

An international intercomparison of marine atmospheric radon ^{222}Rn measurements in Bermuda

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Abstract. As part of an international measurement intercomparison of instruments used to measure atmospheric ^{222}Rn , four participating laboratories made nearly simultaneous measurements of ^{222}Rn activity concentration in commonly sampled, ambient air over approximately a 2-week period, and three of these four laboratories participated in the measurement comparison of 14 introduced samples with known, but undisclosed (“blind”) ^{222}Rn activity concentrations that could be related to U.S. national standards. The standardized sample additions were obtained with a calibrated ^{226}Ra source and a specially designed manifold used to obtain well-known dilution factors from simultaneous flow rate measurements. The exercise was conducted in Bermuda in October 1991. The ^{222}Rn activity concentrations in ambient Bermudian air over the course of the intercomparison ranged from a few hundredths to about 2 Bq m^{-3} , while the standardized sample additions covered a range from approximately 2.5 to 35 Bq m^{-3} . The overall uncertainty in the latter concentrations was in the general range of 10% at a 3 standard deviation uncertainty interval. The results of the intercomparison indicated that two of the laboratories were within very good agreement with the standard additions and almost within expected statistical variations. These same two laboratories, however, at lower ambient concentrations, exhibited a systematic difference with an averaged offset of roughly 0.3 Bq m^{-3} . The third laboratory participating in the measurement of standardized sample additions was systematically low by about 65–70%, which was also confirmed in their ambient air concentration measurements. The fourth laboratory, participating in only the ambient measurement part of the intercomparison, was also systematically low by at least 40% with respect to the first two aforementioned laboratories.

1. Introduction

In October 1991 an international measurement intercomparison of instruments used to measure trace atmospheric concentrations of ^{222}Rn (radon) was organized by Drexel University and conducted at the Atmosphere/Ocean Chemistry Experiment (AEROCE) test site located at Tudor Hill, Bermuda, which is operated in conjunction with the Bermuda Biological Station for Research, Inc. This intercomparison comprised two parts: (1) measurement comparisons among four laboratories of commonly sampled ambient air over approximately a 2-week test period, and (2) measurement comparisons among three of these four laboratories of a select

number of introduced samples with known radon activity concentration.

Measurements of atmospheric radon in remote marine environments are used to obtain information on the temporal and spatial distributions, which are in turn used to test and validate global models that simulate the transport and removal of trace atmospheric species from continental air masses. Unlike other chemical species, radon is an excellent tracer for such studies because it has a well-characterized source (large landmasses from which radon diffuses ubiquitously) and only one principal “sink” (radioactive decay). For such measurement data to be useful, however, particularly when collected by different laboratories at different global sites using diverse instruments that are based on widely different collection and measurement principles, it is necessary that the collected data have at least a common relative, if not an absolute, reference basis. The intent of this intercomparison was to provide that basis for the participating laboratories.

The participating laboratories in the intercomparison were Environmental Measurements Laboratory, U.S. Department of Energy (New York); Atmospheric Chemistry Laboratories, Drexel University (Philadelphia, Pennsylvania, U.S.A.); Australian Nuclear Science and Technology Organisation (Menai, New South Wales); and the Centre des Faibles Radioactivités, Laboratoire Mixte Centre National de Recherche Scientifique–Commissariat à l’Energie Atomique (Gif-Sur-Yvette,

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France); hereinafter referred to as Lab E, Lab D, Lab A, and Lab F, respectively. The first three laboratories performed simultaneous measurements from a common streamline on an ambient air sampling tower. Lab F, in contradistinction, sampled ambient air nearly adjacent to the inlet of the sampling tower and therefore participated in only the ambient air inter-comparisons.

The National Institute of Standards and Technology (NIST) was invited to participate in this intercomparison to serve as the “referee” and, if possible, to provide an “absolute” reference basis for the participants’ measurements. The planned scheme for the latter role consisted of NIST’s being able to provide standardized sample additions of known, but undisclosed (“blind”) radon concentrations that could be related to U.S. national standards. The standardized sample additions were to be introduced over sampling periods of several hours into a common streamline on the sampling tower used by the participants for their measurements. In addition to being a “blind” intercomparison in terms of the radon activity concentrations, the timing and duration of the standard sample additions were also largely unknown to the participating laboratories. Radon concentrations for the sample additions were planned to vary from approximately a few times typical ambient concentration levels up to about 1000 times ambient. This necessitated being able to provide well-known sample dilutions over a wide dynamic range.

