RADON AND WATER VAPOR CO-ADSORPTION ON SOLID ADSORBENTS

by

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ABSTRACT

The potential health hazard posed by radon and its daughters has led to increased efforts to develop effective methods for reducing radon concentrations in indoor air. One promising method for reducting radon in homes is to adsorb it on solid adsorbents such as activated charcoal, silica gel, and molecular sieves. Activated charcoals are currently used for the measurement of radon concentrations in indoor environments, whereas silica gel and molecular sieves are finding increasing application in desiccant based air conditioning systems. Although radon measurements are carried out in humid air, literature data describing radon adsorption in the presence of water vapor are limited.

An experimental system has been designed to measure radon concentrations in the solid and gas phases simultaneously at equilibrium. The uptake of radon by commercially available BPL activated charcoal, silica gel (grade 40), and molecular sieve-13X were measured at room temperature (298 K) from dry nitrogen and moist nitrogen under both dynamic and static conditions. Radon adsorption isotherms were of Type III for all the three adsorbents with adsorption capacities being highest for activated charcoal and the lowest for silica gel. The presence of water vapor reduces the adsorption capacities for radon on BPL activated charcoal considerably. The applicability of these data to improve the radon measurement by charcoal canisters and to design a removal system are also discussed.

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INTRODUCTION

The ability of activated charcoals to adsorb and retain radon has been employed in the design of charcoal canisters that are used to measure radon concentrations indoors. The amount of radon that is adsorbed per unit weight of charcoal at a particular temperature is a function of the gas phase concentration. This relationship can be expressed by a curve known as "isotherm". Therefore, radon adsorbed from air by charcoals in a canister can reach equilibrium corresponding to its gas phase concentration, provided sufficient time is allowed. From the knowledge of solid phase radon concentration, the equilibrium isotherm can be used to measure the concentration of radon in the gas phase. However, physical properties of the charcoal such as surface area, pore size distribution, and chemical nature of the surface play an important role in the uptake capacity. The presence of water vapor also can influence the adsorption process.

Several researchers have studied the effects of these parameters on the radon adsorption capacities of charcoals. Most researchers agree that an increase in the temperature or relative humidity or both decreases the uptake of radon. However, Cohen (1) stated that the correction due to the change in relative humidity was not more than 6%. However, George (2), Ren and Lin (3), Scaripitta and Harley (4), and Ronca-Battista and Gray (5) concluded from their experimental results that relative humidities can decrease the radon uptake by as much as 50% when relative humidities changed from 20 to 100%. Ren and Lin (3) and George (2) also reported that the amount of radon adsorbed by canisters did not change significantly when temperature was changed from 17 to 27°C. On the other hand, Cohen (1) observed a change of 1.5% in adsorption capacity for each 1°F change in temperature. Pojer (6) assessed the effects of temperature and humidity, both theoretically and experimentally, on the performance of a diffusion barrier charcoal canister. The adsorption capacity for radon decreased by 30% when the temperature was increased from 13 to 35°C, and by a factor of 3 when the relative humidity was increased from 15 to 90% at 35°C.

The effects of relative humidity and temperature on the adsorption capacity of radon by charcoal have been taken into account by employing a "calibration factor" which has a dimension of Lmin^{-1}. This procedure has also been adopted by the United States Environmental Protection Agency for measuring radon concentration in homes. Recently, the General Accounting Office, GAO (7), found that the radon detectors recommended by the EPA can give an average concentration error ranging from 16 to 40%. The charcoal canister type detector can give an error as high as 133% with an average error of ±19%.

Although adsorption isotherm data are needed to determine radon concentrations, there does not appear to be any recent data in the open literature. Most studies were conducted from 1950 to 1960 (8-12). Also, the equilibrium data were taken on adsorbents that were specially

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prepared or are not commercially available at the present time. In those previous studies, tl equilibrium data were obtained by using air, argon, hydrogen, nitrogen, and carbon dioxide as carrier gases at atmospheric pressure and near room temperature. The experimental data from the: studies also indicated that the radon adsorption capacities were less for silica gel and molecular sieves than for activated charcoal.

Although activated carbons are used to measure radon concentration, they have not been employed in the design a radon removal unit. In the past, however, activated charcoal has bee used to control radon concentrations in uranium mines (13-16). Such a radon removal methc_ could have several advantages over present radon removal techniques (increased ventilation sealing of cracks and and joints, and source control). For example, an adsorption process may t more energy efficient than one that employs increased ventilation, since radon can be allowed to decay in the bed and the bed would not require a great deal of energy for regeneration. A fe: studies have been reported that relate to the development of a commercial radon removal unit (16-19). In those studies, the effects of temperature, relative humidity, radon concentration, air flo· rate, and the concentration of carbon dioxide on radon adsorption were investigated. Recently, Bocanegra and Hopke (20) investigated the adsorption of radon on several types of activate ¨ carbons in the presence of several pollutants including iso-octane, ethylene chloride, anu formaldehyde. The dynamic adsorption coefficients and the number of theoretical stages also wer⁻ obtained at 20 ^{o}C. No dynamic studies have been reported in the literature where either silica gel c molecular sieves were employed as adsorbents.

In the present study, the equilibrium uptake of radon by commercially available BP: activated charcoal, silica gel (grade 40), and molecular sieve-13X were measured at 298 K from dry and moist nitrogen under both dynamic and static conditions. The equilibrium data wer correlated with a modified Freundlich equation. The applicability of these data to improve the radon measurement by charcoal canisters and to design a removal system are discussed.

