Calibration of Electret-Based Integral Radon Monitors Using NIST Polyethylene-Encapsulated $^{226}$Ra/$^{222}$Rn Emanation (PERE) Standards

1. Introduction

The National Institute of Standards and Technology (NIST) has over the past 3 to 4 years worked on the development of a new emanation standard for $^{222}$Rn measurement calibrations as described by Collé et al. [1]. This new standard is based on a polyethylene-encapsulated $^{226}$Ra solution that has been demonstrated to emanate a well-characterized and known quantity of $^{222}$Rn when employed in an “accumulation mode.” The encapsulated standard was intended to serve as a more convenient, easier-to-use, alternative to the conventionally employed $^{226}$Ra solution standards that have been disseminated by NIST for $^{222}$Rn emanation measurements for the past 40 or more years [2–4]. The latter standards were, of course, only certified for the $^{226}$Ra mass content or at later times (circa mid-1980s) the $^{226}$Ra radioactivity content. The new encapsulated standards that are certified in terms of two parameters, both the $^{226}$Ra activity and the $^{222}$Rn emanation fraction, have...
of necessity, a larger overall calibration uncertainty. Nevertheless, it was envisaged that the encapsulated standards would be sufficiently accurate and efficacious for calibrating instruments used in a variety of measurement applications, particularly those involving routine screening and monitoring of indoor radon air quality.

This paper describes the first demonstration of an application of the use of these polyethylene-encapsulated $^{226}\text{Ra}/^{222}\text{Rn}$-emanation (PERE) standards for the calibration of a routine monitoring technique and measurement method. It applies to passive integral measurements of average $^{222}\text{Rn}$ concentrations in air with "E-
PERSM"$^2$ electret ionization chambers. The use, characteristics and performance of these monitors has been previously and extensively described by Kottrappa et al. [7,8].

Use of Rad Elec Inc. (REI) electret capsule monitors is probably the most widely employed measurement technique in the United States for evaluating radon levels within buildings. The U.S. Environmental Protection Agency (EPA) administers and conducts a measurement proficiency program for commercial vendors of radon measurement services. EPA currently estimates (based on participation in the EPA proficiency program) that of the 600 or more such vendors who maintain their own primary "in house" measurement capability approximately 200 to 250, or at least 30% to 40%, utilized the REI E-PERM electret ionization chambers. The second-most widely employed measurement method in the EPA proficiency program is used by less than half this number. REI estimates that the method is used by 300 to 400 laboratories in 15 countries.

$^{1}$The PERE standard is currently available as NIST Standard Reference Material SRM 4968 [5]. This paper was prepared in early 1993 and was withheld from submission for publication pending completion of the PERE standard calibration. The presently described study was performed with an earlier prototype version of SRM 4968. This prototype utilized mechanical compression seals, as described herein, which were found to be inadequate over long times. As a result, in the interim period following this study, a new heat-sealing procedure based on complete polyethylene encapsulation was developed for SRM 4968. A complete recalibration (and confirmation) of the previously obtained calibration factors for the compression-seal prototypes was also performed [6]. The mean emanation factor $f$ obtained for the earlier prototype capsule used in this work and that for SRM 4968 is virtually indistinct (0.888 compared to 0.890). Subsequent electret measurements conducted during the period July–August 1993 with a set of 14 of the revised heat-sealed PERE standards confirmed the findings presented in this paper. Three independent trials with multiple replications of specific capsule, detector types, and accumulation times were used to perform this confirmation.

$^{2}$Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

2. Experimental Methodology

The NIST encapsulated emanation standards [1] consist of right circular cylinders of polyethylene having a 0.32 cm outside diameter and a 1.0 cm effective length along the emanating surface (overall length is ~2 cm), and are gravimetrically filled with $\approx 0.08$ g of calibrated $^{226}\text{Ra}$ solutions having a known activity concentration. The ends of the polyethylene tubes are stoppered with two 0.5 cm teflon plugs and are crimp sealed with stainless steel bands around the outer circumference.

The standards are certified by NIST in terms of two parameters that, when used in some type of suitable closed accumulation vessel, allow calculation of the $^{222}\text{Rn}$ activity accumulated in the vessel after a given accumulation time. The two parameters are the total $^{226}\text{Ra}$ activity $A_{\text{Ra}}(t)$ contained in the capsule at some reference time, $t_r$, and the $^{222}\text{Rn}$ emanation fraction, $f$ (i.e., the fraction of the total $^{222}\text{Rn}$ generated by decay of $^{226}\text{Ra}$ that is released from the capsule and contained within the volume of the accumulation vessel). Both parameters are calibrated in terms of measurements that can be directly related to the U.S. national radon measurement calibration standard (i.e., the pulse-ionization-chamber-based primary radon measurement system [3,9]) and to national and international radium standards maintained by NIST.

For a capsule having a $^{226}\text{Ra}$ activity content of $A_{\text{Ra}}^0$ at the start of an accumulation (time $t = 0$) and a constant emanation fraction $f$, the growth of $^{222}\text{Rn}$ activity as a function of time $t$ within a closed accumulation vessel may be given in approximate form as

$$A_{\text{Rn}} = f A_{\text{Ra}}^0 (1 - e^{-\lambda_{\text{Rn}} t}) + A_{\text{Ba}}^0 e^{-\lambda_{\text{Ba}} t}$$

(1) since the $^{226}\text{Ra}$$–^{222}\text{Rn}$ genetic relationship satisfies the condition of radioactive secular equilibrium (i.e., $\lambda_{\text{Rn}} \gg \lambda_{\text{Ra}}$, where $\lambda_{\text{Rn}}$ and $\lambda_{\text{Ra}}$ are the decay constants for $^{222}\text{Rn}$ and $^{226}\text{Ra}$, respectively). In Eq. (1), $A_{\text{Ra}}^0$ is the initially present $^{222}\text{Rn}$ activity in the accumulation vessel (i.e., for the boundary condition $A_{\text{Rn}} = A_{\text{Ra}}^0$ at $t = 0$). The initial $^{226}\text{Ra}$ activity $A_{\text{Ra}}^0$ is just given by $A_{\text{Ra}}^0 = A_{\text{Ra}}(t_r) e^{-\lambda_{\text{Rn}} T_D}$, where $T_D = (t_0 - t_r)$ is the decay-time interval, and where all other terms were defined previously. When the encapsulated standards are used in an accumulation mode with integral detectors, e.g., the electret chambers used here, it is necessary to consider the total integral activity over the total accumulation or detector deployment time. The time integral of Eq. (1) gives the total integrated $^{222}\text{Rn}$ activity $I_{\text{Rn}}$ accumulated over some total accumulation time $T_A$, integrating from $t = 0$ to $t = T_A$ yields
\[
\int_0^{T_A} A_{Ra} \, dt = I_{Ra} = f A_{Ra}^0 \int_0^{T_A} \left( 1 - e^{-\lambda_{Ra} t} \right) \, dt \\
+ A_{Ra}^0 \left( \frac{1}{\lambda_{Ra}} \right) \, (1 - e^{-\lambda_{Ra} T_A}).
\]

