

# **Radon diffusion and the emanation fraction for NIST polyethylene capsules containing radium solution**

*Peter Volkovitsky*

National Institute of Standards and Technology, Gaithersburg MD 20899-0001

Ionizing Radiation Division, Building 245, C110, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg MD 20899-8462, USA  
Fax 1 301 926 7416, E-mail: peter.volkovitsky@nist.gov

## **Abstract**

The national standard for radon ( $^{222}\text{Rn}$ ) measurements in the United States is based on Standard Reference Materials (SRMs) prepared at the National Institute of Standards and Technology (NIST), Gaithersburg, MD. NIST radon standards are hermetically sealed polyethylene capsules, filled with radium ( $^{226}\text{Ra}$ ) solution. In preparation of standard reference materials for  $^{222}\text{Rn}$ , it is necessary to understand precisely the emanation fraction of radon from the internal radium solution, through the walls of the polyethylene container, to the surroundings. In preparation of a new radon SRM, it was found that the emanation fraction dependence on accumulation time is not accurately described by the standard ingrowth factor. A mathematical description of the emanation model is presented, which is in agreement with the empirical results for NIST radon emanation standards. It is shown that the radon accumulated inside the polyethylene walls of the capsule is significant and measurable. The radon diffusion coefficient of polyethylene is estimated to be 200 times less than the radon diffusion coefficient of water, while radon solubility in polyethylene is estimated as approximately 2/3 of the solubility of radon in water. This approach could be applied to describe the emanation of radon through other materials.

**Keywords:** radon, standards, emanation factor, radon diffusion

## 1. Introduction

The national standard for radon ( $^{222}\text{Rn}$ ) measurements in the United States is based on Standard Reference Materials (SRMs) prepared at the National Institute of Standards and Technology (NIST), Gaithersburg, MD. NIST radon standards are hermetically sealed polyethylene capsules, filled with radium ( $^{226}\text{Ra}$ ) solution. The first production run of NIST radon emanation SRMs was developed more than 10 years ago (Collé and Hutchinson, 1993). These standards are used widely as primary radon standards for calibration of radon detectors and monitors (Collé et al., 1995, Kotrappa and Stieff, 1994). These early radon SRMs (SRM 4968) were produced in 1993 in sealed polyethylene capsules with total radium solution activities of approximately 5 Bq, 50 Bq, and 500 Bq. With the depletion of this SRM stock, a new series of SRM was produced near the end of 2003. In this case, each activity level was assigned a unique SRM identification (i.e., SRM 4971 for 5 Bq capsules, SRM 4972 for 50 Bq capsules, and SRM 4973 for 500 Bq capsules). The overall dimensions of the cylindrically shaped polyethylene capsules used for the new series are nominally 26 mm in length by 4.4 mm diameter, with an inner solution-containment capacity ( $v_{in}$ ) of approximately  $0.180\text{ cm}^3$  (Figure 1).

The method of measurement involves physical separation of gaseous radon from the parent radionuclide (by emanation of the gas through the walls of the containment capsule), and quantitative transfer of the gas to ionization chambers for measurements. The emanation fraction, the activity of  $^{222}\text{Rn}$  outside the capsule vs the activity of  $^{226}\text{Ra}$  solution confined inside the capsule is the most important parameter of  $^{222}\text{Rn}$  standards. A complete description of the gas purification and counting apparatus is presented elsewhere (Colle et al., 1990). In this paper, we restrict our discussion to understanding the mechanism of radon diffusion through capsule walls and to contribution of the polyethylene walls of the containment capsule to the emanation of radon.

In the work presented here, the activity of confined radium solution  $A_{Ra}$  was measured at a reference time 01/01/2004 12:00 EST with an uncertainty of 1.12% (coverage factor  $k = 2$ , see Taylor and Kuyatt, 1994). The radium solution is contained in a polyethylene cylinder (capsule) with the length of internal volume of 20 mm and an inside diameter of 3.4 mm (Figure 1). When such a capsule is placed into a closed vial filled with air at almost 100% humidity and normal temperature and pressure, and kept there for some accumulation time  $t$ , radon diffuses through the polyethylene walls of the capsule into the vial, and the activity of radon outside the capsule  $A_{out}$  can be written as  $A_{out} = fA_{Ra}$ , where  $f$  is an emanation fraction. In this paper, calculation of  $f$  as a function of accumulation time,  $t$ , is presented first in a simple diffusion-based two-box model. The results of calculations are compared with experimental data obtained in preparation of the new radon emanation standards and thus to determine the emanation fraction and its uncertainty for new radon emanation standards. It is found that radon accumulated inside the polyethylene walls of the capsule is significant and measurable. A mathematical model is presented that is in agreement with the experimentally determined radon activity. The approach to development of the revised model could be applied to describe the emanation of radon through other materials.