The sample additions were made with a commercially available, solid ^{226}Ra source, calibrated by NIST in terms of the available ^{222}Rn concentration as a function of flow rate through the source. The source was employed in conjunction with a sampling and dilution gas-handling manifold also provided by NIST. Grab samples from the sampling streamline were also taken with sample bulbs that were returned to NIST for assaying the ^{222}Rn concentration. These grab samples were taken as confirmatory measurements to ensure that the source and manifold were not performing differently at the test site than at NIST, where the source calibrations were made.

2. Measurement Methods of the Participating Laboratories

Each of the instruments and measurement methodologies employed by the four participating laboratories were based on different analytical approaches. The main characteristics for each are summarized in Table 1.

The instrumentation used by Lab E was based on a two-filter ^{222}Rn measurement method [Thomas and LeClare, 1970]. Simply, the method consists of the following. Sample air is pumped through two filters in series that are separated by a large decay volume to permit decay of the radon. The first filter removes all progeny in the ^{222}Rn subseries ($^{218}\text{Po} - ^{214}\text{Pb} - ^{214}\text{Bi} - ^{214}\text{Po}$). In the decay volume, some of the ^{222}Rn in the flow stream undergoes radioactive decay, producing new progeny. These progeny are collected on the second, downstream filter and measured with an α -sensitive scintillation detector. The ^{222}Rn concentration in the sample air is derived from the resulting α activity counting rate. The Lab E instrument consists of a 500-L cylindrical decay chamber and utilizes flow rates typically ranging from 350 to 400 L min^{-1} . The instrument is fully automated. The second filter is configured as a ribbon, capable of forward and backward motions that allow rewinding of the filter [Guggenheim and Negro, 1990]. For this intercomparison exercise, the instrument used 1-hour sampling

intervals to collect the ^{222}Rn progeny, after which the filter was transported to a ZnS(Ag) detector for 1-hour measurement intervals. While one section of the filter is being counted, another section is used in sampling.

The instrument used by Lab A was modeled on that described by Whittlestone [1985]. The methodology is based on a modification of the two-filter method that incorporates an aerosol particle generator. Its main principles of operation are as follows. Sample air was continuously pumped at a flow rate of 40 L min^{-1} through a 200-L drum to allow decay of short-lived (55-s half-life) ^{220}Rn (thoron), then through an absolute filter into a large 2000-L plastic chamber. Submicron particulate condensation nuclei (CN) were injected into the chamber so that the ^{222}Rn progeny would become attached to the CN rather than to the chamber walls. The attached progeny, after an average residence time of 50 min in the chamber, were filtered onto a membrane filter that was continuously monitored with a ZnS(Ag) scintillator. Average ^{222}Rn concentrations were inferred from 30-min accumulations of counts from the decay of the ^{222}Rn progeny on the filter. A calibrated CN counter was incorporated into the system to account for changes in the detector efficiency as a function of CN concentrations.

The ^{222}Rn measurement results of Lab F were based on inferring ^{222}Rn concentrations from collection and assay of the short-lived ^{222}Rn progeny that are attached to aerosols in ambient air. The methodology assumes that the ^{222}Rn and its progeny are in radioactive equilibrium (or are in a state of known equilibrium ratio). The assumption of radioactive equilibrium (with an equilibrium ratio of unity) is usually considered to be valid at sampling locations distantly far from continental sources of radon and not influenced by local landmasses. The instrument used by Lab F consisted of a large circular filter fixed on a rotating disk that divided the filter into 12 sampling locations. The instrument was automated for simultaneous 2-hour sampling and measurement intervals. After an aerosol sample was collected at one sampling location on the filter, it was automatically rotated to an α -sensitive scintillation detector for counting while the next sample was collected.

The methodology utilized by Lab D was a nonfilter method based on separating radon from air samples and subsequently assaying it in one of six Lucas-type ZnS(Ag) scintillation cells. The instrument was fully automated and operated with the following sequential steps. An air sample at a flow rate of 28 L min^{-1} was aspirated into the instrument, compressed and dried, and flowed through a cooled charcoal trap where the radon was separated from the air stream by adsorption. Following a 2-hour sampling interval, the collected radon was heat and vacuum transferred to a secondary cooled charcoal trap to effect separation with other gases contained in the main charcoal trap. A preevacuated scintillation cell, having a predetermined background counting rate, was then filled by transferring the radon from the secondary trap. Sample separation and processing times were of the order of 2.5 hours and, with the 2-hour sampling interval, resulted in a sampling frequency to about one sample every 4.5 hours. Reported ^{222}Rn activity concentrations were derived from the total α -counting rates from the scintillation cells after about 4 hours, when the ^{218}Po and ^{214}Po progeny follow ^{222}Rn decay in transient equilibrium.