EXPERIMENTAL SECTION

Materials: The adsorbents used in this study were BPL activated charcoal provided by Calgo: Carbon Corporation, and molecular sieve 13X and silica gel (grade 40) provided by Davidson Chemical Division of the W.R. Grace & Co., Baltimore, Maryland. The properties of thes· adsorbents are presented in Table I. Radon gas was generated from a model Rn-1025 Pylon flow-through source by flowing dry nitrogen gas from a cylinder. The source is a sealed container containing dry powder of ^{226}Ra with a stated activity of 22.6 kBq. The source is capable of producing a constant radon gas at 2.847 Bq/min (76.87 pCi/min). A certified gamma calibratior source, model Ra-226-Sc, obtained from The Nucleus, Inc., Oak Ridge, Tennessee, was used as a

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reference to calibrate the NaI(TI) spectroscopy system before each run. It had a stated activity of 548 Bq (14800 pCi).

PROCEDURES:

Equilibrium Adsorption: The equilibrium adsorption studies were carried out using an all glass apparatus. A schematic diagram of the system is shown in Figure 1. The sample holding tube was a 0.5 m x 48 mm diameter glass tube that was made with a flat bottom to match the geometry of the gamma calibration source. A copper circulation coil wrapped around the sample holding tube was used to control the adsorption temperature within ± 0.1 K of the desired value by circulating water through the coil. The bottom of the tube was positioned to provide direct contact with a lead-shielded 50 mm x 50 mm NaI(TI) detector, which was coupled to a multichannel pulse height analyzer with associated electronics. Radon gas was continuously flushed into a 2.8-liter glass chamber by flowing dry nitrogen from a cylinder through the source at a constant flow rate. The flow rate was monitored by a flow meter. The radon-laden nitrogen was vented through a fume hood equipped with filters. The method of calibration prior to each run and radioactivity calculation was described in our previous paper (21). Adsorbent samples were spread uniformly on the bottom of the sample holding tube, which has the same geometry as the gamma calibration source. By trial and error, it was found that 5 g of the sample is sufficient to achieve statistically significant counts from the NaI(TI) detector. The 5 g of the sample was generally stacked in a 2-3 layers at the bottom of the sample tube. It was noticed that when larger amounts of the sample were used, radon was adsorbed on the top layer of the adsorbent and the gamma activity decreased significantly before being detected by the NaI(TI) detector; a longer time was required before any significant count was obtained from the detector. When amounts smaller than 5 g of the sample were used, however, the counts from the detector were insignificant relative to the background level, even after adsorption was continued for 40 hours.

The sample was regenerated by heating it under vacuum at a temperature of 573 ± 0.1 K for 12 hours. After regeneration, the sample was cooled to the desired adsorption temperature, and a background count obtained from the Lucas cell was recorded. The sample holding tube was then placed directly on the top of the NaI(TI) detector and radon-laden nitrogen was introduced into the system in small pressure increments of approximately 50 mmHg. After each increment, 3.5 hours were allowed for radon and its daughters on the adsorbent to reach radioactive equilibrium; It should be noted that this equilibrium is different from the adsorption equilibrium, which was established between radon in the gas and solid phases in approximately 15 minutes. This was explained earlier (21). Once radioactive equilibrium was reached, the gas phase and solid phase

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counts were obtained simultaneously at ten minute intervals. Subsequent data points were obtained by admitting more radon-laden nitrogen into the system and following the same procedure.

The isotherm data of radon and water vapor co-adsorption were obtained by initially equilibrating the adsorbent with water vapor up to the desired relative humidities i.e., 40%, 60%, 80%. The radon-laden dry nitrogen was then introduced into the system in small pressure increments of approximately 50 mmHg, and radon and its daughters were allowed to equilibrate in the usual manner. The dry radon-laden nitrogen stream from the radon source was bubbled through water in two saturators in series. The saturators were immersed in a constant temperature bath whose temperature was controlled within ± 0.1 K to maintain the desired relative humidity of the gas stream. The gas stream could be admitted into either a 2.8-liter glass chamber, so that humid radon in nitrogen can be introduced into the system in small pressure increments, or directly passed through the packed bed during the dynamic study.

Dynamic Adsorption: The adsorption column was packed with approximately 50 grams of adsorbent sample. A bed diameter to particle ratio of 17.5 was maintained in the bed to avoid channeling and wall effects. A superficial gas velocity of 0.198 Lmin^{-1} was maintained in the bed during experimental runs. The concentration of radon in the inlet nitrogen stream was maintained at 220 ± 20 pCi/L throughout the experiments. The bed was regenerated by flowing dry nitrogen at 473± 0.1 K for 10 hours. After regeneration, the adsorbent bed was cooled to the desired adsorption temperature, and a background measurement was obtained using the Lucas flow-through cell. The nitrogen was directed to the source, which was flushed for one hour at a constant flow rate. The dry or moist radon-laden nitrogen was then passed from the top of the column, and the radon activity at the column exit was measured by the Lucas cell along with the AB-5 radiation monitor at five minute intervals. The radon was allowed to flow into the column until the breakthrough was complete and the counts of the effluent reached a maximum constant value, equal to that of the inlet gas stream.

RESULTS AND DISCUSSION

Equilibrium Isotherm Data: The equilibrium data of pure water vapor were first obtained on BPL activated charcoal, silica gel, and molecular sieve 13X at 298 K. As can be seen from Figure 2, the shapes of the isotherms are different for different adsorbents. The isotherms are Type I on silica gel, Type II on molecular sieve-13X, and Type V on activated charcoal, which suggest different adsorption mechanisms. Small amounts of water vapor were adsorbed on charcoal for relative humidities below 40%, followed by a sharp rise in the uptake at relative humidities from 40 % to 60%. This is mainly due to the pore filling of the capillaries.