## 2. Diffusion equations for the capsule

Consider the accumulation of radon in a glass vial of volume  $v_{out}$ , where  $v_{out}$  is much larger than  $v_{in}$ . Assume that radon both inside and outside of the capsule has a uniform

concentration (i.e., constant concentration throughout solution and air volumes). This assumption is quite reasonable because the diffusion of radon in the air and in the radium solution is a much faster process than the radon diffusion through polyethylene. The radon diffusion coefficient of the air is  $D_a = 0.1 \text{ cm}^2/\text{s}$  (NCRP, 1988), and the radon diffusion coefficient of water is  $D_w = 10^5 \text{ cm}^2/\text{s}$  (Rona, 1917, Broecker and Peng, 1974). The radon diffusion coefficient of polyethylene  $D_p$  has not been measured, however, based on the results of experiments presented here, the value of  $D_p$  is more than two orders of magnitude less than that of water.

Convection of radon in air and in water greatly decreases the time needed to achieve constant concentration – both inside and outside the capsule. It will be shown that experimental results clearly indicate that, with accumulation time, the amount of radon in the walls of the polyethylene becomes a measurable quantity, which should be accounted for. Moreover, it will be demonstrated that the fraction of radon inside the polyethylene of a capsule is not only measurable, but also significant relative to radon accumulated inside the radium solution.

To begin, we consider the basics of diffusion of gases. One-dimensional gas diffusion in terms of flux  $J$  is described by Fick's First Law, which states that the diffusive flux is directly proportional to the concentration gradient:

$$J = -D \frac{\partial c}{\partial x} \quad (1)$$

where  $J = 1/S \cdot \partial N / \partial t$  is the flux of radon through the area  $S$ ,  $c = N/v$  is the concentration of  $N$  gas atoms in the volume  $v$ ,  $x$  is the dimension along which flux takes place, and  $D$  is the diffusion coefficient.

Under the above assumptions we can write two equations for the number of radon atoms inside ( $N_{in}$ ) and outside ( $N_{out}$ ) of the capsule:

$$\begin{aligned} \frac{dN_{in}}{dt} &= A_{Ra} - \frac{SD_p}{d} \left( \frac{N_{in}}{v_{in}} - \frac{N_{out}}{v_{out}} \right) - \lambda N_{in}; & (a) \\ \frac{dN_{out}}{dt} &= \frac{SD_p}{d} \left( \frac{N_{in}}{v_{in}} - \frac{N_{out}}{v_{out}} \right) - \lambda N_{out}. & (b) \end{aligned} \quad (2)$$

Here  $A_{Ra}$  is the total activity of radium solution in decays per second (Bq), i.e. the rate of radon atom production inside the capsule and  $S$  is the side-surface area of the capsule (neglecting the thick sealing plugs at each end). Decay of  $^{226}\text{Ra}$  (half life  $\sim 1600$  years) is considered to be small for this discussion. With dimensions shown in Figure 1,  $S = 2.45 \text{ cm}^2$ .  $d$  is the thickness of a side wall of the capsule, which is equal to 0.05 cm.  $v_{in}$  and  $v_{out}$  are the volumes inside and outside the capsule. With dimensions in Figure 1,  $v_{in} = 0.18 \text{ cm}^3$ . The bubbler, where the capsule was embedded for radon extraction, has volume  $v_{out} = 200 \text{ cm}^3$ . The ratio  $k = v_{in} / v_{out} = 9 \cdot 10^{-4}$ .  $\lambda$  is the decay constant of radon,  $\lambda = 2.09822 \cdot 10^{-6} \text{ s}^{-1}$  (ENSDF, 2004).

It is convenient for this discussion to simplify and rewrite these equations in terms of activities by denoting  $\mu = SD_p/v_{in} d$ , the time constant of diffusion, and introducing the activities of radon  $A_{in} = \square N_{in}$  and  $A_{out} = \square N_{out}$ . In this way, one obtains the following equations:

$$\begin{aligned} \frac{dA_{in}}{dt} &= \lambda A_{Ra} - (\lambda + \mu)A_{in} + k\mu A_{out}; & (a) \\ \frac{dA_{out}}{dt} &= -(\lambda + k\mu)A_{out} + \mu A_{in} & (b) \end{aligned} \quad (3)$$

Adding these two equations, the standard equation for the total radon activity  $A_{Rn} = A_{in} + A_{out}$  is obtained:

$$\frac{dA_{Rn}}{dt} = \lambda(A_{Ra} - A_{Rn}) \quad (4)$$

with the stationary solution  $A_{Rn}^s = A_{Ra}$ , and the general solution in the form:

$$A_{Rn}(t) = A_{Ra} [1 - \exp(-\lambda t)] + A_{Rn}(0) \exp(-\lambda t) \quad (5)$$

here  $A_{Rn}(0)$  is the amount of radon inside the capsule before the bubbler was sealed and diffusion started.