Table 1. Comparative Summary of the Instruments and Measurement Methodologies Used by the Participating Laboratories

	Lab E	Lab A	Lab D	Lab F
Instrument and methodology	automated, intermittent two-filter tube method; 500-L decay chamber; moveable filter ribbon	continuous two-filter tube method; 200-L drum followed by 50-min residence in 1000-L chamber with introduced condensation nuclei (controlled and calibrated)	automated, intermittent, cryogenic separation of ^{222}Rn from air on charcoal; transfer to counting cells	automated, intermittent collection of ^{222}Rn progeny on filters; infer ^{222}Rn with equilibrium ratio assumptions; rotating tray of 12 filters
Detector	ZnS(Ag) scintillator for α detection	ZnS(Ag) scintillator for α detection	six Lucas-type ZnS(Ag) scintillation cells for α detection	α -sensitive scintillator
Sampling flow rate	350–400 L min ⁻¹	40 L min ⁻¹	28 L min ⁻¹	200 L min ⁻¹
Sampling and measurement time	1-hour sample collection on moveable filter; 1-hour measurement of filter	continuous measurement “smoothed” by 90-min time constant; 1 hour measurement intervals reported; 30-min filter accumulation	2-hour sample collection every 4.5 hours; multiple-hour measurement after secular equilibrium	2-hour sample collection on moveable filter; 2-hour measurement of filter
Sensitivity (efficiency/detection limit)	0.1 count s ⁻¹ (Bq m ⁻³) ⁻¹ ; LLD = 0.12 Bq m ⁻³ equivalent ^{222}Rn concentration	0.25 count s ⁻¹ (Bq m ⁻³) ⁻¹ ; LLD = 0.01 Bq m ⁻³ equivalent ^{222}Rn concentration	LLD = 0.004 Bq m ⁻³ equivalent ^{222}Rn concentration	25% α -counting efficiency; LLD = 0.0004 Bq m ⁻³ equivalent ^{222}Rn concentration
Background	measurement every 30 hours; 0.02 counts s ⁻¹ ; known thorium contamination	<0.02 Bq m ⁻³ equivalent ^{222}Rn concentration	2-hour background counts on each cell before each measurement; 0.07–0.17 Bq equivalent ^{222}Rn concentration	0.0006 counts s ⁻¹
Calibration	in EML Radon, Thoron, and Progeny Exposure Facility	internal, solid $^{226}\text{Ra}/^{222}\text{Rn}$ reference standard; and with standardized ^{222}Rn injection at ANSTO	internal, commercial (Pylon) $^{226}\text{Ra}/^{222}\text{Rn}$ reference standard	α efficiency relative to β^- counting of ^{222}Rn progeny in equilibrium on same kind of filter
Uncertainty	overall calibration uncertainty <10%; see discussion in section 4.1 for statistical (Poisson) counting precision	calibration accuracy $\pm 15\%$; see discussion in section 4.1 for statistical (Poisson) counting precision	± 3.4 to $\pm 3.9\%$ over intercomparison concentration range; measurement precision $\pm 2.8\%$ over range (see discussion in section 4.1).	$\pm 2\%$ α -counting efficiency precision; overall estimated uncertainty $\pm 20\%$ in range 0.07–0.02 Bq m ⁻³
References	Thomas and LeClare [1970], Negro [1979], Guggenheim and Negro [1990], Chieco <i>et al.</i> [1992], R. J. Larsen (private communications, 1992–1994)	Whittlestone [1985, 1990], Gras and Whittlestone [1992], Whittlestone <i>et al.</i> [1992], S. Whittlestone (private communications, 1992–1994)	G. Polian (private communication, 1992)	J. G. Kay (private communications, 1992–1993)

Participating laboratories are as follows: Lab E, Environmental Measurements Laboratory (EML); Lab A, Australian Nuclear Science and Technology Organisation (ANSTO); Lab D, Atmospheric Chemistry Laboratories, Drexel University; and Lab F, Centre de Faibles Radioactivités. LLD, lower limit of detectability.