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The experimental data for radon adsorption on BPL activated charcoal, silica gel (grade 40), and molecular sieve 13X at 298 K are shown in Figure 3. The error in the count rate of the gas phase was determined at the one sigma significance level and it ranged from 4.79 % to 11.92 %. The minimum detectable activity due to background count was found to be 21.2 counts per minute at the three sigma significance level. Adsorption measurements were repeated for each run to check the reproducibility of the data. Although radon adsorption is a random process, the experimental data were reproducible, with an average error of less than 5%, as indicated in Figure 3. The uptake of radon by activated charcoal was considerably higher than that of silica gel and molecular sieve 13X. However, molecular sieve 13X exhibited a higher affinity for radon than was found for Type 5A (10). This may be due to the larger pore diameter of Type 13X. The silica gel exhibited a relatively low radon adsorption capacity. The equilibrium data exhibited a Type III isotherm. Once an atom or a molecule is adsorbed, adsorbate-adsorbate interactions promote the adsorption of further atoms or molecules so that the isotherm becomes convex to the pressure axis. The Type III isotherms were also obtained by Przytycka (11), Brutt and Kurbatov (12), and Coleman et al. (10).

The equilibrium data of radon on BPL activated charcoal, pre-adsorbed with water vapor at 40%, 60%, and 80% relative humidities are compared in Figure 4 with that obtained for dry nitrogen. The isotherms were also of Type III in the presence of water vapor. However, the amount of radon adsorbed on a pre-equilibrated activated charcoal was lower than that adsorbed on a dry charcoal. It may be noted that when radon-laden nitrogen was introduced into the system a small amount of water vapor was desorbed from the charcoal. In a separate run, radon-free nitrogen was introduced into the system under similar conditions and the same results were observed, suggesting that probably some other impurities in nitrogen is displacing water vapor from the charcoal surface. The interaction between radon and charcoal is not strong enough to displace the preadsorbed water vapor. Thomas (17) and Strong and Levins (18) made the same conclusion from their dynamic adsorption studies; however, the results contradicted other investigators' conclusions (6,2).

Dynamic Adsorption Data : Breakthrough curves for radon on BPL activated charcoal, silica gel (grade 40), and molecular sieve 13X are shown in Figure 5. The bed lengths for activated charcoal, silica gel, and molecular sieve were 10.16, 11.43, and 13.97 cm. respectively. The superficial velocity for nitrogen gas through the adsorbent bed was 0.198 cm/min, and the pressure drop across the bed varied from 10 to 15 mmHg. The flow rate of nitrogen through the radon source was maintained approximately constant at 0.35 Lmin^{-1}. This flow rate produces an inlet radon concentration of about 220 pCi/L (radon partial pressure of 1.2×10^{-12} mmHg) with minor fluctuations of $\pm$ 20 pCi/L for all experimental runs. It was noted that the various solid adsorbents

exhibit different steady state outlet concentrations for the same inlet radon concentration. According to Madey (22), the steady state concentration of radioactive gas at the outlet of a column of length I is related to the inlet concentration through the expression

$$C_{outlet} = C_{inlet} \exp(-\gamma L) \qquad (1)$$

where γ is the decay constant for the radioactive gas. The breakthrough curves for radon from the radon-water vapor mixture on BPL activated charcoal were measured at different relative humidities. The results are shown in Figure 6. The steady state radon concentration at the column outlet was found experimentally to be more than the inlet concentration. This may be due to increased radon plate out on the inside of the Lucas cell. A similar observation was reported earlier by Boncanegra and Hopke (20), who found that the presence of water vapor causes neutralization of ^{218}Po ions and results in their deposition in the detector. The adsorption of radon on BPL activated charcoal from humid nitrogen is considerably less than that from a dry nitrogen stream. The presence of water vapor in the nitrogen stream reduced the uptake capacities for radon due to the strong competition by water vapor molecules for the available sites. However, it is interesting to note that radon broke through the bed approximately at the same time irrespective of the relative humidities of the nitrogen stream. Water vapor molecules, having a stronger affinity for activated charcoal than radon, might be adsorbed near the inlet section of the bed at a faster rate. As adsorbed water front progresses through the bed it is displacing radon, resulting in a faster radon breakthrough from the bed. As shown in Figure 7, repeated experiments for radon adsorption from dry and moist nitrogen on the activated charcoal verified the reproducibility of the results.

Equilibrium Data Correlation: The Freundlich equation has been modified to correlate the equilibrium adsorption data of radon from dry nitrogen. The modified equation can be written as

$$q = k_1 \left(\frac{P}{P_0}\right)^n \qquad (2)$$

or

$$\ln q = \ln k_1 + n \ln\left(\frac{P}{P_0}\right) \qquad (3)$$

where q is the amount of gas adsorbed, P is the system pressure. P_0 is a reference pressure and is arbitrarily set to 10^{-14} mmHg. Here, k_1 is a measure of the volume of gas adsorbed per unit mass of adsorbent and n is the intensity of adsorption. Figure 8 shows good agreement between the

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experimental data and the predicted values. The value of n was set to 1.75 and k_1 has the following temperature dependence:

$$k_1 = 2.10 \times 10^{-11} - 6.58 \times 10^{-14} \, T \qquad (4)$$

Thus, the amount of radon adsorbed on BPL activated charcoal corresponding to the gas phase concentration can be expressed as

$$q = (2.10 \times 10^{-11} - 6.58 \times 10^{-14} \, T) \left(\frac{P}{1 \times 10^{-14}} \right)^{1.75} \qquad (5)$$

Knowing the solid phase concentration, the gas phase concentration can be obtained in pCi/L from the equation

$$C = \frac{5.48 \times 10^3 \, q^{0.571} \, T^{-1}}{(2.10 \times 10^{-11} - 6.58 \times 10^{-14} \, T)^{0.571}} \qquad (6)$$

The equilibrium isotherms of radon, such as the ones shown above, can be used for measuring radon concentrations in homes provided accurate isotherm data are available for the activated charcoal. From the knowledge of the solid phase radon concentration, the equilibrium isotherms corresponding to the particular field conditions, temperature and humidity, can be used to determine the concentration of radon in the gas phase.

