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An update on the NIST radon-in-water standard generator: its performance efficacy and long-term stability

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Abstract

A ^{226}Ra–^{222}Rn generator that could be used as a transfer standard for radon-in-water measurement calibrations was previously developed and described. The generator utilized a novel ^{222}Rn emanation source that was comprised of a ^{226}Ra solution encapsulated in polyethylene. The long-term performance of this standard generator has now been investigated and evaluated. The evaluation included exhaustive and more reliable measurement uncertainty analyses for the generator's performance and routine operation. Modifications to the original protocol for operation of the generator has also resulted in improved precision in the ^{222}Rn activity concentration in a dispensed aliquant. The evaluation results indicate that the generator performance has remained stable, and that the calibration parameters are still well within their given uncertainty intervals for the originally determined canonical values. Over a period of approximately six years, experimentally determined values of the ^{222}Rn emanation fraction, the most critical parameter, have remained constant and invariant of conditions within statistical variations of about 0.3% (corresponding to a relative standard deviation of the mean). All evaluation measurements were performed by 4π-$\alpha\beta$ liquid scintillation spectrometry of gravimetrically determined aliquants dispensed from the generator.

Keywords: Calibration; Emanation; Liquid scintillation; Measurement; Polyethylene; Radioactivity; Radium-226; Radon-222; Standard; Water

1. Introduction

In 1986, the National Institute of Standards and Technology (NIST, then called the National Bureau of Standards) completed the development of a "generator" that could be used as a transfer standard for ^{222}Rn-in-water measurement calibrations [1, 2]. The standard is primarily intended for use with liquid scintillation (LS) measurements of aqueous ^{222}Rn concentrations [3–9]. The generator[2] consists of a polyethylene-encapsulated

^{226}Ra solution source in a small-volume accumulation chamber and an ancillary mixing and dispensing system which is partially automated with motor-driven, 50 ml "gas-tight" syringes. The entire, self-contained generator is maintained and operated under air-free conditions. Unlike other ^{222}Rn-in-water calibration standards then and still in use (cf. Refs [5–9]), this standard can be used to generate and accurately dispense radium-free ^{222}Rn solutions of known concentration, without invoking assumptions or difficult corrections for a ^{226}Ra component in the calibration standard. Use of ^{226}Ra calibration standards (sometimes with large accompanying ^{210}Pb concentrations that are poorly quantified [10]) for LS measurements of ^{222}Rn can introduce significant analytical uncertainties. Many, if not all (cf. Refs. [6–9]), so-called ^{222}Rn measurement "calibration protocols" that rely on ^{226}Ra sources, such as those utilizing immiscible mineral-oil/water LS cocktails, will not withstand critical scrutiny. These calibration standards, using either ^{226}Ra on selective ion-exchange resins or ^{226}Ra solutions directly, rely upon the presumption that the ^{226}Ra (and possibly ^{210}Pb) remains

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[2] An earlier prototype of the generator [1] utilized a solid source of ^{226}Ra which was deposited on an ion-exchange filter and sandwiched between two layers of thin polyethylene tape. Although this solid-source generator was subsequently found to be inadequate in terms of its stability over long times, this earlier work established the validity of the polyethylene-diffusion principle as applied to the encapsulated ^{226}Ra sources, and it gave other physical characteristics of the generator system.

exclusively in the aqueous phase without an LS counting interference.

The standard generator, as described previously [1, 2], was calibrated and certified in terms of several parameters (most importantly the ^{222}Rn emanation fraction f) that allow calculation of the ^{222}Rn concentration or total activity in an aliquant dispensed from the generator when a detailed operating protocol is rigorously followed. The total propagated uncertainty of the calibration, in terms of an assumed relative standard deviation, was estimated at the time to be approximately 1.2%. The original standard generator, as described by Hutchinson et al. [2], was delivered and reposited at the Las Vegas laboratory of the U.S. Environmental Protection Agency (EPA) in 1987. Readers may wish to consult the original references [1, 2] for detailed schematics that illustrate the construction and operation of the generator.

In 1988, NIST initiated the fabrication of a nearly identical, duplicate generator. It was intended for internal use at NIST, and for evaluations of the performance of the generator over time. Representative examples of its internal use at NIST include a verification of a bias in the calibration of electret-based integral radon monitors [11] and preparation of samples used for a precise determination of the ^{222}Rn half-life [12]. A version of this generator, incorporating identical operating principles and a similar polyethylene-encapsulated ^{226}Ra source, is also reported to be under development for use as a national calibration standard in UK [13].

Since the publication of the earlier papers [1, 2], the generator has undergone various evaluations of its long-term stability and performance efficacy. This paper describes the results of these evaluations, and provides more reliable uncertainty estimates. Modifications to the original operating protocol for the generator [2], resulting in improved precision in the ^{222}Rn activity concentration for a dispensed aliquant, are also given.

2. Generator and experimental considerations

The source used for this second standard generator consists of a heat-sealed polyethylene capsule having a total mass of approximately 288 mg, and containing (initially) approximately 170 mg of a ^{226}Ra solution in 118 mg of low-density polyethylene. The solution consists of a calibrated ^{226}Ra solution of nominal 1 mol l^{-1} hydrochloric acid containing approximately 2 mg BaCl$_2$ per gram of solution. The capsule is in a right-circular cylinder configuration with an outer diameter of roughly 0.4 cm, a length of about 2.0 cm, and a nominal average wall thickness of 0.07 cm.[3] It contains a total ^{226}Ra activity of 1167 ± 11 Bq as of 9 September 1991, where the cited uncertainty is an "expanded uncertainty".[4] At the time of the initial encapsulation of the solution, the

capsule contained a small air void estimated to be less than 0.008 cm^3 out of a total internal volume of about 0.180 cm^3. The capsule was subsequently kept completely immersed in water within the generator's accumulation chamber. Over the passage of several years, the air void diminished as a result of transpiration of water into the capsule until the void was no longer visible. The ratio of total polyethylene mass to total water mass in the accumulation chamber was more favorable in this second generator (in terms of ^{222}Rn emanation) compared to the earlier generator located at EPA.[5] All other fabrication details for the generator, such as the materials used (gas-tight syringes, valves, joints, and tubings, etc.) and

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[3] The capsule before filling was fabricated by hand-crafted drawing of a polyethylene tube and therefore is not likely to have a constant wall thickness across its length. The equivalent average wall thickness was estimated from the total and polyethylene masses, known densities, and considerations of the geometry and exterior dimensions.

[4] The specification of measurement uncertainties and the uncertainty analysis procedures used throughout this paper follow the normal conventions of the NIST Radioactivity Group. These conventions are wholly compatible with those adopted by the principal international metrology standardization bodies [9, 10]. All individual uncertainty components are expressed in terms of estimated (experimental) standard deviations (or standard deviations of the mean where appropriate) or quantities assumed to correspond to standard deviations irrespective of the method used to evaluate their magnitude. All of these component quantities 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 [9]. By recently established NIST policy [10], the combined standard uncertainty is multiplied by a "coverage factor" of $k = 2$ to obtain an "expanded uncertainty" which is assumed to provide an uncertainty interval with a confidence of roughly 90–95%. For comparative purposes, it should be noted that previous certifications (e.g., for Standard Reference Materials) issued by the NIST Radioactivity Group used comparably-based uncertainty coverage factors of $k = 3$. This former practice was historically rooted and was assumed to provide certified uncertainty intervals with somewhat higher confidence levels, approaching 95–99%.

[5] The capsule dimensions and polyethylene and solution masses reported for this earlier generator, as given by Hutchinson, et al. [2] are wholly inconsistent. We strongly suspect that the reported polyethylene mass given therein is in error by perhaps as much as a factor of two or more. Excepting the careful gravimetric filling of the earlier capsule with the ^{226}Ra solution, neither the constituent masses nor physical dimensions were as controlled (or as documented) as for the preparation of the source used in the present generator described here.

internal volumes, were virtually identical to those described earlier [2].

Operating details were also nearly identical to those given earlier [2]. The principal differences were improvements in determining the total dilution of the accumulated ^{222}Rn activity and the dispensed aliquant sizes, and in reproducing the total filling volume.

Originally, the standard generator was calibrated and certified on a volume basis in terms of the ^{222}Rn activity concentration K or total activity A in a given aliquant of volume v dispensed from the generator. These quantities could be calculated from a general expression containing certified parameters, when the accompanying operating protocol was invoked. The following parameters were certified: the total ^{226}Ra activity in the encapsulated source A_0; the ^{222}Rn emanation fraction f; a "dead volume" (given by the volume of tubing between the two syringes) which was used along with the filling volume of the two syringes to obtain the total dilution volume V; and, for convenience, a conversion factor k_x for the volume of a dispensed aliquant v in terms of the number of turns on the dispensing-syringe motordrive.[6] Since then, it was found that substantially greater precision could be achieved by firstly increasing the "dead volume" to reproduce its magnitude more precisely, and secondly by directly measuring the total mass of blank water m_D used to perform the dilution. The revised procedure tries to ensure that the starting position of the syringes (which defines the "dead volume") is returned to, as nearly as possible, at the end of the dispensing operations. This was achieved by slightly off-setting the syringe plunger from a fully inserted position and thereby increasing m_d. The total dilution mass M can be given by the mass of this "dead volume" m_d plus the mass m_D. The dilution mass m_D is determined gravimetrically by adding the masses m of all component aliquants dispensed from the generator plus the initial mass of solution used to flush the dispensing needle and the mass of any remaining solution in the dispensing syringe. In other words, the total mass of all of the solution that exits the generator in returning the syringes to their starting positions is directly measured. The "dead volume" m_d is estimated from dimensional measurements and geometrical considerations. It must be noted however, that the emanation fraction f, as defined and experimentally determined, is a function of m_d. The total [or "absolute" (sic)] uncertainty in determining m_d is therefore unimportant. Rather, it is only the uncertainty in reproducing m_d from one use of the generator to the next that propagates as an uncertainty component for the accumulated and diluted ^{222}Rn activity concentration. This uncertainty component, in turn, obviously, is merely dependent on the

reproducibility in returning the syringes to their starting positions.

