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A METHOD FOR TESTING THE DIFFUSION COEFFICIENT OF POLYMER FILMS

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ABSTRACT

This project developed and evaluated a method to measure the diffusion of radon through thin polymer films. The system was designed so that the simple, one-dimensional transport model developed by Mosley (1996) could be used. The system uses radium-bearing rock as a high level radon source. The test film is sealed in the system with the high concentration radon gas on one side and an alpha detector sealed on the other side. The activity-versus-time data are collected and fitted using a non-linear least squares method. The system measurements and the three fit coefficients are used to calculate the system efficiency and diffusion coefficient. Three polymer films with published values of the radon diffusion coefficient (polyethylene, polyester, and latex) were tested in duplicate to evaluate the method and determine its comparability to values in published literature. The results show good repeatability (10%) and some comparability to similar published data (20 to 200%).

ACKNOWLEDGEMENTS

We want to recognize and extend our appreciation to Eastman Chemical Company for supporting this research to develop methods and data for evaluating the radon diffusion barrier resistance of construction membranes and to Dupont Films Group and The Hygenic Corporation as independent suppliers of commercially available thin film materials to be used for reference purposes in the study.

BACKGROUND

The United States Environmental Protection Agency (U.S. EPA) through its Radon Action Program has been involved in a public health program whose goals have been to (1) determine the content and nature of indoor radon problems and (2) reduce exposures to indoor radon through (a) the development of informed public and private sectors of society and (b) providing cost-effective measurement and control techniques for indoor radon. Since the initial efforts by EPA in 1986-87, substantial progress has been made towards the Radon Action Program goals, the maturation of applied indoor radon control technology, and the extent to which it has been incorporated into existing and new buildings.

EPA's research, development, and demonstration of indoor radon control technology for new and existing buildings has resulted in the application of passive and active control techniques to produce radon (entry) resistant buildings. These techniques and technologies, literally from the ground up, address (a) selection of low entry potential building sites, (b) site and foundation preparation and construction features, (c) design, construction, and operation of radon soil gas collection systems, (d) design and construction of radon entry limiting sub-slab barrier configurations, involving construction membranes , footings, and floor slabs, (e) maintenance of balanced ventilation conditions to prevent radon entry driving forces in buildings, and (f) removal and cleaning of indoor air to limit indoor radon exposures.

One of EPA's main objectives within the Radon Action Program is to ensure that the public and private sectors have the most cost-effective means for reducing indoor radon exposure. In this context the Indoor Environment Management Branch of EPA's Air Pollution Prevention and Control Division has entered into a Cooperative Research and Development

Agreement with Eastman Chemical Company of Kingsport, Tennessee, to establish the technical basis for evaluating the radon barrier effectiveness of innovative prototype construction membranes. These membranes have been developed for ease of application and with significant production cost advantages. Evaluation of the Eastman supplied prototype membranes will be completed and reported in a later paper. This paper will address only the development of the methodology for testing thin film membranes.

Well designed sub-slab construction barriers can limit radon entry and thus indoor radon concentrations to approximately 0.01% of the concentrations found in the soil beneath a building. In most cases this reduction is sufficient to keep indoor radon levels below the EPA action level of 148 Bq m^{-3} (4 pCi/L). In other instances, especially in high radon potential areas, the diffusion barrier resistance of slab-on-grade foundation construction is not sufficient to meet the indoor radon action level concentration. In these circumstances, improved radon entry limiting construction membranes can be very cost effective.

The EPA Radon Barrier Testing Facility, as a programmatic entity, was developed in direct technical support of the Florida Radon Research Program, a cooperative research program between the EPA and the State of Florida, whose goal was to provide the technical basis for standards for the construction of radon resistant buildings in Florida.