Another application for the dynamic and static adsorption data is in the design of an adsorber unit for removing radon from indoor air. The design of such a unit may range from a single packed column to a complex system of multiple columns.

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NOMENCLATURE

k_1 first empirical constant in the modified Freundlich equation

n constant in the modified Freundlich equation

P equilibrium partial pressure of radon (mmHg)

P_o reference pressure (mmHg)

q volume of radon adsorbed per unit weight (cm^3 Rn/g adsorbent)

R gas constant

T temperature (K)

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Table I. Properties of Microporous Solid Adsorbents.

Property	BPL Activated Charcoal	Silica Gel (Grade 40)	Molecular Sieve 13X
Particle size, $(\text{Å})^b$	6 x 16 mesh	6 x 12 mesh	8 x 12 mesh
Surface area, S $(m^2/g)^a$			
micropores	823	663	294
meso and macropores	50	9	101
total	874	672	395
Pore volume, V $(cm^3/g)^a$			
micropores	0.47	0.38	0.14
meso and macropores	0.10	0.02	0.27
total	0.57	0.40	0.41
Average pore diameter, $4V/S$ $(\text{Å})^a$	26	24	41.7^c
Bulk density $(g/cm^3)^b$	0.60	0.72	0.72
Equilibrium water capacity (% wt.)^b	-	-	29.5
Moisture content as shipped (% wt.)^b	<1	-	< 1.5

[a] Analysis made by Porous Materials, Inc. Ithaca, New York.

[b] Analysis provided by the manufacturer.
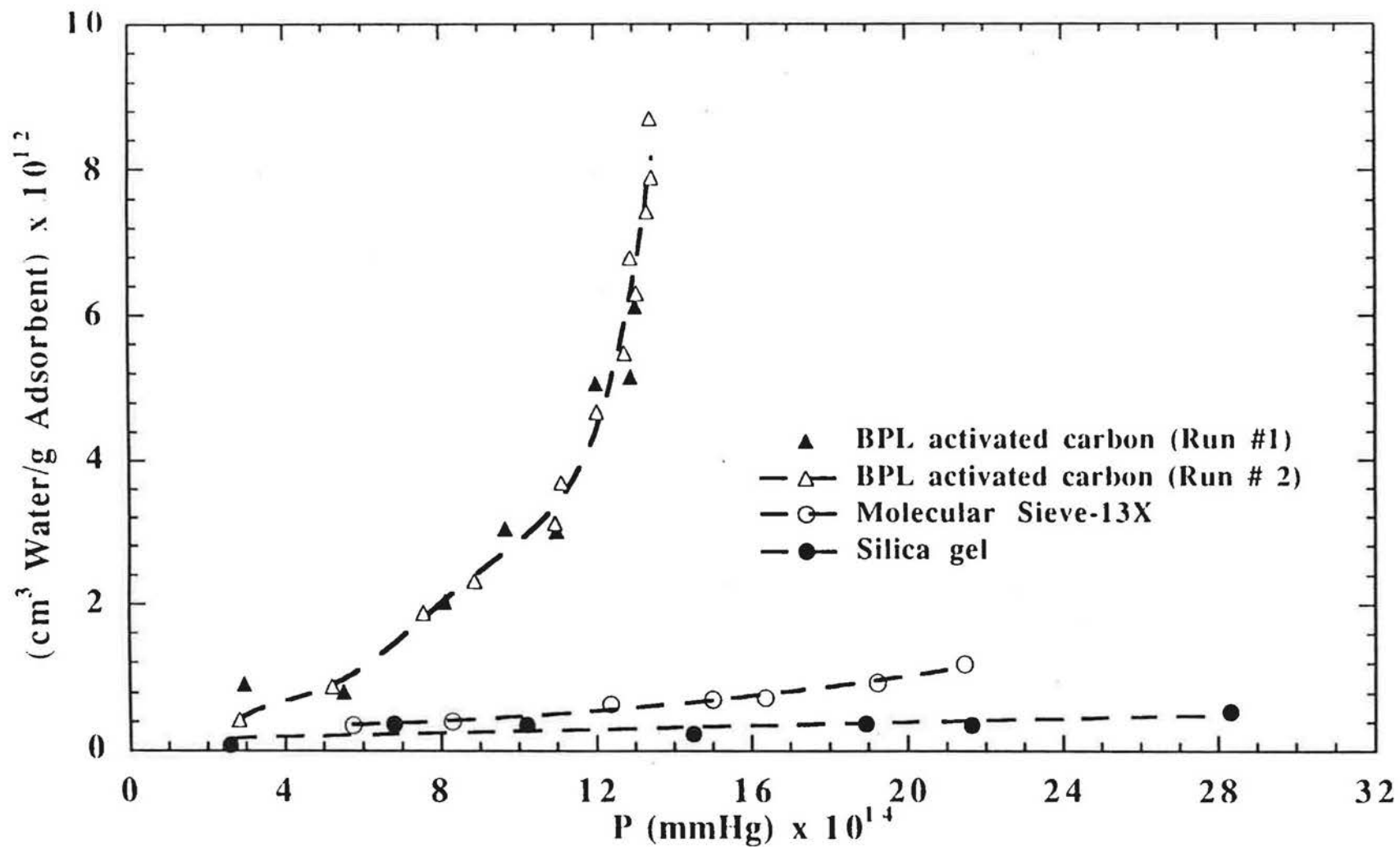
[c] based on total surface area and pore volume.