Following the notation previously utilized [2], the ^{222}Rn activity concentration K and the total ^{222}Rn activity A in an aliquant dispensed from the generator are thus given by

$$K = A/m = fA_0 \exp(-\lambda_{Ra}t_d)[1 - \exp(-\lambda_{Rn}t_a)]/M, \quad (1)$$

where m is the gravimetrically measured mass of a dispensed aliquant; f is the source emanation fraction (the fraction of the total ^{222}Rn generated in the source by the decay of ^{226}Ra that is released to the water in the accumulation chamber); A_0 is the total ^{226}Ra activity in the source at reference time t_0; λ_{Ra} is the ^{226}Ra decay constant; t_d is a decay time interval given by the difference between t_0 and the start time t_1 of an accumulation; λ_{Rn} is the ^{222}Rn decay constant; t_a is an accumulation time interval given by difference between t_1 and the end time t_2 of an accumulation; and M is the total mass of solution containing ^{222}Rn which is given by a defined "dead volume" m_d and a gravimetrically-measured dilution mass m_D. The adopted decay constants are $\lambda_{Ra} = (1.186 \pm 0.005)10^{-6} \, \text{d}^{-1}$ [16] and $\lambda_{Rn} = 0.18130 \pm 0.00002 \, \text{d}^{-1}$ [17].

For routine operation of the generator, the available ^{222}Rn activity concentration K may be varied by adjusting the accumulation time t_a and the total solution mass M. For $M \simeq 55 \, \text{g}$, K ranges from about 2 Bq g^{-1} for an accumulation with $t_a \simeq 1 \, \text{d}$ to about 14 Bq g^{-1} for $t_a > 20 \, \text{d}$. This range may be increased to higher concentrations by use of smaller dilution volumes (and M). Operation of the generator, however, has been found to be most reproducible by using a near maximum $M \sim 55 \, \text{g}$.

All of the performance evaluation measurements described herein were based on 4π-$\alpha\beta$ liquid scintillation (LS) spectrometry of gravimetrically determined aliquants dispensed from the generator. The routine gravimetric procedures used in our laboratory as they apply to the preparation of LS counting sources, as well as estimations of their associated uncertainties, have been treated at length previously [18–22]. Mass determinations for the dispensed aliquants m have relative standard uncertainties of about $\pm 0.05\%$. The generator dispensings and LS measurement procedures used for this study were similar to those given earlier [2]. Two different LS spectrometers were employed. Their principal operating characteristics are outlined in Table 1. Descriptions of these operating characteristics, their respective performance, and use within this laboratory for various radionuclidic calibrations are available [18–22]. Specific aspects of the LS procedures as they apply to ^{222}Rn measurements have been given by Collé, et al. [11, 12]. The LS counting sources (i.e., cocktails) contained ^{222}Rn-laden aqueous solutions ranging from as small as

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[6] The dispensing conversion factor was actually determined in terms of the mass of dispensed aliquant per turn [2].

Table 1
Characteristics of the LS spectrometers used for the evaluations of the Radon-In-Water Standard Generator

Characteristic	System B	System P
LS spectrometer model	Beckman LS7800	Packard Tri-carb A2500TR
Operating mode	Sum-coincidence	Sum-coincidence
Photomultiplier tubes	Hamamatsu R331-05	Hamamatsu R331-08
Operating temperature	Ambient	Ambient
Coincidence resolving time	22 ns	18 ns
Sum-coincident pulse amplification	Logarithmic	Linear
Pulse resolving time	5–33 μs (variable with pulse height)	12 μs (fixed)
Spectral analog-to-digital converter (ADC) capacity	1000 channels	2048 channels
Nominal conversion gain (energy per channel)	Variable (with logarithmic energy)	$\simeq 1$ keV
Detection threshold (nominal)	≤ 1 keV	≤ 1 keV
Live-time determination method (and uncertainty)	Gated oscillator (scaled) ($\pm 0.1\%$)	Gated oscillator (scaled) ($\pm 0.1\%$)
Quench indicating parameter (QIP)	Horrocks number (H)	Transformed Spectral Index of the External Standard ($tSIE$) (proprietary)
External γ-ray source for QIP determination (and location)	[137]Cs (side)	[133]Ba (bottom)

Table 2
Scintillants (commercially prepared) used for the evaluations of the Radon-In-Water Standard Generator

Commercial scintillant	Acronym descriptor	Manufacturer	Density (g ml⁻¹)	Composition
PCS	PCS	Amersham	0.92	Xylene; 2-ethoxyethanol (a surfactant); unspecified fluor
Ready Safe	RS	Beckman	0.97	Phenylxylylethane (PXE), 50-80%; non-ionic surfactant, 20-50%; 2,5-diphenyloxazole (PPO), < 1%
Instagel XF	IG	Packard	$\simeq 0.9$	1,2,4-trimethylbenzene (pseudocumene); with unspecified emulsifiers; PPO and bis(2-methylstyryl)benzene (bis-MSB) fluors

a few tenths of a gram up to nearly 5 g in various proportions (typically 15–20 ml) of several commercially available scintillants (Table 2).[7] The cocktails were contained in glass, nominal 20 ml LS vials having aluminum-backed liners on plastic screw caps. Previous studies to evaluate possible radon losses in the LS vials, and to determine ^{222}Rn LS detection efficiencies, were made in flame-sealed glass LS vials [12]. In all cases, the LS cocktails were compared with matched blanks of nearly identical composition for background subtractions. The blanks were prepared with aged, ion-exchanged, "radon-free", doubly distilled water having a total α- or β-emitting radionuclidic impurity, in terms of an equivalent ^{222}Rn activity concentration, of less than 0.003 ± 0.001 Bq g⁻¹. Generator dilutions were performed with the same blank water supply. Measurements were initiated only after the cocktails contained ^{222}Rn in radioactive equilibrium with its short-lived ^{218}Po–^{214}Pb–^{214}Bi– ^{214}Po subseries (i.e., after a minimum of 5–6 h). The overall LS detection efficiency is almost exactly 5 counts s⁻¹ Bq⁻¹ resulting from a very nearly 100% efficiency for the three α decays (^{222}Rn, ^{218}Po, and ^{214}Po) and an almost comparable 100% efficiency for the two energetic β decays (^{214}Pb and ^{214}Bi). The efficiency is nearly invariant of reasonable sample quenching, but is dependent on the water fraction in the cocktail (as it affects the radon solubility) and on the size of the air space in the LS vial above the cocktail. Based on an efficiency tracing method [23–25] using theoretical

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[7] Most initial measurements in the period prior to 1991 exclusively used the xylene-based PCS scintillant, which is no longer commercially available. The other scintillants (RS and IG) were intercompared to PCS in an interim period from 1991 to 1994. Only the latter two scintillants were used since 1994.
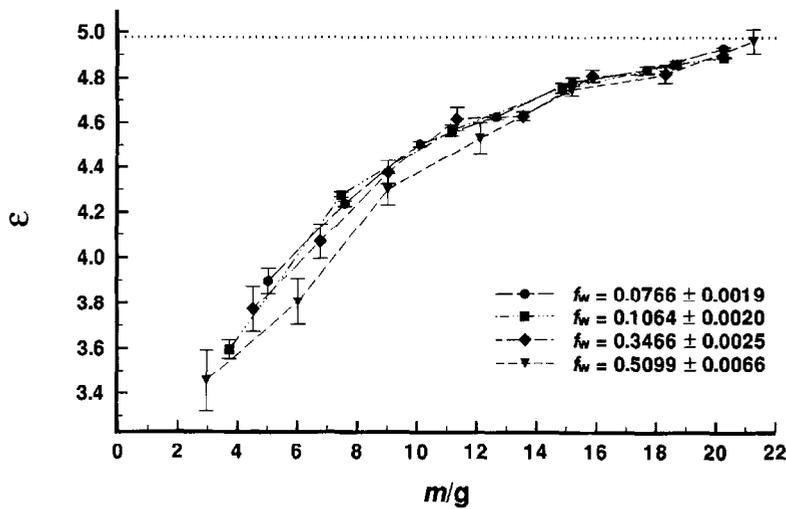
Fig. 1. Experimentally determined LS detection efficiencies ε for ^{222}Rn subseries decay as a function of total cocktail mass m_c (in units of g) for four H_2O mass fractions f_w. Each cocktail consists of $f_w m_c$ g of ^{222}Rn-laden H_2O in $(1 - f_w)m_c$ g of PCS scintillant in a nominal, flame-sealed 20 ml glass LS vial. The value of ε_s (cited in the text) for an "unquenched" cocktail with no radon losses to the air space is shown by the dotted line. The uncertainty interval on each datum correspond to v_c for $6 \leq n_m \leq 12$ replicate measurements on each cocktail (see text).

modelling calculations and measurements with matched sets of ^{3}H-standard LS cocktails, the LS counting efficiency for the ^{222}Rn subseries in "unquenched" (sic) samples was found to be $\varepsilon_s = 4.977^{+0.008}_{-0.015}$ counts s^{-1} Bq^{-1} [12]. The efficiency-tracing quench corrections included appropriate extrapolations for the scintillant-to-water ratio in the LS cocktail; for partitioning of radon between the scintillant-water cocktail mix and the air space in the LS vials; and for count-rate-versus-energy extrapolations to zero energy. Fig. 1 illustrates some representative experimental efficiencies for the ^{222}Rn subseries as functions of the cocktail compositions variables: f_w, the H_2O mass fraction in the cocktail; and m_c, the total cocktail mass.[8] LS cocktail stability over the measurement times was typically estimated from variations in quench indicating parameters [20]. The ^{222}Rn LS detection efficiency was independently verified [2] by confirmatory measurements with the NIST pulse-ionization-chamber-based primary ^{222}Rn measurement system which serves as the U.S. national radon measurement standard [26, 27].

