effect of bubble size on Rn concentration of water stored in glass vials for 4 d. Curves are calculated, but experimental points are provided for samples K-6 and J-18 supplied during the recent laboratory intercomparison study (Hahn 1990).
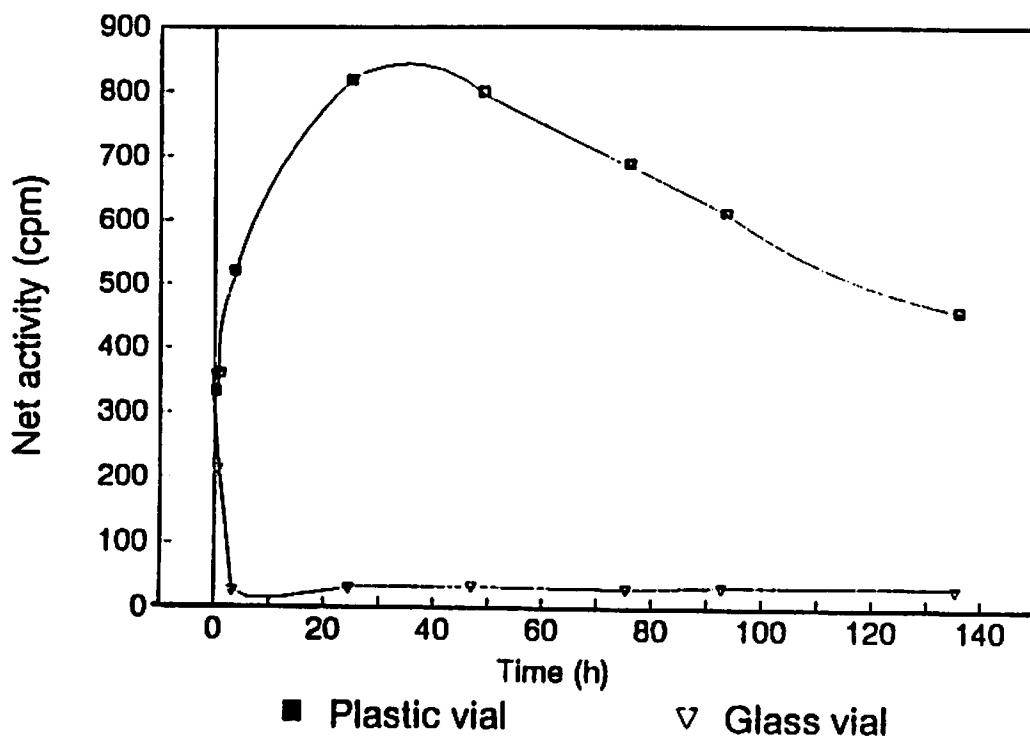
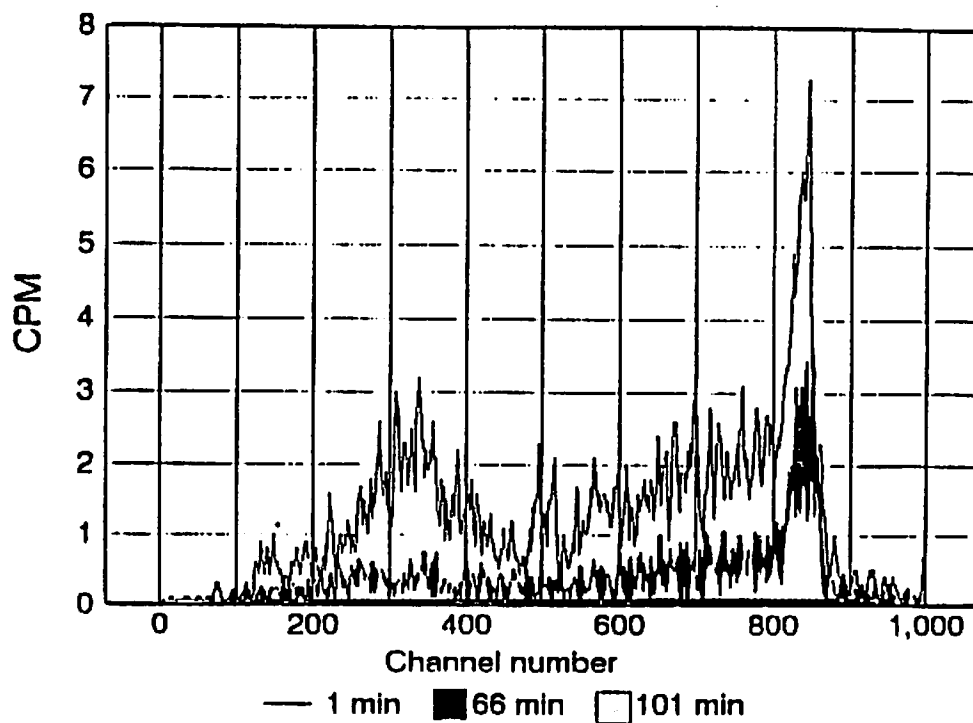Fig. 5. Changes in total activity in plastic and glass vials used to store water containing high concentrations of Rn after water was discarded and cocktail added to the vial.