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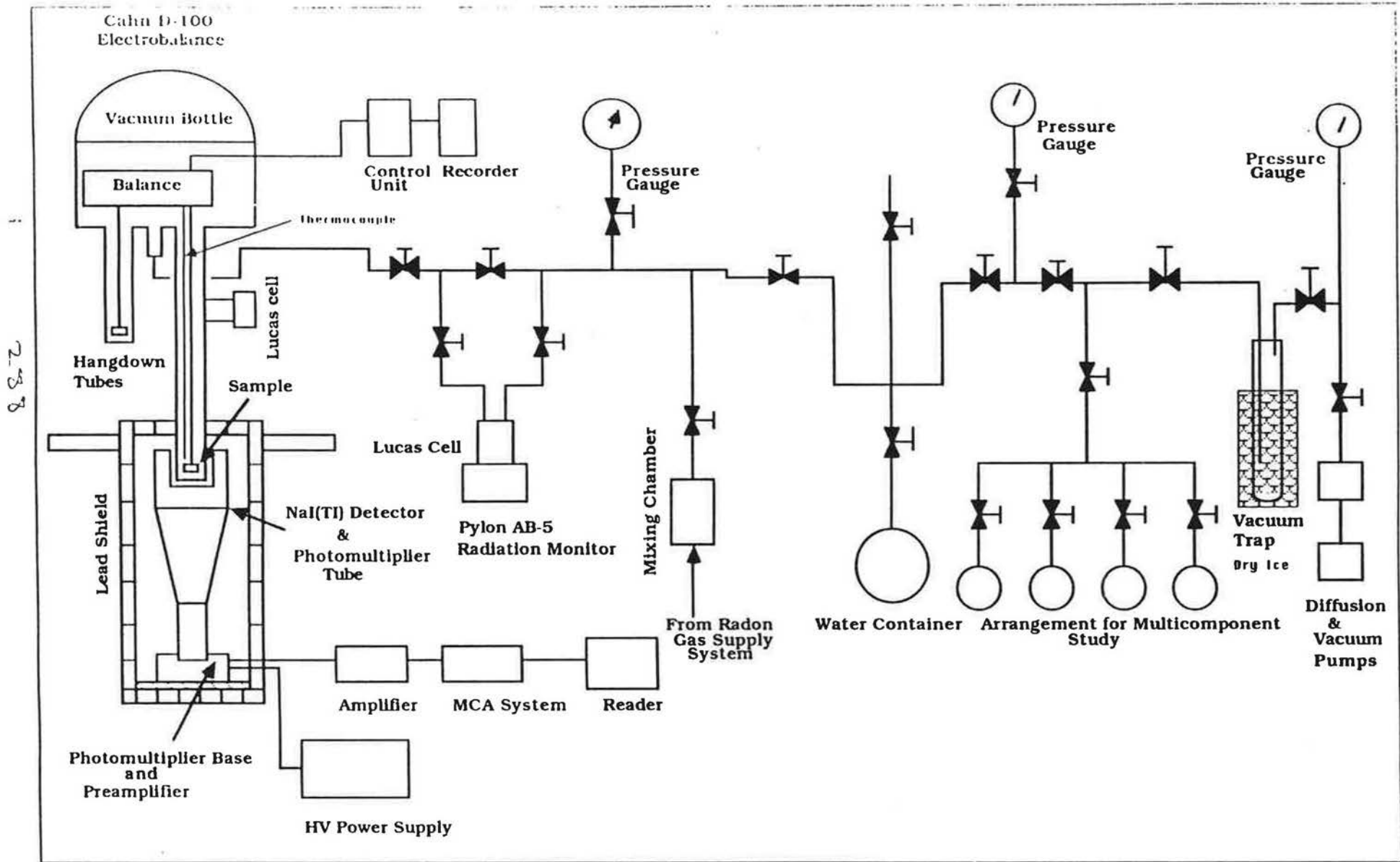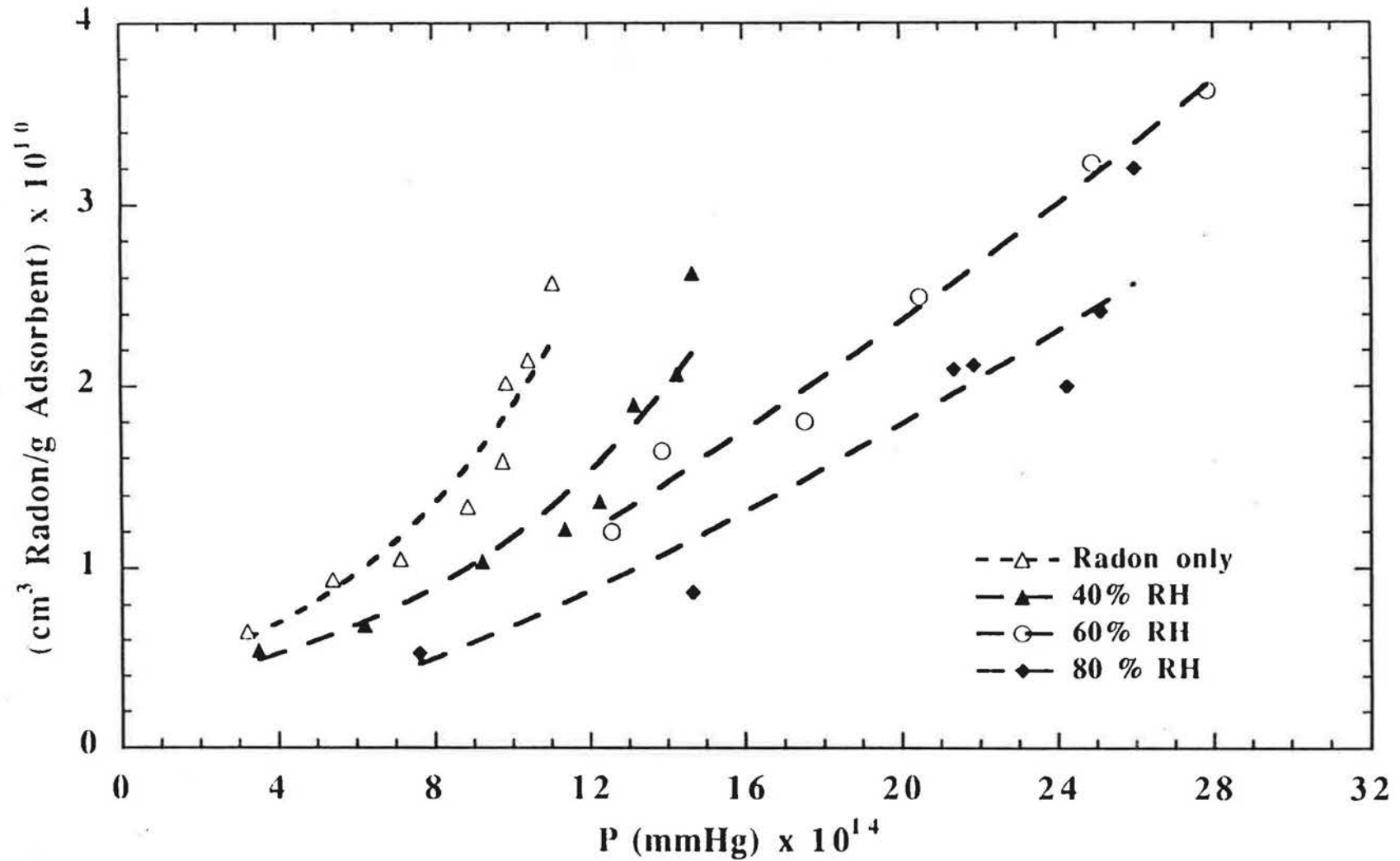
Figure 1. Schematic Flow