3. NIST Calibration and Standardized Sample Additions

3.1. Instrumentation and Methodology

The experimental arrangement used for the intercomparison is illustrated in the schematic of Figure 1. Ambient air was sampled continuously from the top of a sampling tower located at the Tudor Hill, Bermuda, test site. The sampling stack consisted of a nominal 10.2-cm-diameter aluminum tube whose inlet was approximately 20 m above ground level. The inlet at the top of the tube was a gooseneck, which was inverted to minimize the intake of rain and covered with a plastic mesh to prohibit the intake of birds, insects, etc. A similar diameter polyvinyl chloride (PVC) tube was coupled to the aluminum tube about 2.5 m above a horizontal section of the stack that was used by the participants. Air flow within the tube was maintained by sampling pumps that were part of the measurement instrumentation for three of the participating laboratories (Labs A, D, and E). These instruments were located at the

terminus of the horizontal section. One laboratory (Lab F) performed measurements at the top of the sampling tower nearly adjacent to the inlet and, as was mentioned previously, did not participate in the intercomparison of standardized additions. The standardized additions of known ^{222}Rn activity concentration, with known dilution factors, were made into the sampling stack at ground level at the foot of the sampling tower as shown in Figure 1.

The NIST manifold was designed to obtain known radon concentrations from a calibrated ^{226}Ra source, to provide standardized dilutions of this concentration, and to introduce them into the sampling streamline. The manifold also allowed the filling of sample bulbs that were used for confirmatory measurements of the provided radon concentration.

In an ideal situation it would have been desirable to conduct this experiment using “radon-free” air rather than ambient air and to provide standardized additions in a way that would be independent of the varying flow rate demands of the partici-

