

DETERMINATION OF ENVIRONMENTAL ^{222}Rn BY ADSORPTION IN A DIFFUSION BARRIER ACTIVATED CARBON COLLECTOR USING LIQUID SCINTILLATION COUNTING

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ABSTRACT

Activated carbon collectors using gamma-ray spectroscopy have been used successfully for the past 15 years for short-term measurements of indoor radon (^{222}Rn). The collectors are usually 10 to 20 times heavier than the 20 ml vials that use alpha and beta liquid scintillation counting (LSC). Because several steps were required to prepare the samples for analysis, the LSC method did not enjoy the popularity of the more direct gamma counting method. An attractive alternative LSC method was investigated, developed, and made more direct by eliminating steps such as; the need for a desiccant, sample transfer, and the risk of sample degassification. A 20 ml clear polyethylene terephthalate (PET) plastic vial containing 2 g of very sensitive activated carbon is capped with a screw cap with a 6 mm opening fitted with a 1 mm filter paper that serves as the diffusion barrier. The extraction of ^{222}Rn from the exposed collector is carried out in the same plastic vial using a cocktail with a very high xylene content. The extraction efficiency increases to 85% after 3 hours of contact time and to 100% in 15 hours. The PET vial was found to be impervious to ^{222}Rn and cocktail. Analysis for ^{222}Rn is performed with a Beckman LS 5000TD Liquid Scintillation System in a two-phase orientation. Calibration of the collector at different conditions of ^{222}Rn concentration (1-50 pCi/L), relative humidity (30-70%), and exposure time (2-7 days) show adequate sensitivity. The Lower Limit of Detection (LLD) is 0.25 pCi/L for a 4 day exposure with analysis 3 days post exposure. The measurement errors at the 95% confidence level for 1 pCi/L (37 Bq/m³) and 4 pCi/L (148 Bq/m³) are 25% and 8% respectively, when counting time is 10 minutes.

INTRODUCTION

In the past few years, measurements for ^{222}Rn in air increased dramatically to address different exposure problems. The need to obtain and analyze a large number of samples for indoor ^{222}Rn concentrations made it necessary to develop simple, reliable, and inexpensive monitoring devices. Although there are different EPA approved devices and methods for measuring indoor ^{222}Rn , the more popular, available and cost effective are those that are used for short-term or screening measurements. Usually, results of ^{222}Rn concentration measurements in air are available within a week after the end of exposure. These test devices are ideal for identifying "hot" houses during typical exposures from 2-7 days. Most of the present devices for measuring ^{222}Rn are available and are based on open-faced or diffusion barrier activated carbon collectors used for periods of 2-7 days (George, A.C. 1984); (George, A.C. and Weber, T. 1990); (Cohen and Nason 1986); (Gray and Windham 1987). Other devices employing different principles of detection include electret ionization chambers for short and long-term exposures (Kotrappa et al. 1988) and solid state alpha track detectors for long-term exposures (Alter and Fleischer 1981). The use of LSC techniques for measuring ^{222}Rn in water is well established (Pritchard and Gesell 1977). Although LSC for measuring ^{222}Rn in air has been in use for the last 10 years by some testing companies, it did not become popular because of proprietary reasons and the lack of published information in scientific journals. The advantage of the modified device is its small size requiring minimal sample preparation, no sample transfer, and unattended operation in an automatic sequential sample analyzer. Because of the low background of the entire analytical system the LLD is 0.25 pCi/L (9 Bq/m³).

DESIGN CONSIDERATIONS

The modified version of the LSC collector consists of a 20 ml clear PET vial containing 2 g of very sensitive activated carbon. Freshly regenerated carbon is placed inside the vial that is sealed with an airtight foil lined polypropylene screw cap. The overall weight of the sealed vial as sent for exposure weighs about 10.5 g. Although humidity plays a minor role between 20-50% RH, the net water gain is documented and is incorporated in the calibration curve obtained at different conditions of humidity and duration of exposure. To extend the device's measurement period so it may incorporate several diurnal cycles and minimize the effect of humidity, the collector is fitted with a diffusion barrier screw cap during exposure. ^{222}Rn and water vapor diffuse through a 6 mm opening which is fitted with a 1 mm thick filter paper. The need for a desiccant bag or desiccant mixed with carbon is eliminated altogether. Although the diffusion of ^{222}Rn and water vapor are slowed down, the sensitivity of the method is adequate for ^{222}Rn concentrations <1.0 pCi/L. The analyzed collector is disposed of because the carbon is altered during the extraction period and cannot be recycled.