The generator, for any given performance evaluation, was used to dispense and prepare a series of n_s LS samples, ranging from $n_s = 6$ to $n_s > 20$. The evaluations used varying, but well-determined, accumulation times t_a from $t_a \simeq 0.9$ d to $t_a > 40$ d. The relative standard uncertainty in t_a (due largely to the finite time needed to dilute and transfer the ^{222}Rn in the accumulation cham-

ber) ranged from approximately 0.05% for a $t_a \simeq 1$ d accumulation to about 0.002% for a $t_a \simeq 30$ d accumulation. Each of the dispensed ^{222}Rn solution aliquants used to prepare the LS cocktails had an independently determined mass m_j (with $j = 1, 2, 3, \dots, n_s$). Each sample, along with matched blanks for background subtractions, was then measured on either LS spectrometer a number n_m replicate times, which was typically in the range $5 \leq n_m \leq 12$ but which varied (for special tests) from a minimum of $n_m = 3$ to $n_m = 120$. The counting time intervals for each LS measurement was typically 15 or 20 min in duration, and ranged from 5–60 min in extremes. The decay-corrected, net counting rate concentration for sample j during measurement cycle i (with $i = 1, 2, 3, \dots, n_m$) was obtained from

$$R_{j,i} = [C_{j,i} - C_{B(i)}]/[\exp(-\lambda_{Rn}T_i)t_i m_j], \tag{2}$$

where $C_{j,i}$ is the gross integral counts in the full-energy LS spectrum for the jth sample at measurement time T_i; $C_{B(i)}$ is the corresponding gross integral counts for background obtained from a spectrum of a matched blank LS sample in the same ith counting cycle; λ_{Rn} is the ^{222}Rn decay constant; T_i is the decay time interval from the midpoint of the measurement time interval to a common reference time (typically taken as the previously-defined end time t_2 of the accumulation); t_i is the counting (live) time interval for measurement of both the source and matched blank; and m_j is the mass of the dispensed ^{222}Rn solution used in the jth sample.

Routine evaluations of the generator performance (over time) were typically performed with $m_j \simeq 1.5$ g in

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[8] For a cocktail with given f_w and m_c, the cocktail volume v_c may be approximated by $v_c \simeq m_c[f_w + (1 - f_w)/\rho]$ where ρ is the density of the scintillant (Table 2).

about 18.5 g of scintillant to form cocktails with $f_w \simeq 0.1$ and $m_c \simeq 20$ g, although other conditions were also employed for special tests as noted below.

3. Uncertainty (statistical) model considerations

Generator performance was analyzed and could be better understood by considering the underlying uncertainty components, using one-way-classification analysis of variance (ANOVA) techniques for a random-effects statistical model [28].

Relative standard deviations $v_{P(i)}$ in percent for the total Poisson "counting error" (sic) for any single measurement of $R_{j,i}$ would normally be obtained from the usual expression $100 [C_{j,i} + C_{B(i)}]^{1/2}/[C_{j,i} - C_{B(i)}]$ on assuming that the measurement process is Poisson distributed.[9] However, the t_i counting intervals used in this study were typically long or comparable to the half-lifes of the individual members of the ^{222}Rn subseries. As a result, the above expression used to estimate the so-called statistical counting error is not valid since the short-lived ^{222}Rn daughters do not follow the Poisson statistics for independently decaying species. Following the methodology of Lucas and Woodward [29] in which the standard deviation associated with the "counting statistics" for long decay chains is given by $s \simeq (JN)^{1/2}$ with $J = \sigma^2/\mu$ (the quotient of the variance in the mean number of observed events and the mean), the previous expression can be modified to give $v_{P(i)} = 100 [J_{j,i}C_{j,i} + C_{B(i)}]^{1/2}/[C_{j,i} - C_{B(i)}]$. Lucas and Woodward [29] have tabulated values of J for the ^{222}Rn subseries for a variety of combinations of counting time interval and detection efficiency under the condition that only the three α emitters in the decay subchain are counted. The LS results presented here detect (in 4π geometry) the three α emitters as well as the two β emitters with virtually 100% efficiency so that the tabulations of Lucas and Woodward [29] could not be directly applied. Instead, $J_{j,i}$ factor approximations for each ith measurement and jth sample condition were calculated (using the identical approach of Lucas and Woodward [29]) to estimate $v_{P(i)}$. The exact magnitudes of $v_{P(i)}$, of course, were explicitly dependent on the t_i counting times and on the total ^{222}Rn content in the cocktails. The latter in turn was merely dependent on the previously-defined t_a accumulation times and on the m_j sample sizes. It may be of

interest to note that the first (and usual) expression for the counting errors would result in underestimates by a factor of about 2.2 in the limit of very long counting times – as compared to more-exact calculations of $v_{P(i)}$ using J factors. For the present experimental conditions, the $v_{P(i)}$ would have, in any worse case, been underestimated by a factor of considerably less than 2 and in general would have resulted in underestimates of about 50% to 60%.

For n_m replicate measurements, the overall relative "counting error" for a single jth sample can be obtained from summing the total counts over all measurements of that sample;

$$v_P = 100\{\Sigma_i [J_{j,i}C_{j,i} + C_{B(i)}]^{1/2}/\Sigma_i [C_{j,i} - C_{B(i)}]\}.$$

The "counting error" (assuming no ^{222}Rn decay over the course of the measurements) would reduce to approximately $v_P \simeq v_{P(i)}/\sqrt{n_m}$. For most of the calibration results given herein, values of v_P were typically $\leq 0.2\%$.

The variability in the $R_{j,i}$ values (for constant j) would reflect the overall LS measurement precision, and would include the v_P "counting error" component, as well as any other components of random variation in the measurement process. This measurement variability may be characterized either by a relative standard deviation v_C computed from the data set of $R_{j,i}$ values, or by a relative standard deviation of the mean $v_C/\sqrt{n_m}$ (with $n_m - 1$ degrees of freedom). For any given generator run, the $R_{j,i}$ values could be averaged across the n_m measurement cycles to obtain mean $\langle R_j \rangle$ values for each sample in the series. The variability among these $\langle R_j \rangle$ mean values (for constant m_j), which again may be expressed as either calculated relative standard deviations v_R or relative standard deviations of the mean $v_R/\sqrt{n_s}$, would reflect the measurement precision given by the v_C component plus any sample variability. Further averaging the $\langle R_j \rangle$ means across all n_s samples (assuming constant m_j) results in a grand mean $\ll R \gg$ for the given generator run. The accumulated and diluted ^{222}Rn activity concentration in the generator with a mean $\langle K \rangle$ can then be related to $\ll R \gg$ through $\langle K \rangle = \ll R \gg/\varepsilon_s q$ where ε_s is the extrapolated LS detection efficiency for ^{222}Rn in "unquenched" samples (given previously) and q is a combined correction for the effects of radon losses (composition dependent) and chemical quenching in the cocktails. The product quantities $\varepsilon_s q$ are the experimentally-determined efficiencies ε given, for example, in Fig. 1. From Eq. (1), the emanation fraction f may then be obtained directly from determinations of $\langle K \rangle$ along with the decay-corrected ^{226}Ra source strength $[A_0 \exp(-\lambda_{Ra}t_d)]$, ^{222}Rn accumulation factor $[1 - \exp(-\lambda_{Rn}t_a)]$, and dilution mass M. The variability in replicate determinations of f from evaluation run to run would then reflect the uncertainties in determining all of the above component quantities.

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[9] The term "counting error", a gross misnomer, arises from the assumption that the radioactive decay process itself (but *not* necessarily the counting process) is Poisson distributed (with equal mean μ and variance σ^2 for the distribution) such that its variance ($N = \sigma^2$) is equal to the mean number of total observed counts ($N = \mu$).

The individual components of variance may be evaluated as follows. The overall measurement variability, given by v_C for n_m measurements on a single cocktail, may be considered to be related to the Poisson "counting error" v_P through $v_c^2 = v_P^2 + n_m v_{LS}^2$ where v_{LS} is the relative standard deviation for an additional component of variance for the measurement process. Similarly, the overall variability between samples, given by v_R, can be considered to be comprised of the v_C component and an additional component of variance, given by a relative standard deviation v_S, for the differences between samples: $v_R^2 = v_C^2 + n_s v_S^2$. The variability in the mean $\langle K \rangle$ for a given generator run, given by a relative standard uncertainty v_K, is largely reflected in v_R plus random variations in ε_s and in q.[10] It follows that the observed variability in n_f replicate determinations of f, given by a relative standard deviation v_f, can be related to v_K (or v_R) plus an additional component for the variability among generator runs: $v_f^2 = v_K^2 + n_f v_G^2$.

Hence, the following uncertainty components (all expressed as relative standard deviations) are derivable from the experimental evaluation measurements:

- v_P, the overall Poisson "counting error" for n_m multiple measurements of a single sample, obtained directly from the LS counting data for the samples and blanks;
- v_C, the overall replication precision for n_m multiple measurements of R for a single sample, computed from determinations of $R_{j,i}$ for a given sample j and having $(n_m - 1)$ degrees of freedom;
- v_{LS}, the LS measurement precision for a single sample which arises from temporal instrument and cocktail instabilities, and from random variations in the ^{222}Rn decay corrections and livetime determinations, obtained from evaluations of v_P and v_C and having $(n_m - 1)$ degrees of freedom;
- v_R, or v_K, the overall replication precision in determining R for n_s multiple samples, computed from the mean $\langle R_j \rangle$ values and having $(n_s - 1)$ degrees of freedom;
- v_S, the sampling precision which arises from solution inhomogeneity (or sample-to-sample variability) and random variabilities in measuring the sample masses m_s, obtained from evaluations of v_C and v_R and having $(n_s - 1)$ degrees of freedom;
- v_f, the overall replication precision in determining f, computed from n_f multiple determinations of f having $(n_f - 1)$ degrees of freedom; and
- v_G, the generator precision, which arises from random variabilities in determining the total dilution mass M (primarily in turn arising from determining

the "dead volume" m_d) and in the decay-corrected ^{226}Ra source strength A_0 and the ^{222}Rn accumulation factor, obtained from evaluations of v_K and v_f and having $(n_f - 1)$ degrees of freedom.