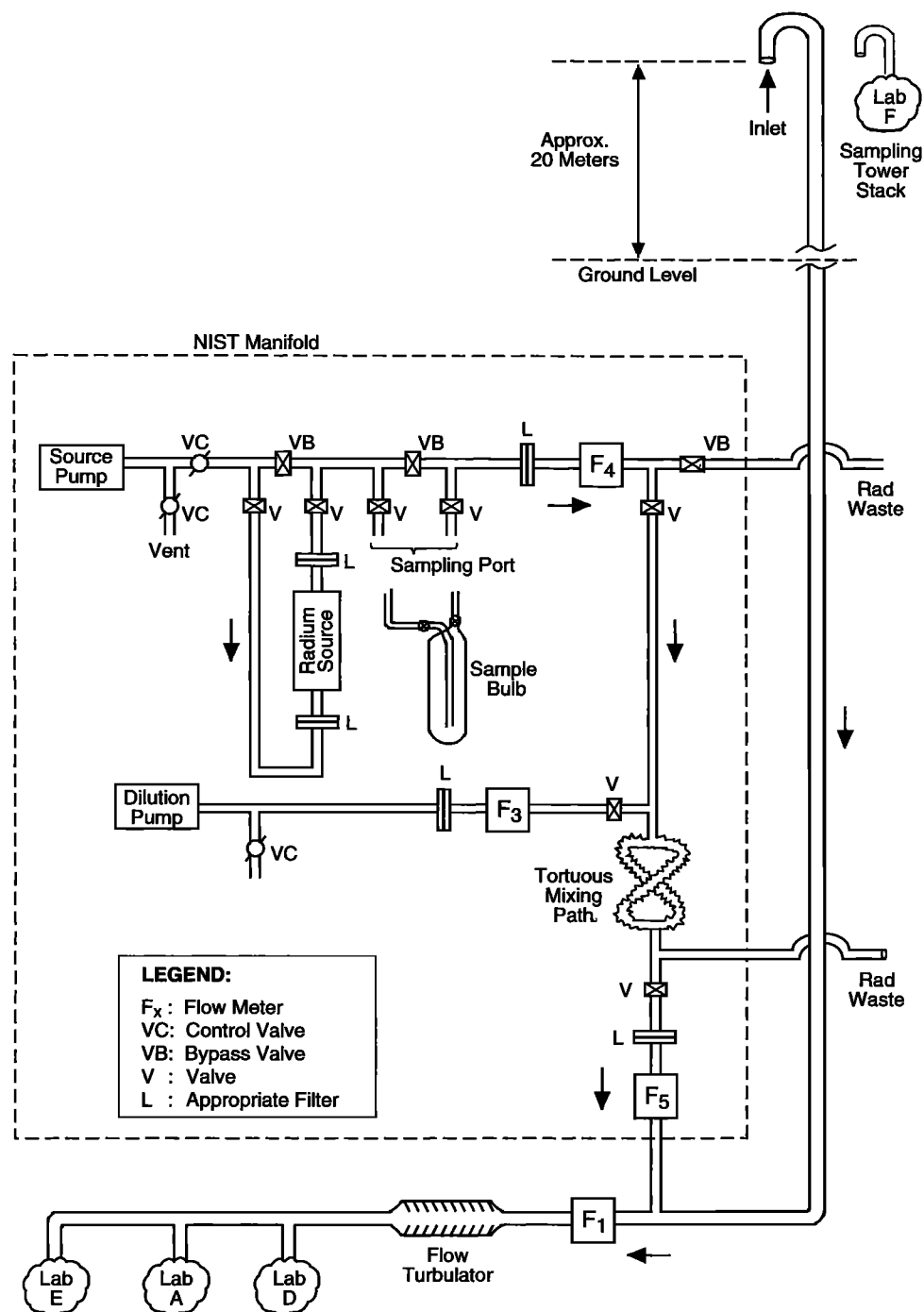


Figure 1. Schematic of the experimental configuration used for the measurement intercomparison showing the National Institute of Standards and Technology (NIST) manifold that was employed to provide standardized additions of known radon concentration and the relative sampling locations for the participating laboratories.

participating laboratories' instruments. Unfortunately, the constraints of time, cost, and practicality prevented these refinements. Although the factors added somewhat to the task of the experimental design and conduct, they did not affect the basic integrity of the experiment, as will be subsequently demonstrated.

The manifold was constructed, for the most part, of 1/4- and 3/8-inch (0.635 and 0.953 cm) stainless steel tubing with compression Swagelok and international pipe thread (IPT) threaded

pipe fittings. All of the valves were of high-vacuum, stainless steel construction. The two pumps were simple, vibrating-diaphragm aquarium pumps which had maximum flow rates of approximately 1.5 L min^{-1} and which utilized ambient air outside their housings. The two control valves (VC in Figure 1) located after the source pump were used to vary and control the flow rate through the radium source. With the use of an appropriate triad of valves, the flow rate could be adjusted with the streamline bypassing the source. A similar triad of valves

was used at the sampling port either to bypass the port or to direct the streamline of air through a sample bulb. The ^{226}Ra source was a commercially available, flow-through source (Pylon Electronic Development Co., Ottawa, Canada), which was independently calibrated by NIST and will be subsequently described in section 3.2 of this paper. The flow rate through the radium source (f_4) was measured with flowmeter F_4 . The streamline after flowmeter F_4 could be either bypassed to a waste stream or directed to the sampling stack for a standard addition. The flow rate from the dilution pump (f_3) was adjusted with a single control valve teed off its streamline. This rate was measured with flowmeter F_3 . Flows f_4 and f_3 were added and mixed through a tortuous mixing path that consisted of a crossed path of flexed stainless steel bellows tubing which served as a flow turbulator. Its efficacy and the adequacy of mixing were demonstrated by confirmatory measurements that will be reported in section 3.4. A portion of the combined ($f_4 + f_3$) flow rate could be diverted (with flow f_x) through a control valve to a second waste line. The net flow (f_5) after this diversion was measured with flowmeter F_5 . The three flowmeters (F_4 , F_3 , and F_5) were matched and intercalibrated mass flowmeters (Matheson Gas Products, East Rutherford, New Jersey) having a range of 0 to 3 L min $^{-1}$ with standard volume conditions of 21°C and 760 mm Hg (1.013×10^5 Pa), and having a reported calibration accuracy of 1.0%. Confirmatory measurements of their in situ intercalibration are also reported in section 3.4. The two waste streamlines, which at times contained appreciable radon concentrations, were directed by flexible plastic hose to distances considerably away from the sampling stack. The waste hose outlet was located 30 to 40 m southeast of the tower base for the first few standard additions and was subsequently relocated about 30 m down the hill from the tower (which would place the outlet 40 to 50 m below and west of the intake at the top of the tower). None of the diversions were considered to have appreciably altered any ambient radon concentration levels.

The outlet of the NIST manifold with flow rate f_5 was directed into the main sampling stack where the flow of the combined streamlines was measured with flowmeter F_1 and mixed with a commercial high-efficiency flow tubulator prior to sampling by the instrumentation of Labs A, D, and E. Meter F_1 was a 0 to 50 foot 3 min $^{-1}$ (i.e., 1416 L min $^{-1}$) mass flow meter (TSI, Inc., St. Paul, Minnesota) with standard volume conditions of 70°F (20.1°C) and 14.7 pounds inch $^{-2}$ (i.e., 1.013×10^5 Pa) and a reported "tolerance" of $\pm 2\%$ of reading plus 0.2% of full scale.