Diagram of Radon Adsorption Apparatus
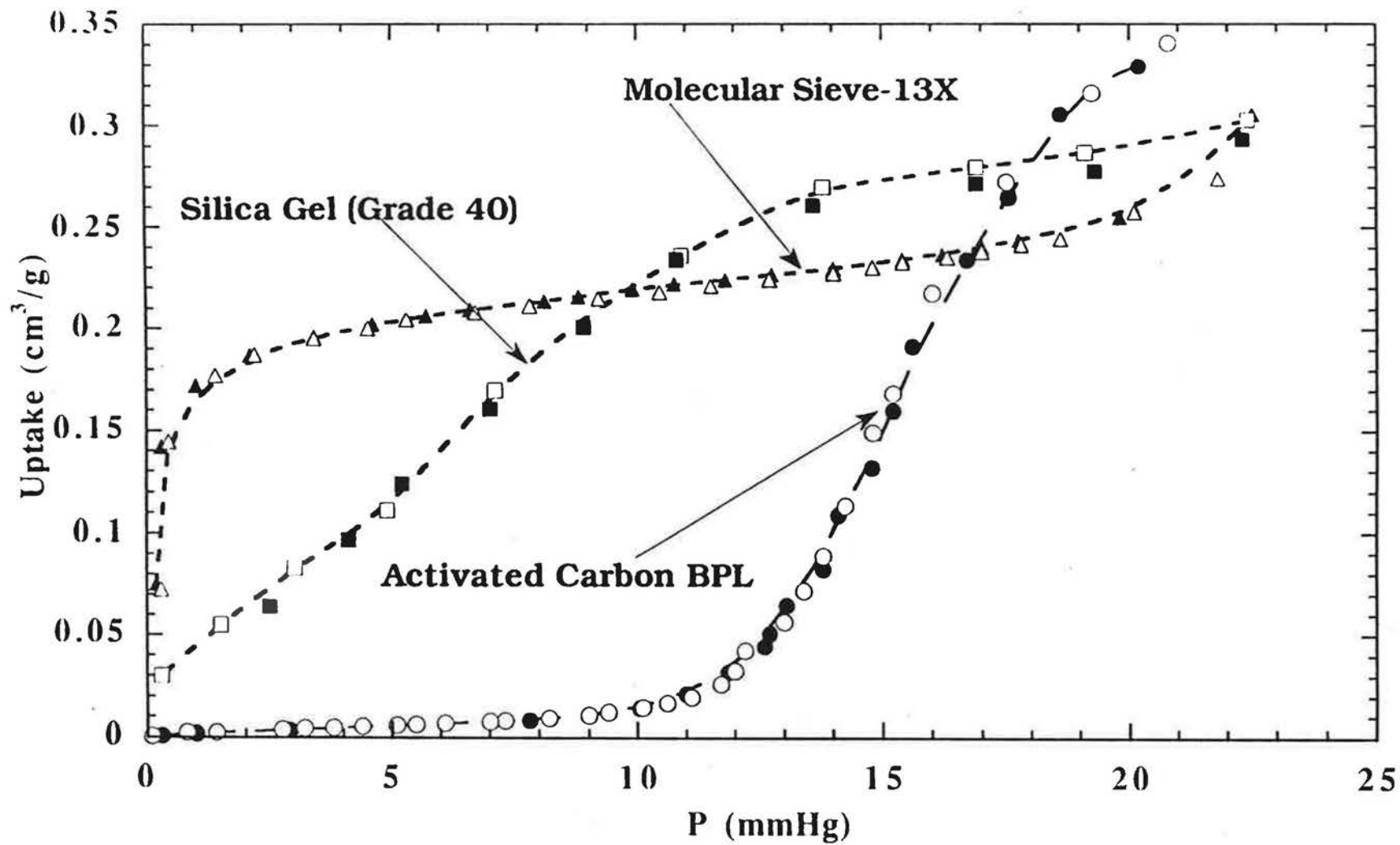
Figure 2. Adsorption isotherms of water vapor on various solid adsorbents at 298 K.