These uncertainty components evidently consist of a nested array. The components v_P, v_C, v_R (or v_K) and v_f are directly obtained from measurement data of replications; whereas v_{LS} is derived from v_P and v_C, v_S is derived from v_C and v_R, and v_G is derived from v_R and v_f.

4. Results of the performance evaluations

The left-hand side of Fig. 2 gives the first four experimental determinations (labelled $\alpha 1$, $\alpha 2$, $\alpha 3$ and $\alpha 4$) of the emanation fraction f when the generator was employed by following the original operating protocol [2]. In these cases, the total dilution was obtained by volumetric estimations and the "dead volume" was approximately 0.53 ml. All four determinations used comparable accumulation times t_a of 1 to 2 days, and were made over a relatively short two-week interval. The determinations were also based on roughly the same total dilution volume of $V = 51.5$–52.0 ml, the same number of samples $n_s = 7$ to $n_s = 10$ using sizes of $1.1 \text{ g} \leq m_j \leq 1.5 \text{ g}$ in 15 ml of the same PCS scintillant, and each sample was counted an equivalent $n_m = 10$ number of times which resulted in very comparable Poisson "counting errors" v_P. The uncertainty intervals shown on the individual datum points in Fig. 2 reflect only the standard deviations v_R in determining the $\ll R \gg$ values (defined above), and do not include any uncertainties in the total solution volume V or mass M. The dispersion in the four determinations of f (given by the standard deviation v_f) in comparison to the precision estimators v_R clearly indicates that there is an additional and large component of uncertainty whose magnitude can not be attributed to uncertainties in either the decay-corrected ^{226}Ra content of the source or the ^{222}Rn accumulation factor [see Eq. (1) and previous discussion]. This additional uncertainty component can only be due to the inherent variability in the volumetric estimation of V (or M).

This is evident on examination of the right-hand side of Fig. 2 which illustrates the next four experimental determinations (labelled $\omega 1$, $\omega 2$, $\omega 3$ and $\omega 4$) of f that were obtained after the operating protocol was revised to more accurately reproduce and quantify the total dilution mass M (as described previously). In these latter four cases (in which $M = m_D + m_d \simeq 57.57$, 56.08, 57.58 and 55.12 g, respectively) the total mass of blank water m_D used to perform the dilution was gravimetrically determined (as obtained by summation of all masses m_j dispensed in returning the dispensing syringe to its starting position) with an estimated relative standard uncertainty of approximately 0.15% and the reproducibility in M was estimated to be better than 0.2%. This

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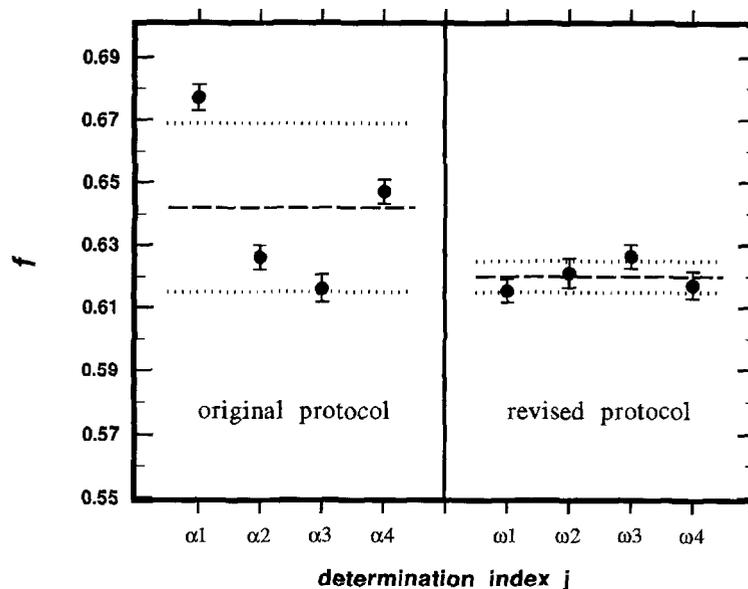[10] In actuality, v_K is equivalent to the variability in $\langle R_j/m_j \rangle$ for constant $\varepsilon_s q$.

Fig. 2. Replicate determinations of the ^{222}Rn emanation fraction f using the original volumetric-based operating protocol and a revised gravimetrically based protocol. The uncertainty interval bars on the individual datum values correspond to the standard deviations fv_K. The horizontal dashed and dotted lines, respectively, correspond to the two calculated mean f values and their standard deviations fv_f.

may be contrasted with the relative uncertainty in determining V (or M) using the original protocol which is now estimated to be greater than $\pm 1\%$.[11] All other experimental conditions for determinations $\omega 1$ through $\omega 4$ were comparable and similar to those for $\alpha 1$ through $\alpha 4$: $t_a = 1$–3 d; $8 \leq n_s \leq 12$ cocktails per determination; 1.1 g $\leq m_j \leq 1.4$ g in 15 ml of PCS; and $n_m = 10$–12 measurements per cocktails. The relative uncertainties v_R for each determination (given by the illustrated uncertainty interval bars in Fig. 2) were comparable for both the original and revised protocols. The relative standard deviation v_f, however, for the revised protocol is roughly 5 times smaller than that for the original protocol ($v_f = 0.8\%$ compared to $v_f = 4.2\%$). All subsequent evaluation data (and results) given here are based on use of this revised protocol.

Before addressing sample homogeneity (i.e., variation in ^{222}Rn concentration from sample to sample), it is useful to first consider the uncertainties associated with the LS measurements on any one sample. Fig. 3 provides estimates of the measurement precision (*repeatability*) v_C (defined previously) with $3 \leq n_m \leq 20$ on each determination (as obtained from independent evaluations with 183 different cocktails from a variety of generator runs). These v_C values vary somewhat widely, from about 0.2%

to well over 1%, and with a mean of 0.75% and median of 0.73%. The wide dispersion is just indicative of sampling v_C from a relatively broad χ^2 distribution of v_C^2. From evaluations of the total "counting error" v_P on each determination, one can in turn estimate the additional uncertainty component v_{LS} (see above uncertainty model discussion). The determinations were chosen to cover a range $0.05\% \leq v_P \leq 1.5\%$. These 183 estimates of v_{LS} are also illustrated in Fig. 3, and have a mean of 0.24% and median of 0.23%. It is apparent from the findings: that there is an additional component of variability v_{LS} in the LS measurement process (beyond that due to the "counting error" v_P); that the magnitude of this component is generally $v_{LS} \simeq 0.3\%$; and that the overall measurement variability v_C for n_m measurements on a single cocktail can be approximated by $v_C \simeq (v_P^2 + n_m v_{LS}^2)^{1/2}$, which has a corresponding standard deviation of the mean $v_C/\sqrt{n_m}$ which is generally in the range 0.3–0.4% for most determinations with $v_P \leq 0.1\%$. The estimates of v_{LS} were invariant of the magnitude of v_P, i.e., the v_P and v_{LS} components of v_C were uncorrelated. The magnitude of these v_C and v_{LS} uncertainty components comport well with those found in other measurements with our LS systems [18–22].

Homogeneity (or between-sample variability) was originally estimated to be the largest contributing source of uncertainty in the ^{222}Rn concentration in a given dispensed aliquant. This uncertainty component was presently evaluated in two ways: first, by consideration of the variation in measured R_j/m_j values for a set of samples

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[11] It is now believed that the originally reported relative uncertainty in determining V, given as 0.3% [2], was underestimated.
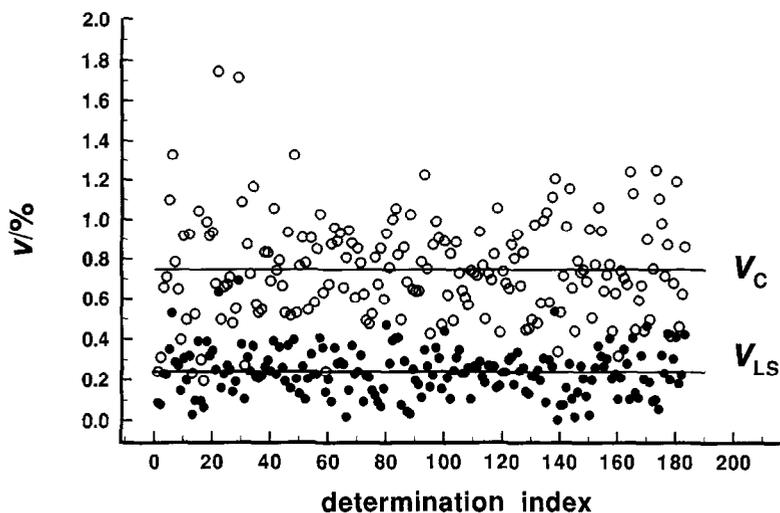
Fig. 3. Evaluations of the relative uncertainty components (in %) for the overall replication precision v_C for $3 \leq n_m \leq 12$ multiple measurements of a single cocktail and the LS measurement precision v_{LS} (as derived from 183 independent estimates of v_C and the total "counting error" v_P). Refer to text. The relative standard deviation of the mean $v_C/\sqrt{n_m}$ for any given cocktail is typically 0.3–0.4%.

obtained from any given generator run; and second, by consideration of R_j/m_j when the size of the aliquant m_j varied over a fairly large range. Additionally, it is evident that these variations would, of course, depend upon the adequacy of the mixing procedure in the operating protocol.

