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EMANATION OF RADON FROM SOLID SAMPLES

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NOVEMBER 1991

Sudbury Neutrino Observatory Project Report SNO-STR-91-068

MINING RESEARCH LABORATORY  
DIVISION REPORT 91- (TR)

## EMANATION OF RADON FROM SOLID SAMPLES

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## ABSTRACT

This report presents a brief review as well as some theoretical background on radon ( $^{222}\text{Rn}$ ) emanation methods from solid samples. This is followed by a description of an experimental apparatus built at the Elliot Lake Laboratory (Mining Research Laboratory, CANMET, E.M.R.) to measure the  $^{222}\text{Rn}$  emanation rate from  $^{226}\text{Ra}$ -bearing solid materials by the vacuum emanation method. Experimental data are presented on three materials, namely, Viton<sup>TM</sup> 'O'-ring, coaxial cable Belden M9067, and a molecular sieve (zeolite). The results of this study and other investigations presently in progress are relevant to the Sudbury Neutrino Observatory (SNO) Project.

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Key words: Radon emanation; Pathways; Measurement techniques.

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## INTRODUCTION

Uranium-238,  $^{232}\text{Th}$ , and  $^{235}\text{U}$  are the parents of three naturally occurring radioactive decay chains which are more or less uniformly distributed on the crust of the earth. Through a series of radioactive decays  $^{238}\text{U}$ ,  $^{232}\text{Th}$ , and  $^{235}\text{U}$  form, respectively,  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ , and  $^{223}\text{Ra}$ . These metal radionuclides decay, respectively, into the radioactive gases  $^{222}\text{Rn}$  (radon),  $^{220}\text{Rn}$  (thoron), and  $^{219}\text{Rn}$  (actinon), which readily diffuse through solids and dissolve in liquids. Because  $^{235}\text{U}$  only represents a small fraction (~0.7%) of the natural U content, the contribution of  $^{235}\text{U}$  to the natural radioactivity environment is often neglected in most practical applications.

The natural abundance of  $^{238}\text{U}$  and  $^{232}\text{Th}$  varies with geographical location, depth, and other factors. The abundance of  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  depends on meteorological and geological factors, as well as with the chemistry and physical characteristics of the soil environment. These and other variables and factors, partly determine (through selective leaching processes,  $\alpha$ -recoil mechanisms and transport phenomena) radionuclide disequilibrium ratios in the radioactive decay chains.

The  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  content in a given material or chemical compound may be of 'natural' origin, or the result of a physico-chemical reaction, or an industrial manufacturing process. It may also be the product of prolonged contact with soil materials in the ground, or some other natural radioactive medium or environment such as Ra-containing water. Furthermore,  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  may be more or less uniformly and isotropically distributed within the material, or may, on the other hand, be selectively distributed within the material or deposited on its surface, e.g., surface contamination.

Because  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  decay, respectively, into  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$ , which diffuse through the  $^{226}\text{Ra}$ - and  $^{224}\text{Ra}$ -containing materials, the resulting radioactive gases will emerge from the surface of the material. However, not all the  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  formed in the material will emerge from

its surface because some fraction of the gases produced will be trapped irreversibly in the capillary network or pore space of the material. The fraction (of the total) that emerges from the material depends on the radioactive decay constant,  $\lambda$ , of the radioactive gas, the physical dimensions and shape of the material, and the diffusion coefficient and permeability of the material to  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  which, in turn, depend on the physical characteristics of the material. The fraction that emerges from the material is usually referred to as the emanation coefficient,  $E_c$ . Usually  $E_c < 100\%$ , except for surface contamination which for all practical purposes can be set to 100% for most cases of interest. Once  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  emerge from the surface of the material they will decay into their short-lived decay products, i.e., progeny. (Progeny formed within the material will not emerge from it because their diffusivity is virtually nil!)

In summary, whatever the origin may be, materials do contain measurable amounts of  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$ . And whether  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$ , or  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$ , or their respective progeny are the relevant radionuclides of particular interest, they can seriously interfere with unrelated low-level radioactivity measurements.

The emanation of  $^{222}\text{Rn}$  from  $^{226}\text{Ra}$ -containing materials is of particular interest in the Sudbury Neutrino Observatory (SNO) project at Creighton Mine because the mine walls, construction materials and components of the observatory are potential sources of  $^{222}\text{Rn}$  and its progeny. One  $\gamma$ -ray emitting radioisotope of the short-lived  $^{222}\text{Rn}$  progeny decay chain is a most likely candidate to interfere with the detection of neutrinos at the SNO.

This report presents work regarding the emanation of  $^{222}\text{Rn}$  from materials of interest in the SNO Project. The emanation of  $^{222}\text{Rn}$  from several materials has been measured by vacuum emanation techniques. The report describes the design of the apparatus used for the measurement of  $^{222}\text{Rn}$  emanation rates, the technique used in the calibration of the apparatus, as

well as emanation data for three materials of interest. This work is part of a cooperative program between the SNO Project and the Elliot Lake Laboratory (Mining Research Laboratory, CANMET, Energy, Mines and Resources Canada).

#### THEORETICAL BACKGROUND

The rate of change in the number of radioactive gas ( $^{222}\text{Rn}$  and  $^{220}\text{Rn}$ ) atoms in a bulk volume of a porous (ore-bearing, e.g.,  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$ ) medium where radioactive gas production, radioactive decay, and diffusion and transport of gas takes place is given by the continuity condition (1):

$$\delta C / \delta t = -(1/\eta) \nabla \cdot J_T - \lambda C + \phi \quad (1)$$

where,  $C$  is the radioactive gas ( $^{222}\text{Rn}$ ,  $^{220}\text{Rn}$ ) concentration, number of atoms per unit volume of interstitial space;

$J_T$  is the total current density (flux density) of radioactive gas atoms, number of atoms per unit time per unit geometric area 'transported' by molecular diffusion and interstitial fluid (air) flow;

$\lambda$  is the radioactive decay constant of the gas;

$\phi$  is the radioactive gas production rate, number of atoms produced per unit time per unit volume of medium;

$\eta$  is the porosity of the medium, ratio of void to bulk volume.

In Equation 1,  $J_T$  can be written as a sum of two terms:

$$J_T = J_D + J_t \quad (2)$$

where,  $J_D$  and  $J_t$  are respectively, the diffusion and transport current densities. The term  $J_D$  is given by Fick's Law of diffusion, whereas  $J_t$  is determined by Darcy's Law:

$$J_D = -DVC \quad (3)$$

$$J_c = Cv \quad (4)$$

where, 
$$v = -(k/\delta)\nabla P \quad (5)$$

In Equations 3 to 5:

D is the bulk diffusion coefficient of the radioactive gas in the medium;

v is the fluid volume current density (Equation 5), volume of interstitial fluid flowing per unit time per unit geometrical area for pressure-induced flow;

k is the medium permeability;

$\delta$  is the dynamic viscosity of interstitial fluid;

P is pressure.

The source of  $^{222}\text{Rn}$  or  $^{220}\text{Rn}$  (as 'viewed' externally from the volume containing the source), i.e.,  $\phi$ , in Equation 1, can be written as:

$$\phi = E_c \lambda_i C_i \quad (6)$$

where,  $\lambda_i$  and  $C_i$  are, respectively, the radioactive decay constant and concentration (in atoms per unit volume) of the parent product, i.e.,  $^{226}\text{Ra}$  for  $^{222}\text{Rn}$  and  $^{224}\text{Ra}$  for  $^{220}\text{Rn}$ . The symbol  $E_c$  is a dimensionless quantity called the emanation coefficient for  $^{222}\text{Rn}$  or  $^{220}\text{Rn}$  in the material. This quantity indicates the fraction of the radioactive gas formed by the decay of its parent that actually 'escapes' the pore spaces and crystal structures of the medium. The rate of emanation of  $^{222}\text{Rn}$  or  $^{220}\text{Rn}$  from a material is a function of the structure and uniformity of the mineral crystal lattices, the distribution of the parents  $^{226}\text{Ra}$  or  $^{224}\text{Ra}$ , the pore space, microfractures, cracks, and the degree of branching and the size of capillary networks. The extent of de-emanation, i.e.,  $E_c$ , is usually less than 100% as a fraction of the radioactive gas formed is trapped irreversibly in crystal structures.

The production rate of  $^{222}\text{Rn}$  or  $^{220}\text{Rn}$  in the medium can be expressed by:

$$dC/dt = \phi - C\lambda \quad (7)$$

The solution to this equation is:

$$C = (\phi/\lambda) (1 - e^{-\lambda t}) \quad (8)$$

Equation 8 indicates that for a sufficiently long time, i.e.,  $t \gg T_{1/2}$  for which  $e^{-\lambda t} \ll 1$ , Equation 8 reduces to:  $C(t \rightarrow \infty) = \phi/\lambda$ , i.e., a constant value, or steady-state condition. (The symbol  $T_{1/2} = 0.693/\lambda$ , stands for the radioactive half-life of the radioisotope of interest.) For the  $^{226}\text{Ra}$ ,  $^{222}\text{Rn}$  system, C reaches a constant value after a few weeks, whereas for the  $^{224}\text{Ra}$ ,  $^{220}\text{Rn}$  system this occurs in a matter of a few minutes. Equation 8 can be used to express the concentration of radioactive gas in a sealed container of finite dimensions into which the sample has been placed. It also gives the concentration of radioactive gas in the interstitial space of the material if the boundary between the material surface and the outer space (e.g., air volume) is assumed to be impervious to the gas.

For a medium of physical dimensions considerably larger than the diffusion length  $L_D$  ( $=\sqrt{D/\eta\lambda}$ ) of the radioactive gas in the medium, the emanation coefficient,  $E_c$ , is very small because only the gas formed within a few diffusion lengths separating the radioactive medium from the external medium surrounding it, e.g., air, can diffuse out. The rest of the radioactive gas formed in the bulk material decays away before reaching the medium/air boundary. For an infinite medium, the emanation coefficient  $E_c$  becomes vanishingly small. Because  $E_c$  depends on the physical dimensions of the medium, and, as will be shown below, also on its geometry, i.e., shape, this quantity is often referred to as the 'apparent' or 'effective' emanation coefficient. This variable is, therefore, not an intrinsic property of the medium.