or
\[
\bar{A}_{Ra} = f A_{Ra}^0 \left[ 1 - \left( \frac{1}{\lambda_{Ra} T_A} \right) \right] \left( 1 - e^{-\lambda_{Ra} T_A} \right)
\]

for the simplified case of \( A_{Ra}^0 = 0 \).

Four of the prototype encapsulated standards were used in this study. They ranged in \(^{226}\text{Ra}\) activity \( A_{Ra}^0 \) from approximately 15 Bq to 540 Bq (see Table 1). The uncertainty in \( A_{Ra}^0 \) for each capsule, in terms of a relative "expanded combined standard uncertainty" (i.e., a coverage factor \( k = 2 \) and thus a 2 standard deviation estimate \([10,11]\)), was approximately \( 2 \mu A_{Ra}^0 = 0.87 \% \). The \(^{222}\text{Rn}\) emanation fraction for the prototype capsules was determined \([1]\) to be \( f = 0.888 \) with a relative expanded uncertainty of \( 2 \mu f = 3.4 \% \).

By normal conventions of the NIST Radioactivity Group, which for the most part are wholly compatible with those adopted by the principal international metrology standardization bodies \([10,11]\), all individual uncertainty components are expressed in terms of experimental standard deviations (or experimental standard deviations of the mean where appropriate) or quantities assumed to correspond to standard deviations.

Table 1. Results of 16 accumulation trials comparing E-PERM electret chamber responses to integral \(^{222}\text{Rn}\) activities provided by NIST encapsulated \(^{226}\text{Ra}\) standards

| Capsule identification | \(^{226}\text{Ra}\) activity in capsule \( A_{Ra}^0 \) (Bq) | Accumulation volume \( V_A \) (L) | Accumulation time \( T_A \) (d) | Detector type (and number deployed) | E-PERM response Mean \( E_{Ra} \) (Bq · d) | \( s_m \) (%) | Integral \(^{222}\text{Rn}\) activity \( I_{Ra} \) (Bq · d) | Ratio \( E_{Ra} / I_{Ra} \) |
|-------------------------|---------------------------------|-----------------------------|-----------------|-------------------------------|--------------------------|--------|-----------------------------|---------------------|
| CR-10                   | 14.80                           | 3.622                       | 1.000           | SST (2)                       | 1.005                    | 8.0    | 1.122                       | 0.896               |
|                         |                                 | 3.622                       | 3.000           | SST (2)                       | 8.421                    | 2.6    | 9.013                       | 0.934               |
|                         |                                 | 3.622                       | 7.000           | SLT (2)                       | 39.32                    | 1.2    | 39.93                       | 0.985               |
|                         |                                 | 3.622                       | 14.00           | SLT (2)                       | 106.4                    | 1.0    | 117.2                       | 0.908               |
|                         |                                 | 3.567                       | 33.00           | LLT (5)                       | 318.5                    | 1.3    | 361.4                       | 0.881               |
| CR-21                   | 147.4                           | 3.622                       | 1.000           | SST (2)                       | 9.515                    | 2.1    | 11.18                       | 0.851               |
|                         |                                 | 3.622                       | 3.000           | SLT (2)                       | 85.72                    | 1.0    | 89.78                       | 0.955               |
|                         |                                 | 3.622                       | 7.000           | LLT (4)                       | 349.3                    | 3.0    | 397.2                       | 0.879               |
|                         |                                 | 3.622                       | 14.00           | LLT (4)                       | 1033.1                   | 1.8    | 1168.0                      | 0.884               |
| CR-12                   | 514.8                           | 3.622                       | 1.000           | SLT (2)                       | 33.88                    | 2.6    | 39.04                       | 0.868               |
|                         |                                 | 3.622                       | 3.000           | SLT (2)                       | 280.2                    | 1.5    | 313.6                       | 0.893               |
|                         |                                 | 9.820                       | 2.792           | SLT (5)                       | 242.9                    | —      | 277.5                       | 0.875               |
|                         |                                 | 3.622                       | 7.000           | LLT (4)                       | 1271.2                   | 0.85   | 1387.0                      | 0.916               |
| CR-4c                   | 543.8                           | 10.15                       | 1.000           | LST (4)                       | 38.51                    | 0.76   | 41.24                       | 0.934               |
|                         |                                 | 10.09                        | 2.667           | LST (5)                       | 252.1                    | 0.47   | 266.7                       | 0.945               |
|                         |                                 | 3.622                       | 4.000           | LST (4)                       | 513.4                    | 1.4    | 557.5                       | 0.921               |

\(^{3}\) The PERE standards, issued as SRM 4968, were certified with slightly revised uncertainties of \( 2 \mu A_{Ra}^0 = 0.93 \% \) and \( 2 \mu f = 4.0 \% \). The revisions arose from more exhaustive uncertainty component considerations in the recalibration \([5,6]\).
irrespective of the method used to evaluate their magnitude. All of these uncertainty components are designated as "standard uncertainties." A propagated uncertainty, termed a "combined standard uncertainty," is expressed as what is assumed to be an estimated standard deviation which is equal to the positive square root of the total variance obtained by summing all variance (square of the standard uncertainty) and covariance components, however evaluated, using the law of propagation of uncertainty for the specific mathematical function given by the model of the measurement procedure [10].