OVERVIEW

Diffusion is the movement (transport at the atomic/molecular level) of one material through another as a result of a difference (gradient) in the concentration of the material in motion. Gas diffusion is the movement of a gas through a different solid/liquid/gas caused by a concentration gradient of the gas. The diffusion coefficient describes the property of a material to permit the concentration-driven movement of a specific atomic or molecular species. The diffusion coefficient (for a given set of materials) is modeled as purely a property of the material, independent of the material thickness, geometry, and concentration. The simplest geometry to model is that of one-dimensional transport with a fixed concentration on one side of the material being tested (infinite source), zero concentration on the opposite side (infinite sink), and a uniform, fixed material thickness.

The method used in these tests is an adaptation of one-dimensional transport. One side of the film is exposed to a high concentration of radon gas in air, and the radon concentration on the opposite side of the film is measured as a function of time. The radon gas is derived from rock which contains naturally occurring uranium, the radon precursor. The rock is in a 30-gallon (114-liter) drum with a small mixing fan. The radon gas is pumped out of the drum, through a rotameter and filter, into the lower chamber of the test apparatus, and then back into the drum. The filter eliminates the radon daughters in the air being pumped from the drum. The film is sealed to the top of the lower chamber, and the detector and a spacer are sealed to the top of the film. The amount of radon passing through a unit area of film per unit time is proportional to the thickness of the film and the diffusion coefficient. The amount of radioactivity detected is automatically recorded by a computer.

DESIGN GOAL

This project developed and evaluated a method to measure the diffusion of radon through thin polymer films. The system was designed with several objectives: 1) the simple, one-dimensional transport model could be used, 2) it should be easy to set up and use, 3) it should be relatively inexpensive per test, and 4) it should not require long test runs (less than 1 week). To accomplish this, there had to be a constant, high-concentration radon source on one side of the film; the detector, film, and chamber needed to be the same diameter, and the system had to be leak- tight and easily assembled. The system described in this paper meets these requirements. Three polymer films with published values of the radon diffusion coefficient were tested to evaluate the method and determine its comparability.

SYSTEM DESCRIPTION

The system consists of:

- Radon source
- Filter
- Flowmeter
- Diaphragm pump
- Test chamber
- Alpha-particle detector system
- Desktop PC with battery backup
- Radon measurement equipment using a scintillation cell
- Air reservoir

The arrangement of the system is shown in Fig. 1. The pump draws the air/radon mixture out of the source drum and through the 0.45 μm filter to remove the daughter products. The valve on the flowmeter is used to regulate the flow to 8×10^{-4} $m^3 s^{-1}$ (0.5 lpm). The test chamber is connected as closely as possible to the source drum and the air reservoir to minimize any pressure differential across the film in the test chamber. The system operates closed-loop to minimize the fluctuations in the radon source and maximize the radon concentration.

Initially, a Basic-language program was used to control the instrument and collect the data automatically. This program collected data to a disk file and displayed the last 24 datapoints on the computer display. After the test was complete, the data were transferred to a spreadsheet for display and analysis. An improved system was developed using the WinWedgePro®[1] to handle the interface between the serial communications and a spreadsheet. This system uses a spreadsheet macro to control data collection and store it directly into the spreadsheet. A screen graph plots the data as they are collected. This new software allows the operator to see the progress of the test as the radon concentration comes to equilibrium in the upper chamber.

METHODOLOGY

Before the start of a test, a continuous ambient radon monitor is checked to ensure that the radon concentration in the testing room (a modified paint spray booth) is not above background (approximately 37 Bq m^{-3}) which would indicate a system leak and a health hazard.

The test cell is prepared for the membrane testing by cleaning the sealing surface of the cell and the 0.5 inch (12.7mm) thick spacer with a degreasing hand cleaner which can remove the sticky residue left by the sealing material. The system is purged with ambient air before the test to ensure a low radon background for the start of the test. During purging, the flow is adjusted to the 8×10^{-4} $m^3 s^{-1}$ (0.5 lpm) rate used in the testing. After purging, three new sealing gaskets are made from a non-hardening, clay-type sealing material. One is used on the top of the source chamber, and the other two are used on the spacer (see Fig. 2).