Figure 3. Adsorption isotherm data for radon on various solid adsorbents at 298 K.

Figure 4. Radon and water vapor co-adsorption data on BPL activated carbon at 298 K.

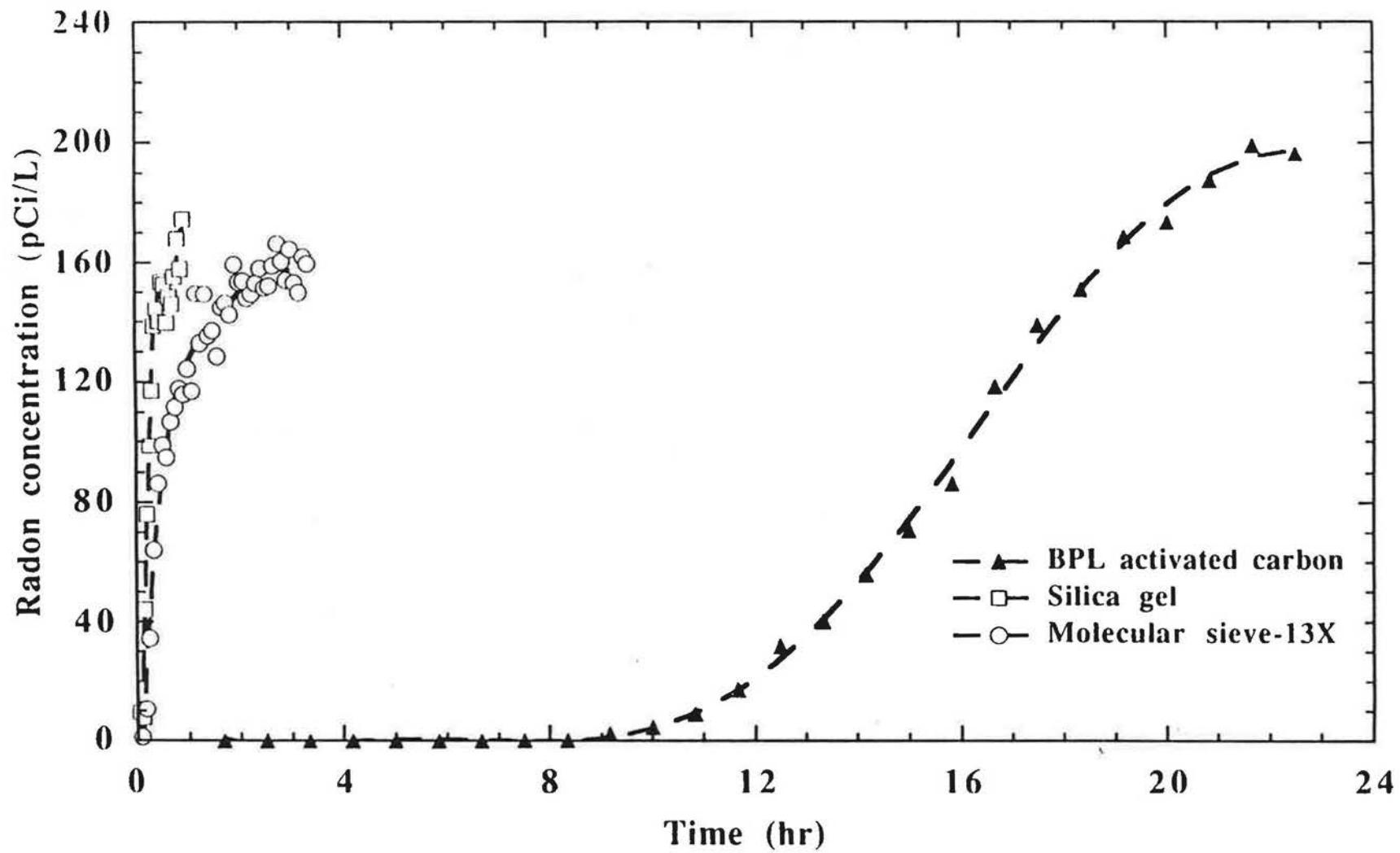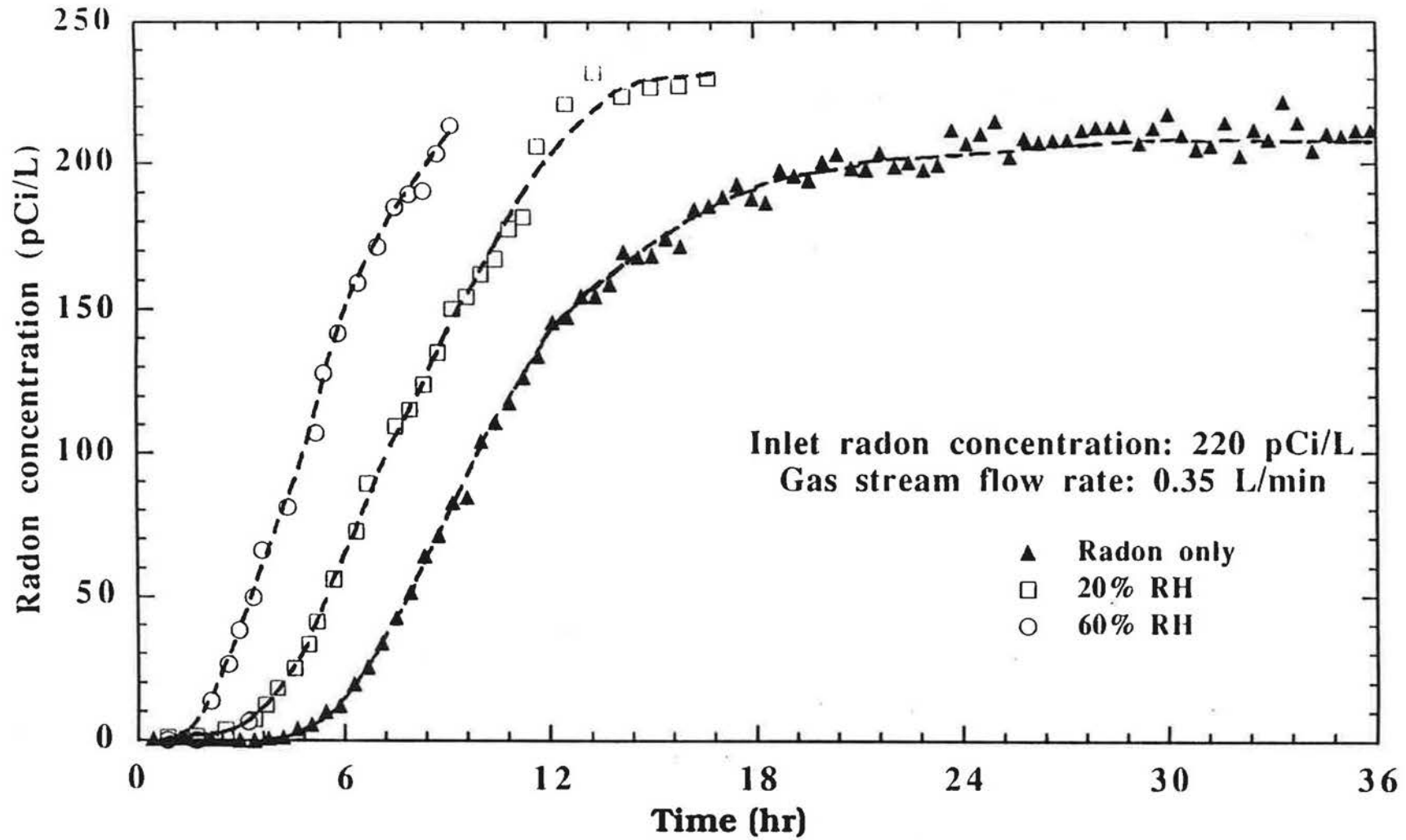Figure 5. Experimental breakthrough curves for radon on solid adsorbents at 298 K.