By recently established NIST policy [11], the uncertainty component $u_e$ due to a $^{226}$Ra calibration factor used in the determination of $f$ and $A_{0}^{Rn}$, Its magnitude is roughly $u_e = 0.4 \%$. The estimated relative uncertainties $2u_{A_{0}^{Rn}}$ in $A_{0}^{Rn}$ [Eq. (1)] and $I_{0}^{Rn}$ [Eq. (3)] are thus approximately

$$2u_{A_{0}^{Rn}} = 2u_{I_{0}^{Rn}} = 2\sqrt{u_I^2 + u_{Al_{0}^{Rn}}^2} - u_I^2 \approx 3.4 \%.$$ 

The NIST encapsulated standards were used in accumulation vessels provided by REI. The majority of the accumulation measurements were performed with nominal "one U.S. gallon," screw-capped and gasketed glass jars that are a component part of the REI radon-in-water measurement test kit [12,13]. The jar lids were further sealed with compression collars fabricated out of thick sleeves of natural rubber that were clamped with metal bands. The total volume of the jars was independently measured by REI and by NIST by filling them with known volumes of water, and the total accumulation volume after subtracting the excluded volume for the E-PERM chamber housings was determined to be $V_{A} = 3.622$ L in most cases (see Table 1). The NIST-determined total volume (3.871 L) agreed with that of REI (3.842 L) within 0.8 %. The uncertainty in the NIST-determined total volume was estimated to be $u_{V_{A}} = 0.6 \%$ and on consideration of the uncertainties in the volume excluded by the detectors, the estimated uncertainty in the accumulation volume was taken to be $u_{V_{A}} \approx 1 \%$.

$$2u_{I_{0}^{Rn}} = 2\sqrt{u_I^2 + u_{Al_{0}^{Rn}}^2} + \left[\frac{A_{0}^{Rn} T_{A} e^{-\lambda_{0} T_{A}}}{1 - e^{-\lambda_{0} T_{A}}}\right]^2 (u_{A_{0}^{Rn}}^2 + u_{T_{A}}^2) \quad (5)$$

and

$$2u_{I_{0}^{Rn}} = 2\sqrt{u_I^2 + u_{Al_{0}^{Rn}}^2} + \left[\frac{T_{A} (1 - e^{-\lambda_{0} T_{A}})}{\lambda_{0} (1 - e^{-\lambda_{0} T_{A}})} - 1\right]^2 u_{I_{0}^{Rn}}^2 + \left[\frac{1 - e^{-\lambda_{0} T_{A}}}{T_{A} - \frac{1}{A_{0}^{Rn}} (1 - e^{-\lambda_{0} T_{A}})}\right]^2 u_{A_{0}^{Rn}}^2 \quad (6)$$

where the standard uncertainties $u$ in each case are assumed relative standard deviations (e.g., $u_I = s/Ix$ for any variable $x$). Throughout this study, the magnitude of the uncertainties $u_{A_{0}^{Rn}} \approx 0.05 \%$ and $u_{T_{A}} \approx 0.01 \%$, even in propagation over long accumulation times of up to $T_{A} = 33$ d, are negligible in comparison to $u_I = 1.7 \%$ and $u_{A_{0}^{Rn}} = 0.43 \%$. The quantities $f$ and $A_{0}^{Rn}$ are, however, correlated. Their uncertainties include a common uncertainty component $u_{T_{A}}$, and in each case are as

---

4 Using revised uncertainty estimates for $u_I$ and $u_{Al_{0}^{Rn}}$, as given for SRM 4968, the relative expanded uncertainties $2u_{A_{0}^{Rn}}$ and $2u_{I_{0}^{Rn}}$ are approximately 4.0 \%.
To investigate possible systematic accumulation volume effects or discrepancies that might have resulted from the arbitrary choice of accumulation volume, a second, larger accumulation vessel was used for a few experiments. This vessel was a nominal 10 L, commercially available,\(^3\) plastic vacuum desiccator that provided accumulation volumes \(V_a\) of about 9.8 L and 10.1 L when used in configurations with different numbers of deployed detectors. The manufacturer specified that it could hold a vacuum of 3.3 kPa (25 Torr) for up to 24 h, and thereby provided some assurance of the vessel’s integrity against leaks.

Depending on the needs for a particular measurement in terms of the average \(^{222}\)Rn activity concentration expected and the chosen detector deployment time, E-PERM detectors of three different chamber volumes and two different sensitivities are commercially available from REI. E-PERM chambers of nominal 50 mL volume (designated “L”), and nominal 210 mL volume (designated “ST’’), and electrets of both high sensitivity (designated “ST’’ for short-term deployment) and low sensitivity (designated “LT’’ for long-term deployment) were used in this work. This resulted in a combination of four detector types, designated SST, SLT, LST, and LLT for (i) large-volume chamber and high-sensitivity electret; (ii) large-volume chamber and low-sensitivity electret; (iii) small-volume chamber and high-sensitivity electret; and (iv) small-volume chamber and low-sensitivity electret, respectively. The E-PERM chambers were originally designed and fabricated so that the excluded volume of two L chamber housings (55 mL each) is approximately that of one S chamber housing (110 mL). Thus, nearly identical excluded volumes (and hence accumulation volumes \(V_a\)) could be obtained using 2 SST (or 2 SLT) or 4 LLT (or 4 LST) detectors.

The detector response for an E-PERM electret chamber is a measured voltage change that is proportional to the ionization produced by the integral \(^{222}\)Rn activity concentration to which it is exposed. Each detector type has an independently determined calibration factor that relates the voltage change to an average \(^{222}\)Rn activity concentration \(C_E\). This calibration factor is not linear, but is a function of the electret voltage. Calibration details may be found in Kotrappa et al. \([7,8]\). For this study, the REI determined and reported average \(^{222}\)Rn activity concentrations \(C_E\) (as obtained from their electret measurement and independent calibrations) were converted into integral activity responses

\[
E_{Ra} = C_E V_A T_A, \tag{7}
\]

which could be compared to the integral \(^{222}\)Rn activity \(I_{Ra}\) [Eqs. (2) or (3)] provided by the encapsulated emanation standards in an accumulation volume \(V_A\) over accumulation time interval \(T_A\).

Alternatively, the measured and reported values of the average \(^{222}\)Rn activity concentration \(C_E\) could be compared to \(\bar{A}_{Ra}/V_A\) [using \(\bar{A}_{Ra}\) from Eq. (4)], which is mathematically equivalent to the comparison of \(E_{Ra}\) to \(I_{Ra}\) (i.e., \(C_E/\bar{A}_{Ra}/V_A = E_{Ra}/I_{Ra}\), since \(E_{Ra} = C_E V_A T_A\) and \(\bar{A}_{Ra} = I_{Ra}/T_A\)).