A film test sample approximately 6 by 6 inches (152 by 152 mm) is selected and examined to verify that it is free of any apparent defects or foreign material. The sample film is then placed on the cell. An alpha detector, that has had no exposure to radon gas for several days, is selected and paired with a ratemeter. The alpha detector calibration sheet is used to verify that a calibrated pair has been selected and to set the high voltage for that particular detector. Next, the spreadsheet and WinWedgePro programs are started. Several macros in the spreadsheet control the counting process and handling of the data. The startup time is recorded in the log book.

[1] registered trademark of TAL Technologies, 2027 Wallace Street, Philadelphia , PA 19130

The detector is placed on the table for a 10-minute background count. If the background counts are less than 10 counts per minute, the spacer and the detector are placed on top of the film and aligned. Pressure is applied as uniformly as possible to the detector to compress the gasket material and ensure a good seal. The distance between the detector face and the film material is measured and should be about 18 mm

The valves to the radon source drum are opened, the pump is started, and the flow rate adjusted (if necessary). The time is recorded in the log book and is considered the beginning of the run or film exposure to the radon gas. The test room ambient air conditions, temperature, relative humidity, and barometric pressure are recorded and monitored during the run.

Scintillation cell samples are collected three times during the run to determine source strength. The background counts of the cell are measured and recorded in the log book. Then the cell is connected into the system. The valve diverts the radon gas flow through the sample cell. The gas in the system is allowed to circulate through the cell for 2 minutes. The valve is then returned to normal operating position before the scintillation cell is disconnected from the system. The cell containing the radon gas is placed on a discharge pad for 2 to 4 hours before counting. The cell is then counted for a 5-minute interval. Typical source radon concentrations are approximately 3×10^6 Bq m^{-3} (8×10^4 pCi/l). Table 1 shows the measured radon source concentrations for each radon sample and the deviations from the run average and the overall average for the six test runs. The data show that the largest variation within a test run and for the overall test series is approximately 6%.

Table 1. Source Term Measurements

Test Run average	Concentration (MBq m^{-3})	% RPD* within run	% RPD from overall
Polyethylene #1	2.74	-1.86	-6.29
Polyethylene #1	2.85	1.86	-2.75
Polyethylene #2	2.77	-5.82	-5.33
Polyethylene #2	3.12	5.81	-6.36
Polyethylene #2	2.95	0.01	-0.54
Latex #1	2.79	-1.14	-4.67
Latex #1	2.86	1.14	-2.48
Latex #2	2.91	-0.78	-0.75
Latex #2	2.95	0.78	0.81
Polyester #1	3.03	0.27	3.34
Polyester #1	3.01	-0.25	2.8
Polyester #1	3.02	-0.02	3.03
Polyester #2	3.07	3.06	4.91
Polyester #2	2.93	-1.79	-0.03
Polyester #2	2.94	-1.27	0.50
Maximum	3.12	5.81	6.36
Minimum	2.74	-5.82	-6.29

* Relative Percent Deviation

The run is terminated when the linear portion of the curve is complete or detector-side alpha activity has reached equilibrium. The longer tests (to equilibrium) are used to determine the system efficiency (number of alpha particles detected per decay event) and diffusion coefficient. After determining the system efficiency, shorter runs can be used to screen different polymer films. The source pump is then turned off, the test room exhaust fan turned on, and the system is disassembled. The exhaust fan is allowed to run for 1 hour to ensure that the radon gas vented into the room is flushed outdoors.

EXPERIMENTAL RESULTS

Three plastic films were tested as candidates to evaluate the method and the system. The films were 1) 0.15 mm (6 mil) Hygenic® [2] natural latex, 2) 0.15 mm (6 mil) Film-Gard® [3] polyethylene, and 3) 0.013 mm (0.5 mil) Mylar ® [4] polyester. These materials were chosen for their availability, documented values in the literature, their diffusion coefficients span a large range, and they are relevant materials to the testing of other barrier membranes.