Fig. 6. Spectra obtained by adding cocktail to glass vials that had been used to store water samples containing Rn and progeny. Peaks due to inert Rn are absent.
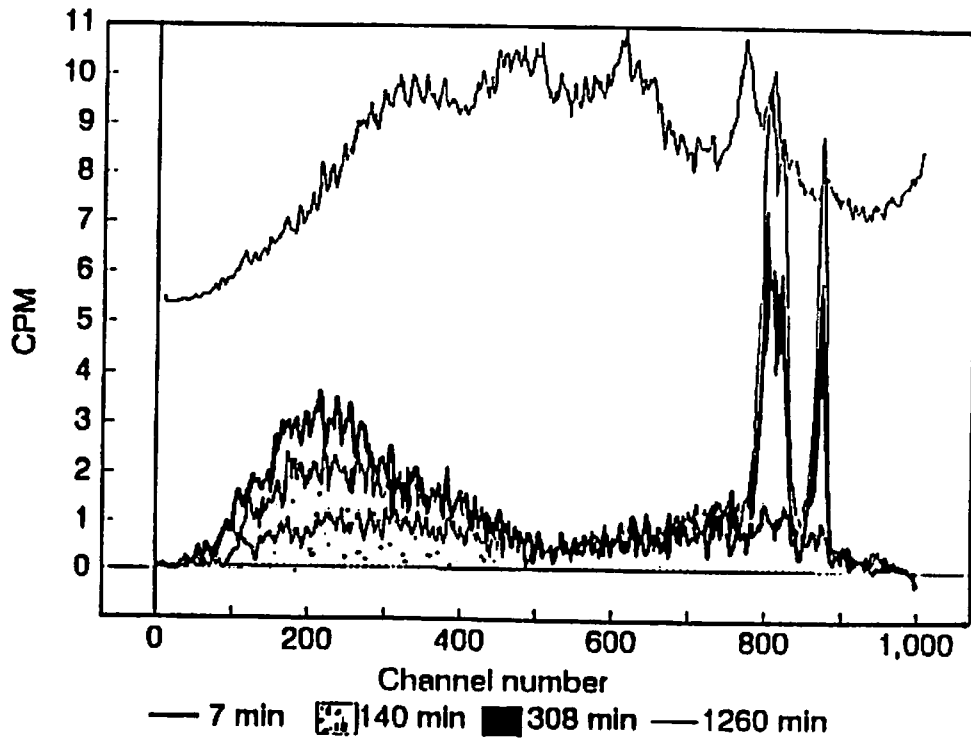
Fig. 7. Spectra obtained by adding cocktail to plastic vials that had been used to store water samples containing Rn and progeny. Radon had diffused into the plastic, and initially nearly all activity was in the 300-500 channel region. After 2 mo, the spectrum at the top of the figure was obtained. The peaks in the top spectrum had maxima around 0.1 cpm.
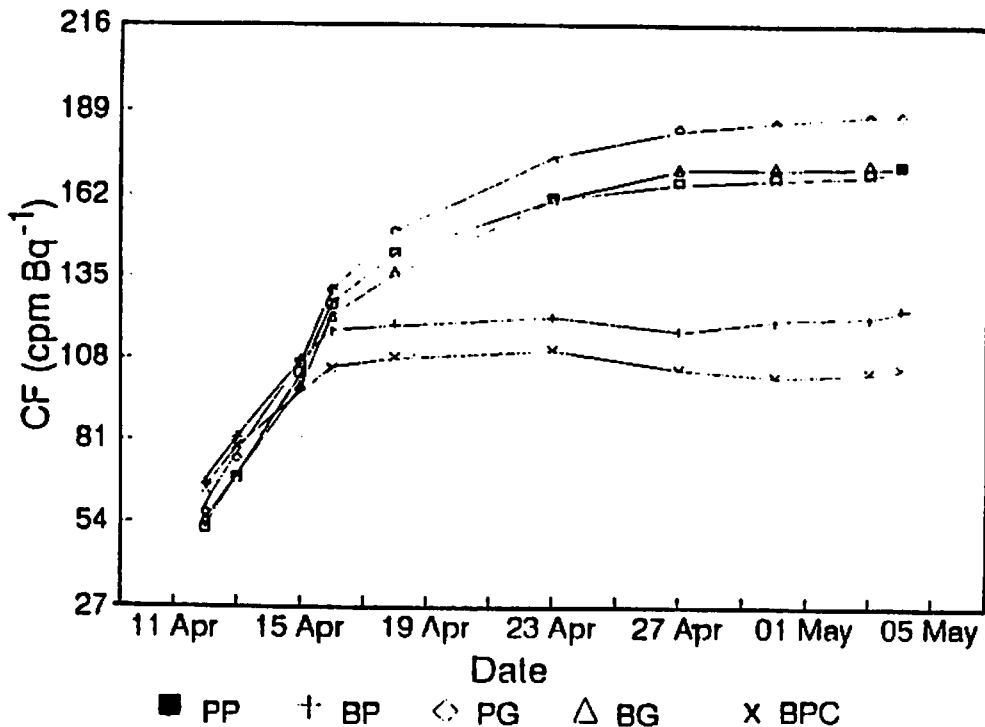