The stationary solutions of equations (3) are:

$$\begin{aligned} A_{in}^s &= A_{Ra} \frac{\lambda + k\mu}{\lambda + \mu + k\mu} \approx A_{Ra} \frac{\lambda}{\lambda + \mu}; & (a) \\ A_{out}^s &= A_{Ra} \frac{\mu}{\lambda + \mu + k\mu} \approx A_{Ra} \frac{\mu}{\lambda + \mu} & (b) \end{aligned} \quad (6)$$

Since the volume inside the capsule is small, the ratio of inside to outside volumes,  $k$ , is always a small number (less than  $10^{\square} \div 10^{\square}$ ). For the stationary solution, the emanation fraction  $f_0 = \mu/(\lambda + \mu)$ . If radon diffusion is much faster than the radon decay ( $\square \gg \square$ ),  $f_0 = 1$ ; in the opposite limit ( $\square \gg \square$ ),  $f_0 = 0$ , and there will be no radon outside of the capsule.

To measure  $f_0$  directly, the accumulation time of radon in the bubbler,  $t$ , should be much larger than  $1/(\square + \square)$ , which may be as great as a few weeks. Fortunately, when many sequential measurements were to be accomplished (as is the case for the current work), by modeling the time dependence of the emanation fraction  $f$  for finite time  $t$ , much shorter accumulation periods could be used (on the order of days).

The general solution of equations (2) has the forms:

$$\begin{aligned}
A_{in}(t) &= A_{in}^s + kC_1 \exp(-\lambda t) + C_2 \exp(-(\lambda + \mu + k\mu)t); & (a) \\
A_{out}(t) &= A_{out}^s + C_1 \exp(-\lambda t) - C_2 \exp(-(\lambda + \mu + k\mu)t) & (b)
\end{aligned}
\tag{7}$$

At  $t = 0$  there is no radon outside the capsule:  $A_{out}(0) = 0$ . Denote  $A_{in}(0) = A_0$ . Constants  $C_1$  and  $C_2$  can be determined from these initial conditions, and the solution (7 b) for  $A_{out}(t)$  has the form:

$$A_{out}(t) = A_{Ra} f_0 [1 - \exp(-(\lambda + \mu)t)] - (A_{Ra} - A_0) \exp(-\lambda t) [1 - \exp(-\mu t)] \tag{8}$$

Before the capsule is loaded into the bubbler, it was kept in a closed vial with volume  $20 \text{ cm}^3$ . The outside volume is still much bigger than the inside one, and  $k \ll 1$ . Under these conditions  $A_0 = A_{Ra} \lambda / (\lambda + \mu) = A_{Ra} (1 - f_0)$  (see equation (6 b)). In this case,  $C_2 = 0$  and equation (8) is reduced to:

$$A_{out}(t) = A_{Ra} f_0 [1 - \exp(-\lambda t)] \tag{9}$$

and  $f(x)/x = A_{out}(x)/xA_{Ra} = f_0$ , where  $x = 1 - \exp(-\lambda t)$ . Under this assumption the emanation fraction  $f_0$  was determined in previous work (Collé and Hutchinson, 1993).

### 3. Results of measurements and modification of the model

The recent experimental data exhibits some dependence of  $f(x)/x$  on  $x$  (Figure 2). This dependency suggested a measurable accumulation of radon in the polyethylene walls of the container. Measurements were performed with the NIST Radon Pulse Ionization Chambers facility described in Collé, 1990. Capsules were stored in closed glass vials with volume of  $20 \text{ cm}^3$ , prior to use and then transferred into bubblers with volume of  $200 \text{ cm}^3$ . Radon was allowed to accumulate inside the bubbler for time interval  $t$  between 1 and 18 days. A total of 62 measurements were performed — 17 of which measured capsules that were “preconditioned” according to the recommendations of Collé and Hutchinson, 1993. Preconditioning of these 17 capsules consisted of interim storage of the capsules in a standard fume hood for one day after removal from the glass vial and before being placed into the bubbler for accumulation and counting. A summary of the modeled experimental results is given in Table 1. No significant difference was observed between “preconditioned” and “non-preconditioned” capsules. The infinitely large volume under the hood gives the ratio of volumes,  $k = 0$ , while  $20 \text{ cm}^3$  volume of a glass vial corresponds to  $k = 0.01$ , which is considered here as negligible. In accordance with the model, data shown in Figure 2 do not reveal any noticeable difference between “preconditioned” and “non-preconditioned” capsules.

A more detailed description of capsule production and measurement will be given elsewhere.

To explain the observed dependence of  $f(x)/x$  on  $x$ , the initial activity of radon inside the capsule should be somewhat bigger than  $A_0 = A_{Ra} (1 - f_0)$ , namely  $A_0 = A_{Ra} (1 - f_0 + \alpha)$ .