CALIBRATION

Before exposure, 2 g of regenerated carbon is placed inside the clear PET vial and sealed with the airtight screw cap. The integrity of the sealed plastic collector was investigated to determine that ^{222}Rn does not diffuse through the plastic walls. Sealed collectors exposed for 13 days in a ^{222}Rn test chamber at 37 pCi/L showed no radioactivity above background as determined with identical unexposed sealed glass vials. Two types of LSC vials were prepared for comparison with the modified device: 1) LSC vials containing 3 g of carbon, and 2) LSC vials containing 3 g of carbon and a 2.75 g bag of desiccant (SORB-ITTM). After exposure for 7 days in a ^{222}Rn atmosphere of 36 pCi/L at 40% RH and temperature of 19.6°C, the LSC vial with 2 g of carbon only was 1.12 times more sensitive than those with 3 g of carbon. The amount of water adsorbed by each type was the same (0.08 g). However, the collector with 3 g of carbon and a desiccant bag adsorbed 0.27 g of water and its sensitivity was 5-10% lower than that with 2 g of carbon only. The desiccant bag appeared to collect about 2% of the adsorbed radon. From these tests it is obvious that the diffusion barrier filter used in the plastic vial collector is adequate for integration periods up to 7 days. The sensitivity of the 2 g collector was the same whether one or two filters were used as diffusion barriers.

The calibration factors of the collectors were determined at different conditions of ^{222}Rn concentration ranging from 1-50 pCi/L, relative humidities ranging from 30-70%, and for exposure periods ranging from 2-7 days. At the start of the exposure, the vials are fitted with the diffusion barrier screw caps. At the end of the exposure the vials are sealed with the original airtight screw cap and sent to the laboratory for analysis. The net weight of water vapor adsorbed by the carbon inside the vial is measured with a sensitive balance and recorded for incorporation into the calibration curve. Typical gain during a 4 day exposure at 50% relative humidity is 50 mg of water.

The exposed collector is prepared for analysis by quickly adding 15.0 ml of a xylene based LSC cocktail above the carbon bed. The advantage of this modified collector is that there is no sample transfer and thus less opportunity for radon degassing. The cocktail is commercially available from Packard as INSTA-FLUORTM consisting of 90-100% O-Xylene and 3% N-Pentanol with scintillators. The sealed collector is shaken for 5-10 minutes in an automatic agitator and is left to stand for several hours for maximum extraction of ^{222}Rn from the carbon bed.

Analysis for ^{222}Rn is performed with a Beckman LS 5000TD Liquid Scintillation System in a two-phase orientation. The detector energy window was set in the region between channel 500-900 for the best resolution of the three alphas from ^{222}Rn , ^{218}Po , and ^{214}Po , with background of 15 cpm. Figure 1 shows the analyzers response obtained with an LSC collector exposed in a ^{222}Rn chamber for 4 days. With this region of interest, a counting efficiency of 2.5 CPM/pCi was obtained using a ^{226}Ra standard solution in equilibrium with ^{222}Rn and its decay products.

To determine the maximum extraction of ^{222}Rn from a field sample, a curve was determined empirically by analyzing the sample collector from 1.3 hours to 38 hours after the cocktail was added. Figure 2 shows the extraction rate of ^{222}Rn versus contact time. After 13 hours, the extraction is almost 99% and the maximum (100%), occurs in about 18 hours with no change up to 38 hours. Analysis after only 3 hours of contact may underestimate the ^{222}Rn concentration by as much as 15%.