The uncertainty in \(C_E\), based on an uncertainty analysis by REI that is given as part of their routine measurement methodology, is approximately 5 % to 6 % for a relative 1 standard deviation uncertainty interval \([8]\). Comparatively, the uncertainties in \(V_A\) and \(T_A\) are almost negligible (\(\mu V_A = 1\%\) and \(\mu T_A = 0.01\%\)) so that the uncertainty in \(E_{Ra}\), \(u(E_{Ra})\), may be considered to be of a comparable 5 % to 6 % at a relative one standard deviation uncertainty interval.

Insofar as the E-PERM electret detectors operate as a type of ionization chamber, they are sensitive to environmental gamma-radiation exposure-rate fields and exhibit a corresponding background response. The routine measurement methodology used by REI for calculating \(C_E\) provides an appropriate gamma-radiation background correction \([7,8]\). The encapsulated \(^{226}\)Ra standards used in this work are not believed to have significantly increased the gamma-radiation background in the accumulation vessel above natural ambient levels. The magnitude of the effect can be approximated by considering the activity content of the capsule and typical capsule-to-detector geometry in the accumulation vessel. The exposure rate for a 500 Bq \(^{226}\)Ra point source at 10 cm can be expected \([14]\) to be roughly 0.01 Gy \(\cdot h^{-1}\) (1 \(\mu R \cdot h^{-1}\)) compared to gamma-radiation ambient levels of typically 0.1 Gy \(\cdot h^{-1}\). Hence, the effect is estimated to be \(\approx 10\%\) of a relatively small correction \([7,8]\).

The experimental configuration used for the accumulation trials consisted of suspending the encapsulated standard from a thin thread so that it was located about in the center of the accumulation vessel. The various deployed detectors were distributed, somewhat randomly, about the remaining accumulator volume. A minimum of two detectors were deployed for any given experimental trial. When two detectors were used, one was located above the encapsulated standard and the other was located nearly equidistantly below. When four or five of the smaller-volume electret chamber detectors were deployed, they were of necessity, located at varying distances from the capsule. As will be discussed subsequently, this somewhithered, haphazard detector placement had the result of randomizing effects due to

---

\(^3\) Bel Art product #42072, Bridgeport, New Jersey.
possible $^{222}\text{Rn}$ activity concentration gradients as a function of distance from the encapsulated standard.

The experimental protocol consisted of maintaining identical timing and capsule preconditioning before and between each accumulation trial. The encapsulated standards when not in use are stored in water-saturated air. Before each use, the capsules are “equilibrated” for a minimum of 24 h in an open space, i.e., in an infinite volume of air, so that the external $^{222}\text{Rn}$ activity concentration approximates zero prior to their placement in the vessel and the start of an accumulation. A similar 24 h open-air equilibrium was performed between experimental trials so that each accumulation started under identical diffusion boundary conditions.

For each trial, an accumulation vessel with a preconditioned encapsulated standard and with the deployed detectors was sealed in the vessel’s ambient air at some chosen start time $t = 0$. The surface voltage of each detector’s electret was measured just preceding placement of the detector in the vessel. After the passage of a selected accumulation time interval $T_s$, the vessel was opened and the detectors were removed. The electret voltage of each deployed detector was immediately re-measured, thereby permitting calculation of the integral average activity concentration $C_t$ for each detector [7,8].

Inasmuch as the accumulation vessels were sealed with ambient air, the integrated activity concentrations $C_t$ include the electret responses due to ambient $^{222}\text{Rn}$. This is the contribution due to the second terms for $A_{15}^{\text{Ra}}$ in both Eqs. (1) and (2). Given that the ambient $^{222}\text{Rn}$ activity concentrations were typically less than 0.015 Bq·L$^{-1}$, the effect is rather small. The ratio of the second to first terms in Eq. (2) is < 0.02 (or < 2 % of $I_{15}^{\text{Ra}}$) for an accumulation time of 3 d for even the lowest-level 15 Bq encapsulated standard. At longer accumulation times the effect rapidly becomes negligible. The ambient contribution at shorter times down to $T_s = 1$ d for the 15 Bq source is still less than 4 %.

The four detector types were deployed with the four encapsulated standards in the two different accumulation volumes over accumulation times ranging from 1 d to 33 d.

This study was conducted in the period September 1990 to May 1991 prior to the completion by NIST of the emanation fraction calibration and performance testing of the encapsulated emanation standards. The presented results, however, are based on the since-completed, final calibrations [1].

3. Results and Discussion

The results of 16 different accumulation trials are summarized in Table 1. The integral $^{222}\text{Rn}$ activity in the accumulations ranged from about 1 Bq·d to over 1300 Bq·d. Values for the integral activities $I_{15}^{\text{Ra}}$ provided by the NIST encapsulated standards were calculated from Eq. (3) using the tabulated values of $A_{15}^{\text{Ra}}$ and $T_s$ with a well-determined (subsequently certified) emanation fraction of $f = 0.888$. Recall that the overall $2\sigma$ relative expanded uncertainty in $I_{15}^{\text{Ra}}$ was estimated to be 3.4 %.

The E-PERM responses are tabulated as the mean $E_{15}^{\text{Ra}}$ [Eq. (7)] averaged over the measurements on two to five electret-chamber detectors for each accumulation. The relative standard deviation of the mean, $s_m$, in the E-PERM response for each accumulation was in the range of 0.5 % to 3.0 %, with one exception. As might be anticipated, the excepted $s_m = 8$ % was obtained in the case of expected least precision, that for an integral $^{222}\text{Rn}$ activity of $I_{15}^{\text{Ra}} = 1$ Bq·d acquired with the lowest-level 15 Bq $^{226}\text{Ra}$ source in a short $T_s = 1$ d accumulation time interval. The REI estimated total uncertainty $u_{E_{15}^{\text{Ra}}}$ of 5 % to 6 % is well borne out by the observed $s_m$ values.