Figure 6. Breakthrough curves for radon from moist nitrogen stream on BPL activated carbon at 298 K.

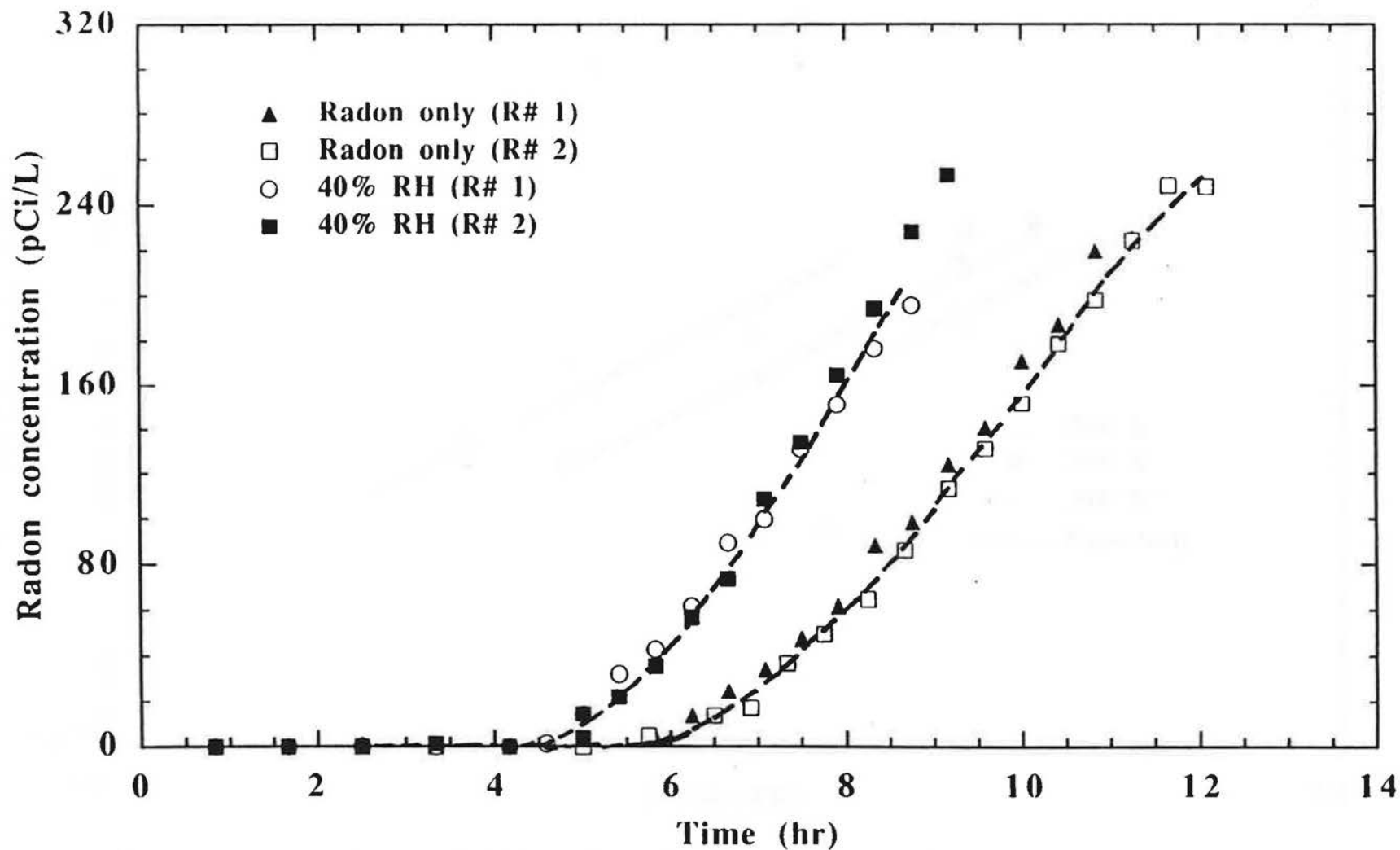Figure 7. Reproducibility of radon breakthrough curves on BPL activated carbon 298 K.