Now, in the first case, one can estimate the homogeneity from an evaluation of v_S as obtained from determinations of v_K and v_C (using an analysis similar to that given above for obtaining v_{LS} from v_P and v_C). Table 3 gives the results for v_S as obtained from 11 generator runs (each with cocktails having $f_w \simeq 0.1$ and $m_c \simeq 20$ g). Each run had a computed v_K (or v_R) for n_s dispensed samples (as tabulated). From the mean v_C obtained by averaging $v_{C(j)}$ across all samples within a given run (with each individual $v_{C(j)}$ computed from the results of n_m measurements on each sample), one can estimate the v_S for that run. As expected, v_K and v_S vary widely (again, considering the statistical sampling from broad χ^2 distributions of v_K^2 and v_S^2). For illustrative purposes, Fig. 4 gives relevant data for the first two runs. In Fig. 4(a), the computed v_K for the 9 dispensed samples was $v_K \simeq 1.2\%$. The mean v_C for the 9 samples was $v_C \simeq 0.67\%$ (with median $v_C \simeq 0.69\%$) which yields an estimate of $v_S \simeq 0.33\%$. In Fig. 4(b), the computed estimates of v_K and v_C are virtually equal, yielding an estimate of $v_S \simeq 0.$[12]

In the second case, Fig. 5 illustrates typical results for the relative invariance in the derived massic activity

Table 3
Evaluation of the relative standard deviation v_S (in %) for the sampling precision (homogeneity) as obtained from estimates of the relative standard deviations v_K and v_C in 11 generator runs

	v_K (%)	Mean v_C (%)	n_s	v_S (%)
	1.2	0.73	9	0.33
	0.74	0.75	7	—
	1.5	0.20	7	0.56
	1.0	0.23	7	0.38
	2.2	0.32	10	0.69
	0.93	0.65	10	0.21
	1.8	0.72	9	0.54
	1.4	0.85	7	0.40
	2.5	0.65	9	0.80
	1.3	0.44	9	0.41
	2.3	0.53	10	0.71
Median	1.4	0.65	9	0.47
Mean	1.5	0.55	8.7	0.50

K (proportional to R_j/m_j) obtained with cocktails having a large range of m_j. Each cocktail for this sample series was prepared with near constant $f_w \simeq 0.34$ (by the addition of a variable quantity of blank H_2O plus m_j to $\simeq 13$ g PCS) and $m_c \simeq 20$ g. The m_j-varying aliquants were dispensed in order of increasing m_j. As indicated there are no substantial differences in K between cocktails prepared initially with small aliquant sizes ($m_j < 1$ g) and with later ones having large multiple-gram aliquants. For comparative purposes with Table 3, v_K, in this case, was $v_K \simeq 0.95\%$ and the mean v_C (across all 25 cocktails) was $v_C \simeq 0.47\%$ (with median $v_C \simeq 0.45\%$), which yields an estimate of $v_S \simeq 0.2\%$.

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[12] In fact, v_S, in this case, is indeterminate with a magnitude of imaginary number (square root of a negative number) since the estimates of v_K and v_C had $v_C > v_K$.
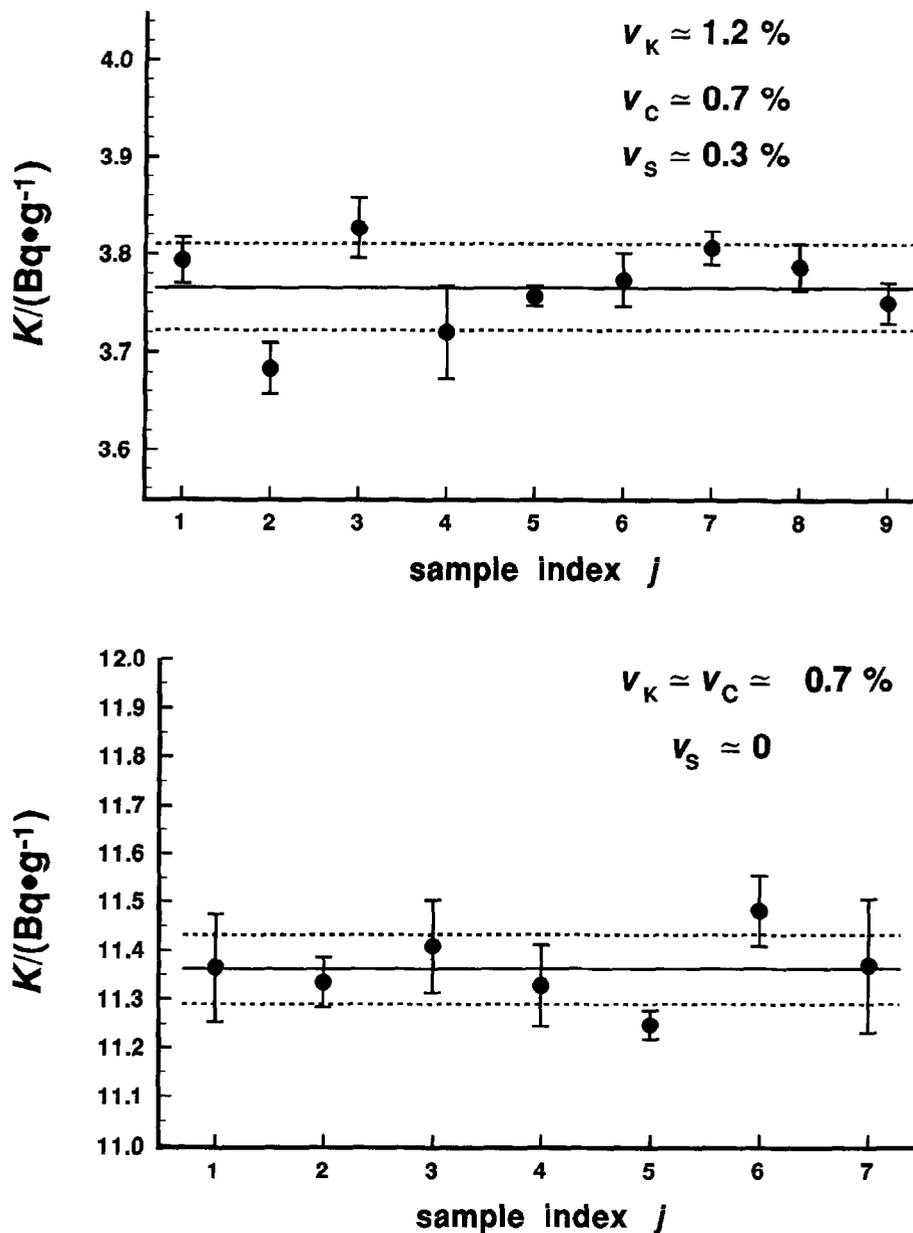
Fig. 4. Representative data for the LS-assayed ^{222}Rn activity concentration K (in units of Bq g^{-1}) in a series of dispensed aliquants with near constant m_j as obtained in two different generator runs (with $n_s = 9$ (upper) and $n_s = 7$ (lower) aliquants, respectively). The uncertainty interval on each datum corresponds to the standard deviation Kv_C for n_m replicate LS measurements on the given aliquant. The solid and dashed horizontal lines, respectively, correspond to the mean K obtained for the run and its standard deviation Kv_K interval for the n_s samples. The "sampling precision" v_S is derived from estimates of v_C and v_K (refer to text).

This same sample series could also be used to evaluate, very thoroughly, the conversion factor k_x for the dispensed mass of an aliquant per turn of the dispensing-syringe motordrive. Each aliquant was dispensed with a given number (or fraction) of turns and had a gravimetrically determined m_j for that aliquant. Hence, the conversion factor k_x could be evaluated for each dispensing

(Fig. 6). The mean k_x and standard deviation from this generator run (obtained with widely varying m_j, i.e., with $\frac{1}{4}$ to 7 turns) were $k_x = 0.7840 \pm 0.0012$ g (per turn). This precision is not typical, however, since extraordinary care was taken during this run to very precisely control the number of motordrive turns (particularly for the fractional numbers). Other evaluations of k_x from additional,
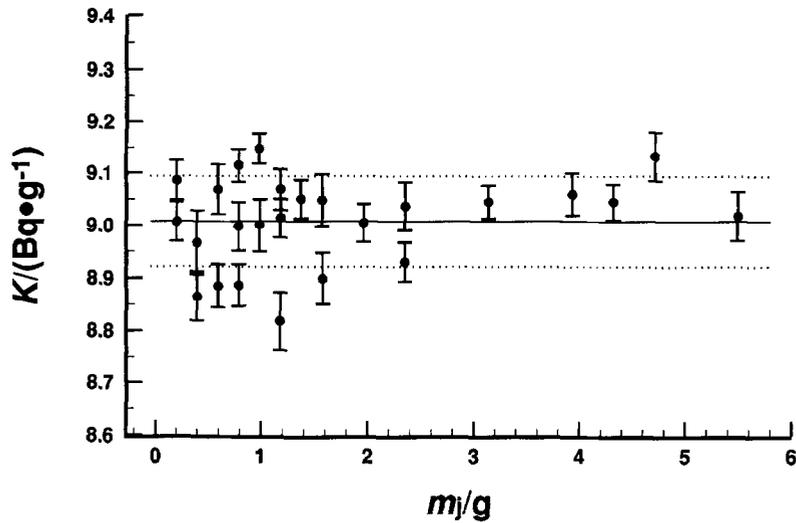
Fig. 5. ^{222}Rn activity concentration K (in units of $Bq\,g^{-1}$) as a function of dispensed aliquant mass m_j (in g) over a large m_j range. The uncertainty interval on each datum corresponds to the standard deviation Kv_C for n_m replicate LS measurements on the given aliquant. The solid and broken horizontal lines, respectively, correspond to the mean K obtained for the run and its standard deviation Kv_K interval for the n_s samples.
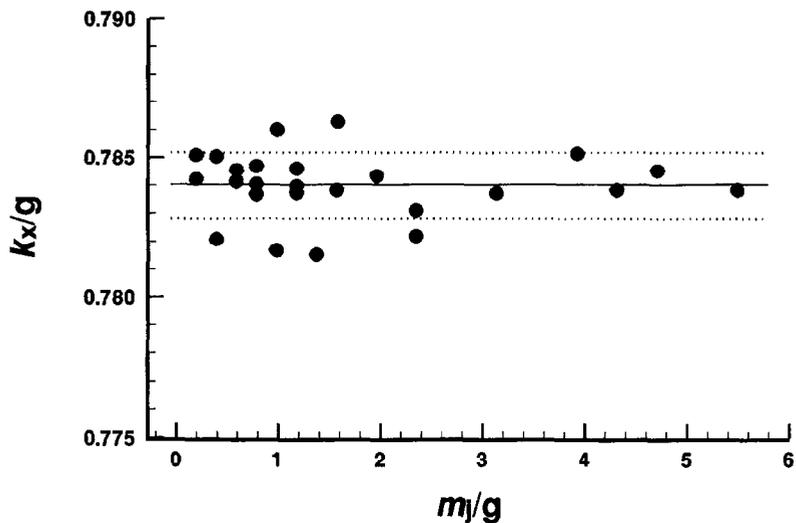