Constant  $\alpha$  may be considered as a fraction of radon inside of a polyethylene of a capsule. Then:

$$A_{out}(t) = A_{Ra} f_0 [1 - \exp(-\lambda t)] + \alpha A_{Ra} \exp(-\lambda t) [1 - \exp(-\mu t)] \quad (10)$$

As it follows from Figure 2, constant  $f_0 \approx 0.85$  and  $\mu \approx 5.7\lambda$ . For  $t \geq 1/\lambda$ ,  $\exp(-\mu t) \ll 1$ , and in terms of  $x = 1 - \exp(-\lambda t)$ , introduced above, equation (10) can be rewritten as:

$$A_{out}(t) = A_{Ra} f(t) = A_{Ra} \{f_0 [1 - \exp(-\lambda t)] + \alpha \exp(-\lambda t)\} = A_{Ra} [f_0 x + \alpha(1 - x)] \quad (11)$$

and

$$f(x) = f_0 x + \alpha(1 - x) \quad (12)$$

#### 4. Experimental data fits and parameter determination

In Figure 3 the fit of all experimental data with formula (12) is shown. The fit gives  $f(x) = (82.14x + 5.09)\%$  with  $f_0 = (87.23 \pm 0.72)\%$ ,  $\alpha = (5.09 \pm 1.20)\%$ . Uncertainties in parameters correspond to two standard deviations of regression parameters (see, for example, Draper and Smith, 1981). The total fraction of radon both dissolved in the radium solution inside the capsule and inside the polyethylene walls of the capsule is equal to  $1 - f_0 = 0.128$ . Given  $\square = 0.051$ , this means that the radium solution contains  $1 - f_0 - \alpha = 0.077$  of total radon produced, and the polyethylene walls contain approximately 2/3 of the radon dissolved in the radium solution inside the capsule. Based on this fit, one can determine the  $\mu = 6.85\lambda = 1.44 \cdot 10^{-5} s^{-1}$ , and the radon diffusion coefficient of polyethylene  $D_p = \mu dv_{in}/S = 5.2 \cdot 10^{-8} cm^2 s^{-1}$ , which is approximately 200 times less than the radon diffusion coefficient of water.

Figures 4, 5, and 6 show fits with formula (12) for each SRM individually.

The obtained results are summarized in Table 1. All emanation fractions  $f_0$  coincide on the level of three sigma uncertainties, however on the level of two sigma uncertainties the preconditioned 50 Bq capsules give  $f_0$  less than others. Parameters  $\square$  determined for all measurements coincide on the level of two sigma uncertainties.

#### 5. Conclusions and future experiments

The emanation factor  $f_0$ , obtained in previous measurements with polyethylene capsules (Collé and Hutchinson, 1993) was  $f_0 = (89.0 \pm 3.6)\%$ . Based on the results of our present measurements, the value of  $f_0 = (87.23 \pm 0.72)\%$  (coverage factor  $k = 2$  for both uncertainties), which is in agreement with the previous result, given the stated uncertainties. However, while Collé and Hutchinson observed no noticeable dependence of  $f(x)/x$  on  $x$ , the results presented here show a dependence of  $f(x)/x$  on  $x$  similar to that observed by Dean and Kolkowski, 2004 for measurements of radon accumulation from polyethylene capsules in a radon-in-water generator. These experimenters observed an  $f(x)/x$  dependence on  $x$  in independent sets of experimental measurements of radon diffusion in data collected in 1996 and 2003. Although the radon diffusion coefficient in water is much less than that of air, the value is much bigger than the radon diffusion coefficient of polyethylene. Thus, Eq. (12), presented in this paper, should be valid for accumulation in a radon-in-water generator.

Measurements of emanation factor in the NIST radon-in water generator (see Collé and Kishore, 1997) are planned for future work.

One of the results of the present work is an estimate for the radon diffusion coefficient of polyethylene  $D_p = \mu dv_{in}/S = 5.2 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  by measurement of emanation coefficient. A method similar to the one of the present work may be used for other materials to measure the radon diffusion coefficient.

## Acknowledgements

The author is indebted to Ron Collé, Dan Golas, Robin Hutchinson, Larry Lucas, and Mike Unterweger for discussions and to Andrew Rukhin for explanation of uncertainties of the regression fit parameters. I would like to express my sincere gratitude to Mike Schultz for careful reading of the manuscript and many valuable remarks.