Because of the dependence of the diffusion length,  $L_D$ , of the radioactive gas on the material, sample preparation and geometry

standardization are recommended practices in order to eliminate the dependence of the emanation coefficient,  $E_c$ , on the geometry of the sample, and hence, attain reproducible results. In other words, meaningful comparative studies of  $E_c$  for different materials are best accomplished by preparing samples of the same physical dimensions and shape.

In its simplest version, a typical emanation experiment consists of placing the sample in a sealed container where the radioactive gas emanated is collected. The sample is kept in the container for a period of time and the gas build-up in the container is measured as a function of time. Alternatively, the total gas accumulated after a fixed period is measured. It is important to bear in mind that in the first case, measurements should be carried out until a radioactive steady-state is reached (see Equation 8). If, as in the second case, the method of measurement consists of a single radioactive gas measurement conducted after a period of gas in-growth, this measurement should also be made when steady-state conditions have been attained.

Emanation studies can be done with the sample at essentially atmospheric pressure, or under vacuum conditions. Alternatively, the sample can be immersed in a fluid, usually water. The different experimental alternatives available will be examined in a separate section devoted to a description of experimental techniques and procedures.

The emanation coefficient of a given material of simple regular geometrical shape can be calculated according to:

$$E_c = F_g(J/\phi_i) \quad (9)$$

where  $\phi_i = \lambda_i C_i$  (see Equation 6), and the symbol  $J$  represents the flux of radioactive gas across the boundary between the external surface of the material and the medium surrounding it. The symbol  $F_g$  is a geometrical factor given by  $F_g = S/V$ , where  $S$  is the surface area of the material, and  $V$  is the

volume enclosed in S.

Alternatively, Equation 9 can be rewritten as:

$$E_c = \eta C_n \lambda_n / \phi_i \quad (10)$$

where,  $C_n$  represents the concentration of radioactive gas (radioactive decay constant,  $\lambda_n$ ) in the pore volume. But  $C_n = \phi_n / \lambda_n$ . Hence,

$$E_c = \eta (\phi_n / \phi_i). \quad (11)$$

According to the shape of the sample, the ratio of its physical dimensions and the conditions of the experiment,  $F_g$  and  $J$  assume different forms. Cylindrical, spherical, and 'slab' shapes are commonly used, or encountered, in practice.

### 1. CYLINDRICAL SHAPE

If  $C_1$  and  $C_2$  are the concentrations of  $^{222}\text{Rn}$  or  $^{220}\text{Rn}$  in the interstitial space of the material and outside the material, respectively, Equation 1, assuming  $J_t = 0$  (Equation 4, i.e., no Darcy's flow), can be rewritten in cylindrical coordinates as:

$$\frac{\delta C_1}{\delta t} = D \left( \frac{\delta^2 C_1}{\delta r^2} + \frac{1}{r} \frac{\delta C_1}{\delta r} \right) - \lambda C_1 + \phi \quad (12)$$

where,  $r$  is the distance in the radial direction. In this geometry it is assumed that the upper and lower circular ends of the cylinder are impervious to  $^{222}\text{Rn}$  or  $^{220}\text{Rn}$ .

When the sample is placed in a 'receiver' (confined) volume, the radioactive gas builds up at a rate according to:

$$\frac{\delta C_2}{\delta t} = -(D/h) \left. \frac{\delta C_1}{\delta r} \right|_{r=r_0} - C_2 (\lambda_n + \lambda_1) \quad (13)$$

where,  $r_0$  is the radius of the cylinder. The symbol  $h$  is given by the expression:  $h = V/S\eta$ . The symbol  $\lambda_1$  represents the decay constant due to the

radioactive gas leaking from the detection system associated with the receiver volume.

The solutions of Equations 12 and 13, subject to various boundary conditions can be obtained by the methods of Leplace transform and Fourier analysis. The solution of  $C_1$  by Fourier analysis assumes the solution to be of the form:

$$C_1(r,t) = \sum_{n=0}^{\infty} E_n J_0(k_n r) e^{-\omega t} + C_1(r,\infty) \quad (14)$$

where,  $\omega = Dk_n^2 + \lambda$ .  $J_0$  is the zero-order Bessel functions of argument  $k_n r$ . The symbol  $k_n$  is used to represent the roots of the transcendental equation. The coefficients  $E_n$  assume values according to the boundary conditions.

Equation 14 gives the radioactive gas concentration in the pore space for  $r < r_0$ . For  $r = r_0$ , Equation 14 gives the concentration in the 'receiver' volume. The above equation can be rewritten in terms of the emanation coefficient and the  $^{226}\text{Ra}$  or  $^{224}\text{Ra}$  concentration of the sample:

$$C(r,t) = \left(\frac{E_c}{\eta}\right) \left(\frac{C_i \lambda_i}{\lambda_n}\right) \left(\frac{\lambda_n}{\phi_n}\right) \left[ \sum_{n=0}^{\infty} E_n J_0(k_n r) e^{-\omega t} + C(r,\infty) \right] \quad (15)$$

The flux,  $J = -D \frac{\delta C}{\delta r} \Big|_{r=r_0}$ , across the surface of the sample can be calculated

using Equation 15.

## 2. SLAB SHAPE

The diffusion through a slab of length  $L$  can be solved by the Fourier series method. It can be shown:

$$C(z,t) = \left(\frac{E_c}{\eta}\right) \left(\frac{C_i \lambda_i}{\lambda_n}\right) \left(\frac{\lambda_n}{\phi_n}\right) \left[ \sum_{n=0}^{\infty} E_n \cos(k_n z) e^{-\omega t} + C(z,\infty) \right] \quad (16)$$

It is clear from Equations 10, 15 and 16 that  $C(r,t)$  (cylindrical geometry), and  $C(z,t)$  (slab geometry), and hence  $E_c$ , depend on the geometry of the sample and its physical dimensions. Hence, the need for geometry and physical size standardization. The theoretical implications of the above discussion and the different solutions of the diffusion equation for the different shapes and boundary conditions using the Laplace transform method, in addition to the Fourier series method, will be the subject of a forthcoming report.

#### EXPERIMENTAL METHODS FOR MEASURING RADIOACTIVE GAS EMANATION FROM SOLID MATERIALS

The experimental determination of the emanation coefficient of  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  from solid materials can be done using  $\alpha$ -particle and  $\gamma$ -ray measuring techniques. In both cases, gross (total) counting and spectrometric methods can be used. Depending on the  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  content of the sample, and the physical characteristics of the material (which determine the diffusion length,  $L_D$ ), emanation measurements can be broadly divided into moderate to high activity measurements, and low to very low activity measurements. Although the basic first step in the experimental procedure for determining  $E_c$  remains essentially the same, the operational procedure beyond this point will differ quite substantially depending on the  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  concentrations in the sample. For the sake of simplicity, the experimental procedures of practical interest are discussed below separately. Unless otherwise specified, it will be assumed that  $\alpha$ -particle counting techniques are used.

##### 1. MEASUREMENTS AT AMBIENT PRESSURE

The experimental procedure in this case is fairly simple: the sample is placed in an emanation chamber and the concentration of  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  emanating from the material are measured after steady-state

radioactive conditions have been attained (i.e., -30 days for  $^{222}\text{Rn}$ ). If for practical reasons, a shorter in-growth time for the radioactive gas is chosen, then allowance (correction) should be made to take into account the (theoretical) growth of radioactive gas in the container subject to the initial and final conditions:  $C(t=0) = 0$ , and  $C(t=\infty) = C$  of Equation 8.

After the in-growth period, the concentration  $C(t)$  of radioactive gas in the emanation chamber is measured, and the emanation coefficient,  $E_c$ , and/or the rate of gas emanation can be determined. The experimental arrangement used is very simple and is shown in Figure 1. In this experimental arrangement the emanation chamber is connected to a two-port scintillation cell coupled optically to a photomultiplier tube (PMT) and a scaler. The system is provided with two on/off valves, V1 and V2, and a low airflow rate ( $\sim 1 \text{ Lmin}^{-1}$ ) sampling pump, SP. Radioactive gas concentration measurements are carried out by opening V1 and V2 and running the SP (i.e., connecting points A and B) until perfect mixing is attained. In this method care should be exercised that the pump does not initiate unwanted air currents that may enhance the diffusion of the radioactive gas, or produce dead 'spaces' (volumes) that could lead to erroneous readings. These unwanted conditions may arise depending on the airflow rate used. Connections between the emanation chamber and the scintillation cell (usually by means of flexible tubing) should be as short as possible to minimize the total volume of the system. It is clear that the radioactive gas concentration measured according to the arrangement shown in Figure 1, say,  $C_{TS}$ , is different from that corresponding to the emanation chamber,  $C_{EC}$ . Calling  $V_{EC}$ ,  $V_t$  and  $V_{SC}$  the volume of the emanation chamber, the connecting tubing and the scintillation cell, respectively, one can write:

$$C_{EC} = (\sum_i V_i / V_{EC}) C_{TS} \quad (17)$$

where,  $\sum_i V_i = V_{EC} + V_t + V_{SC}$ .

From  $C_{EC}(t)$ ,  $V_{EC}$ ,  $t$ , and Equation 8, the emanation rate for the radioactive gas from the sample can readily be calculated; and if the concentrations of  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  in the material are known (i.e., radiochemical analysis or  $\gamma$ -spectrometry), the emanation coefficient,  $E_c$ , can be calculated.

