

Measurement of radon diffusion and solubility constants in membranes

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We have measured the radon permeability of various foil materials of interest in special applications. After describing the apparatus used to determine radon diffusion and solubility constants in thin membranes by means of the time-lag method, we give results for commercially available PVC, Polyamid, Polyurethane, Plexi and rubber membranes.

1. Introduction

Radon isotopes are known to permeate through membranes of polymers. Some efforts have been made to select a suitable material to serve as a radon barrier [1], to discriminate between different radon isotopes [2] or to investigate the permeability characteristics of membranes to radon and thoron [3,4]. The permeability of the membranes was usually measured under steady-state conditions. This was most readily done by comparing count rates of two radon detectors exposed to the same, constant radon concentration. The first detector was covered with the investigated membrane and the other with a porous material of very high permeability to allow free passage of radon. Under steady-state condition i.e., for measurement times $t \gg \tau$ (where τ is the mean life of ²²²Rn) the count rate of the detector behind the membrane remains constant. The permeability of the investigated membrane was then derived from the ratio between the count rates for the two detectors.

Still, the diffusion-, solubility- and permeability coefficients of polymers to radon are not generally available in the literature.

Here we describe an apparatus and, following Barrer [5] and Müller [6], the modified method to obtain diffusion constants, solubility constants and the permeability of ²²²Rn in plastics by analyzing nonstationary flows through membranes.

2. The method

The theory of diffusion in isotropic substances is based on the hypothesis that the rate of transfer of a

diffusing substance through unit area of a membrane is proportional to the concentration gradient measured normal to the membrane i.e.

$$F = -D \frac{\partial C}{\partial x} = \frac{D(C'_1 - C'_2)}{d}, \quad (1)$$

where F is the rate of transfer per unit area, C the concentration of the diffusing substance, C'_1 , C'_2 the surface concentrations in the membrane, x the space coordinate measured normal to the membrane, d the thickness of the membrane and D is the diffusion coefficient [$\text{cm}^2 \text{s}^{-1}$].

If the diffusion coefficient is isotropic and constant in time, and if there is a linear relationship between the external concentration of a nondecaying diffusing substance and the corresponding equilibrium concentration within the membrane, we then have

$$C'_1 = SC_1 \quad \text{and} \quad C'_2 = SC_2, \quad (2)$$

where C'_1 and C'_2 are the surface concentrations in the membrane in equilibrium with external concentrations C_1 and C_2 , respectively, and S is the solubility.

Steady-state flow considers the case of diffusion through a plane sheet of thickness d , whose surfaces, $x = 0$, $x = d$, are maintained at constant concentrations C_1 , C_2 , respectively. After a time, a steady-state is reached in which the concentration remains constant in time at all points of the membrane. Also, the rate of transfer of diffusing substance is the same across all sections of the membrane (provided a nondecaying diffusing substance):

$$F = DS(C_1 - C_2)/d, \quad (3)$$

where the constant $P = DS$ is referred to as the permeability constant.

In ref. [7] the approach to steady-state flow through a membrane as analyzed. In the present work the

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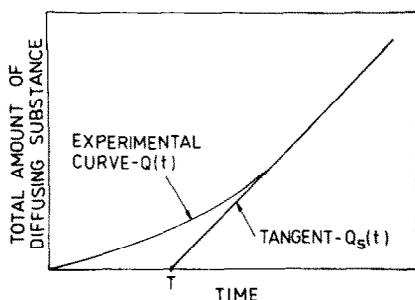


Fig. 1. Approach to steady-state flow through the membrane.

steady-state and the transient methods [5,6] are used in combination in the time-lag method.

Usually, in the experimental arrangement the membrane is initially at zero concentration and the concentration C_2 (at the face through which diffusing substance emerges) is maintained at low concentration levels compared to the opposite face.

Fig. 1 illustrates the behaviour of the total amount diffused as a function of time $Q(t)$ for $C_1 > C_2$. $Q(t)$ is given by:

$$Q(t) = SdC_1 \left\{ \frac{Dt}{d^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_1^{\infty} \frac{(-1)^n}{n^2} \times \exp\left(\frac{-Dn^2\pi^2 t}{d^2}\right) \right\}. \quad (4)$$

The straight line $Q_s(t)$ obtained when extrapolating the upper part of the curve $Q(t)$ to zero concentration is given by:

$$Q_s(t) = \frac{SDC_1}{d} \left(t - \frac{d^2}{6D} \right), \quad (5)$$

where the slope is the steady-state flow rate

$$F = \frac{SDC_1}{d} \quad (6)$$

and the intercept on the t -axis

$$T = \frac{d^2}{6D} \quad (7)$$

is referred to as the "time-lag". Thus from the determination of the intercept, T , D is obtained by eq. (7) and from the steady-state flow rate, F , S follows from eqs. (5) and (6).