Fig. 8. Increase in conversion factors for two types of cocktail in two types of vial. Standards were prepared from Ra solution with (1) Packard Optifluor-O cocktail in plastic vials (PP), (2) Beckman Ready Organic cocktail in plastic vials (BP), (3) Packard cocktail in glass vials (PG), (4) Beckman cocktail in glass vials (BG), or (5) Beckman cocktail in plastic vials with added carrier (BPC).
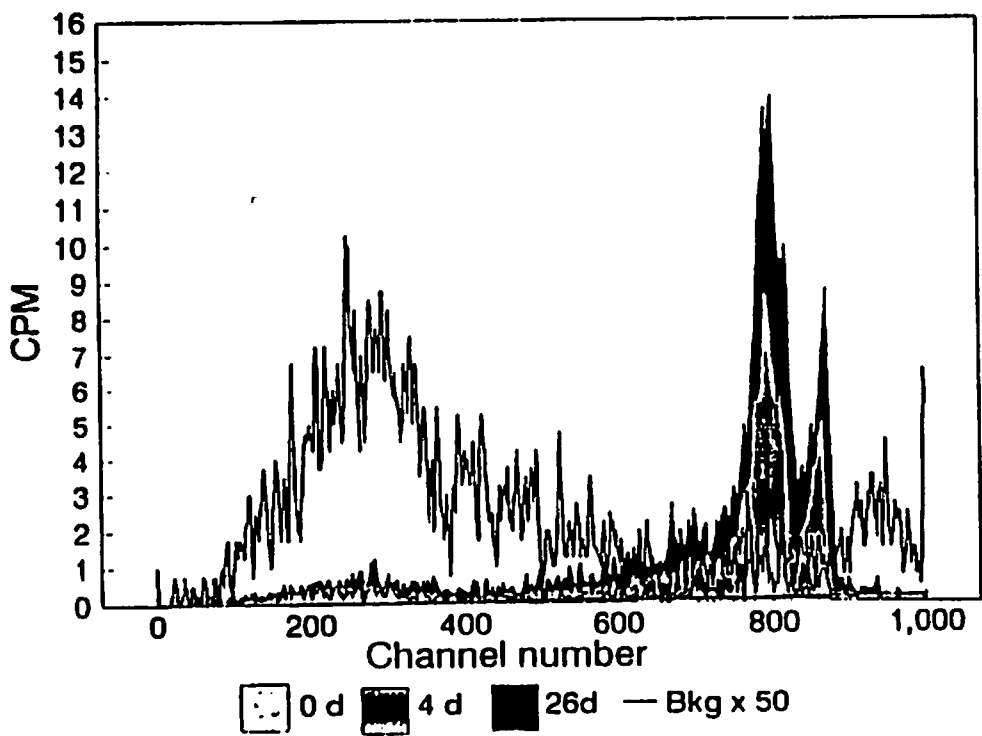
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Fig. 9. Increase in spectral peaks with time for standards in glass vials with Packard Optifluor cocktail, and typical background spectrum amplified 50×.