In the experimental procedure outlined a sampling pump was used to:

- a) introduce a sample of radioactive gas into a scintillation cell at the same pressure as the rest of the experimental apparatus, i.e., ambient pressure;
- b) circulate, stir, and hence, mix the radon-laden air in the emanation chamber with the air in the rest of the system to produce a homogeneous radioactive gas concentration throughout the experimental apparatus;

An alternative to the above procedure is to have  $V_1$  and  $V_2$  closed, points A and B disconnected, i.e., pump not running and take a sample of gas from the emanation chamber at a convenient time (by opening  $V_1$  or  $V_2$ ) by means of an evacuated scintillation cell. If this procedure is followed, the following should be considered:

- a)  $V_{SC}$  is small compared with  $V_{EC}$ . If this conditions is not satisfied the pressure differential created during the taking of the sample can enhance emanation of radioactive gas from the interstitial space of the sample by transport (convective) mechanisms;
- b) the counting efficiency of a scintillation cell is dependent on the pressure in the cell when the physical dimensions of the latter are larger than the range of the  $\alpha$ -particles in the cell volume. Hence, if the final pressure of the cell after the sample of radioactive gas has been completed is less than ambient, i.e., the case of reduced pressure, corrections to the counting efficiency will be necessary. This elementary fact is quite frequently overlooked and can lead to significant errors in

the calculation of  $E_c$  and emanation rates.

The experimental procedure discussed above is only applicable to cases in which the concentrations of  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  in the material are moderate or high. In these cases, only elementary care and precautions in carrying out the measurements are necessary. However, when the concentrations of  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  are low or very low, then special precautions have to be taken to ensure meaningful and reliable measurements. In this case special attention should be paid to the materials used in the design of the experimental apparatus used, i.e., these materials should have the lowest possible emanation rates (lowest  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  content possible). In addition, improved techniques for the collection of the radioactive gas should be developed to increase the signal to noise ratio, i.e., true emanation rate from the material as compared with the emanation rate, or background, from the materials used in the construction of the experimental system. Adsorption losses of the radioactive gas onto the surfaces of the materials used in the experimental system is also a serious consideration. A method developed for measuring very low emanation rates of  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  from materials is described and discussed below.

## 2. MEASUREMENTS UNDER VACUUM CONDITIONS

Measurements of radioactive gas emanation from samples under vacuum conditions are suitable for materials of low and very low  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  content (2,3). However, it should be stressed that measurements under vacuum conditions do not truly represent normal or natural conditions. This is so because an artificial pressure differential between the sample's interstitial space and the volume external to the sample is imposed. Under these conditions, the usual expressions describing pure diffusion processes no longer apply because the emanation of radioactive gas from the sample is governed by forced convective transport processes, in addition to pure diffusion mechanisms. Under these conditions, the simplification  $J_t = 0$  (no

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Darcy's flow) is no longer possible, and Equations 12 to 16 are no longer valid in the present case. Hence, Equation 1 must be solved taking into account Equations 2, 4 and 5, where VP can be described by a step function. However, the solutions to Equation 1 for VP  $\neq$  0 is beyond the scope of this report.

Another important consideration when measuring radioactive gas emanation rates from materials of low or very low  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  content is the adsorption of  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  on large surfaces. Three cases are of interest in the context of this discussion, namely, adsorption of radioactive gas:

1. On the surface of the emanating material (sample);
2. Upon contact of the sample with 'laboratory air' before placing the sample in the emanation chamber (see below);
3. On the surfaces of components of the experimental apparatus.

In all of the above cases, the  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  are, in part, irreversibly adsorbed. Data on adsorption of  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  on material surfaces is virtually non-existent, and a subject of interest worthwhile investigating in some detail. Items 1 and 3 will result in underestimating the emanation rate of radioactive gases from the samples. However, item 2 will result in the opposite, i.e., overestimation of the emanation rate. Items 1 to 3 are not the only complicating factors to contend with. Another difficulty arises when the porosity of the material and the 'mechanical layout or configuration' of the sample are taken into account. In the first case,  $^{222}\text{Rn}$  can diffuse into the sample (reverse or back-diffusion) upon contact with 'laboratory air', prior to inserting the sample into the emanation chamber. Part of the  $^{222}\text{Rn}$  may remain trapped in the pore space until it decays away. In the second case,  $^{222}\text{Rn}$  entering samples, arranged in layers of different materials, may be trapped between layers and diffuse through the layers slowly, and so on. (For  $^{220}\text{Rn}$  the above effects can be

safely disregarded because of its short half-life, ~56 s.)

A further consideration when measuring low emanation rates is the  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  content of the materials used in the experimental apparatus, e.g., emanation chamber, tubing, cold traps, valves, scintillation cells, and vacuum gauges, to name a few components. Hence, materials should be chosen for the components of the system with the minimum possible amount of  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$ . If the content of these radionuclides in the system is significant, in other words easily measurable, then estimation of emanation rates will not be an easy task.

The discussion above suggests that measurements of emanation rates and emanation coefficients of materials under vacuum conditions are rather complex, delicate, and time consuming. In general, the experimental procedure used in this method can be summarized in the few steps below. However, because this is the method and procedure followed in obtaining the emanation rates data presented in this report, the experimental procedure used, as well as the different components of the experimental apparatus (hereafter referred to as the emanation system, or the system, for short) will be described in detail elsewhere in this report. The main steps followed in the emanation method under vacuum conditions are:

1. Outgasing of the emanation system without the sample in place (i.e., emanation chamber);
2. Sample is placed in emanation chamber and the emanation system is maintained under vacuum for a pre-set length of time. This operation is done to remove  $^{222}\text{Rn}$ : a) adsorbed on the surface of the material; b) trapped in surficial pore spaces; c) trapped between layers of different materials making up the sample, etc. Items a) to c) occur when the sample is in contact with  $^{222}\text{Rn}$ -laden atmospheres, e.g., 'laboratory air', for a prolonged period of time;
3. The emanation chamber is disconnected from the rest of the emanation

system, and the radioactive gas in the sample is left to diffuse out of it into the emanation chamber. The latter is designed to maintain the vacuum conditions prevailing in the emanation system previous to disconnecting the emanation chamber from the rest of the system, with minimum leakage. This operation is commonly referred to as the in-growth period;

4. After a given in-growth period the emanation chamber is 'reconnected' to the rest of the emanation system and the radioactive gas in the emanation chamber is collected in a liquid nitrogen ( $\text{LN}_2$ ) cold trap; and
5. The radioactive gas collected in the  $\text{LN}_2$  cold trap is released (by warming the Cu-coil that makes up the cold trap) and transferred to the scintillation cell, where the radioactive gas concentration is measured.

Because of the low radioactive gas concentrations to be measured, the background of the emanation system, i.e., contribution without the sample, plays an important role and should be known as accurately as possible. For this reason, the procedure outlined in items 1 to 5 should be carefully repeated without the sample. This contribution, i.e., background, should be subtracted from the results obtained when measurements are conducted with the sample.

It is also important to carry out measurements with the same sample for different in-growth times to verify that the growth of radioactive gas concentration in the emanation chamber with time follows Equation 8. Non-conformance with Equation 8 is clearly indicative of a faulty experiment or measurement, as well as, or, effects, contributions, or mechanisms other than pure diffusion of, say,  $^{222}\text{Rn}$  from the sample.

Although the method described here has been classified before as rather artificial, this method would be in perfect accordance with situations in which materials were subjected to vacuum conditions as part of their natural environment, and the emanation of, say,  $^{222}\text{Rn}$ , was of importance. Such cases may not be difficult to envisage.

### 3. MEASUREMENTS BY THE LIQUID IMMERSION METHOD

Emanation of radioactive gases from solid materials submerged in liquids, particularly water, is another case of importance, both from the theoretical and the experimental standpoints (3). The emanation method used in this case is very similar to the method used under vacuum conditions, except for some notable differences, e.g.:

1. The emanation system is kept at ambient pressure; hence, no vacuum pump is necessary (a slight variation of the method in which collection of radioactive gas is done under vacuum conditions will be described below);
2. The emanation chamber is filled with ultra-high purity water. The sample is immersed in the water and kept in the emanation chamber for a given period, i.e., the in-growth period. During this time, the radioactive gas emanating from the sample will dissolve in the water, from which it must be extracted;
3. The radioactive gas dissolved in the water is extracted by bubbling an inert carrier gas such as He through the water for a length of time.

The rest of the experimental procedure is similar to the previous case investigated (emanation under vacuum conditions) and uses, except for the emanation chamber, the same emanation system and follows the same analytical procedure.

In this method, special care must be exercised with regards to the purity of the water and the gas carrier (He) used. In order to reduce the background of the system, the water used should contain  $<1$  ppm of suspended solids, and have a resistivity of  $\sim 18$  M $\Omega$ . This can be accomplished by passing distilled water through a combination of ion-exchange and de-ionizer columns, in conjunction with special 'final' filters. This procedure will eliminate the majority of the  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  content in the water. Radon-222 dissolved in the water must also be removed before immersing the sample in it. This can be done by bubbling He through the water. However,

because He is not  $^{222}\text{Rn}$ -free, the carrier gas is passed through a  $\text{LN}_2$  cold trap, to remove any trace of  $^{222}\text{Rn}$ , before entering the emanation chamber.

Once the sample is placed in the emanation chamber and after a given in-growth period, the radioactive gas dissolved in the water can be extracted as indicated above, namely, by passing  $^{222}\text{Rn}$ - and  $^{220}\text{Rn}$ -free He. However, the He/radioactive gas mixture exiting the emanation chamber will contain substantial amounts of water vapour which, for a variety of reasons, must be removed from the gaseous mixture before the radioactive gas is collected in the  $\text{LN}_2$  cold trap. This can be done by placing a  $\text{CO}_2$  cold trap at the exit of the emanation chamber, upstream of the  $\text{LN}_2$  cold trap.

If the emanation chamber is not large, it is possible to 'de-emanate' the radioactive gas by applying a vacuum to the emanation chamber (through the rest of the emanation system) so that the radioactive gas dissolved in the water will bubble through.

Because of the special conditions under which measurements are conducted in this particular type of experiments, the properties of water as a solvent and leaching agent should be considered. The solubility and leachability of the sample due to the prolonged action of the water acting upon the sample are largely unknown, and some degree of interference with the diffusion process should be expected. In addition, water can diffuse into the interstitial pore space of the sample dissolving the radioactive gas diffusing through the material. It is possible that this effect may retard the diffusion process. Also some transport of radioactive gas mediated by water is likely to occur. All these factors should be considered carefully. Hence, the growth characteristics for the radioactive gas depicted by Equation 8 is not likely to apply to the present case.