## References

- Broecker, W.S., Peng T.H. 1974, *Gas Exchange Rates between Air and Sea*, Tellus **26**, pp 21-35;
- Collé, R., Hutchinson J.M.R., and Unterweger M.P., 1990, *The NIST Primary Radon-222 Measurement System*, J. Res. Natl. Inst. Stand. Technol., **95**, pp 155-165;
- Collé, R. and Hutchinson, J.M.R., 1993, *Technical Notes on the Use of Standard Reference Material. Radon-222 Emanation Standard*, NIST Technical Report **4968**;
- Collé, R., Kotrappa, P., and Hutchinson, J.M.R., 1995, *Calibration of Electret-Based Integral Radon Monitors Using NIST Polyethylene-Encapsulated  $^{226}\text{Ra}/^{222}\text{Rn}$  Emanation (PEPE) Standards*, J. Res. Natl. Inst. Stand. Technol., **100**, pp 629-639;
- Collé R. and Kishore, K., 1997, *An update of the NIST radon-in-water standard generator: its performance efficacy and long-term stability*, Nucl. Instr. Meth., **A 391**, pp 511-528;
- Dean, J.C.J. and Kolkowski, P., 2004, *The development of a  $^{222}\text{Rn}$  Standard Solution Dispenser at NPL*, Applied Radiation and Isotopes **61**, pp 95-100;
- Draper, N.R. and Smith H., 1981, *Applied Regression Analysis*, John Wiley & Sons, 2nd Ed.;
- ENSDF , 2004, *Evaluated Nuclear Structure Data File*, <http://ie.lbl.gov/ensdf/welcome.htm>;
- Kotrappa P. and Stieff L.R., 1994, *Application of NIST  $^{222}\text{Rn}$  Emanation Standards for Calibrating  $^{222}\text{Rn}$  Monitors*. Radiation Protection Dosimetry, **55**, pp 211-218;
- NCRP 1988, *Measurement of Radon and Radon Daughters in Air*, Report No **97**;
- Rona, E., 1917, *Diffusionsgrosse und Atomdurchmesser der Radiumemanation*, Zeitschrift für Physikalische Chemie **92**, pp 213-218;

Taylor B.N. and Kuyatt C. E., 1994, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Technical Note **1297**.

## Tables

Capsule type	Number	$f_0$ (%)	$\alpha$ (%)
All capsules			
All	62	$87.23 \pm 0.36$	$5.09 \pm 0.60$
5 Bq only	19	$88.39 \pm 0.58$	$6.38 \pm 1.20$
50 Bq only	20	$86.04 \pm 0.47$	$3.86 \pm 0.78$
500 Bq only	23	$86.98 \pm 0.47$	$5.64 \pm 0.68$
Preconditioned capsules			
All	17	$87.36 \pm 0.73$	$4.99 \pm 0.92$
5 Bq only	5	$89.18 \pm 0.70$	$6.13 \pm 1.81$
50 Bq only	6	$84.75 \pm 0.30$	$3.82 \pm 0.37$
500 Bq only	6	$87.25 \pm 0.87$	$6.09 \pm 0.67$
Non-preconditioned capsules			
All capsules	45	$87.14 \pm 0.46$	$5.24 \pm 0.89$
5 Bq only	14	$87.68 \pm 0.86$	$7.23 \pm 1.62$
50 Bq only	14	$86.50 \pm 0.64$	$3.87 \pm 1.27$
500 Bq only	17	$87.36 \pm 0.66$	$4.41 \pm 1.29$

Table 1. Results of experimental data fit. Uncertainties correspond to one sigma level.

## Figures

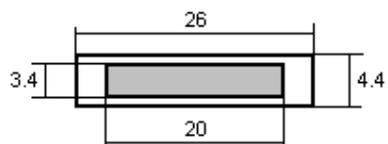


Figure 1. Dimensions of the polyethylene capsule used for preparation of NIST radon standard reference materials.