Averaging over all 16 accumulations, the comparison ratio $E_{15}^{\text{Ra}}/I_{15}^{\text{Ra}}$ mean was 0.908 with a relative experimental standard deviation of the mean of 0.99 %. For any given single accumulation, the comparison of $E_{15}^{\text{Ra}}$ to $I_{15}^{\text{Ra}}$ can barely exclude the possibility of their equivalence on consideration of their respective total uncertainties.

The two-sided uncertainty interval \( \left( E_{15}^{\text{Ra}}/I_{15}^{\text{Ra}} \pm k \sqrt{u_{E_{15}^{\text{Ra}}}^2 + u_{I_{15}^{\text{Ra}}}^2} \right) \), obtained by propagating $u_{E_{15}^{\text{Ra}}}$ and $u_{I_{15}^{\text{Ra}}}$, overlaps unity at almost any confidence probability ($p$) level $\alpha \leq 0.1$ (i.e., $\geq 90$ % confidence coefficient for $p = 1 - \alpha$) with normalized variate $k \geq 2$. Yet, many of the component uncertainties, of which $u_{E_{15}^{\text{Ra}}}$ and $u_{I_{15}^{\text{Ra}}}$ are composed, are clearly fixed and common between accumulations. Therefore, one might expect that the propagated uncertainty $u_{E_{15}^{\text{Ra}}}/I_{15}^{\text{Ra}} \geq 6.3$ % would thereby overestimate the statistical variations expected to be observed from just the experimental condition repetitions. The considerably smaller observed $s_m = 1$ % in the mean $E_{15}^{\text{Ra}}/I_{15}^{\text{Ra}}$ ratio is indicative of this. In addition, the data of Table 1 clearly show that the results for $E_{15}^{\text{Ra}}/I_{15}^{\text{Ra}}$ do not fluctuate about unity with a large statistical variation, but rather exhibit a definite systematic bias trend. In every accumulation case, $E_{15}^{\text{Ra}}$ is systematically less than $I_{15}^{\text{Ra}}$ with a range of 0.87 $\leq E_{15}^{\text{Ra}}/I_{15}^{\text{Ra}} \leq 0.99$.

This systematic bias was further evidenced when the comparison ratios $E_{15}^{\text{Ra}}/I_{15}^{\text{Ra}}$ were analyzed and averaged across the four variables of the specific encapsulated standard used (Table 2), the accumulation volume (Table 3), accumulation time (Table 4), and detector type (Table 5). In all four cases, the mean ratios of $E_{15}^{\text{Ra}}/I_{15}^{\text{Ra}}$ within each variable subset of data were invariant within statistical variations compared to the overall mean for all 16 accumulation trials. Several examples can be used to illustrate this invariance. When averaging across the
four capsules (Table 2), the mean $E_{Ru}/H_{Ru}$ ratio for any given capsule differed from the overall mean $E_{Ru}/H_{Ru} = 0.98$ by $-2.3\%$ (for CR-12) to $+2.8\%$ (for CR-4c). Similarly, when averaging across the six $T_A$ time intervals (Table 4), the mean $E_{Ru}/H_{Ru}$ ratio for any given $T_A$ differed from the overall mean by $-3.1\%$ (for $T_A = 33$ d) to $+2.1\%$ (for $T_A = 7$ d), even though two of the six $T_A$ values were based on single accumulation trials. When comparing the data for the two different accumulation vessels and their respective volumes (Table 3), the maximum range difference in the two means for $V_A = 3.6$ L and $V_A = 10$ L was $1.4\%$. Again, averaging across the four detector types (Table 5), the mean ratio in $E_{Ru}/H_{Ru}$ for any given detector type differed from the overall mean by $-1.6\%$ (for SST) to $+3.5\%$ (for LST). Interestingly, but perhaps of no significance, is the observation that these two extremes were obtained with detectors having electrets of high sensitivity (‘‘ST’’). They were, however, also the averages obtained with the fewest number of accumulations. Lastly, one may observe that the grand averages of the means for each variable (last rows of Tables 2, 4, and 5) differ from the overall mean $E_{Ru}/H_{Ru} = 0.908$ by less than $0.4\%$ of the overall mean in every case: the four capsule means (0.909) differ by $+0.11\%$; the six capsule means (0.908) differ from the overall mean by $-0.33\%$; and the four detector-type means (0.911) differ by $+0.33\%$.

Additional statistical tests were performed on the data set. These included $\chi^2$-tests of the homogeneity in subsets of the observed sample variances (across the variables), $F$-tests of the homogeneity in the various subset sample means discussed above, $t$-tests of differences between the various means, and tests of possible variable correlations and biases using analysis of variance (ANOVA) techniques with sequential two-way classifications of the four variables. None of the tests indicated any statistically significant differences in any of the tested subset sample means or sample variances (although it must be mentioned that in many of the cases, the sensitivity and power of the test was low because of the small sample sizes and the small degrees of freedom).

One may, therefore, conclude that the mean comparison ratio $E_{Ru}/H_{Ru} = 0.91$ is a reasonably good indicator of the performance of the E-PERM electret chambers compared to the NIST encapsulated emanation standards when the latter are employed to obtain accumulated integral $^{222}$Rn activities. The comparison ratio was invariant across the four tested variables, and the confidence interval for the mean $E_{Ru}/H_{Ru}$ is $\pm 15\%$ at a $99\%$ confidence level.

The observed invariance in $E_{Ru}/H_{Ru}$ across the four tested variables leads one to exclude several possible causes of biasing effects. This is important to consider,
particularly in view of the observed average 9 % systematic difference between the E-PERM responses and the integral $^{222}\text{Rn}$ activities provided by the NIST encapsulated standards.

One obvious possible bias effect, of course, is leakage loss of $^{222}\text{Rn}$ from the accumulation vessel. This could occur as real ventilation leaks at the seals of the vessel lids or as losses of $^{222}\text{Rn}$ diffusing into components of the vessels (e.g., the plastic lids or rubber gaskets with the 3.7 L jar, or the plastic 10 L accumulation vessel itself). The use of the two very different types of accumulation vessels having substantially different volumes and composition materials, and yet yielding virtually identical $E_{\text{Rn}}/I_{\text{Rn}}$ values, would seem to exclude this as a biasing effect. Similarly, any kind of leakage loss is not likely to be proportionately constant over the wide variation in accumulation times from $T_A = 1$ d to 33 d as was observed in the constant $E_{\text{Rn}}/I_{\text{Rn}}$ ratios over these intervals. A leakage loss can normally be considered to have a representative time constant $\lambda_L$ such that the growth functions for $^{222}\text{Rn}$ [e.g., Eq. (1)] would be modified by substituting an effective rate constant $\lambda = \lambda_L + \lambda_{\text{Ra}}$ for the $^{222}\text{Rn}$ decay constant $\lambda_{\text{Ra}}$. The integral activity $I_{\text{Rn}}$ given by Eq. (3) calculated with $\lambda = \lambda_L + \lambda_{\text{Ra}}$, and calculated with just $\lambda_{\text{Ra}}$ would not be proportionately constant in the two cases over widely different $T_A$ intervals.