A final word of caution is in order. In this report, frequent reference to radioactive gas is made as opposed to specific mention of  $^{222}\text{Rn}$  or  $^{220}\text{Rn}$ . This is done because the methodologies described here

apply, in most cases, to radioactive gases with half-lives sufficiently long for these experimental procedures to be effective. This is certainly the case for  $^{222}\text{Rn}$ , but not for  $^{220}\text{Rn}$ , where its short half-life (~56 s) renders the above procedures useless. However,  $^{224}\text{Ra}$  and  $^{220}\text{Rn}$  must always be taken into consideration because once  $^{220}\text{Rn}$  is formed, its progeny ( $^{212}\text{Bi}$  and  $^{212}\text{Po}$ ) can seriously interfere with  $^{222}\text{Rn}$  measurements unless  $\alpha$ -particle spectrometry is used to discriminate  $^{220}\text{Rn}$  progeny from  $^{222}\text{Rn}$  and its progeny. Unfortunately, the detectors suitable for  $\alpha$ -particle spectrometry (e.g., silicon barrier, SiB, and diffused-junction, DJ, detectors) have much lower  $\alpha$ -particle counting efficiencies than scintillation cells. (A well designed scintillation cell can easily have an  $\alpha$ -particle counting efficiency at least three times as high as a conventional SiB or DJ detector, which have counting efficiencies of approximately 20%.) Hence, what is gained in spectral information is lost in  $\alpha$ -particle counting efficiency. Fortunately,  $^{220}\text{Rn}$  progeny formed in the emanation system plate-out most efficiently on the wall surfaces of the system because of the low aerosol concentration, particularly under vacuum conditions.

Radon-220 emanation measurements from solid materials are difficult to carry out by the liquid immersion method. They are considerably easier to conduct at ambient pressure, or under vacuum conditions, but the emanation system used for  $^{222}\text{Rn}$  emanation measurements must be modified substantially. The easiest way to conduct  $^{220}\text{Rn}$  emanation measurements is by placing an  $\alpha$ -particle detector in the emanation chamber and conducting continuous, 'real-time' measurements, either at ambient pressure or under vacuum conditions. This technique, as well as some measurements conducted on some materials, will be described in a forthcoming report.

Emanation measurements by the liquid immersion method are of great practical interest, particularly with regards to the Sudbury Neutrino Observatory (SNO). Measurements by this method will be the subject of another

forthcoming report.

#### 4. MEASUREMENTS BY GAMMA-RAY COUNTING

Finally, and for the sake of completeness a method for determining the emanation of  $^{222}\text{Rn}$  from materials by  $\gamma$ -ray counting will be outlined briefly (4,5). This method has been used preferentially to determine the emanation coefficient of  $^{222}\text{Rn}$  from U-ore samples. This method is commonly known as the Gamma-Only Assay Method, and it uses a NaI(Tl)  $\gamma$ -ray detector and its associated electronic circuitry. (Other detectors, such as High Purity Germanium, HPGe, detectors could of course also be used.)

The method consists of placing the sample in a suitable small 'can', and sealing the latter immediately after. The gamma-ray activity is followed from  $t=0$ , i.e., insertion of sample in can and sealing of the can, until  $t=\infty$ , i.e., steady-state conditions (several weeks) (5). In a modified version, named the prediction method (4), two gamma-activity measurements are made at suitable times after the sample is sealed in the can. From these measurements, extrapolations are made to find the  $\gamma$ -ray activity at sealing time ( $t=0$ ),  $N_0$ , and at equilibrium ( $t=\infty$ ),  $N_\infty$ . Calling  $N_1$  and  $N_2$  the two measurements at times  $t_1$  and  $t_2$ , respectively, it can be shown that:

$$N_\infty = N_1 + \frac{N_2 - N_1}{1 - \exp[-\lambda(t_2 - t_1)]} \quad (18)$$

$$N_0 = N_\infty - [N_\infty - N_1] \exp [\lambda(t_1 - t_0)] \quad (19)$$

From Equations 18 and 19 the emanation coefficient,  $E_c$ , can be calculated:

$$E_c = [1 - (N_0/N_\infty)] \times 10^2 \quad (20)$$

The emanation rate can be calculated from  $N_\infty$  (Equation 18). The ultimate sensitivity of the gamma-only method depends a great deal on the environmental gamma-ray background in the laboratory where measurements are

conducted. The sensitivity of the technique can be improved by adequate shielding and by the use of high energy resolution  $\gamma$ -detectors such as HPGe detectors. Although this method has not been used at our laboratory for very low  $^{226}\text{Ra}$  or  $^{238}\text{U}$  content samples, it works reasonably well for conventional U-samples. It is, however, doubtful that it would be sensitive enough, because of high environmental  $\gamma$ -ray backgrounds, for our particular application with regards to the SNO Project.

This report presents data obtained with the emanation method under vacuum conditions. The following section is devoted to a detailed description of the emanation system used, and the experimental procedure followed for both, the calibration of the emanation system, and the determination of emanation rates from materials. Data for three materials are reported.

#### DESCRIPTION OF THE APPARATUS (EMANATION SYSTEM)

The vacuum emanation system used in this series of measurements is shown in Figure 2. The system consists of the following components:

1. An acrylic emanation chamber. There are several cylindrical chambers available of different dimensions to accommodate different types of samples and amounts of the material samples of interest. The dimensions of the chambers range from 12.5 to 29 cm in diameter and 19 to 175 cm in height, thereby covering a volume ranging from 3.6 L to ~60 L. The chambers are provided with 2 to 3 connecting or sampling ports fitted with 'quick-connectors' of the Swagelok<sup>TM</sup> type;
2. The gas emanated from the sample and released into the emanation chamber during the 'in-growth' period was directed to two cold traps (CT). One cold trap contains 'dry-ice' ( $\text{CO}_2$ ) in order to remove water vapour, whereas the second CT, placed downstream of the  $\text{CT}(\text{CO}_2)$ , contains liquid

N<sub>2</sub> (LN<sub>2</sub>) to condense <sup>222</sup>Rn and/or <sup>220</sup>Rn;

3. All the steps of the experimental procedure are carefully pressure-monitored by means of three vacuum sensors, and their associated vacuum gauges, and two Hg-manometers. Each pressure (P) sensitive device is strategically located in the emanation system 'train' to accurately monitor P during the different operations carried out in the experimental procedure. The different steps conducted during the procedure are effected by means of several needle valves, each designed to perform a given function;
4. Radon-222 and/or <sup>220</sup>Rn are released from the CT(LN<sub>2</sub>) and transferred to the counting system. This operation is normally done using a <sup>222</sup>Rn-free carrier gas, e.g., He in our case. (The He is first passed through a LN<sub>2</sub> fold trap to remove all traces of <sup>222</sup>Rn.) The counting system consists of a scintillation cell of the flow through type, operating in conjunction with a photomultiplier tube (PMT) and an automated, fully programmable, 'scaler'. In cases where spectral information, and/or radioisotope discrimination are important, the gross  $\alpha$ -particle counting system indicated above (i.e., scintillation cell and associated PMT/scaler system) has been substituted by a special electrostatic chamber, equipped with a silicon barrier detector in conjunction with their electronic circuitries and computer-based system;
5. The different components of the emanation system were connected together by means of thin-walled metal tubing (3/8" O.D.), including elbows, 'tees', unions, quick connectors, and so on. Three emanation systems have been built which differ only in the tubing material used. The data reported here were obtained using Cu-tubing. The other two systems were constructed using, respectively, stainless steel and Pyrex<sup>TM</sup>. A fourth, recently built emanation system only differs in the size of the tubing, unions, etc. This system was built with 1/8" O.D. Cu-tubing and is

significantly shorter and smaller than the others. This 'microsystem' has an internal surface area considerably smaller than that of the other systems, and was designed to further reduce the  $\alpha$ -particle background of the emanation system. The idea behind using different materials was to determine which had the lowest background to be used for very low emanation studies;

6. Other components of the emanation system include (flexible) Tygon<sup>TM</sup> tubing which was found to be the most suitable for connecting the emanation chamber and the scintillation cell to the rest of the system. Connections between the different components of the emanation system were effected by means of brass or stainless steel 'quick connectors'. This 'modular' option provided the system with a great degree of flexibility as it was very easy to reassemble, transpose and interchange components within the same system, or from one system to another;
7. The cold traps placed in the emanation system (see item 2) differed in size, shape and material. Usually, the cold traps used were of the coil-type with about six complete turns and approximately 7 cm diameter. Cold traps were made of Cu, stainless steel, and Pyrex<sup>TM</sup>; and
8. A vacuum pump at one end of the emanation system train provided the desired vacuum for proper operation of the system. The pump was rated at  $1 \times 10^{-4}$  Torr ( $1.33322 \times 10^{-5}$  kPa).

The experimental procedure followed to measure the emanation of  $^{222}\text{Rn}$  (or  $^{220}\text{Rn}$ ) by the vacuum method will be described in detail elsewhere.

#### CALIBRATION OF THE EMANATION SYSTEM

The calibration of the emanation system can be divided into three parts, namely:

1. Calibration of the detection system, e.g., scintillation cell (SC), in

- conjunction with the PMT and associated scaler (s), or SC/PMT/S, for short;
2. Measurement of the background of the system; and
  3. Determination of the efficiency of radioactive gas ( $^{222}\text{Rn}$ ,  $^{220}\text{Rn}$ ) transfer.