For a decaying diffusing substance, the non-stationary, one-dimensional (x -axis) flow, can be described by

$$\frac{\partial C}{\partial t} = D \frac{d^2 C}{dx^2} - \lambda C, \quad (8)$$

where λ is the decay constant of the diffusing isotope. The solution of this equation is rather difficult. We have used then eqs. (6) and (7). Next, the results were cor-

rected for Rn decay in the active volume of the detectors.

If the measured time-lag of the membrane is much smaller than the Rn half-life then the correction of the diffusion- and solubility coefficients regarding Rn decay in the membrane can be neglected. For that reason, the thickness of the investigated membrane ought to be as small as possible, especially for the materials with expected low diffusion coefficient.

3. Apparatus and experimental procedure

The apparatus to measure the diffusion coefficients and the solubilities of Rn in plastic materials consists of two Rn detectors and an Rn reservoir (fig. 2). As Rn detectors scintillation chambers have been used. Only the quartz-window of the chamber is covered by ZnS(Ag) scintillator. The light generated in the ZnS(Ag) by alpha particles emitted by Rn and its progeny, is detected by a photomultiplier. The standard electronics consists of an amplifier, a single channel analyzer and a scaler-time with printer. Beta electrons and gamma rays were discriminated by a properly adjusted electronic threshold. The active volume of each detector is $V_d = 27 \text{ cm}^3$.

The active volume of the first detector is separated from the Rn reservoir by a paper filter in order to have the same Rn concentration as in the reservoir and identical active volumes for both detector chambers. The count rate of this detector is proportional to the Rn concentration in the reservoir when equilibrium with the progeny is reached, and to the active volume of the detector.

The active volume of the second detector is separated from the reservoir by the membrane investigated. At the beginning of the measurement $C_2 = 0$. The surface area of the membrane through which Rn diffuses from the reservoir to the detector volume corresponds to $A = 29.7 \text{ cm}^2$. With a special gasket system care was taken that Rn could not leak through the membrane mounting. The corrected count rate of the second detector with regard to the Rn decay is almost proportional to the total amount of Rn diffused through the investigated membrane. The weak disequilibrium between Rn diffused and its progeny leads to correction of the

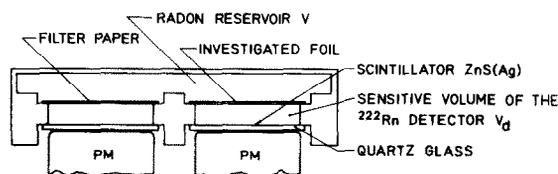


Fig. 2. Apparatus for the measurement of diffusion- and solubility coefficient in membranes.

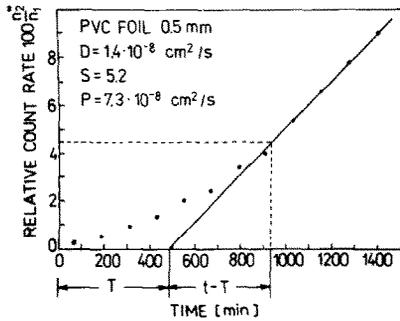


Fig. 3. The dependence of the relative count rate on time for a PVC membrane.

time-lag T . The straight line in fig. 1 shows the linear growth of the Rn concentration in the active volume of the second detector. Rn reaches the radioactive equilibrium with its daughters after about three hours. The straight line which represents the growth of the count rate (count rate is proportional to the Rn- and its daughters activity) will be then parallel shifted. For our scintillation detector the calculated shift is $\Delta T = 16$ min.

The relative efficiency of both detectors has been determined with filter paper on both sides.

After the Rn was introduced into the reservoir ($V = 255 \text{ cm}^3$) equilibrium in the Rn concentration between the reservoir and the first detector was reached within minutes. Then the count rate of the first detector, n_1 , increases during about three hours due to the growth of Rn-daughters ($n_1 \propto C_1$) and finally decreases as a result of the Rn decay.

The Rn concentration in the active volume of the second detector and its count rate (from radon and its short-lived α -emitting progeny), n_2 ($n_2 \propto C_2$), (fig. 3) starts to increase after a certain time-period, depending on the material type and thickness of the membrane. The measurement was terminated when the count rate n_2 reached a few percent of the n_1 count rate according to the condition for eq. (5).