FOOTNOTES

(1) Beckman Instuments Company, 2500 Harbor Road, Fullerton, CA 92634.

(2) Packard Instrument Corporation, 2200 Warrenville Road, Downers Grove, IL 60515.

(3) DuPont Biotechnology Systems, NEN Research PRoducts, 240 University Avenue, Westwood, MA 02090. The current high-efficiency mineral oil scintillator (NEF 957A) was formerly marketed under product numbers PSS-007H and NEF-9999.

(4) ICN Biomedicals, Inc. Radiochemicals Division, Irvine, CA 92713.

(5) National Diagnostics, 303 Cleveland Ave, Highland Park, NJ 08904.

(6) Rainin Instrument Company, Woburn, MA 01801.

(7) Lotus Development Corporation, 55 Cambridge Parkway, Cambridge, MA 02142.

(8) National Instruments Corporation, 12109 Technology Boulevard, Austin, TX 78727.

(9) Wheaton Instruments, 1301 North 10th Street, Millville, NJ 08332.

(10) Cole Parmer Catalog #6409-14, 7425 North Oak Park Avenue, Chicago, IL 60648.

(11) Fischer Scientific, 711 Forbes Avenue, Pittsburg, PA 15219.

(12) Sun Brokers, P.O. Box 2230, Wilmington, NC 28402.

REFERENCES

Cross, F.T.; Harley, N.H.; Hofmann, W. Health effects and risks from ²²²Rn in drinking water. Health Phys. 48:649-670; 1985.

Dundulis, W. P.; Bell, W. J.; Keene, B. E.; Dostie, P. J. Radon-222 in the gastrointestinal tract: A proposed modification of the ECRP Publication 30 model. Health Phys. 47:243-452; 1984.

Hahn, P. B. NRA-XCK radon in water collaborative study. Las Vegas, NV: Nuclear Radiation Assessment Division, United States Environmental Protection Agency, Environmental Monitoring Systems Laboratory; 1990.

Hess, C. T.; Beasley, S. M. Setting up a laboratory for radon in water measurements. In: Cothern, C. R.; Rebers, P. A. Radon, radium and uranium in drinking water. Chelsea, MI: Lewis Publishers; 1990.

Hess, C. T.; Michel, J.; Horton, T. R.; Prichard, H. M; Coniglio, W. A. The occurrence of radioactivity in public water supples in the United States. Health Phys. 48:553-586; 1985.

Horton, T. R. Methods and results of EPA's study of radon in drinking water. Montgomery, AL: U.S. EPA Office of Radiation Programs, Eastern Environmental Radiation Facility; EPA 520/5-83-027; 1983.

Lucas, H. F. A fast and accurate survey technique for both radon-222 and radium-226. In: Adams, J. A. S.; Lowder, W. M. The natural radiation environment; Chicago, IL; University of Chicago Press; 1964:315-329.

Nussbaum, E. Radon solubility in body tissues and in fatty acids. Rochester, NY: University of Rochester, Atomic Energy Project; UR-503; 1957. Available from NTIS, Springfield, VA.

Partridge, J. E.; Horton, T. R.; Sensintafar, E. L. A study of radon-222 released from water during typical household activities. Montgomery, AL: U.S. EPA Office of Radiation Programs, Eastern Environmental Radiation Facility; EPA ORP/EERF-79-1; 1979.

Prichard, H. M.; Gesell, T. F. Rapid measurements of Rn-222 concentrations in water with a commercial liquid scintillation counter. Health Phys. 33:577-581; 1977.

Vitz, E. Preliminary results of a nationwide waterborne radon survey. In: Proceedings of the 1988 symposium on radon and radon reduction technology, 18-21 October 1988; Denver, Co: EPA; 1988.

Whittaker, E. L; Akridge, J. D.; Giovino, J. Two test procedures for radon in drinking water: Interlaboratory collaborative study. Las Vegas, NV: U.S.EPA Environmental Monitoring Systems Laboratory Office of Research and Development: EPA 600/2-87/082; 1989.