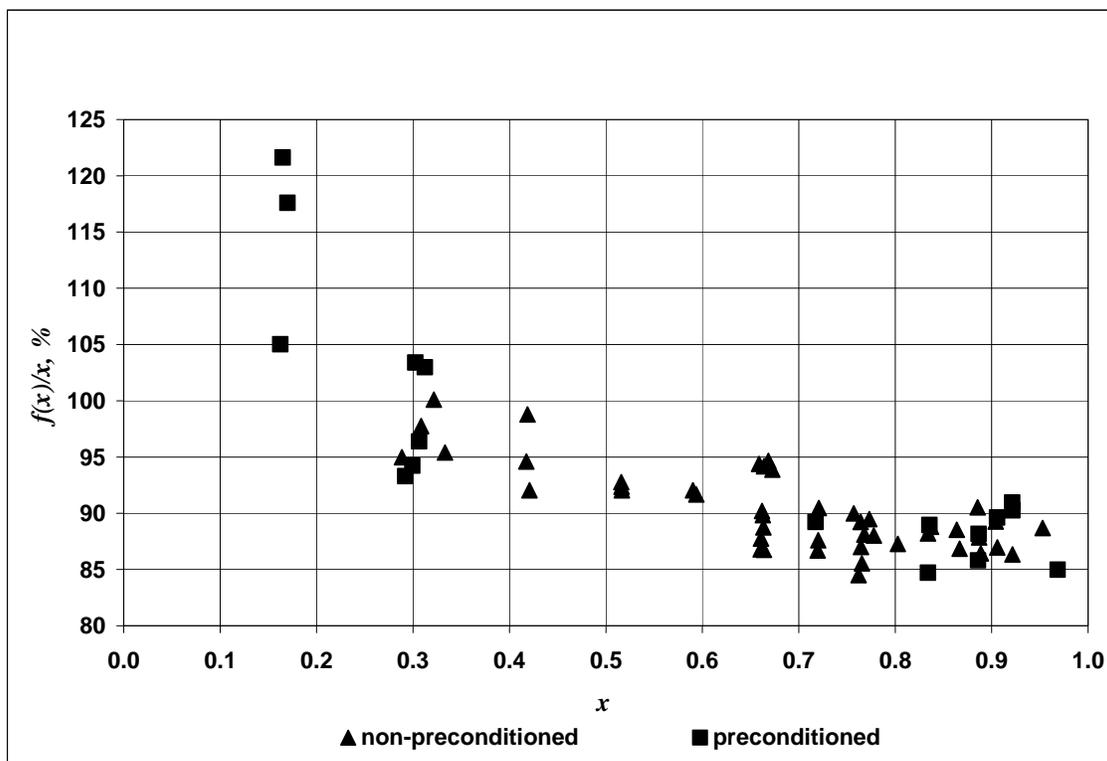


Figure 2.