#### 1. CALIBRATION OF THE RADIOACTIVITY DETECTION SYSTEM

The  $\alpha$ -particle efficiency of the SC/PMT/S system depends on the PMT/S settings (e.g., threshold, high voltage, and the like) and the scintillation cell itself. Assuming the PMT/S to be an invariant of the system, the efficiency of the counting system mainly depends on scintillation cell parameters such as shape, physical dimensions, and ZnS(Ag) coating thickness. Calibration of scintillation cells is a standard, well known procedure. However, for special applications, such as low-activity emanation studies under vacuum conditions, special care must be exercised to take into account a number of important factors as follows. Usually, scintillation cells are calibrated at ambient pressure conditions and at relatively high  $^{222}\text{Rn}$  concentrations. However, in the present case measurements were conducted either under vacuum, or reduced pressure conditions, or at ambient or reduced pressure conditions in the presence of a carrier gas, such as He. The counting efficiency of a scintillation cell depends on the pressure inside the cell and the type of gas carrying the  $^{222}\text{Rn}$ . One way of eliminating this dependence is by making the dimensions of the cell equal or smaller than the range of the  $\alpha$ -particle at atmospheric (ambient) pressure. However, this has a drawback, namely, it reduces the total  $\alpha$ -particle count because the total amount of  $^{222}\text{Rn}$  inside the cell is proportional to its volume. But it also has an advantage: the background of the cells, which is proportional to its internal total surface area, decreases with decreasing surface area.

In the present case, new scintillation cells of volume  $\sim 280$   $\text{cm}^3$ , filled with the  $^{222}\text{Rn}$ /carrier gas (He) mixture at atmospheric pressure

have been used. Under these conditions, the counting efficiency of the cells is greater than when the cells are filled with the  $^{222}\text{Rn}$ /air mixture at the same pressure. This is so because the range of  $\alpha$ -particles of a given energy is larger for gases with low atomic number, such as He, than for gases such as  $\text{O}_2$  and  $\text{N}_2$ , the main components of air. It should be noted that in addition to the relatively large scintillation cells ( $\sim 280 \text{ cm}^3$ ) indicated above, much smaller cells ( $\sim 100 \text{ cm}^3$ , and  $< 50 \text{ cm}^3$ ) have also been used under the same conditions.

The  $\alpha$ -counting efficiency, K, of scintillation cells vary, as indicated above, with the cell volume and shape. For the scintillation cells used here K was  $\sim 1.45 \text{ cpm/pCiL}^{-1}$  ( $39.2 \text{ cpm/mBqm}^{-3}$ ).

## 2. BACKGROUND OF THE EMANATION SYSTEM

The main contribution to the background, B, of the emanation system arises from the  $^{226}\text{Ra}$  content (Bq/g) of the components of the system (including the emanation chamber and the Scintillation cell), as well as the total emitting (internal) surface area of the system. Another undefined potential contribution to the background may arise from adsorption of  $^{222}\text{Rn}$  on the walls of the system, particularly from the calibration procedure which usually necessitates the injection of significant amounts of  $^{222}\text{Rn}$ , which may later desorb during emanation studies.

The background of the emanation system varies with time depending on its use and the activity concentration measured. In general, B increases with time due to the steady build-up of  $^{210}\text{Pb}/^{210}\text{Po}$  from the decay of the short-lived decay products of  $^{222}\text{Rn}$ . This contamination is very undesirable because of its long half-life ( $\sim 22 \text{ y}$ ). Hence, once the contamination becomes appreciable, the scintillation cell must either be discarded, or alternatively, the ZnS(Ag) coating needs to be removed and the cell recoated again. The background may also change because of microleaks in the system. Because the emanation system is under vacuum, air from outside

may find its way into the system, which even in small amounts may significantly contribute to B. This type of contamination or contribution is affected by environmental factors.

Background (B) measurements should be carried out frequently and extensively, i.e., for extended (continuous) periods. Accurate measurements of B are critically important for the precise assessment of emanation rates from materials. These measurements should be conducted under the same conditions, i.e., in-growth period, and experimental procedure, as the 'real' emanation study except that no sample should be inserted in the emanation chamber. Thus far, B measurements have been conducted quite frequently over the last seven months for periods ranging from 1 day to several weeks. The range of values found for B depended on the emanation chamber and scintillation cell (type and volume) used. An average value for the background of the total emanation system  $\approx 16$  counts per day (cpd) has been measured.

### 3. TRANSFER EFFICIENCY FOR THE RADIOACTIVE GAS

Not all the radioactive gas emanated from the sample into the emanation chamber reaches the  $\alpha$ -particle detector, e.g., scintillation cell. There are several reasons for this:

- a) Part of the radioactive gas is irreversibly adsorbed on the walls of the emanation chamber and other components of the emanation system, including the cold traps. Although direct measurement under our experimental conditions of adsorption phenomena is not straightforward, this effect could conceivably be significant for 'low-emanating' materials where the signal-to-noise count ratio is rather low;
- b) Not all the radioactive gas 'trapped' in the cold trap can be transferred to the scintillation cell. This is mainly due to two reasons, depending on whether the transfer is effected under vacuum (or reduced pressure) conditions, or, alternatively, using a carrier gas, such as He, to effect

the transfer. In the first case, insufficient pressure (vacuum) differential between the cold trap and the scintillation cell is responsible for inefficient transfer, whereas in the second case the most probable cause is an insufficient amount of carrier gas to 'push' all the radioactive gas from the cold trap to the scintillation cell, hence part of the radioactive gas remains in the 'in-between' space (tubing, and so on).

The transfer efficiency of the emanation system can be determined by injecting a known amount of  $^{222}\text{Rn}$  into the (empty) emanation chamber and following the usual experimental procedure for the measurement of  $^{222}\text{Rn}$  emanated from samples, by the vacuum method. Special precautions should be taken in the transfer procedure to minimize sources of error, namely, a given amount of  $^{222}\text{Rn}$  from a standard source is transferred into a well calibrated scintillation cell, i.e., cell A, and the  $\alpha$ -particle count of cell A is recorded carefully by an independent counting system, S1, before injecting the sample into the empty emanation chamber. After the transfer has been completed, cell A is counted again in the counting system S1. This operation is important in order to verify that all the  $^{222}\text{Rn}$  in cell A has been transferred to the emanation chamber. If this is not the case, the fraction of the total amount of  $^{222}\text{Rn}$  in cell A transferred to the emanation chamber should be known accurately. It should be noted that because of the plate-out of  $^{222}\text{Rn}$  progeny on large surfaces, such as the walls of scintillation cells, the second measurement of cell A should be done about 4 h after the  $^{222}\text{Rn}$  transfer to the emanation chamber has been effected. The residual activity is due to the cell background and any  $^{222}\text{Rn}$  still remaining in the cell.

Numerous measurements following the procedure described above indicate that the average transfer efficiency for the system used here is,  $\epsilon(\text{tr}) = 0.85$  (i.e., -85%). (Subsequent modification in the system gives

correspondingly higher values for  $\epsilon(\text{tr})$ .)

#### FURTHER COMMENTS ON THE CALIBRATION OF THE SYSTEM

Subsections 1 (Calibration of the Radioactivity Detection System), 2 (Background of the Emanation System), and 3 (Transfer Efficiency for the Radioactive Gas) of this section are the main considerations regarding the calibration of the emanation system. Hence, the  $\alpha$ -particle count,  $N_\alpha$ , obtained with the  $\alpha$ -particle counting system of the emanation apparatus must be corrected for:

1. Background, B;
2.  $\alpha$ -particle counting efficiency of the scintillation cell/photomultiplier tube/scaler (SC/PMT/S) system, K; and
3. Transfer efficiency  $\epsilon(\text{tr})$ .

Neglecting effects other than the ones discussed above, one may write for the true  $\alpha$ -particle count from the sample, i.e.,  $N_S$ :

$$N_S = (N_\alpha - B)/K \epsilon(\text{tr}) \quad (21)$$

If  $N_\alpha$  and B are given as count rates (e.g., counts per minute, cpm) and K in terms of  $\text{cpm/Bqm}^{-3}$ ,  $N_S$  will be in  $\text{Bqm}^{-3}$ . Calling  $V_{SC}$  the volume of the scintillation cell, the product  $N_S V_{SC}$  (Bq) represents the total emanated radioactivity resulting from the sample, i.e.,  $A_T$ . This quantity must now be related to some 'extensive' quantity of the sample, such as volume, surface area or mass in order to properly quantify the emanating characteristics of the sample. At this point it is important to be reminded again of the effect of shape and physical dimensions on the emanating characteristics of samples. For comparison purposes, this dependence can be eliminated by preparing standardized, i.e., identical samples, from the 'geometry' standpoint. However, it is clear that this is not always possible because of practical considerations and constraints. Results from samples of

different geometries should be interpreted accordingly.

Expression 21 presupposes that radioactivity measurements have been taken at, or after, steady-state conditions in the emanation chamber have been reached, i.e.,  $t=t_{ss}$ , where ss stands for steady-state. This conditions is reached when  $e^{-\lambda t_{ss}} \ll 1$ . If  $t = t_{IG} < t_{ss}$ , where IG indicates in-growth period, Equation 21 should be modified accordingly by dividing by  $1 - e^{-\lambda t_{IG}}$ . Again, the assumption is implicitly made that the radioactivity measured arises from the decay of, say,  $^{226}\text{Ra}$  in the sample. But this does not necessarily need to be the case because the presence of  $^{222}\text{Rn}$  could be partly due to causes other than decay of  $^{226}\text{Ra}$  in the sample, namely:

1.  $^{222}\text{Rn}$  adsorbed in the surface or pore space close to the surface of the sample during contact with air;
2.  $^{222}\text{Rn}$  trapped between layers of material if the sample is of the multilayered type.