RESULTS AND DISCUSSION

The preweighed PET vials with 2 g of carbon were exposed for calibration for 2-7 days in ^{222}Rn test chambers in which the ^{222}Rn concentration, temperature, and relative humidity were well documented. The ^{222}Rn concentration ranged from 6.5-50.0 pCi/L, the humidity between 30-70%, and the temperature from 18-22°C. The exposed collectors were postweighed and the water adsorbed was determined. The extraction of ^{222}Rn in the presence of the liquid scintillation cocktail was always more than 15 hours to maximize extraction count rate. The calibration factor (Cf) was determined from the following expression (George, A.C. 1984).

$$\text{Cf} = \frac{\text{Net CPM}}{\text{E} \times \text{Ts} \times \text{Df} \times \text{Rn}}$$

Where: Cf = Calibration factor, Radon adsorption rate, L/min.
 Net CPM = (Gross CPM - Background CPM)
 E = The detector efficiency with ^{226}Ra standard solution, (CPM/pCi)
 Ts = Exposure time, (min)
 Df = Decay factor from the midpoint of exposure to the time of counting

$$\text{calculated from } e^{-\frac{0.693t}{5500 \text{ min}}} \quad \text{and} \quad t = \text{time in min from midpoint of exposure to counting time.}$$

Rn = ^{222}Rn concentration, pCi/L

A series of calibration curves were obtained for 2-7 days of exposure at different humidities ranging from 30-70%. The calibration factors (Cf) were calculated using the equation above. At 0.05 g of water adsorbed the corresponding Cf's are 0.00427, 0.00367, 0.00346, 0.0033, 0.00312, and 0.00296 for 2, 3, 4, 5, 6, and 7 days exposures, respectively. The corresponding Cf's when 0.15 g of water was adsorbed are 0.00383, 0.0034, 0.00306, 0.00283, and 0.0025 respectively. Collectors exposed from 2-7 days in a 50 pCi/L ^{222}Rn atmosphere at 70% RH and temperature at 20.3°C showed that even up to 7 days, they continue to adsorb and accumulate ^{222}Rn as shown in Figure 3. Although the adsorption rate is reduced by about 50% from 2-7 days of exposure, the additional signal is sufficient to render the measurement useful even in an environment with high humidity and without a desiccant bag inside the collector.

The LLD for the plastic vial collector with 2 g of carbon and with a total background of 15 CPM counted for 20 minutes was calculated using the expression $\text{LLD} = 4.65 \text{ SqR CPM/Tb}$ where Tb is the time of background counting (Altshuler and Pasternak 1963). The LLD for a sample collected over a period of 4 days (5,760 min.), analyzed 3 days post exposure with Df = 0.407 and analyzer efficiency of 2.5 CPM/pCi and Cf = 0.00305 with 0.15 g of water adsorbed is calculated as follows:

$$\text{LLD} = \frac{4.65 \text{ SqR } 15/20}{2.5 \times 5760 \times 0.407 \times 0.00305} = 0.22 \text{ pCi/L}$$

If the sample is counted for 10 minutes LLD = 0.32 pCi/L
 If the sample is counted for 50 minutes LLD = 0.14 pCi/L

The counting error at the 95% confidence level for a collector exposed for 4 days in a 49.1 pCi/L ²²²Rn atmosphere and analyzed 3 days later is calculated from the following equation:

$$\% \text{ Counting Error (95\% conf.)} = 1.96 \text{ SqR } \frac{\text{Gross CPM}}{T_s} + \frac{\text{Back. CPM}}{T_b} = \text{cpm}$$

Where: T_s = the counting time of the sample and
 T_b = the counting time of the background.

For the above sample with a 10 minute count time the error is:

$$1.96 \text{ SqR } 882/10 + 15/10 = 18.6 \text{ cpm}$$

$$\text{and } \frac{18.6 \text{ cpm}}{882-15} (100) = 2.1\% \text{ or } 49.1 \pm 1.0 \text{ pCi/L}$$

At 4 pCi/L the error is 8.0 % or 4.0 ± 0.32 pCi/L. If both sample and background are counted longer, the error is reduced accordingly.

CONCLUSIONS

Since a ²²²Rn measurement over a period of several days is desirable, the LSC collector technique was investigated and modified substantially to measure ²²²Rn accurately for as long as 7 days. A PET plastic vial containing 2 g of activated carbon with a diffusion barrier was found to perform adequately when exposed to conditions likely to be found in the indoor environment. The advantages of the modified technique are the ease of field sample handling and subsequent analysis. There is no sample transfer and the opportunity of degassing the adsorbed ²²²Rn is minimized. The clear PET plastic vial is impervious to ²²²Rn and has the same UV light transmission characteristics as the heavier more expensive and fragile glass vial. Calibration of the modified collector at humidity conditions ranging from 30-70% for 2-7 days indicates good performance and shows adequate sensitivity for measurements of environmental levels of ²²²Rn.