The raw data consist of the activity count-rate-versus-time data from the alpha-particle detector, the source concentration, the dimensions for the film (area and thickness), and the dimensions of the chamber. A plot of the polyethylene film data is shown in Fig. 3 and representative time series curves for the three films in Fig. 4.

The early segments of the data are nearly linear with time. This linear section corresponds to a steady-state flux of radon through the film. At long times, the activity will reach an equilibrium value. This equilibrium occurs when the decay rate of the radon is equal to the reduced radon flux through the film into the elevated radon concentration on the detector side of the film.

The mathematical model developed by Mosley (1996) was used to analyze the data and calculate the efficiency and diffusion coefficient. First, the raw data were fitted using a non-linear least squares method to the formula:

$$Activity = A * (1 - e^{-Ct}) + B$$

The model assumes that the first data point is at the origin. The above fit uses the B coefficient to allow for the non-zero activity in the data. The A, B, and C coefficients are then used to calculate the efficiency and diffusion coefficient using these equations:

$$Efficiency = \frac{(A+B)*C}{\lambda_{Rn}*C_s*V_a*(C-\lambda_{Rn})}$$

$$D = \frac{d*L*A*(C-\lambda_{Rn})}{A+B}$$

where:

A = fit constant ($s^{-1}\ m^{-3}$)
B = fit constant ($s^{-1}\ m^{-3}$)
C = fit constant (s^{-1})
C_s = radon source concentration (atoms m^{-3})
d = film thickness (m)
D = diffusion coefficient ($m^2\ s^{-1}$)
L = distance between film and detector (m)
V_a = volume between detector and film (m^3)
λ_{Rn} = decay constant for radon (~ $2.1 \times 10^{-6}\ s^{-1}$)

[2] registered trademark of The Hygenic Corporation, 1245 Home Ave., Akron, OH 44310
[3] registered trademark of Carlisle Plastics, Inc., 1401 W. 94th St., Minneapolis, MN 55431
[4] registered trademark of DuPont Corporation, 400 Pennington Ave., Trenton, NJ 08618

A shorter test run can be performed once the system efficiency is determined from one or more long-time test runs where the activity reaches equilibrium. In the shorter run, the film is tested only until the initial, linear section of the raw data is collected. This linear section corresponds to an approximate steady-state flux of radon through the film, and the diffusion coefficient is computed from the slope of the curve. The slope of the linear section is obtained by linear regression.

The results from the analysis are summarized in Table 2:

Table 2. Comparison of Diffusion Results

Film	Efficiency	Calculated D ($m^2 s^{-1}$)	Literature D (Appendix A) ($m^2 s^{-1}$)	% Difference v. Literature	% Difference v. Duplicate Runs
Polyethylene	0.69	9.7×10^{-12}	3.36×10^{-11} and 7.8×10^{-12}	21 to 97	7
Latex	0.65	1.9×10^{-10}	6.36×10^{-10}	107	10
Polyester	0.11	4.3×10^{-11}	1.95×10^{-13} and 8.36×10^{-14}	199	39

Duplicate tests were performed on the films. The repeatability of the method is good given a difference between the duplicate tests of 7 and 10%, except for the polyester. The comparisons to published values are not as good, ranging from 21 to 199%. These values are not surprising since the published values for some materials differ by as much as a factor of 85 (polyvinylchloride, Appendix A). These differences may be caused by factors such as differences in material (e.g., high-density versus low-density polyethylene), variability in manufacturing, or the uncertainty in the methods.

The system efficiency calculated for the polyester tests was very low when compared to the latex and polyethylene data. This indicates that there is something significantly different about the polyester which is not explained by the model. An examination of the data shows that the initial slope of the data implies a diffusion coefficient similar to latex while the activity at long times indicates a diffusion coefficient which is much lower than for polyethylene. One possible explanation for the difference in the efficiency and in the calculated diffusion coefficient value (when compared to the literature) may be the collection of daughters by charges retained on the surface of the polyester. This would significantly reduce the count rate and lower the efficiency. This also makes the calculated value of the diffusion coefficient unreliable.