Items 1 and 2 could not account for any  $^{222}\text{Rn}$  if the sample was kept out of contact with any contaminating ( $^{222}\text{Rn}$ ,  $^{226}\text{Ra}$ ) material, i.e., if the sample is kept in the emanation chamber under vacuum, and radioactivity measurements are carried out at times  $t \gg 0.693/\lambda$ . The latter quantity represents the half-life of  $^{222}\text{Rn}$ ,  $T_{1/2} (^{222}\text{Rn}) \sim 3.82$  d. Hence, in order to minimize the contribution of  $^{222}\text{Rn}$  from causes other than  $^{226}\text{Ra}$  in the sample, measurements should be conducted at times  $t > 7T_{1/2} (^{222}\text{Rn}) \sim 1$  month. However, this is approximately the minimum time necessary for the  $^{226}\text{Ra} - ^{222}\text{Rn}$  mixture to attain radioactive equilibrium (steady-state conditions), i.e.,  $t_{ss}$ . It is clear from the above, that at least one measurement of the sample should be conducted at  $t > t_{ss}$  ( $\sim 8$  w) to eliminate the potential contribution from 'surface' contamination by adsorption or back diffusion of  $^{222}\text{Rn}$ .

#### EXPERIMENTAL RESULTS AND DISCUSSION

Extensive measurements on three materials, Viton 'O'-ring;

coaxial cable by Belden, M9067; and a molecular sieve (zeolite) have been completed, and tests on other materials (norite, and several concrete mixtures) are in progress. Measurements on each material were carried out for different in-growth periods ranging from 4 to 58 days, for coaxial cable, to 1 to 82 days, for the molecular sieve. The following number of tests were conducted for the different materials: 3 for the Viton 'O'-ring, 12 (4 were discarded for different reasons) for the coaxial cable, and 7 for the molecular sieve. Some physical data of interest are shown in the table below, where the symbols L, S, V, M, and R stand, respectively, for length, surface area, volume, mass and radius.

Material	L(cm)	S(cm <sup>2</sup> )	V(cm <sup>3</sup> )	M(g)	R(cm)	Remarks
Viton 'O'-ring	469	704.3	84.2	154.9	0.239	1 piece
Coaxial cable	17.5 <sup>1</sup>	4795.7*	731.3*	697.4	0.305	143 pieces
Molecular sieve	-	-3200.0 <sup>+</sup>	-215.0 <sup>+</sup>	474.1	-0.2	spheres <sup>++</sup>

\*<sup>+</sup>Total, i.e., corresponding to the 143 pieces (\*), or the  $6.4 \times 10^3$  spheres (<sup>+</sup>). <sup>++</sup> about  $6.4 \times 10^3$  spheres (calculated from M and assuming  $\rho = 2.2 \text{ gcm}^{-3}$ ). <sup>1</sup> length per piece.

Figure 3 shows the results obtained for the molecular sieve, where the emanation rate,  $E_R$ , measured for the sample has been plotted versus the in-growth time,  $t_{IN}$ , in the emanation chamber. Also shown, is the theoretical curve representing the expression:  $E_T(t) = E_R(\infty)[1 - \exp(-\lambda t_{IN})]$ , where,  $E_R(\infty)$  has been taken as the emanation rate measured at  $t = 82$  d. Because of the dependence of  $E_R$  on the shape and size of the sample, and because of the lack of sample standardization, a difficulty arises as to how best to express the emanation rate, namely, per unit surface area ( $\text{Bqm}^{-2}$ , i.e.,  $\text{atoms m}^{-2}\text{h}^{-1}$ ), or per unit mass ( $\text{Bq kg}^{-1}$ , i.e.,  $\text{atoms kg}^{-1}\text{h}^{-1}$ ). Emanation rate values are quoted below in both units, i.e.,  $\text{Bqm}^{-2}$

(atoms  $m^{-2}h^{-1}$ ) and  $Bq\ kg^{-1}$  (atoms  $kg^{-1}h^{-1}$ ). Furthermore, some uncertainty in the specific gravity of the molecular sieve (Zeolite) (a value of 2.2 has been taken), and the somewhat irregular shape of the molecular sieve particles (spheres), which leads to some uncertainty in the measurement of their diameter, suggest that in the present case, the emanation rate per unit mass provides a more accurate description of the emanating properties of the material.

Comparison of experimental and theoretical data is best accomplished by data normalization, a procedure which also eliminates the need to express emanation rate data in terms of mass or surface area. The emanation rate data at  $t \rightarrow \infty$ , e.g.,  $t \sim 82$  d, permit the calculation of the (approximate)  $^{226}Ra$  content of the sample. This calculation would give an accurate value for the  $^{226}Ra$  content if the emanation coefficient,  $E_c$ , were precisely known. However, because of the relatively small size of the zeolite spheres ( $\sim 0.2$  cm), some assumptions can be made. Recalling that the diffusion length,  $L_D$ , is given by  $(D/\eta\lambda)^{1/2}$ , a review of the values for  $D$  in the literature suggests,  $D > 10^{-6}$   $cm^2s^{-1}$ . Hence,  $L_D \gg 0.2$  cm, and  $E_c \sim 1$ . Taking the above into consideration, the  $^{226}Ra$  content in the sample can simply be calculated from the  $^{222}Rn$  emanation rate at  $t \rightarrow \infty$  (i.e., steady-state conditions) from the equality:  $N(^{226}Ra) \lambda (^{226}Ra) = N(^{222}Rn) \lambda (^{222}Rn)$ , where the right hand side of this expression has been experimentally determined as  $628 \pm 36$  atoms  $kg^{-1}h^{-1}$  (see table below).

Theoretical principles and the data of Figure 3 show that to estimate the true value of  $E_R$ ,  $^{222}Rn$  measurements should be made at in-growth times  $> 20$  d. If a shorter in-growth period is chosen, the value obtained for  $E_R$  should be corrected (i.e., divided) by the correction factor  $1 - \exp(-\lambda t_{IN})$ , where  $t_{IN}$  is the in-growth time. However, the simplified procedures indicated above are not recommended because the value estimated for  $E_R$  would depend on a single measurement only. The recommended procedure is to

measure  $E_R$  for at least three in-growth times, one possibly for  $t_{IN} > 20$  d, and verify that the curve drawn through the data points is in agreement with theoretical expectations.

Finally, it should be noted that the value for the  $^{226}\text{Ra}$  content in the sample, i.e.,  $[^{226}\text{Ra}]$ , calculated as indicated above is approximate, suitable only for illustration purposes. In actual practice,  $[^{226}\text{Ra}]$  is usually assayed by wet chemical separation procedures followed by  $\gamma$ - and/or  $\alpha$ -spectrometric measurements. In some cases, however, direct spectrometric measurement of the bulk material, i.e., entire sample, is made. This method is, in most cases, not reliable enough.

Measurements on the coaxial cable showed certain inconsistencies of, as yet, not clearly defined origin. It would appear that after some evacuation periods, which usually lasted between 24 to  $>48$  h (see below), the emanation rate measured, after a given in-growth time, would drop markedly as compared with the values obtained in the previous experiment. This behaviour is consistent (at least partly) with the notion that:

- a) An undefined fraction of the  $^{222}\text{Rn}$  measured is not due to the radioactive decay of the  $^{226}\text{Rn}$  trapped between the different layers of material making up the cable;
- b) Part of the  $^{222}\text{Rn}$  measured arises from adsorption of the radioactive gas on the material (coaxial cable) surfaces;
- c) All, or part of the  $^{222}\text{Rn}$  measured originates from the decay of the  $^{226}\text{Ra}$  in the material, but its diffusion out of the sample is complicated by (and depends on) the different diffusion coefficients making-up the materials of the coaxial cable, and the air space thickness between the layers. All these complicating factors will result in rather complex  $^{222}\text{Rn}$  release characteristics which could conceivably depend on the measurement cycle, i.e., evacuation period, in-growth period, and hence, time elapsed between measurements.

Items a) and b) depend on the exposure (to air) history of the sample, but the effects should become negligible after about  $6T_{1/2}({}^{222}\text{Rn})$  -23 d, unless the sample is again exposed to air between measurements. The effect of sample exposure to air is simply measured by placing the exposed sample in the emanation chamber, as if it had gone through the evacuation and in-growth periods procedure, and then proceeding in the usual manner, as described elsewhere in this report. This was done shortly after the sample had been received and had been exposed to air by an undetermined period. The value measured for this contamination in terms of emanation rate was:  $0.89 \pm 0.31$  atoms  $\text{m}^{-1}\text{h}^{-1}$ . However, it should be noted that an undefined amount of  ${}^{222}\text{Rn}$  (trapped between the layers or in the layers) must also have come from the decay of  ${}^{226}\text{Ra}$  in the material. Additional measurements conducted shortly after the 'contamination' experiment suggest that a large fraction of the radioactivity measured must have come from air contamination. In summary, one may surmise from the above discussion that item c) plays a key role.

The term evacuation period has been introduced above. This is an important operation in which the sample is placed in the emanation chamber, and the latter is evacuated for a given period. This operation is conducted to remove any residual  ${}^{222}\text{Rn}$  trapped in the sample, e.g., in the pore space and on the surface of the material, before the actual in-growth period begins. However, because of the different porosities, permeabilities, and hence, diffusion coefficients, and diffusion lengths of  ${}^{222}\text{Rn}$  in different materials, the period required in each case for each material or array of materials is different. This poses a serious problem that should be investigated in detail. Hence, evacuation period standardization, i.e., same evacuation period for all samples, may not be the best solution as it could result in unnecessary time constraints and other practical difficulties. The question of how long an evacuation period is necessary in each case can be resolved in two ways:

1. By monitoring the pressure of the system, where the sample is under vacuum, until no further decrease in pressure by outgasing is observed. This presupposes that the system is capable of detecting extremely small variations in pressure;
2. By monitoring the  $^{222}\text{Rn}$  concentration in the system until 'background' levels are attained. This method requires the  $^{222}\text{Rn}$  counting system to be of the flow through continuous monitoring type, as the ones used at our laboratories.

The second method has lately been adopted here. However, many early measurements were conducted for arbitrary evacuation periods ranging from 24 to >48 h, based solely on pressure variation (outgasing) considerations.

Figure 4 shows the emanation rate measured for the coaxial cable for different in-growth periods. Also shown is the theoretical curve for the same in-growth period. Extrapolation of the experimental data for  $t \rightarrow \infty$ , gives an emanation rate,  $E_R$ , for the coaxial cable of  $-0.31 \pm 0.13$  atoms  $\text{m}^{-1}\text{h}^{-1}$ .