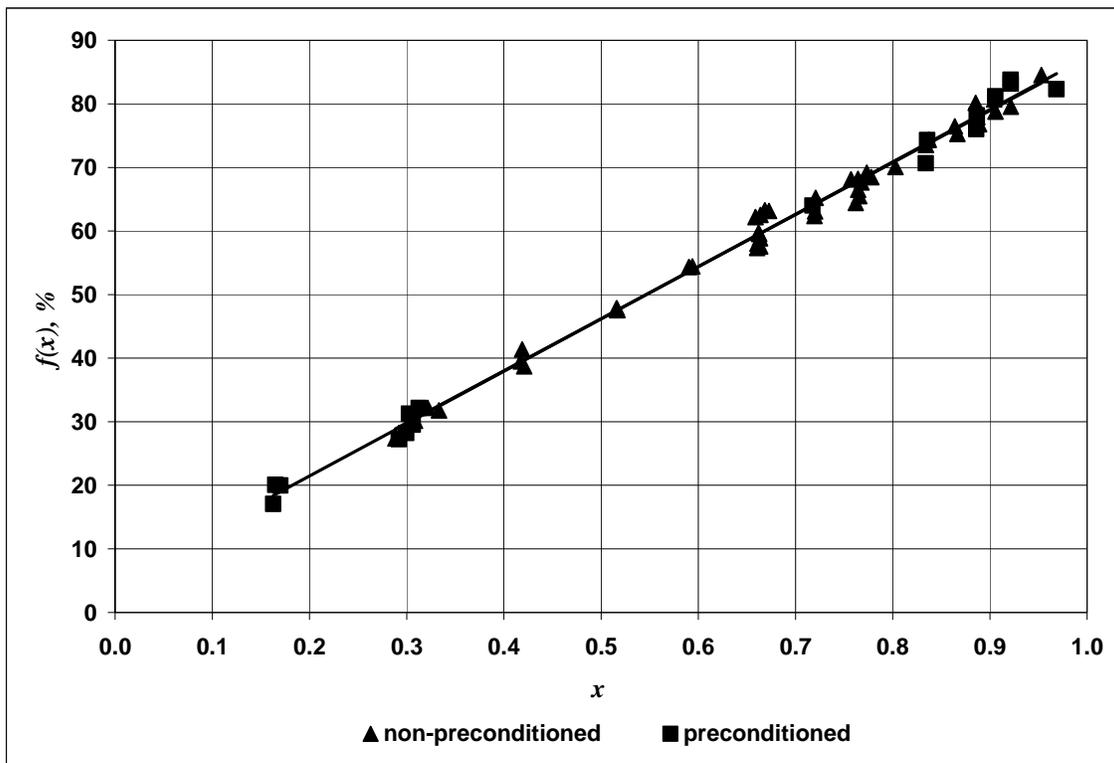


Figure 3

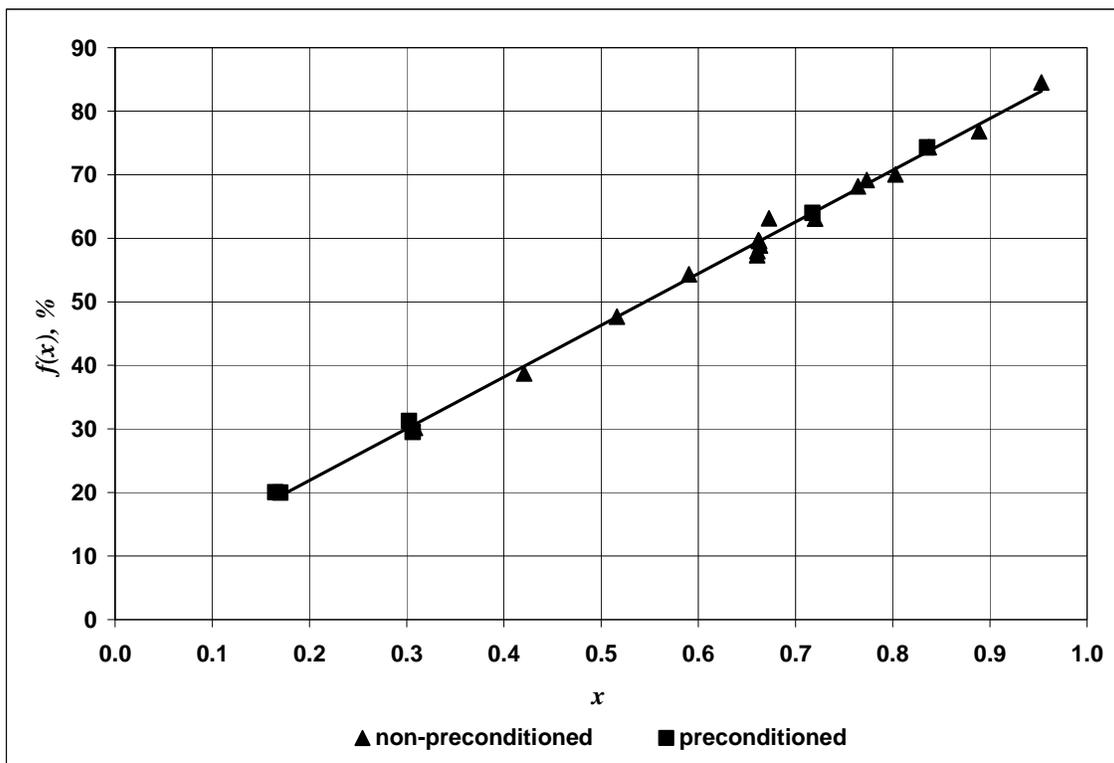


Figure 4

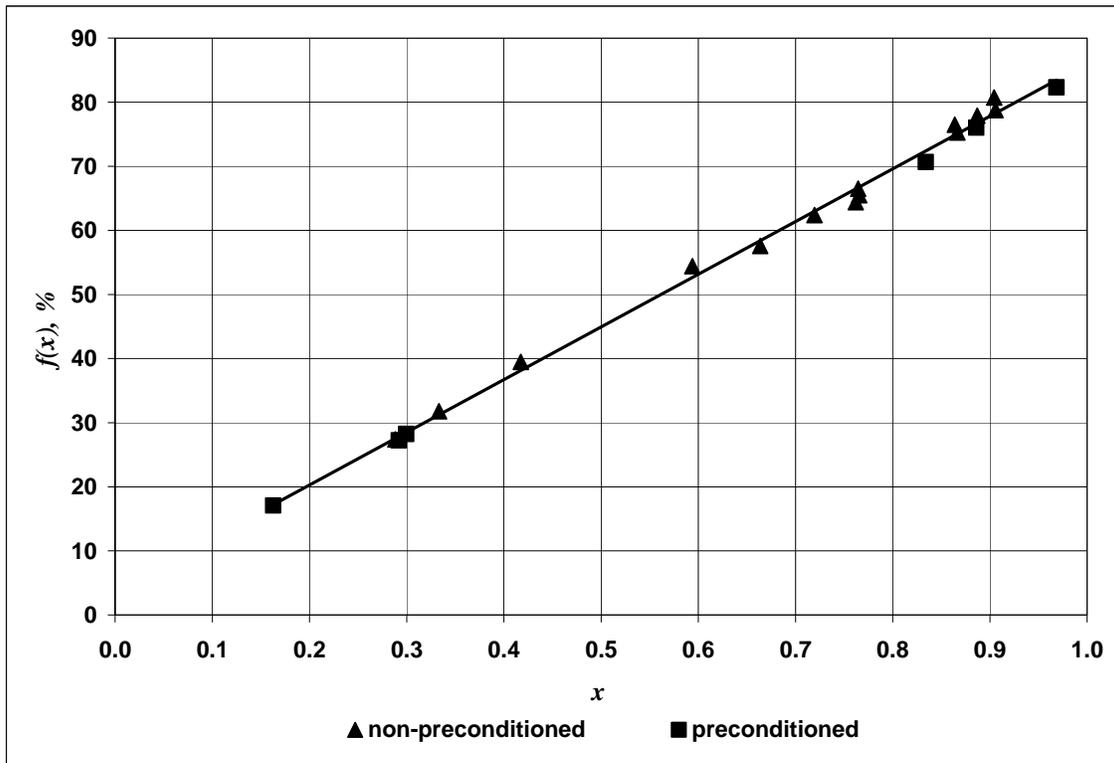


Figure 5.