Fig. 6. Evaluation of the conversion factor k_x for the mass m_j (in units of g) of a dispensed aliquant per number of turns on the dispensing-syringe motordrive. The horizontal solid and dashed lines correspond, respectively, to the mean k_x and its standard deviation interval $k_x v_{kx}$.

more typical, generator runs are summarized in Table 4. The relative standard deviation v_{kx} computed on the grand mean $k_x = 0.7810\,g$ from the 10 generator runs was $v_{kx} \simeq 0.92\%$. Invariably, the uncertainty in k_x (from a particular generator run) is decidedly smaller when the aliquant dispensings have comparable m_j (i.e., are dispensed with equal numbers of turns), have larger m_j, or have an integral (non-fractional) number of turns. The uncertainty in k_x for a typical, routine operation (across

all m_j sizes) can be characterized in terms of a relative standard deviation of the mean $v_m(k_x)$ obtained from the quadratic combination of v_{kx} and a typical relative standard deviation *of the mean* $v_{kx(i)}/\sqrt{n_{s(i)}}$ for any given generator operation; i.e., $v_m(k_x) = [v_{kx}^2 + (v_{kx(i)}/\sqrt{n_{s(i)}})^2]^{1/2}$ since the between-run variability v_{kx} is not homogeneous with the within-run variability $v_{kx(i)}$. The typical $v_{kx(i)}$ may be taken to be the mean (or median) obtained from averaging across all 10 runs, which is

Table 4
Evaluation of the conversion factor k_x for the mass (in units of g) of dispensed solution per turn of the syringe motordrive as obtained in 10 generator runs. Each tabular k_x is that obtained from a given run with n_s dispensed aliquants having a range n_{turn}. The uncertainty estimator $v_{kx(i)}/\sqrt{n_{s(i)}}$ is the relative standard deviation of the mean (in %) for the given generator run

n_{turn} range	n_s	k_x (g)	$(v_{kx(i)}/\sqrt{n_{s(i)}})$ (%)
0.25–7	25	0.7840 ± 0.0012	0.031
0.25–7	8	0.7701 ± 0.0159	0.73
0.25–2.25	10	0.7752 ± 0.0231	0.94
0.25–1.5	7	0.7758 ± 0.0477	2.3
0.5–2	7	0.7725 ± 0.0208	1.0
2–8	7	0.7885 ± 0.0041	0.20
1–5	9	0.7900 ± 0.0081	0.34
1–6	15	0.7800 ± 0.0140	0.46
1–4	12	0.7875 ± 0.0063	0.23
1–5	9	0.7860 ± 0.0067	0.28
Grand mean		0.7810 ± 0.0072	0.65

0.65%. The propagation of $v_{kx} \simeq 0.95\%$ and typical $v_{kx(i)} \simeq 0.65\%$ results in an estimate $v_m(k_x) \simeq 1.1\%$.

To homogenize the ^{222}Rn solution prior to dispensing, the original operating protocol [2] utilized (and was found to require) two complete transfers of the solution between the two syringes. The transfers may be more clearly understood by reference to the schematic layout of the generator as given by Hutchinson, et al. [2]. The diluent blank H_2O (after passing through the accumulation chamber) first filled the left-hand side syringe (L). The ^{222}Rn-laden solution in L was then transferred to the right-hand side syringe (R), then back to L, back to R, and finally back to L for initiation of any dispensing. This invoked operation constituted (by definition) two complete mixing transfers, and was believed to be sufficiently adequate for obtaining a desired degree of solution homogeneity (< 1% differences amongst aliquants). The adequacy of this mixing procedure was re-examined in the present evaluations. Fig. 7 shows the variation in v_K and v_S as a function of the number n_x of mixing transfers. The conditions for each generator run were comparable with $7 \leq n_s \leq 9$ cocktails each containing approximately $m_j \simeq 1.5$ g aliquants in 18.5 g of RS scintillant. As before, v_S was estimated from the computed v_K for each generator run and the mean v_C obtained by averaging over all cocktails for the run. The results for v_S [Fig. 7(b)] suggest that there is a slight improvement in solution homogeneity with $n_x = 3$ compared to that obtained with $n_x = 2$. The improvement however is very slight. Nevertheless, the operating protocol was revised in late 1992 to routinely employ $n_x = 3$ (rather than $n_x = 2$) mixing transfers.

The most critical parameter for the generator, the ^{222}Rn emanation fraction f, was independently evaluated many times over the period from February 1989 to

March 1995. The results for K (for various generator runs) previously presented here constituted some of these f evaluations. The 26 evaluations of f considered here were obtained under a broad array of variable conditions. These include: (1) a ^{226}Ra source with varying "age" (i.e., the time interval between its initial preparation and the start of the accumulation for a given run) ranging from 0.3 a to 6.3 a; (2) variable accumulation times 0.9 d $\leq t_a > 30$ d; (3) somewhat constant, but nevertheless variable total dilution mass 53 g $\leq M \leq 58$ g (gravimetrically determined for each run); (4) variable numbers of mixing transfers $2 \leq n_x \leq 5$, although the first 19 of the 26 determinations were obtained with $n_x = 2$; (5) variable numbers of dispensed aliquants for a given generator run ranging from as few as $n_s = 6$ to $n_s > 20$; (6) prepared cocktails containing near constant m_j aliquants for a given run, as well as with variable 0.2 g $\leq m_j \leq 5$ g within a run; (7) varying f_w and m_c cocktail compositions, although most of these f determinations were obtained with $f_w > 0.07$ and $m_c \simeq 20$ g; (8) cocktails prepared with three different scintillants (Table 2); (9) variable numbers of LS measurements performed on each cocktail ranging $5 \leq n_m \leq 120$, but generally with $v_P < 0.1\%$; (10) LS measurements performed over time intervals of 2 d $> t_i > 12$ d [see Eq. (2)]; and (11) use of two different spectrometers for the measurements (Table 1). All of the f evaluations considered here utilized the "flushing" procedure given in the initial protocol [2] and the revised procedure for determining M by increasing the "dead volume" m_d and gravimetrically determining M_D (as described above). A majority of these f determinations were obtained from runs performed in the first 2 years of operation (i.e., up to 1991).

Fig. 8 gives the results of these 26 f evaluations which have a mean value of $f = 0.6255$. The uncertainty bars on each datum correspond to the computed v_K for that run. The mean v_K across all 26 runs was $v_K \simeq 1.29\%$ (with median $v_K \simeq 1.32\%$). The overall reproducibility in f (in terms of the relative standard deviation v_f) from the 26 evaluations was $v_f \simeq 1.55\%$. With these estimates of v_K and v_f, one can approximate the previously defined "generator precision" v_G to be 0.2%. Re-examination of Fig. 2, alongside Fig. 8, clearly demonstrates the vastly improved precision obtained in going to the protocol revisions. These results also support the conclusion that the total dilution mass M can be determined to a precision of a few tenths of a percent, but that the uncertainty in the volume-based dilutions (for the original protocol [2]) was seriously underestimated previously.

Scientific instinct dictates that two of the more likely variables that may affect f are the "age" of the ^{226}Ra capsule t_{age} and the accumulation time t_a. Fig. 9 demonstrates the invariance in f with both variables. Fig. 9(b) includes some additional points with $t_a < 1$ d not included in the data of Fig. 8. For these comparisons, it must be emphasized that other variables were not
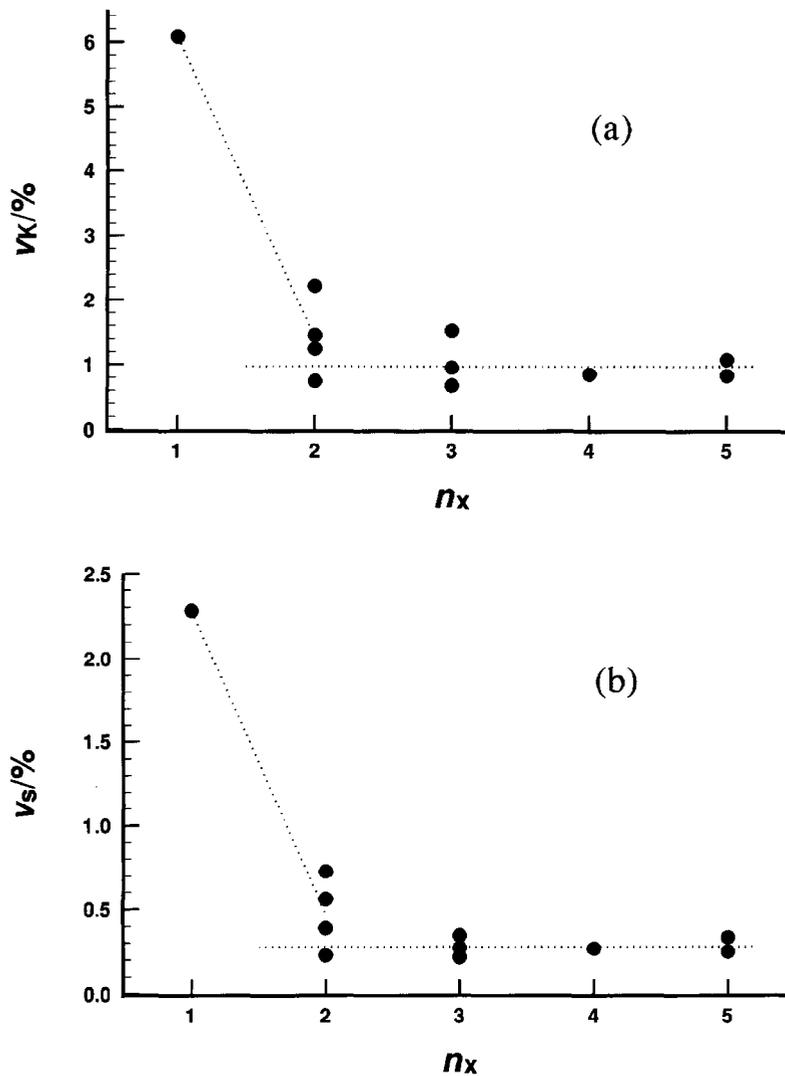
Fig. 7. Variation in the uncertainty estimators v_K and v_S as a function of the number of syringe-transfer mixes n_x.

necessarily held constant (nor were they completely randomized). In particular, the invariance of f with t_{age} was obtained under systematic conditional changes. All initial f determinations (at young t_{age}) were obtained by operating the generator with only $n_x = 2$ mixings. The dispensed aliquants from these initial runs formed aliquants with only the PCS scintillant (Table 2) that were measured only with the system B spectrometer (Table 1). In contradistinction, the more recent f determinations were obtained with $n_x > 3$ mixings and utilized cocktails that were formed with IG and RS scintillants that were in turn measured with both the B and P spectrometers. In addition, the initial air void in the ^{226}Ra capsule (mentioned previously) also continuously diminished with time.