The last material to be reported here (but the first one of the series to be investigated) is a length of Viton 'O'-ring. This material was mainly used to test several experimental procedures, and to run a variety of tests in three different emanation systems made up of different materials and components. However, no extensive series of measurements was conducted of the emanation rate versus the in-growth time. The measurement reported here was obtained for an in-growth period of 3 days. The corresponding value for  $t \rightarrow \infty$  was calculated as described by theory. Hence, the value given is subjected to an undefined uncertainty. The emanation rate so obtained was  $-1.02 \pm 1.12$  atoms  $\text{m}^{-1}\text{h}^{-1}$ .

The table below summarizes  $^{222}\text{Rn}$  emanation data for the three materials investigated. In all cases, the emanation rate is given in

terms of  $^{222}\text{Rn}$  emanated per unit surface area and unit mass of the material. In addition, emanation rate data for the coaxial cable and the 'O'-ring are given as  $^{222}\text{Rn}$  emanated per unit length.

Material	$^{222}\text{Rn}$ Emanation Rate			Remarks
	Atoms $\text{m}^{-2}\text{h}^{-1}$	Atoms $\text{kg}^{-1}\text{h}^{-1}$	Atoms $\text{m}^{-1}\text{h}^{-1}$	
'O'-ring	$68.2 \pm 74.4$	$31.0 \pm 33.8$	$1.02 \pm 1.12$	Viton
Coaxial cable	$16.03 \pm 6.73$	$11.03 \pm 4.63$	$0.31 \pm 0.13$	Belden M9067
Molecular sieve	$930 \pm 54^*$	$628 \pm 36$	-	Zeolite

\*Only approximate because surface area cannot be estimated with certainty.

#### FURTHER COMMENTS

The data reported here were obtained under vacuum conditions. A number of additional measurements (not reported here) were carried out at 'ambient' pressure using He to remove the  $^{222}\text{Rn}$  emanated from the sample in the emanation chamber. The  $^{222}\text{Rn}$  formed was separated from the  $^{222}\text{Rn}/\text{He}$  mixture by means of a cold trap. In this method, the evacuation and in-growth period procedures were followed in exactly the same way as for the emanation under vacuum conditions method. The main difference between the two methods is that the transfer of  $^{222}\text{Rn}$  from the emanation chamber to the cold trap is effected by means of He. One important advantage of the He-method is that 'vacuum tightness' so crucially important in the vacuum method is relatively unimportant in the He-method.

It goes without saying that the accuracy of the measurements for either method improves with the amount of material available for the measurement. However, the larger the amount of available material, the larger the emanation chamber needs to be. Because the emanation chamber is itself a source of  $^{222}\text{Rn}$ , an optimum ratio for the chamber to sample volume

is attained which maximizes the signal (S) to noise (N) ratio, i.e., S/N. With this in mind, the use of the smallest emanation chamber that can hold the sample is strongly recommended. If experimentally achievable, a S/N  $\geq 10$  is desirable.

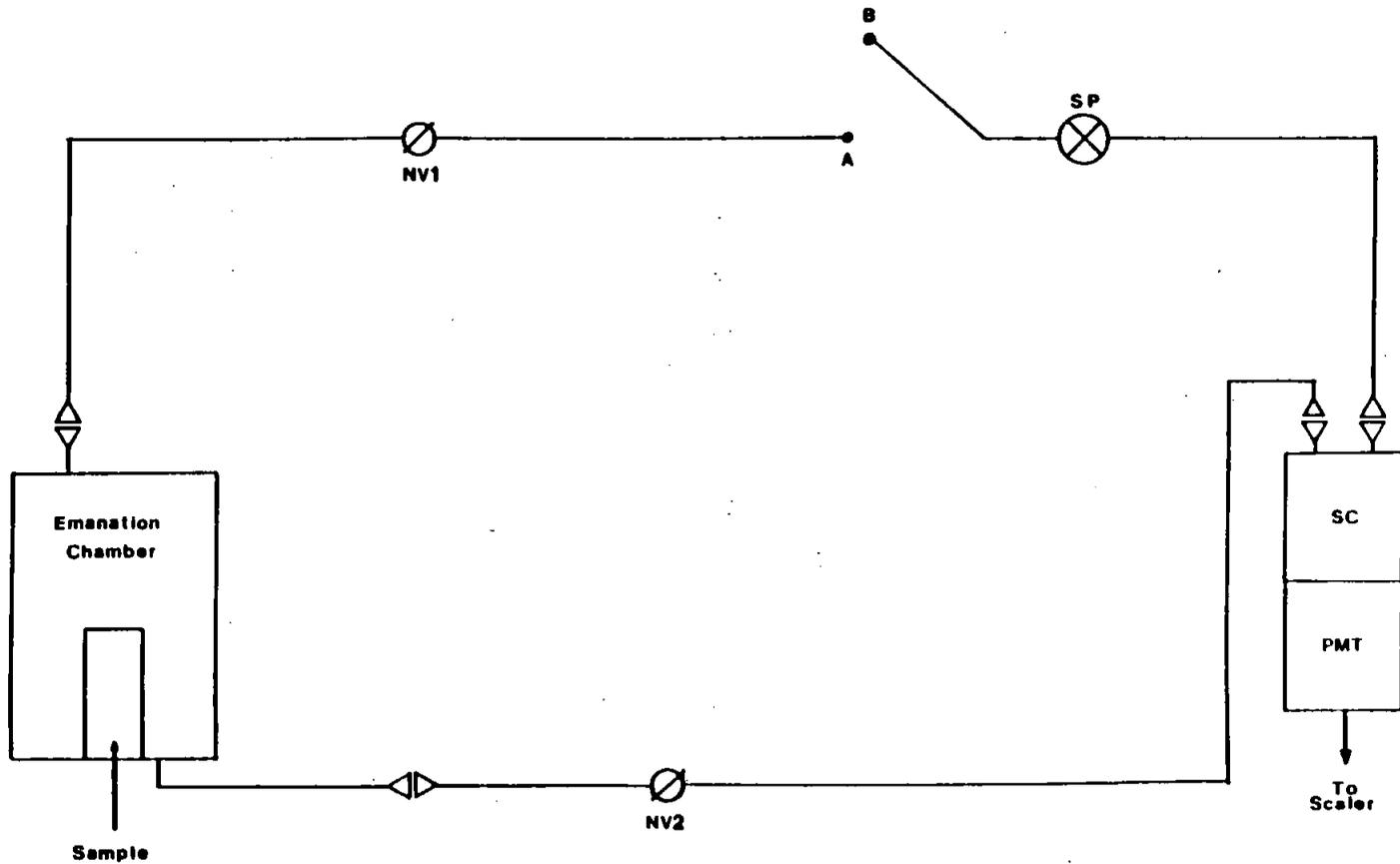
A number of materials other than the ones reported here are presently being studied using the vacuum and the He-method. These materials include norite, and several concrete aggregates which are important for the SNO Project. Also concurrently investigated, are the  $^{222}\text{Rn}$  permeability characteristics of epoxy resins and other polymers. The ultimate goal of these studies is to determine the characteristics of these polymers as  $^{222}\text{Rn}$  barriers when one or more coatings of these materials are applied to mine walls (norite) and building materials (e.g., concrete aggregates) used in the construction of structures for underground laboratory and other experimental facilities. In this type of study, the emanation characteristics of norite and concrete aggregates are investigated before and after coating the samples with epoxy resin, or other suitable  $^{222}\text{Rn}$  barrier material. The study of the  $^{222}\text{Rn}$  emanation characteristics of the material in bulk, and after having been crushed and ground is also of great practical interest.

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# 'AMBIENT' PRESSURE APPARATUS