After background subtractions and correction of n_2 with regard to the Rn decay the dependence of the ratio n_2^*/n_1 was plotted versus time as shown in fig. 3. ($n_2^*/n_1 = C_2^*/C_1$, where n_2^* and C_2^* are n_2 and C_2 , respectively, corrected with regard to the Rn decay). From the intercept of the backwards extrapolated straight line the time-lag T is obtained. After time-lag T correction with regard to the weak disequilibrium between radon diffused and its progeny, the diffusion coefficient D is calculated according to eq. (7).

Assuming that for the upper part of the extrapolated straight line $Q_s(t) = V_d \cdot C_2^*/A$, the solubility from eqs. (5) and (7) can be deduced:

$$S = \frac{(n_2^*/n_1)dV_d}{(t-T)AD} \quad (9)$$

From fig. 3, the slope $(n_2^*/n_1)/(t-T)$ can be found and then the solubility can be calculated.

The measurements were carried out at a constant temperature of 24°C , and constant, low humidity. For background determination the active volume of the second detector and the Rn reservoir were filled with dry nitrogen.

4. Results and discussion

In table 1 we give results of measurements of diffusion-, solubility-, and permeability coefficients as well as diffusion lengths for plastic materials and rubbers. The diffusion length d_e is the distance in a plastic material at which the Rn concentration is $1/e$ of the concentration at the surface under steady-state conditions and for $d \gg d_e$, d_e corresponds to:

$$d_e = \sqrt{D/\lambda} \quad (10)$$

with λ being the decay constant of the Rn. This parameter allows one to calculate e.g. the thickness of walls of Rn hermetic devices or the Rn quantity A_{Rn} dissolved in unit area of walls of Rn container

$$A_{\text{Rn}} = d_e SC \quad \text{for } d \gg d_e, \quad (11)$$

where S is the solubility and C is the Rn concentration at the surface in air or gas.

As mentioned earlier [1,3,6], supronyl (polyamid) is suited as a radon barrier. The permeability coefficient thus obtained is $2 \times 10^{-9} \text{ cm}^2/\text{s}$. This value is almost the geometric mean of the two values reported in the literature $2.5 \times 10^{-8} \text{ cm}^2/\text{s}$ [3] and $1.3 \times 10^{-10} \text{ cm}^2/\text{s}$ [6]. The differences may be attributed to the additives used in the different manufacturing processes.

We have found that the diffusion coefficient and permeability of Rn in butyl rubber is relatively low. Gloves made of butyl rubber are the best among the options tested for Rn-tight glove-box constructions.

Table 1

The diffusion-, solubility-, permeability coefficients and diffusion lengths of Rn in some membranes

Material	Diffusion coefficient D [$10^{-10} \text{ cm}^2/\text{s}$]	Solu- bility S	Permeability P [$10^{-8} \text{ cm}^2/\text{s}$]	Diffusion length d_e [mm]
Rubber soft	1000	12	120	2.2
Butyl rubber	49	4.4	2.1	0.48
PU soft	408	5.6	23	1.4
PU hard	88	7.9	6.9	0.65
PVC soft	420	10	42	1.4
PVC hard	140	5.2	7.3	0.82
PA Supronyl	6.1	3.4	0.2	0.11
Plexi	6.2	8.2	0.5	0.11

The diffusion coefficient and the solubility of Rn in PVC vary between $(1.4-4.2) \times 10^{-8}$ cm²/s and 5.2-10, respectively. The permeability of Rn for soft PVC foils is higher than for foils without softener. The same trend was observed by as for polyurethane membranes.

Acryl glass (plexi) is a very good material for e.g. Rn hermetic windows in devices in which glass windows cannot be applied.

5. Conclusions

The method presented here enables the study of the diffusion and solubility of Rn in membranes with relative little effort. Compared to steady-state investigations it is much less time consuming and leads to the more fundamental constant – the diffusion coefficient [7] in contrast to only the permeability constant [2-4].

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References

- [1] J. Pohl-Rueling, F. Steinhäusler and E. Pohl, *Health Phys.* 39 (1980) 299.
- [2] W.J. Ward III, R.L. Fleischer and A. Mogro-Campero, *Rev. Sci. Instrum.* 48 (1977) 1440.
- [3] J. Bigu, *Nucl. Instr. and Meth.* A251 (1986) 366.
- [4] G. Jha, M. Raghavayya, and N. Padmanabhan, *Health Phys.* 42 (1982) 723.
- [5] R.M. Barrer, *Diffusion in and through Solids* (Cambridge University Press, 1951).
- [6] W. Müller, *Die Diffusions-, Löslichkeits- und Permeabilitätskoeffizienten von Radon-222 in Handelsüblichen Kunststoffen*, Thesis Univ. Heidelberg (1978) in German.
- [7] J. Crank, *The Mathematics of Diffusion* (Clarendon Press, Oxford, 1988).