Throughout the intercomparison of standardized additions, all four flow meters were continuously monitored. Their 0- to 5-V analog outputs were sampled at 10-s intervals and converted to digital signals with a 4096-channel analog-to-digital converter (ADC) and chronologically recorded on a dedicated personal computer (PC). Thus every 10-s file of all of the flow rates provided an exhaustively complete record of all flow rate changes, and thereby the necessary dilution factors, throughout the course of all the standardized additions. The chronological record was maintained with the internal computer clock. This clock was cursorily intercompared with the timing devices of the measurement instruments of the participating laboratories. All clocks were in agreement within a minute or two, and any of the differences in clock times could be demonstrated to have negligible effect on the intercomparison results.

Consideration of the flow network (Figure 1) reveals that

$$C_1 = \left(\frac{f_5}{f_1}\right) \left(\frac{f_4}{f_4 + f_3}\right) C_s + C_A \quad (1)$$

where C_1 is the ^{222}Rn activity concentration in the main stream line sampled by Labs E, A, and D; C_s is the ^{222}Rn activity concentration from the radium source when maintained at flow rate f_4 (see section 3.2); and C_A is the ^{222}Rn activity concentration in ambient air. For discussion purposes, let us call the portion contributed by the standard sample addition C_0 , and call the combined flow rate ratios the dilution factor D , so that $C_1 = C_0 + C_A$; $C_0 = DC_s$; $D = (f_5/f_1) [f_4/(f_4 + f_3)]$. It should be noted that there are two simplified situations: with $f_x = 0$ and $f_3 = 0$, $f_4 = f_5$ and the dilution factor is just $D = (f_5/f_1) = (f_4/f_1)$. Alternatively, with $f_x = 0$, $(f_3 + f_4) = f_5$ and $D = (f_4/f_1)$. For confirmatory purposes, both cases were tested in the series of standardized additions (see section 3.4).

The protocol for initiating the standardized additions consisted of (1) adjusting flow rate f_4 while bypassing the radium source, (2) opening the flow f_4 through the source but diverting it out the waste line to allow time to reach a steady state concentration C_s from the source and to flush the source line, (3) adjusting flow rates f_3 and f_5 with the appropriate control valves, and finally, (4) after all the flow rates are stabilized, and at the commencement of the standard addition, opening the valve after flowmeter F_4 and closing the waste bypass valve to direct C_s into the manifold stream. The standardized additions were typically of 4-hour duration (with one exception) to allow sufficient overlap with the measurement intervals for each of the participating laboratories. Each addition was initiated at the start of one of the hourly measurement cycles of Lab E. The rapid and abrupt change in flow rate f_1 at those hourly intervals (a flow rate change of approximately 400 L min $^{-1}$ over approximately 40 s as the Lab E pump went off and on again) provided a convenient internal timing mechanism. The standard addition was terminated, again at the end of one of the measurement cycles of Lab E, by (1) rapidly diverting C_s from the main streamline to the bypass waste line and (2) readjusting the flow rates (and thereby the dilution factor) for the next standard addition.

3.2. Calibration of the ^{226}Ra Source

The flow-through radium source used for the intercomparison was calibrated in terms of the available ^{222}Rn concentration C_s maintained in a streamline at a constant flow rate f_4 . For these calibration measurements the streamline was sampled by filling flow-through sample bulbs. The source was operated and the streamline was sampled using the upper portion of the identical manifold described above in section 3.1. This portion consisted of the source pump, appropriate control valves to adjust the flow rate through the source, a triad of valves to serve the inlet and outlet ports for the source and a bypass line, another triad of valves for the sampling ports, and flowmeter F_4 .

The sample bulbs which were filled at known flow rates f_4 were assayed for total ^{222}Rn activity using the NIST primary ^{222}Rn measurement system. This system is based on pulse ionization chamber (PIC) measurements calibrated against national ^{226}Ra solution standards maintained by NIST and has been described in detail previously by Collé *et al.* [1990] and Hutchinson *et al.* [1992]. The estimated uncertainty in the measurement of the total activity in the sample bulbs (correspond-

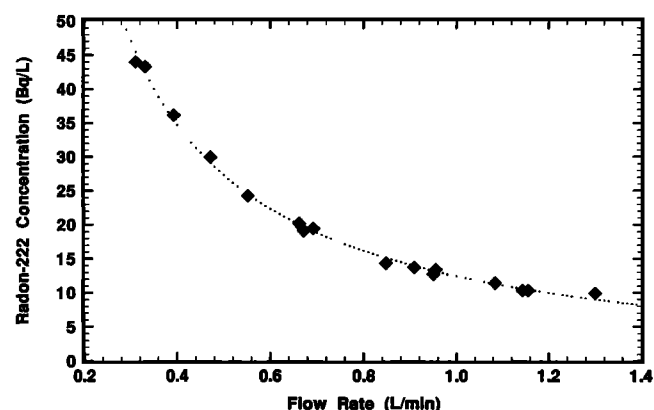


Figure 2. Calibration curve for the ^{226}Ra flow through source in terms of the concentration of ^{222}Rn in a streamline, C_s , as a function of the flow rate f_4 .

ing to an approximate relative standard deviation) is approximately 0.7%.