A second possible biasing effect could arise if the detectors were responding to lower $^{222}\text{Rn}$ activity concentrations than that given by the time-averaged [Eq. (4)] concentration $\bar{A}_{\text{Rn}}/V_A$ because of concentration inhomogeneities and gradients within the accumulation vessel. Again, the results from several of the variable factors would tend to exclude this possibility. No attempt was made to provide any mixing in the accumulation vessels. Yet, the diffusion of radon in air is relatively rapid (with a Fick’s law diffusion coefficient on the order of 0.1 cm$^2$ · s$^{-1}$) compared to the $T_A$ time intervals, and the effect of concentration gradients, particularly on integral measurements, can be expected to be very negligible. In addition, no discernable differences in the detector responses were seen for detectors deployed at varying distances from the encapsulated standard. One would expect that if concentration gradients caused a biasing effect, it would have been manifest in the data for the two substantially different accumulation volumes.

In the absence of any other plausible explanation for the average $\approx 9$ % difference between the REI-measured E-PERM responses and the NIST-provided $^{222}\text{Rn}$ integral activities, one is compelled to question the extent E-PERM calibration. To this end, an independent confirmatory test of the E-PERM calibration was performed in an attempt to verify the observed systematic difference. The test was based on REI measurements of $^{222}\text{Rn}$ activity concentrations in water using their E-PERM system [12,13] compared to the NIST radon-in-water standard generator [16–18] and confirmatory $4\alpha\text{Ra}$ liquid scintillation (LS) measurements. Details for this calibration verification test are provided in Appendix A. The results indicated that a comparison ratio of the average REI E-PERM responses compared to a NIST calibration was 0.936, with a combined relative standard deviation of the mean of $s_{\alpha} \approx 2$ % for the statistical sampling and measurement variations. This observed $6$ % to $7$ % difference is wholly compatible with the $\approx 9$ % difference seen in the accumulation experiments with the PERE standards.$^6$

Another interesting application of these standards was demonstrated previously [15]. They were used to experimentally determine elevation correction factors for radon monitors. If a radon monitor is calibrated at sea level and then used at another elevation, a correction is necessary because of differences in air density at the two elevations. The PERE standards were used to obtain known $^{222}\text{Rn}$ concentration ratios in two accumulation vessels maintained at two different pressures. The ratio of the radon monitor responses in the two vessels establishes the effect of differing pressures which are relatable to different elevations.

### 4. A Concluding Note

This work provided a comparison between the extant REI calibration of their electret-ionization-chamber-based E-PERM systems and accumulated integral $^{222}\text{Rn}$ activities obtained from the recently developed NIST polyethylene-encapsulated $^{226}\text{Ra}/^{222}\text{Rn}$ solution (PERE) emanation standards. The protocol and measurement methodology that was used could, of course, be invoked in a similar fashion to actually provide an independent and direct E-PERM calibration that could be related to U.S. national, and internationally recognized, $^{226}\text{Ra}$ and $^{222}\text{Rn}$ standards. The study, however, went beyond merely serving the interests and calibration needs for one particular $^{222}\text{Rn}$ measurement method—even though the REI electret chamber monitors in terms of their wide-spread use for routine screening and monitoring of indoor radon air quality have a substantial importance. Much more significantly, this work clearly demonstrated the utility and efficacy of the encapsulated emanation standards for a much broader range of measurement applications beyond those previously investigated [1], namely those involving accumulated $^{222}\text{Rn}$ activities for integral measurements.

$^6$ Calibration factors for the E-PERM detectors as provided by REI were revised in late 1994 to account, in part, for these observed systematic biases.
5. Appendix A. A Confirmatory Verification of the E-PERM Calibration Bias Based on 222Rn-in-Water Measurements

An independent confirmatory test of the extant E-PERM calibration was performed in an attempt to verify an observed ≈ 9 % systematic difference in the E-PERM integral 222Rn activity responses $E_{\text{Ra}}$ [Eq. (7)] compared to the integral activities $I_{\text{Ra}}$ [Eq. (3)] provided by NIST polyethylene-encapsulated 226Ra/222Rn emanation (PERE) standards. The test was based on REI measurements of 222Rn in water using their E-PERM system [12,13] compared to the NIST radon-in-water standard generator [16–18] and confirmatory $4\pi \alpha$ liquid scintillation (LS) measurements.

The REI routine procedure for measuring dissolved 222Rn-in-water samples using their “Radon in Water Kit” with E-PERM electret chamber detectors has been described previously [12,13,19]. The procedure, in brief, consists of the following. A small water sample, appropriately collected and contained in a REI sample bottle, is placed in the bottom of a nominal “one U.S. gallon” glass accumulation jar. The protocol calls for efforts to minimize losses of 222Rn in transferring the sample. An E-PERM detector, with a pre-measured initial electret voltage, is suspended in the air space above the water sample. The lid of the jar is closed and sealed, and the jar is then gently agitated to aerate the water sample to accelerate the release of 222Rn into the air space. The methodology relies upon the constant partitioning of the 222Rn between the water and air contained within the accumulation vessel. At the conclusion of a desired accumulation time interval (typically of several days duration), the jar is opened to remove the E-PERM detector for measurement of the post-accumulation final electret voltage. The average 222Rn activity concentration in the air [identical $C_\text{f}$ of Eq. (7)] is calculated by the REI conventional E-PERM procedure that is based on the accumulation time interval and initial and final electret voltage measurements using their provided calibration factors. The average 222Rn activity concentration in the water sample $C_\text{w}$ is then derived from $C_\text{f}$ using a simple partition model [11] that employs the necessary decay and accumulation time intervals, the relative volumes of water and air in the accumulation jar, and the Oswald partition coefficient.