Equally, the temperature of the ^{222}Rn accumulations (as it may affect the solubility and diffusion of radon out of the polyethylene capsule and into the water of the accumulation chamber) was uncontrolled (and largely unmonitored). The f evaluations were performed, however, during all seasons which have known ambient temperature variations ranging from about 17°C to 25°C. The experimentally-determined (and empirically-defined) f for the generator is thereby considered to be valid for a temperature range of 21 ± 3°C. Inasmuch as the encapsulated ^{226}Ra source is wholly immersed in the H_2O of the accumulation chamber and that it appears to act as a purely-diffusive device (with no permeation component) [2], effects due to ambient humidity or atmospheric pressure changes are believed to be non-existent or negligible.

Finally, three other evaluations were also performed. One was to test the adequacy of the "flushing" procedure
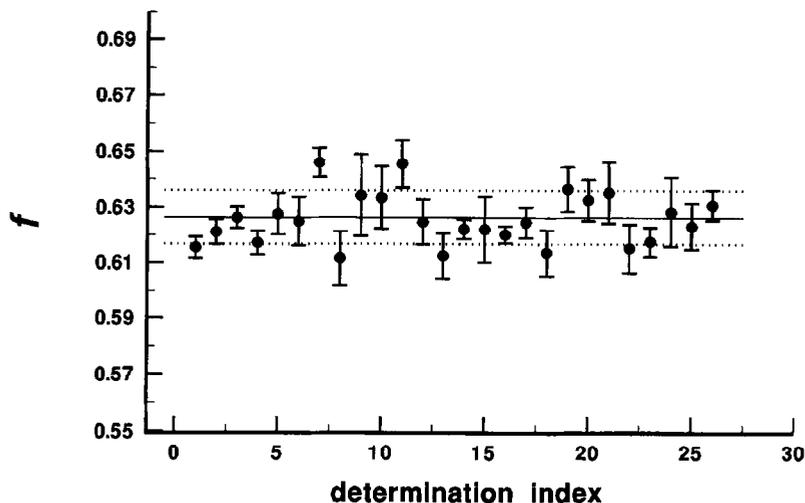
Fig. 8. Evaluation of the ^{222}Rn emanation fraction f for the Radon-In-Water Standard Generator as obtained from 26 evaluations over a period of about 6 years under many variable conditions (see text). The horizontal solid and broken lines correspond, respectively, to the mean f and its standard deviation interval $f v_f$.

to ensure proper initialization conditions for an accumulation (i.e., that the steady-state boundary conditions for the diffusion of radon out of the capsule were reproducibly achieved). The flushing is performed to obtain, at the start of an accumulation ($t_a = 0$), a virtual zero ^{222}Rn concentration in the water contained in the accumulation chamber, and a steady-state diffusive flux of ^{222}Rn out of the polyethylene. The tests were performed by varying both the flushing duration and volume flow rate of rinse H_2O and examining the predicted accumulated ^{222}Rn activity for relatively short ($0.3\,d < t_a < 1\,d$) accumulations. The extant protocol [2] (which consists of an initial rinse of about 50 ml of "radon-free" H_2O, followed by continuous flushing at a flow rate of about $0.1\,1\,h^{-1}$ for a minimum of 6 h to remove any excess ^{222}Rn dissolved in the polyethylene, and finally by a 50 ml rinse that is performed as rapidly as possible) was found to be wholly adequate. A second evaluation was to independently assess the reproducibility in determining the "dead volume" m_d (i.e., the reproducibility in returning the syringes to their starting positions) by replicate measurements of the dilution mass m_D under conditions of near constant $m_d \simeq 1.55$ g and $M = m_d + m_D \simeq 55$ g. This test was intended to independently verify the uncertainty estimator v_G (which contains the uncertainty in determining M) and in estimating the uncertainty on m_d. Gravimetric determinations of m_D from six closely-controlled trials resulted in a relative standard deviation of $v(m_D) \sim 0.14\%$. With $v_M = [(m_d/M)^2 v(m_d)^2 + (m_D/M)^2 v(m_D)^2]^{1/2}$ and assuming that $v_G \simeq 0.2\%$ is wholly due to the relative standard deviation v_M, one obtains an estimate of $v(m_d) \simeq 5.2\%$ (which corresponds to an uncertainty in m_d of about ± 0.08 g). This comports reasonably well with our geometrically-based estimate of $m_d \simeq$

1.55 ± 0.15 g. A third evaluation was to routinely test for possible ruptures or leakage losses of ^{226}Ra from the capsule. This was rather easily performed by LS measurements of cocktails (containing large-volume dispensed aliquants from the generator) after either long ^{222}Rn decay-time intervals (> 40 d) or after purging the ^{222}Rn from the cocktails and merely waiting for the short-lived ^{214}Pb–^{214}Bi–^{214}Po subseries to decay (> 6 h). No losses of ^{226}Ra from the capsule were ever detected, thereby ensuring the integrity of the source and that the ^{222}Rn solutions obtained from the generator (and subsequent ^{222}Rn calibrations) are indeed "radium free".

A considerable number of additional statistical analyses beyond those reported here were performed on the vast data set obtained from these evaluations. They included: (1) sequential time-series analyses to determine if there were any time dependencies or correlations in the order of samples or order of measurements for the various evaluated parameters (e.g., R_j/m_j for a given cocktail within a n_m measurement sequence) or in the various statistical estimators (e.g., v_C or v_K); (2) regression analyses between various combinations of variables (e.g., R_j/m_j versus m_j for cocktails within a given run or for f versus M between runs); (3) divisions of the data (e.g., for quantities like R_j/m_j, v_K, or f) into classes (e.g., those obtained with one scintillant compared to those obtained with the other scintillants, or with one spectrometer versus the other) and testing the resulting subsets of data for differences in the various means using t-tests, and for the homogeneity in the various subset means and variances using χ^2- and F-tests; and (4) sequential two-variable analysis-of-variance (ANOVA) techniques for any differences in similarly constructed subset means and variances. None of the tests (excepting the m_j and
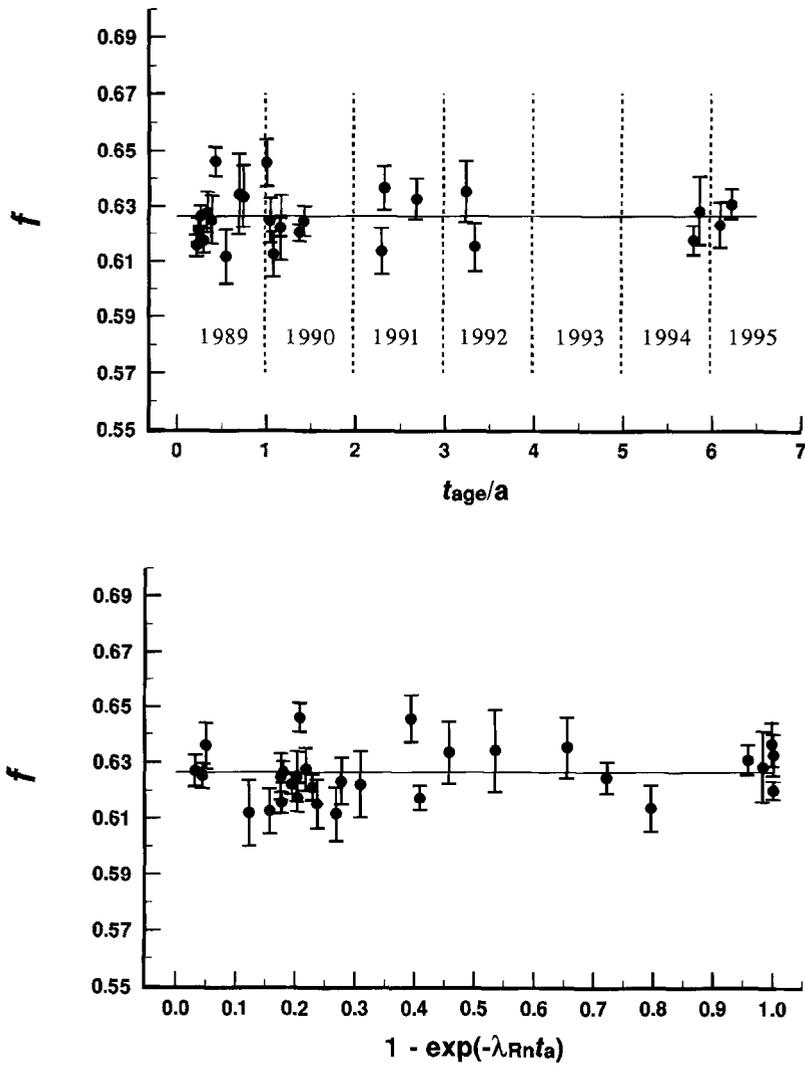
Fig. 9. ^{222}Rn emanation fraction f as functions of the "age" t_{age} (in units of a) of the ^{226}Ra encapsulated source (upper trace) and the accumulation factor $[1 - \exp(-\lambda_{Rn}t_a)]$ for ^{222}Rn growth and accumulation (lower trace).

fractional-turn dependencies on k_x noted above) indicated that there were any statistically significant differences in any of the time dependencies, correlations, or differences in the tested subset sample means and variances.