The volumes of the sample bulbs, used to obtain the activity concentration C_s from the total activity in the assayed samples, were well known from replicate gravimetric determinations using high-purity water of known density at given temperatures. The sample bulbs were of various sizes ranging in volume from about 330 to 670 mL. The estimated overall uncertainty in the volumes is 0.2 to 0.5%, the magnitude of which was primarily controlled by the number of replicates.

Samples were collected and subsequently assayed for ^{222}Rn to determine C_s over a range of flow rates from about 0.3 to 1.3 L min^{-1} . Continuous flow for a minimum of 10 to 20 min (i.e., at least 10 complete air changes through the manifold) was maintained during sampling to flush the manifold and remove all previous air and to insure adequate mixing. The precision of the flow rate measurements during sampling was typically 0.02% (relative standard deviation of the mean). Flowmeter F_4 was calibrated by its manufacturer (Matheson) and was stated to have a calibration accuracy of 1.0% for air over the entire 0 to 3 L min^{-1} flow rate range. Inasmuch as this uncertainty is presumed to correspond to some type of “maximum” confidence interval, the approximate relative standard deviation was taken to be 0.5%.

The calibration results for 16 independent determinations of C_s as a function of mean f_4 are shown in Figure 2. The data were fitted to obtain the χ^2 -minimized regression curve $C_s = a + (b/f_4)$ with $a = -2.386 \text{ Bq L}^{-1} \pm 16.0\%$ and $b = 14.825 \text{ Bq min}^{-1} \pm 1.5\%$ when f_4 is expressed in units of liters per minute. The fitted residuals ranged from 0.1 to 1.4% with a correlation coefficient of $r = 0.9968$. Regressions using other fitting functions, including second- and higher-order polynomials in $1/f_4$ as well as exponentials, were inferior to the given linear function. The uncertainties in C_s (for the flow rate range $f_4 = 0.3$ to 1.3 L min^{-1}) are estimated to be 1.2 to 2.6% (relative standard deviation). This was obtained by propagating in quadrature the combined uncertainty in the sample assays for ^{222}Rn concentration (0.7–0.9%), the flowmeter uncertainty (0.5%), and the uncertainty in C_s from the regression (0.77–2.4%).

3.3. Radon 222 Standardized Additions

Fifteen sets of standardized additions using the methodology described in section 3.1 were performed over 5 days (October

9–13, 1991). Each standard addition was of 4 hours’ duration, with the exception of standard addition 13 which was 3 hours. The ^{222}Rn activity concentrations, C_0 , for the standard additions ranged nominally from 2.5 to 35 Bq m^{-3} (refer to Table 2). One of them (standard addition 4) had to be discarded from the analyses because a bypass valve on the manifold was inadvertently opened during the course of the addition, which diverted the source flow stream from the main sampling line.

The standardized additions were analyzed in terms of calculating a mean C_0 individually for each participating laboratory for each of their sampling/measurement intervals. The start and stop times of the 1-hour sampling intervals for Lab E, were easily obtained from the abrupt changes in the flow rate f_1 data (see section 3.1). For Lab A, whose instrument recorded continuously and gave averaged results that were “smoothed” by a time constant of approximately 90 min, the entire 4-hour (or 3-hour in the case of addition 13) standard addition time interval was used to derive the mean C_0 . For Lab D, the mean C_0 was calculated using the start and stop clock times for their 2-hour sampling/measurement intervals which were submitted with their measurement results.

To obtain a mean C_0 for each standardized addition interval from some start time t_a to stop time t_z for each laboratory’s individual measurement cycle, the flow data could be analyzed in at least three different ways, but all yield essentially the same numerical results.