The estimated range of diffusion coefficients which may be tested using this method ranges from that of latex (10^{-10} $m^2 s^{-1}$), due to assumptions in the mathematical model, to a lower limit of approximately 10^{-16} $m^2 s^{-1}$, estimated on a change in measured activity of three times background over a 1 week period.

CONCLUSIONS

The system to perform the tests has been constructed and a set of reference materials procured. The test procedures have been developed and the reference materials tested to provide data for model validation. The tests to date show that the system is capable of testing a wide variety of films over a large range of diffusion coefficients. Once the system efficiency is determined, much shorter runs (run times from hours to a few days) may be used to determine the diffusion coefficient. A possible limitation is in the extremely low diffusion coefficient range (e.g., polycarbonates) where the current detector may not be sufficiently sensitive.

APPENDIX A: RADON DIFFUSION COEFFICIENT LITERATURE VALUES

Publication →	HA77	JH82	HA86	NI96	PO80
Units	$nm^2/Pa \cdot s$	$m^2 s^{-1}$	$m^2 s^{-1}$	$m^2 s^{-1}$	% @ 4.5d
Material ↓					
Natural Rubber		6.36×10^{-10}			58
Cellulose Nitrate		1.24×10^{-11}			
Cellulose Acetate			7.5×10^{-13}		
Polyvinylchloride	0.03	5.00×10^{-11}	5.8×10^{-13}		70
Polyethylene	14 - 113		7.8×10^{-12}	3.36×10^{-11}	20-70
Polyethylene Terephthalate			3.0×10^{-13}		
Polyester		1.95×10^{-13}			
Polycarbonate	1.4	3.82×10^{-13}	2.4×10^{-12} 5.5×10^{-13}		
Mylar		8.36×10^{-14}			
Tetrafluoroethylene					
Exposure Time	Not Avail.	Not Avail.	30 d	Not Avail.	10 d
Radon Source	Radium solution	Ore, Ra @ 1730 pCi/g	Not Avail.	Mill Tailings	50 nCi/l Rn
Thickness	0.5-15 mil	Not Avail.	0.5, 1, 3 mil	6 mil	2, 8, 40 mil

HA77: Hammon, H.G, Ernst, K., and Newton, J.C. Noble Gas Permeability of Polymer Films and Coatings. Journal of Applied Polymer Science, Vol 21, pp 1989-1997 (1977).

JH82: Jha, G., Raghavayya, M., and Padmanabhan, H. Radon Permeability of Some Membranes. Health Physics, Vol 42, No 5, pp 723-725 (1982).

HA86: Hafez, A. and Somogyi, G. Determination of Radon and Thoron Permeability through some Plastics by Track Technique. Nuclear Tracks, Vol 12, Nos 1-6, pp 697-700 (1986).

MO96: Mosley, R.B. Description of a Method for Measuring the Diffusion Coefficient of Thin Films to Radon-222 Using a Total Alpha Detector. Prepared for Presentation at the 1996 International Radon Symposium, Haines City, FL, Sept 29 - Oct 2, 1996.

NI96: Nielson, K.K., Holt, R.B., and Rogers, V.C., Residential Radon Resistant Construction Feature Selection System. EPA-600/R-96-005 (NTIS PB96-153473), February 1996. U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

PO80: Pohl-Rulling, J., Steinhausler, S., and Pohl, E., Investigation of the Suitability of Various Materials as ^{222}Rn Diffusion Barriers. Health Physics, Vol 39, No 2, pp 229-301 (1980).