5. Generator parameters and uncertainty assessments

Uncertainty evaluations need to consider two distinct assessments. Firstly, there is the assessment needed to evaluate the uncertainties associated with the parameters for the generator's operation. Secondly, and more importantly, is the assessment needed to assign a realistic uncertainty to the total ^{222}Rn activity content A or activity concentration K in an aliquant dispensed from

the generator (when appropriately derived by rigorously invoking the operating protocol). In addition to the statistically evaluated uncertainties (given above), additional uncertainties requiring evaluation are those associated with the activity of the ^{226}Ra source, with the mass determinations, and with the radioactive decay and accumulation (^{222}Rn growth) factors.

The statistically-evaluated uncertainties v_P, v_C, v_{LS}, v_R (or v_K), v_S, v_f, v_G(or v_M), and $v_m(k_x)$ (as defined previously) can be summarized in a very general way as given in Table 5. The quality of these estimates can be characterized in terms of either the degrees of freedom associated with each (given previously) or the variability obtained from replicate evaluations (i.e., the "uncertainty in the uncertainty") of the same estimator (e.g., the

Table 5
Summary of the statistically evaluated uncertainties obtained from the present evaluations of the Radon-In-Water Standard Generator

Estimator	Relative standard deviation
v_P	variable, but generally $v_P < 0.2\%$
v_C	Largely depends on n_m (and v_P), but generally $v_C/\sqrt{n_m} \simeq 0.4\%$
v_{LS}	0.2%
v_R (or v_K)	Largely depends on n_s (and v_C), but generally $v_K/\sqrt{n_s} \simeq 0.5\%$
v_S	0.5%
v_f	0.3%
v_G	0.2%
$v_m(k_x)$	1.1%[a]

[a] $v_m(k_x)$ is a relative standard deviation of the mean for 9 degrees of freedom.

replicate evaluations of v_C and v_{LS} given in Fig. 3 or those for v_K and v_S given in Table 3). If, of course, one had perfect knowledge of the underlying distributions from which the quantities were sampled, then the degrees of freedom would reveal these "uncertainties in the uncertainties." Examinations of the data sets for the various estimators like v_C, v_{LS}, v_R, v_S, or v_{kx} indicates that the relative uncertainty on these uncertainties are typically 50–200% (but can, as seen in some cases, substantially vary more widely). One must therefore recognize that such uncertainty estimators (or any that follow) are very crude, rough quantifications that reflect only general magnitudes or their orders. It is not an extreme statement to generalize that uncertainty estimators for complex experiments with many uncertainty components (even when the experiments are very carefully controlled and when the quantity of available data is vast) are usually very, very poorly known. One should not then place too much emphasis on any explicitly cited magnitude. To wit, for all intensive purposes two relative uncertainties quoted as, for example, 0.8% and 1.2% must be viewed as essentially equal with magnitude of about 1%.

The generator, as presently evaluated, may be described in terms of the parameters [see eq. (1)] and conditions:

$f = 0.625 \pm 0.005$;
$A_0 = 1167 \pm 6$ Bq;
(as of $t_0 = 1200$ EST 9 September 1991);
$\lambda_{Ra} = (1.186 \pm 0.005) \times 10^{-6}$ d^{-1};
t_d = variable from t_0, but presently $t_d > 1.7(\times 10^3)$ d;
$\lambda_{Rn} = 0.18130 \pm 0.00002$ d^{-1};
t_a = variable, but typically $t_a > 1$ d for best precision;
M = variable, with $M = m_d + m_D$ (best precision obtained with $M \simeq 55$ g);
$m_d = 1.55 \pm 0.15$ g;
$k_x = 0.784 \pm 0.009$ g.

The cited uncertainty (defined to be a standard uncertainty) on each of these, excepting that for f, were given in context earlier. That for f is summarized in Table 6. The uncertainty in the total ^{222}Rn activity A (or activity concentration K) for a time t_2 at the end of an accumulation in a given dispensed aliquant from a typical generator run is summarized in Table 7. The assessment in Table 7 assumes that all masses (i.e., those required to obtain m_D as well as the dispensed aliquant m_j) were determined by careful gravimetric measurements. The additional uncertainty that results from use of the "mass per unit turn" conversion factor k_x will be addressed subsequently. To avoid uncertainty correlations (or "double accounting" of uncertainty components such as for A_0), Table 7 utilizes only the reproducibility in f (given by $v_f \simeq 0.3\%$) instead of the entire combined standard uncertainty in f of about 0.8% (Table 6). In addition, however, for any given run (generator operation), one must incorporate the attendant variabilities due to sampling precision (solution homogeneity) v_S and generator precision v_G (the latter of which largely consists of v_M).

It must be emphasized that the assessment of Table 7 is applicable only if m_D is obtained by mass measurements. If M is estimated volumetrically, as in the original protocol [2], then the expanded uncertainties on A and K are likely to be several fold that given in Table 7 (i.e., probably > 3%). This is apparent from re-examination of the between-run reproducibility in Fig. 2. In addition, if the dispensed aliquant m_j is estimated by use of the k_x "mass per unit turn" conversion factor, then the uncertainty component for m_j in Table 7 must be increased to $\sqrt{10 \cdot v_m(k_x)} \simeq 3.5\%$ for any one dispensed aliquant. This

Table 6
Assessment of the uncertainty in the ^{222}Rn emanation fraction f for the Radon-In-Water Standard Generator, given in terms of the relative standard uncertainty (in %) for each uncertainty component

Uncertainty component	Standard uncertainty
Reproducibility v_f in determining f from 26 independent evaluations under many variable conditions	0.30%
Typical LS detection efficiency $\varepsilon_s q$ used to determine ^{222}Rn activity	0.6%
^{226}Ra activity A_0 in source	0.47%
^{226}Ra decay corrections, $\exp(-\lambda_{Ra} t_d)$	< 0.001%
^{222}Rn decay corrections for LS measurements, $\exp(-\lambda_{Rn} T_i)$	< 0.0001%
typical ^{222}Rn growth accumulation factors, $[1 - \exp(-\lambda_{Rn} t_a)]$	< 0.05%
Gravimetric measurement of any one aliquant m_j for LS measurements	0.05%
Gravimetric determination of $M = m_d + m_D$	0.15%
Combined standard uncertainty	0.84%

Table 7

Assessment of the uncertainty in the ^{222}Rn activity concentration K or total activity $A = Km_j$ in an aliquant m_j dispensed from the Radon-In-Water Standard Generator, given in terms of the relative standard uncertainty (in %) for each uncertainty component

Uncertainty component	Standard uncertainty
Reproducibility v_f in determining f from 26 independent evaluations under many variable conditions	0.3%
Sampling precision v_s, including solution homogeneity (sample-to-sample variability)	0.5%
Generator precision v_G, largely reflecting the run-to-run reproducibility in determining M	0.2%
^{226}Ra activity A_0 in source	0.47%
^{226}Ra decay corrections, $\exp(-\lambda_{Ra}t_d)$	< 0.001%
Typical ^{222}Rn growth accumulation factor, $[1 - \exp(-\lambda_{Rn}t_a)]$	< 0.05%
Gravimetric measurement of any one aliquant m_j	0.05%[a]
Gravimetric determination of $M = m_d + m_D$	0.2%
Combined standard uncertainty	0.80%
Expanded uncertainty ($k = 2$)	1.6%

[a] Required only for the uncertainty in the total ^{222}Rn activity $A = Km_j$ in a dispensed aliquant of mass m_j, not for the uncertainty in K.

uncertainty component would obviously dominate the uncertainty in $A = Km_j$. The k_x-factor operating option was incorporated only for user convenience, and its use is not recommended except for applications that do not require a measurement accuracy of better than 5–10%.

6. Summary

The performance efficacy and long-term stability of the NIST Radon-In-Water Standard Generator, previously developed and described [2], has been exhaustively evaluated over a period approaching 7 years.

Two revisions to the original operating protocol have been incorporated; viz., a minor one of increasing the number of syringe-transfer mixings n_x from 2 to 3 (to improve solution homogeneity), and a more substantive change in the method used to determine the total ^{222}Rn solution volume (or mass M) by gravimetric means (to obtain substantially improved reproducibility in the ^{222}Rn concentration in a dispensed aliquant between generator runs). Evaluations of the ^{222}Rn emanation fraction f, the most critical generator parameter, have demonstrated that it has remained constant with a relative standard deviation of the mean of about 0.3%, which indicates that the encapsulated ^{226}Ra source has not deleteriously aged or degraded with time.

The uncertainty (a relative combined standard uncertainty multiplied by $k = 2$) associated with the ^{222}Rn activity concentration K or total activity A in any given dispensed aliquant from the generator (when the generator is operated by following the prescribed protocol) is typically $\pm 1.6\%$.

The laboriously presented uncertainty treatments (with its attendant statistical-analysis model), as presented herein, may have pedagogic value for other researchers. The treatments clearly delineate the nature of nested uncertainties; which are associated with n_m multiple measurements on any given sample, with n_s multiple samples obtained from any given experimental trial (such as from particular runs of the generator as given here), and with multiples of such trials. Appropriate analyses of computed statistics (e.g., the standard deviations of directly measured quantities) can be used to derive underlying, inherent uncertainties in the measurement system itself (e.g., those for v_{LS}, v_s, and v_G given herein). Continuous monitoring (and evaluations) of these system uncertainties can, and will prove to be of great benefit for routine monitoring of the performance of measurement systems and/or of assessing the quality of resultant measurement data obtained from those systems.

Disclaimer

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 are the best available for the purpose.

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