The combination of low background and good counting efficiency of the analytical system renders the modified collector an appropriate device capable to measure ²²²Rn as low as 0.2 pCi/L (7.4 Bq/m³). The integrity of the collector is destroyed after analysis and cannot be reused as is the case with some activated carbon collectors that use the gamma analysis technique. However, the replacement cost is very low to offset the savings realized by recycling the collector.

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Figure 1
Alpha Activity Vs. Channel Number

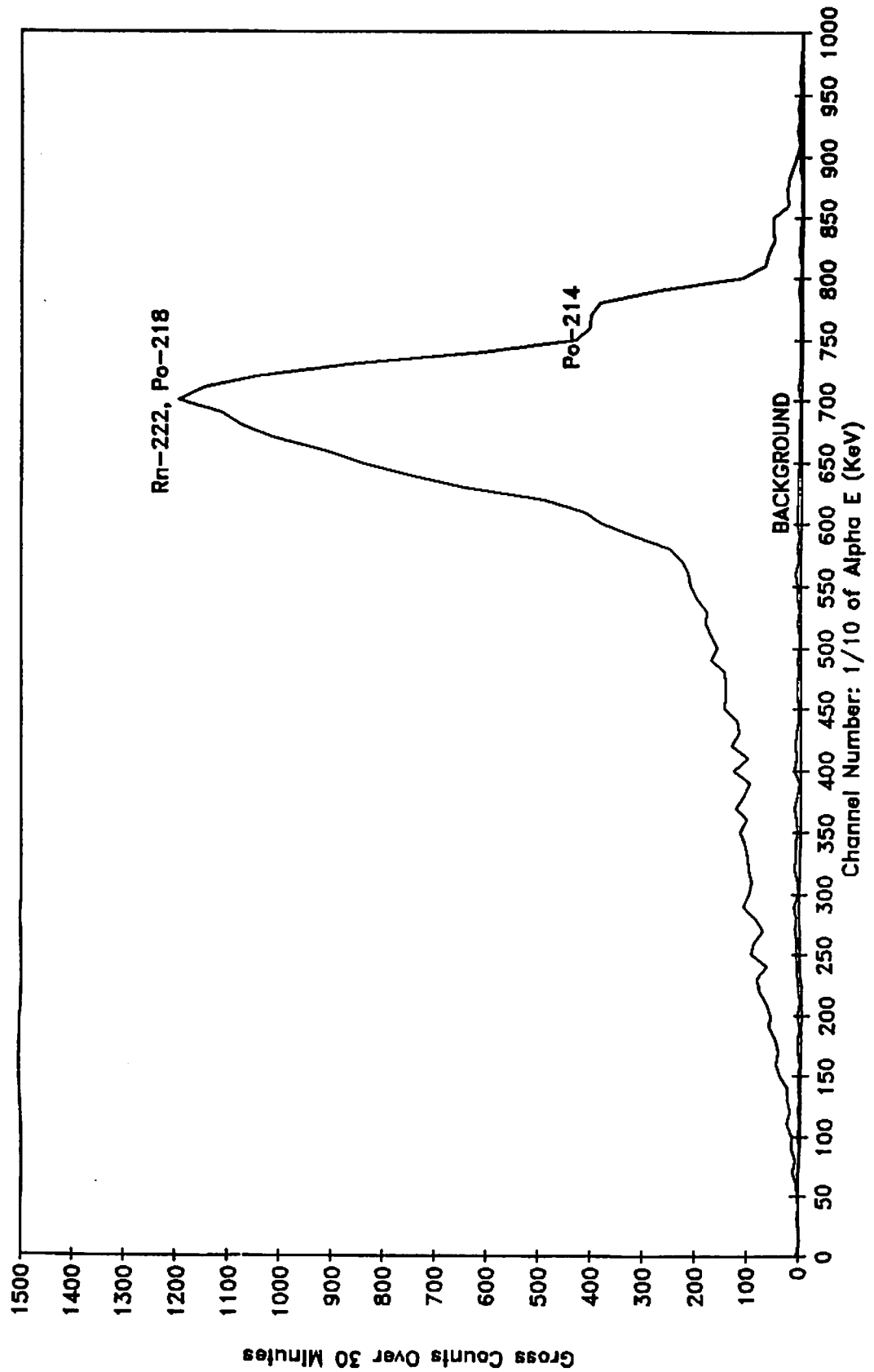


Figure 2
Rn-222 Extraction Vs. Contact Time

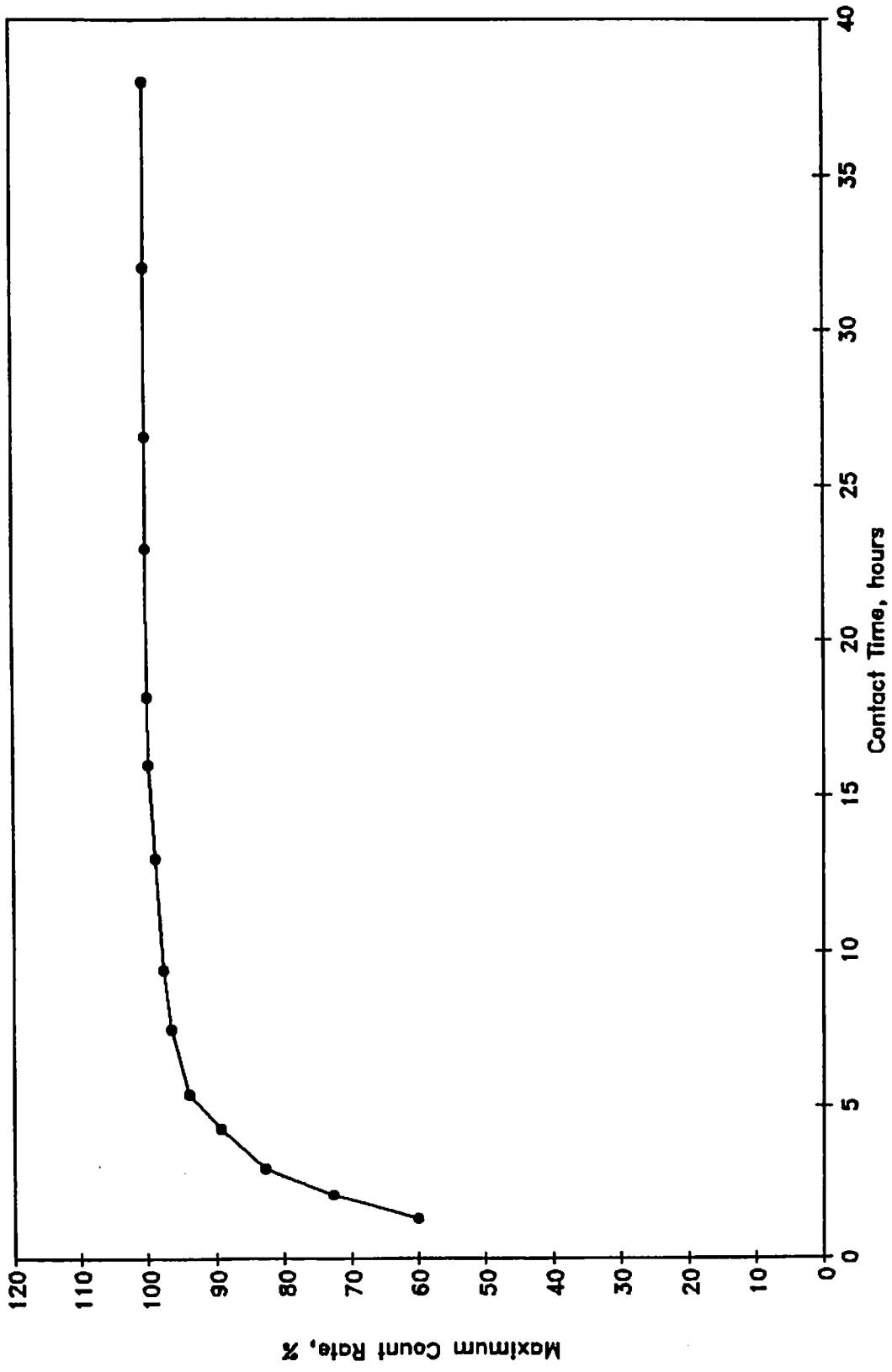


Figure 3
Rn-222 Adsorption from 2-7d Exposure