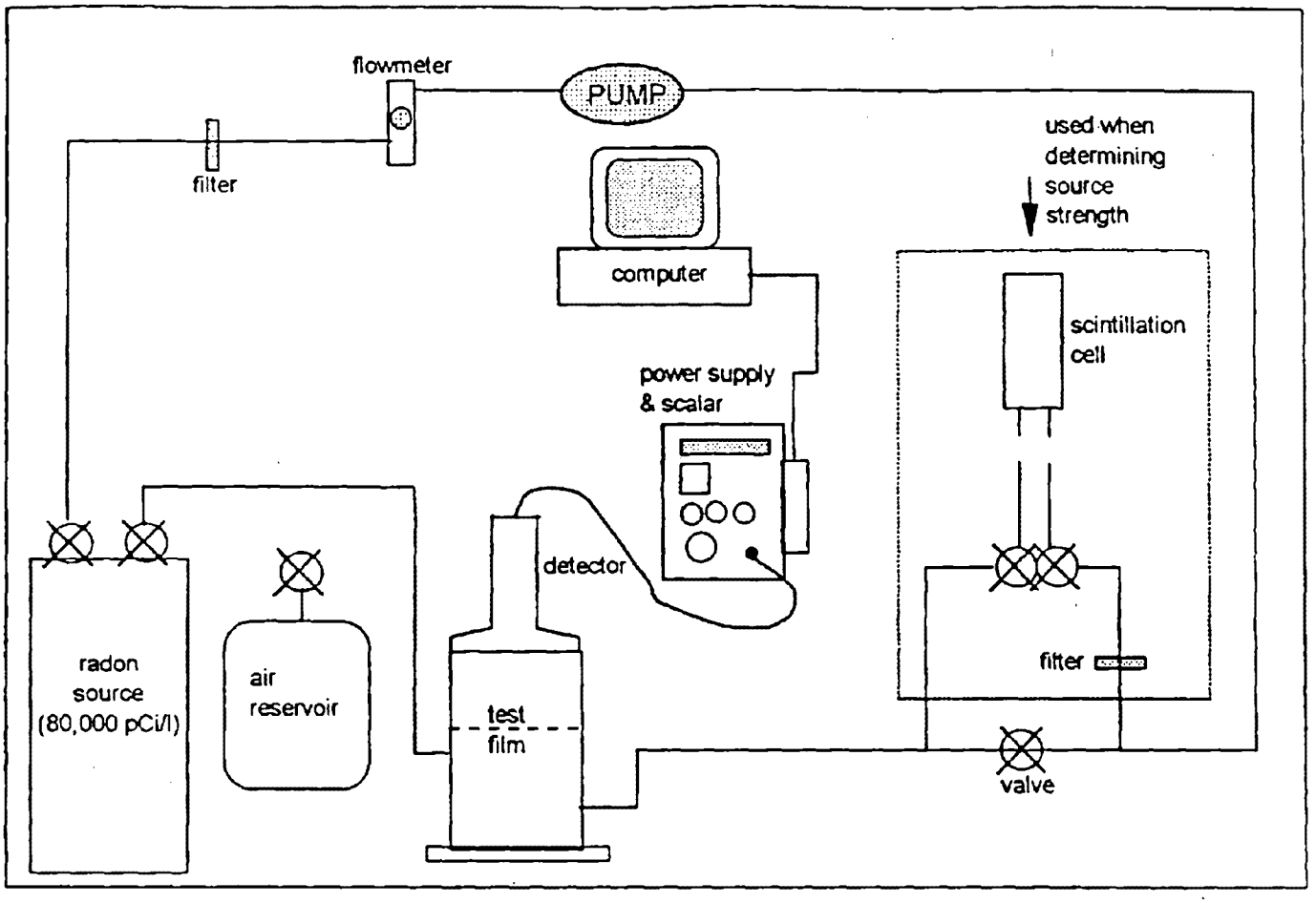

Fig. 1 System Diagram

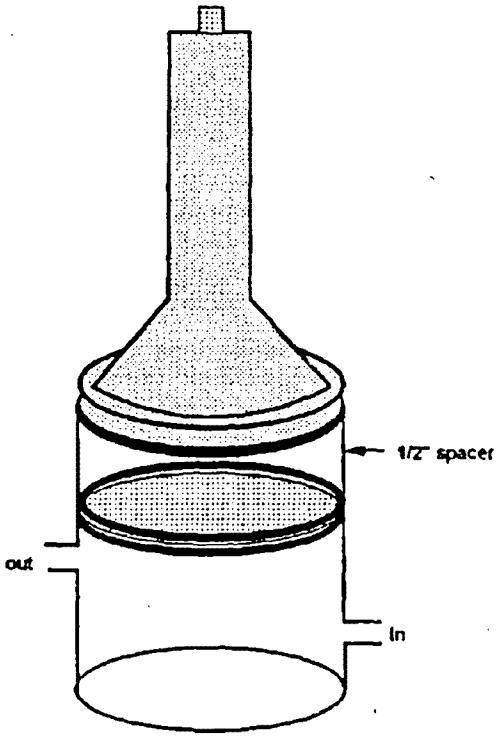

Fig. 2 Radon Diffusion Test Cell

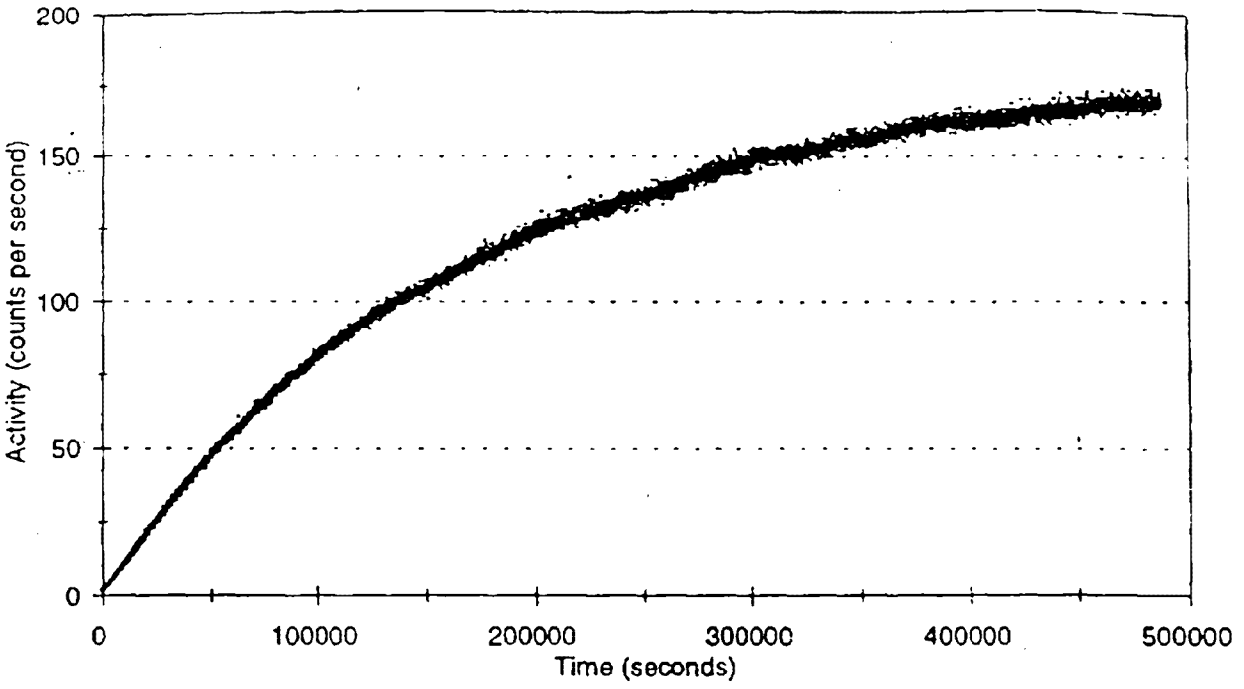

Figure 3. Typical Raw Data for Polyethylene

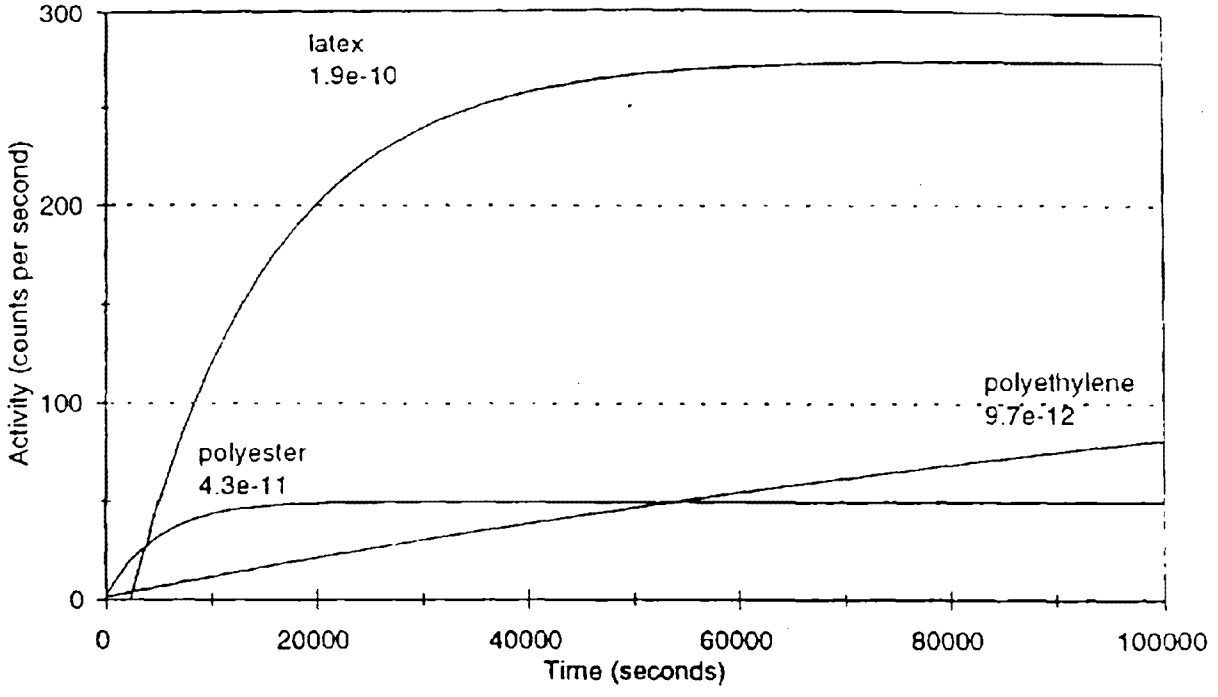

Figure 4. Representative Time Profiles for Reference Materials

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16. ABSTRACT The paper gives results of the development and evaluation of a method to measure the diffusion of radon through thin polymer films. The system was designed so that a simple, one-dimensional transport model could be used. The system uses radium-bearing rock as a high level radon source. The test-film is sealed in the system with high concentration radon gas on one side and an alpha detector sealed on the other side. The activity-versus-time data are collected and fitted using a non-linear least squares method. The system measurements and the three fit coefficients are used to calculate the system efficiency and diffusion coefficient. Three polymer films with published values of the radon diffusion coefficient (polyethylene, polyester, and latex) were tested in duplicate to evaluate the method and determine its comparability to values in published literature. The results show good repeatability (10%) and some comparability to similar published data (20 to 200%).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Polyester Fiber	Pollution Control	13B	11E
Radon	Latex	Stationary Sources	07B	11J
Polymers		Polymer Film	07D	
Diffusion Coefficient			20M	
Measurement			14B	
Polyethylene			11I	

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