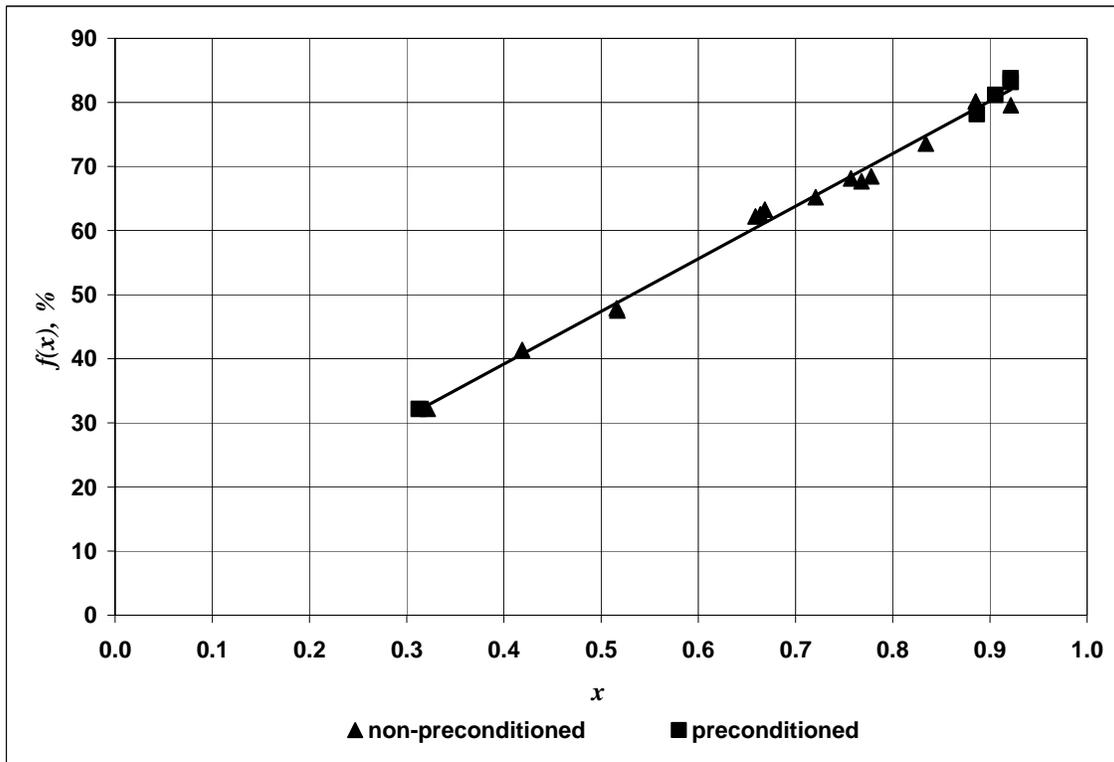


Figure 6.

## Figure captions

Figure 1. The polyethylene capsule with radium solution inside.

Figure 2. Dependence of emanation factor  $f$  on accumulation time  $t$  for all measured capsules;  
 $x = 1 - \exp(-\lambda_{Rn}t)$

Figure 3. Fit for emanation fraction in the form  $f(x) = f_0x + \alpha(1 - x)$ , where  $x = 1 - \exp(-\lambda_{Rn}t)$  for all capsules.  $f_0 = (87.23 \pm 0.72)\%$ ,  $\alpha = (5.09 \pm 1.20)\%$  Coverage factor for uncertainty  $k = 2$ .

Figure 4. Fit for emanation fraction in the form  $f(x) = f_0x + \alpha(1 - x)$ , where  $x = 1 - \exp(-\lambda_{Rn}t)$  for all 500 Bq capsules.  $f_0 = (86.98 \pm 0.94)\%$ ,  $\alpha = (5.64 \pm 1.36)\%$  Coverage factor for uncertainty  $k = 2$ .

Figure 5. Fit for emanation fraction in the form  $f(x) = f_0x + \alpha(1 - x)$ , where  $x = 1 - \exp(-\lambda_{Rn}t)$  for all 50 Bq capsules.  $f_0 = (86.04 \pm 0.94)\%$ ,  $\alpha = (3.86 \pm 1.56)\%$  Coverage factor for uncertainty  $k = 2$ .

Figure 6. Fit for emanation fraction in the form  $f(x) = f_0x + \alpha(1 - x)$ , where  $x = 1 - \exp(-\lambda_{Rn}t)$  for all 5 Bq capsules.  $f_0 = (88.39 \pm 1.18)\%$ ,  $\alpha = (6.38 \pm 2.40)\%$  Coverage factor for uncertainty  $k = 2$ .