For this confirmatory test of the E-PERM calibration, the NIST radon-in-water standard generator [16–18] was used to prepare calibrated water samples with known 222Rn concentrations. The generator utilizes an earlier prototype source of the polyethylene-encapsulated 226Ra solution in a small-volume accumulation chamber and with an ancillary mixing and dispensing system. It generates aqueous solutions of radium-free 226Rn of which multiple aliquots may be dispensed and used as standardized solutions for calibrating 222Rn-in-water assay procedures. As in all other NIST transfer standards for 222Rn, the generator calibration is directly relatable to the NIST primary 222Rn measurement system and in turn to national and international 226Ra standards [3].

The generator was used to prepare four samples in the REI sample bottles (nominal volume 68 mL) and six LS samples for NIST measurement. Each of the REI samples consisted of approximately 55 mL of blank, “radon-free,” distilled water (less than 0.003 Bq · g$^{-1}$ 222Rn); and 0.366 g of 222Rn solution containing $C_{\text{Rs}} = 9.588$ Bq · g$^{-1}$ of 222Rn at the reference time (1336 DST on 26 April 1991). The $2\tau_{\text{Ra}}$ uncertainty in the total 222Rn activity in each sample (89.80 Bq total) is estimated to be about 2.3 % (cf., the uncertainty analyses in Hutchinson et al. [17] and Collé et al. [18]).

The REI samples were prepared by dispensing the 222Rn solution beneath the surface and at the bottom of the sample bottles which had previously been filled with the 55 mL of blank water. The samples were immediately transferred to REI for placement in their measurement jars. Possible losses of 222Rn from samples dispensed in this way was largely unknown, but based on previous REI experience and their measurement protocol it was thought to be minimal.

The six LS samples, each with an average 1.561 g of 222Rn solution as gravimetrically determined, were also dispensed into previously filled LS counting vials. These LS samples were interspersedly dispensed between the REI samples. The sample aliquots were dispensed in the sequence $e_1 : e_2 : E_1 : e_3 : E_2 : e_4 : E_3 : e_5 : E_4 : e_6$ where the lower-case $e$ designator represents an LS sample and the upper-case $E$ is an REI sample.

Two different LS cocktails were used for the measurements, viz., 18.8 g of “PCS” (a xylene-surfactant-based LS cocktail) and 20.0 g of “Ready Safe” (designated RS here, a polyarylalkane-surfactant-based cocktail). Matched blanks of nearly identical composition were also prepared for background subtractions. Each of the six LS samples along with the matched blanks were measured five times over 3 days.

The resultant 222Rn activity concentrations $C_{\text{Rs}}$ for these samples were based exclusively on the present LS measurement assays, although they were also within 2 % agreement with the historical, canonical generator calibration factors [17,18]. The dispensed sample sizes for the REI samples were based on the known dispenser ‘‘mass divided by turn’’ calibration factor for the gener-

---

7 Amersham Corp. Arlington Heights, Illinois.
8 Beckman Instruments Inc., Fullerton, California.
ator [17]. This factor was also reconfirmed in the present measurements from the gravimetrically-determined dispensed masses in the LS samples. The factor (0.7805 g per turn; \( s_m = 0.8 \% \)) was within 1 % of the historical value—although for some inexplicable reason the dispensing precision was nearly a factor of 5 to 10 more variable than past history.

The measurement results for the six LS samples are given in Table A1. The reported value of \( C_{Rn} \) for each sample is the mean of 5 replicate measurements (corrected for \( ^{222}\text{Rn} \) radioactive decay) obtained after the \( ^{222}\text{Rn} \) and its short-lived daughters were in secular equilibrium. The precision of the measurements for each sample in terms of a relative experimental standard deviation of the mean \( s_m \) range from 0.13 % to 0.33 %. The Poisson statistical “counting error” for each of the 30 measurements ranged from 0.1 % to 0.2 %. The LS counting results were corrected for count-rate background from the matched blanks, \( ^{222}\text{Rn} \) partitioning in the LS sample, dead-time losses, count-rate-versus-energy extrapolations to zero energy, and \( ^{222}\text{Rn} \) radioactive decay to obtain the values of \( C_{Rn} \). The mean concentration \( C_{Rn} = 9.588 \text{ Bq g}^{-1} \) over the 6 LS samples has a relative experimental standard deviation of the mean \( s_m(C_{Rn}) = 0.51 \% \). Analysis of the covariance matrix (for the five measurement by six sample matrix) and analysis of variance (ANOVA) calculations indicate no sampling or measurement biases in the calculated mean. The mean and its variance were invariant over the specific LS sample mean, over the five LS counting cycles, over the dispensed sample order, over the timing or sequence of the LS sample measurements, over the dispensed sample masses, and over the LS cocktail used. LS spectra also confirmed the absence of any \( ^{226}\text{Ra} \) in the measured samples.

The mean total \( ^{222}\text{Rn} \) activity from the E-PERM measurements on the four REI samples was 84.06 Bq with a relative experimental standard deviation of the mean of 1.7 %. The mean dispensed mass of the calibrated \( ^{222}\text{Rn} \) solution in the samples was 9.366 g (with an estimated \( s_m = 0.8 \% \)). The mean \( ^{222}\text{Rn} \) activity concentration is then \( C_w = 8.975 \text{ Bq g}^{-1} \) with a combined relative experimental standard deviation of the mean \( s_m(C_w) = 1.9 \% \). The uncertainty in terms of a relative standard uncertainty was estimated by REI to be a canonical \( u_w = 5 \% \) to 6 % based on their routine measurement protocol and experience [12,19].

The average E-PERM response compared to the NIST calibration can then be expressed as the comparison ratio

\[
\frac{C_w}{C_{Rn}} = 0.936
\]

with a statistical sampling and measurement estimator of

\[
s_m = \sqrt{[s_m(C_w)]^2 + [s_m(C_{Rn})]^2}
\]

\( \approx 2 \% \)

and a combined standard uncertainty in the \( C_w/C_{Rn} \) ratio of approximately

\[
u = \sqrt{u_w^2 + u_{rn}^2}
\]

\( \approx 6 \% \)

Expanding the confidence interval \( C_w/C_{Rn} \pm k_u \) for any normalized variate \( k_u \geq 2 \) with confidence coeffi-
cient level $p \geq 90\% \ (\alpha = 1 - p/100 \leq 0.1)$ cannot exclude the possibility that the “true” $C_W/C_{Rn}$ overlaps unity (and thereby the equivalence of $C_W$ and $C_{Rn}$ at that confidence level). Yet, the estimator of central tendency in this case, given by the mean $C_W/C_{Rn} = 0.936$, is wholly compatible with the previously observed approximate $-9\%$ bias in the comparison of the averaged E-PERM responses to the integral $^{222}\text{Rn}$ activities provided by the NIST PERE standards.