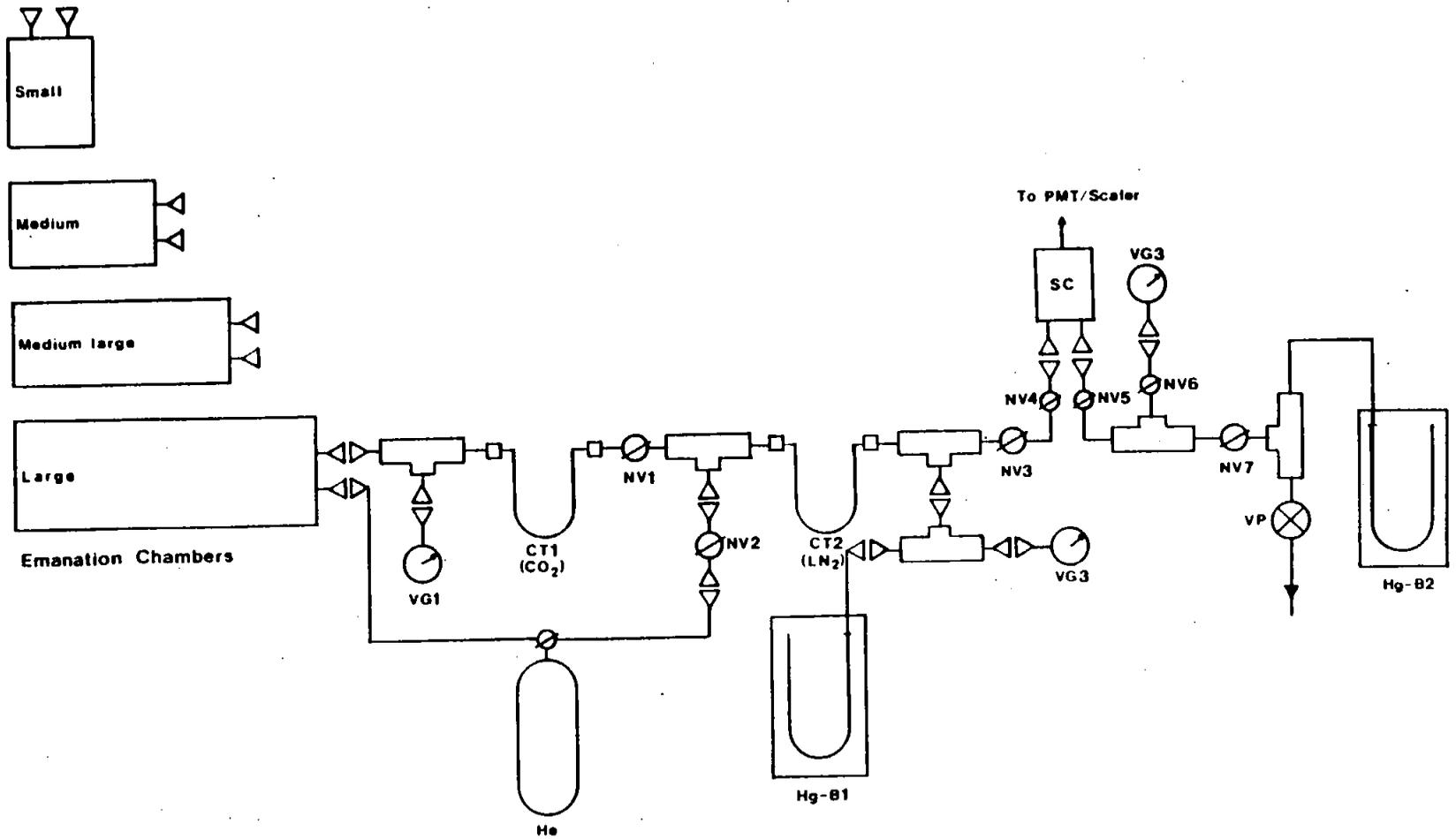


**Legend:**

- NV- Needle Valve
- SP- Sampling Pump
- SC- Scintillation Cell
- PMT- Photomultiplier Tube

Fig. 1 - Ambient pressure emanation apparatus.

# VACUUM EMANATION APPARATUS



**Legend:**

- VG - Vacuum Gauge
- CT - Cold Trap
- NV - Needle Valve
- Hg-B - Mercury Manometer
- SC - Scintillation Cell
- PMT - Photomultiplier Tube

Fig. 2 - Vacuum emanation apparatus.

# Molecular Sieve (Zeolite)

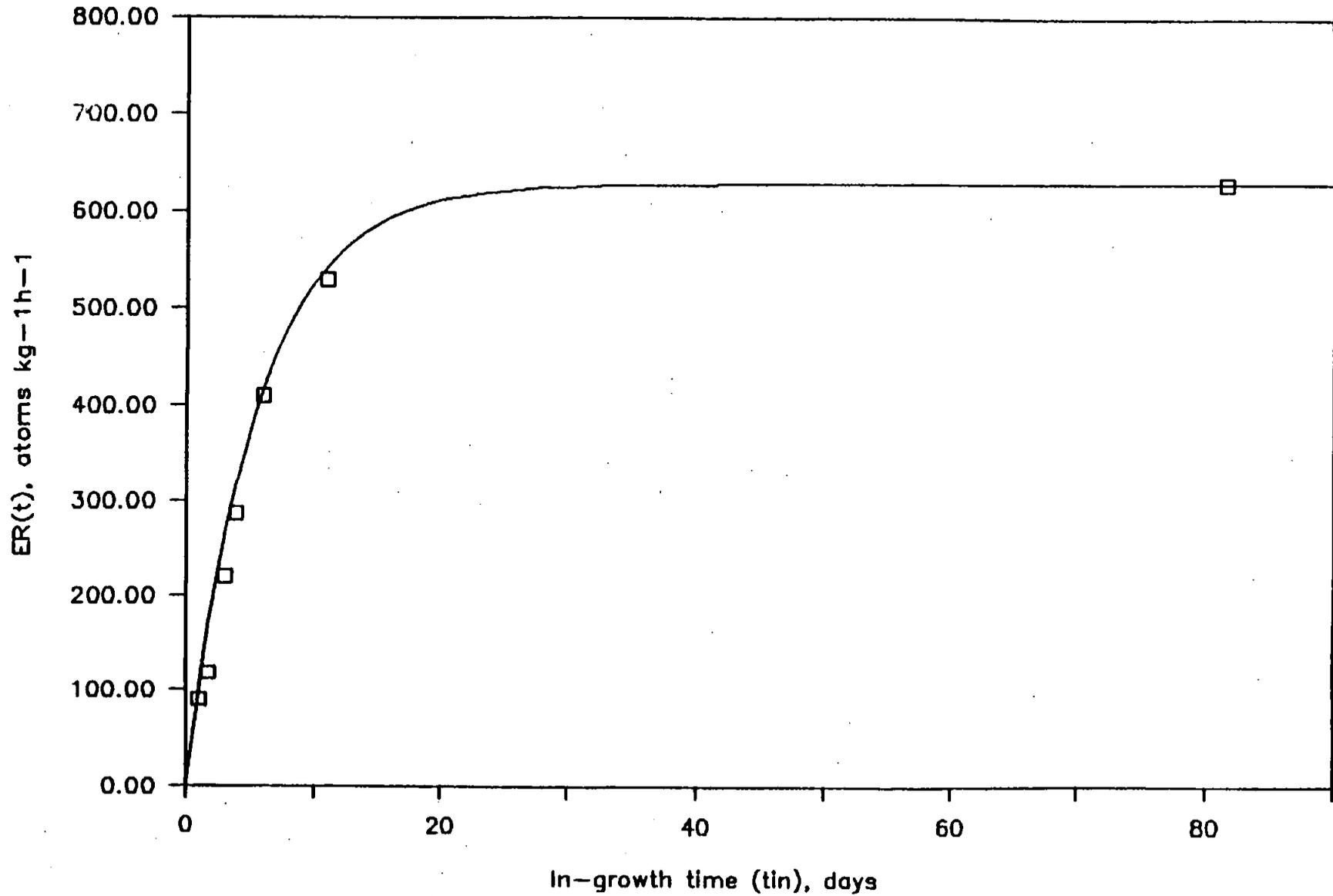


Fig. 3 - Emanation rate versus time for a molecular sieve (Zeolite). (The emanation rate can be highly dependent on the packing configuration of the material. In the present case, the material was highly packed.)

# Coaxial Cable (Belden, M9067)

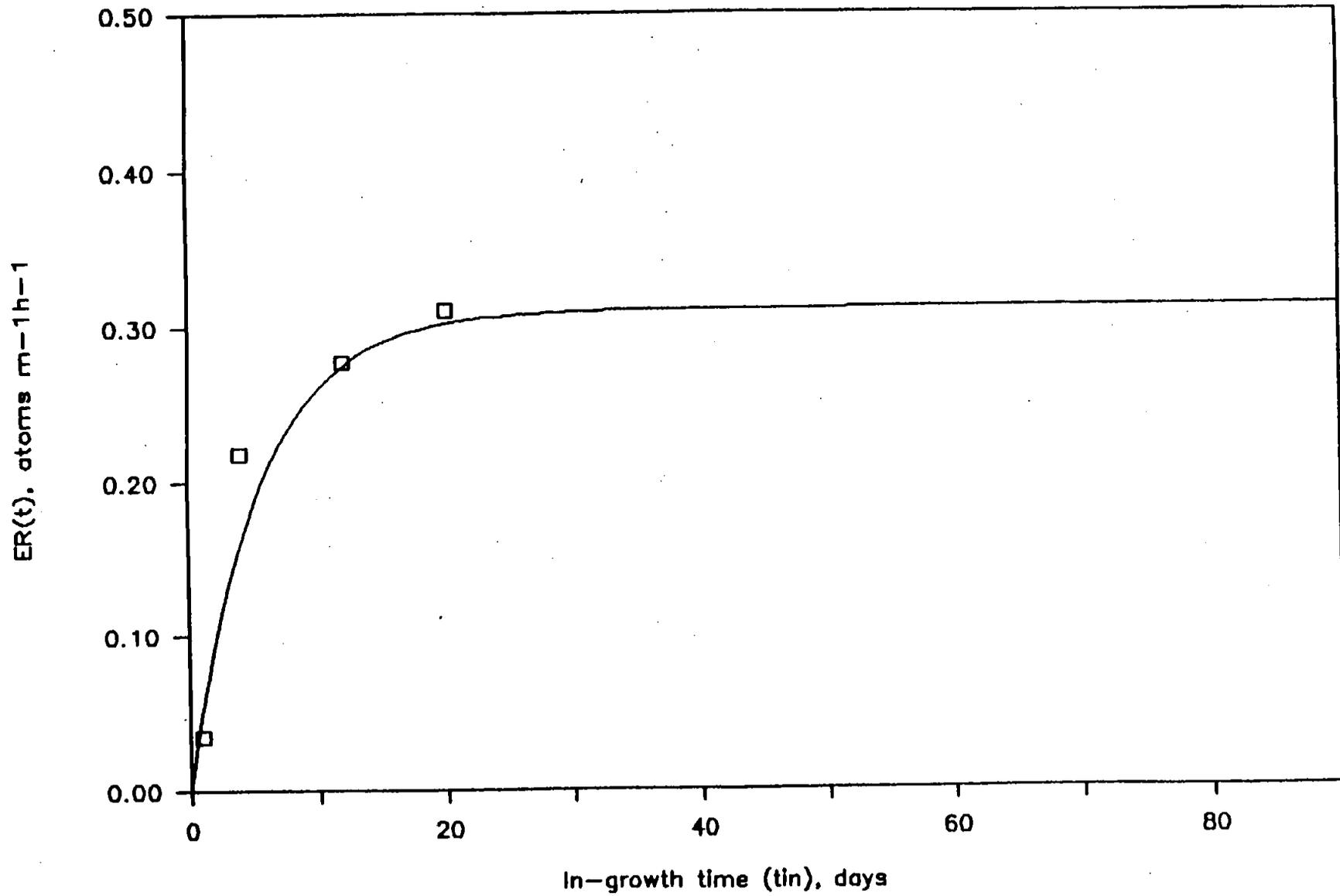


Fig. 4 - Emanation rate versus time for a coaxial cable (Belden, M9067).