Acknowledgments

The authors would like to duly acknowledge the NIST Office of Standard Reference Materials for its support of this work, as well as thank their present and former colleagues in the NIST Radioactivity Group, particularly Ms. P. A. Hodge, Dr. D. D. Hoppes, Dr. M. P. Unterweger, and Ms. J. M. Calhoun, for their underlying contributions to the development of the PERE standards. M. Arthur M. Collé is thanked for proposing the standard’s acronym. The effort of Mrs. Gloria Wiersma in preparing a coherent manuscript from a very messy hand-written draft (and even in uncovering textual inconsistencies) is highly appreciated. Lastly, the senior author heartily thanks and acknowledges Mme. Dr. K. A. Maroufi-Collé for substantial (but somewhat indescribable) sacrifices, contributions, and mathematical and statistical devil’s advocacy without which this work could not have been completed.

6. References

[1] R. Collé, J. M. R. Hutchinson, and P. A. Hodge, Polyethylene-Encapsulated $^{226}\text{Ra}$ Solution Standards: A New NIST Emanation Standard for $^{222}\text{Rn}$ Measurement Calibrations, to be published (1995).
[2] R. Collé and J. M. R. Hutchinson, Radon Measurements and Calibration Standards, in Low-Level Measurements and Their Applications to Environmental Radioactivity, M. Garcia and G. Madurga, eds., World Scientific, Singapore (1988) pp. 79–100.
[3] R. Collé, J. M. R. Hutchinson, and M. P. Unterweger, The NIST Primary Radon-222 Measurement System, J. Res. Natl. Inst. Stand. Technol. 95, 155–165 (1990).
[4] R. Collé. In progress historical review of international and U.S. national $^{226}\text{Ra}$ and $^{222}\text{Rn}$ standards (presently unpublished).
[5] National Institute of Standards and Technology, Certificate for Standard Reference Material SRM-4968, Radon-222 Emanation Standard, issued August 1994.
[6] R. Collé, P. A. Hodge, and J. M. R. Hutchinson, The NIST Polyethylene-Encapsulated-$^{226}\text{Ra}/^{222}\text{Rn}$-Emanation (PERE) Standard, to be published (1995).
[7] P. Kotrappa, J. C. Dempsey, J. R. Hickey, and L. R. Stieff, An Electret Passive Environmental 222-Rn Monitor Based on Ionization Measurement, Health Phys. 54, 27–56 (1988).
[8] P. Kotrappa, J. C. Dempsey, R. W. Ramsey, and L. R. Stieff, A Practical E-PERM® (Passive Environmental Radon Monitor) System for Indoor Radon Measurement, Health Phys. 58, 461–467 (1990).
[9] J. M. R. Hutchinson, J. Cessna, R. Collé, and P. Hodge, An International Radon-in-air Measurement Intercomparison Using a New Transfer Standard. Appl. Radiat. Isot. 43, 175–189 (1992).
[10] International Organization for Standardization (ISO), Guide to the Expression of Uncertainty in Measurements, ISO, Geneva, 1993; published jointly by ISO, International Bureau of Weights and Measures (BIPM), International Electrotechnical Commission (IEC), International Federation of Clinical Chemistry (IFCC), International Union of Pure and Applied Physics (IUPAP), and the International Organization for Legal Metrology (OIML).
[11] B. N. Taylor and C. E. Kuyatt, Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results: 1994 Edition, National Institute of Standards and Technology, Technical Note 1297 (1994).
[12] W. A. Jester and P. Kotrappa, E-PERM Radon Monitors for Determining Waterborne Concentrations of Dissolved $^{222}\text{Rn}$, Trans. Amer. Nucl. Soc. 60, 88–89 (1989).
[13] Rad Elec Inc. Manual for Measurement of Radon in Water Using the E-PERM® System. Frederick, MD (1990).
[14] Bureau of Radiological Health, U.S. Department of Health, Education, and Welfare, Radiological Health Handbook, rev. ed., (1970) pp. 32 and 131.
[15] P. Kotrappa and L. R. Stieff, Elevation Correction Factors for E-PERM® Radon Monitors, Health Phys. 62, 82–86 (1992).
[16] J. M. R. Hutchinson, P. A. Mullen, and R. Collé, Development of a Regenerative Radon-in-Water Radioactivity Standard, Nucl. Instr. Meth. Phys. Res. 223, 451–457 (1984).
[17] J. M. R. Hutchinson, P. A. Mullen, and R. Collé, The NBS Radon-in-Water Standard Generator. Nucl. Instr. Meth. Phys. Res. A247, 385–389 (1986).
[18] R. Collé, Raj Kishore, and J. M. R. Hutchinson, An Update on the Efficacy and Long-Term Stability of the NIST Radon-in-Water Standard Generator, to be published (1995).
[19] P. Kotrappa and W. A. Jester, Measurement of Dissolved Radon-222 in Water Using Electret Ion Chamber Radon Monitors. Health Phys. 64, 397–405 (1992).

About the authors: Dr. R. Collé is a specialist in radionuclidic metrology, and currently serves as a research chemist in the Radioactivity Group of the NIST Physics Laboratory (Ionizing Radiation Division). He has been at NIST since 1974, and his primary interests and responsibilities for the past decade have involved maintaining the national standards for $^{226}\text{Ra}$ and $^{222}\text{Rn}$, and developing new transfer standards and measurement methodologies for them. Dr. Paul Kotrappa is President of Rad Elec Inc., and was a co-developer of the electret ionization chamber technology. Dr. J. M. R. Hutchinson is a physicist who has been at NIST since 1957, and currently serves as the Radioactivity Group Leader. The National Institute of Standards and Technology is an agency of the Technology Administration, U.S. Department of Commerce.