The first approach consisted of calculating individual mean flow rates \bar{f}_4 , \bar{f}_3 , \bar{f}_5 , and \bar{f}_1 , over the given t_a to t_z interval. The mean \bar{f}_4 was then used to obtain a mean \bar{C}_s from the linear calibration function of section 3.2; and a mean dilution factor \bar{D} was obtained from the combination of the individual flow rate means. The mean \bar{C}_0 was thereby approximated by the product of the derived \bar{C}_s and \bar{D} values.

The second approach consisted of calculating the quantities $C_s(t_i)$, $D(t_i)$, and $C_0(t_i)$ from the flow rate measurement data $f_4(t_i)$, $f_3(t_i)$, $f_5(t_i)$, and $f_1(t_i)$ at each t_i measurement point (taken 10 s apart). The set of resulting $C_0(t_i)$ values was then arithmetically averaged over the entire t_a to t_z interval to obtain the mean \bar{C}_0 .

The third approach, considering the temporal variation in C_0 , consisted of numerically integrating the individual $C_0(t_i)$

Table 2. NIST Standardized Sample Additions

Standard Addition	Approximate Time			Nominal Range for the ^{222}Rn Activity Concentration, Bq m^{-3}
	Date, 1991	Day of Year, 1991	Hours, UT	
1	October 9	282	1900–2300	33–37
2	October 10	283	0900–1300	28–30
3	October 10	283	1400–1800	29–31
4	October 11	284	0900–1300	discarded
5	October 11	284	1400–1800	5.3–6.2
6	October 11	284	1800–2200	20–23
7	October 11–12	284–285	2200–0200	3.9–5.0
8	October 12	285	0200–0600	3.8–4.1
9	October 12	285	1200–1600	7.2–7.9
10	October 12	285	1600–2000	12–14
11	October 12	285	2000–0000	32–36
12	October 13	286	0000–0400	30–33
13	October 13	286	1200–1500	15–16
14	October 13	286	1500–1900	5.4–5.8
15	October 13	286	1900–2300	2.4–2.6

values at each point t_i normalized by the total flow (from flow rate f_1) in the main sampling line:

$$\bar{C}_0 = \frac{\int_{t_a}^{t_z} C_0(t) f_1(t) dt}{\int_{t_a}^{t_z} f_1(t) dt} = \frac{\sum_i C_0(t_i) f_1(t_i)}{\sum_i f_1(t_i)}. \quad (2)$$

Inspection of (2) reveals that the numerator represents the total ^{222}Rn activity passing through the sampling line from time t_a to t_z , while the denominator is the corresponding total volume.

The numerical differences in the mean C_0 calculated by the three calculational approaches were in all cases negligible compared with the estimated relative standard deviations of the mean (s_m) for C_0 calculated by any one of the approaches. These differences, depending on the specific standardized addition in question, ranged from less than 0.01% to about 2.0 to 4.0% in worst cases. The specific case-to-case variation in the precision in mean C_0 may be seen in Tables 3, 4, and 5, which provide the calculated results of the standardized additions for the three participating laboratories. Estimates of s_m for C_0 may be obtained directly from s_m for the mean dilution factor D , since the latter is the singularly dominant source of imprecision in C_0 . These estimates of s_m range from about 0.03% to 3.0% for Lab E, and from about 0.2 to 3.6% for Lab A and Lab D. The wide variations merely reflect the actual wide variations in the flow rates (mainly f_1) from case to case, as will be discussed shortly. Nevertheless, any differences due to the chosen calculational approach for a given case were clearly reflected and embodied within the estimated s_m for that case.

The final calculational approach chosen for the intercomparison of standardized additions consisted of a combination of the first two approaches outlined above. This choice was somewhat arbitrary, since all of the approaches gave essentially identical results. None of the results and conclusions of the intercomparison would change as a result of a different calculational choice. For the adopted method chosen, the mean C_S was obtained from a mean f_4 as in the first approach; the mean dilution factor D was derived as in the second approach; and the mean C_0 was just the product of these values of C_S and D . These are the values tabulated in Tables 3, 4, and 5.

As indicated in the tables, the ^{222}Rn activity concentrations C_0 in the standardized sample additions ranged from approximately 2.5 to 35 Bq m^{-3} .

Perusal of the actual flow rate measurement data for a typical standardized sample addition may be helpful in understanding the experimental aspects of the intercomparison and the quality of the results. Figures 3 through 6 give the flow rate measurement data for f_4 , f_3 , f_5 , and f_1 , respectively, obtained during standardized addition 11. The illustrated data consist of nearly 1440 simultaneous measurements of the four flow rates, taken approximately every 10 s over a 4-hour interval.

The means for the relatively stable flow rates f_4 , f_3 , and f_5 were somewhat overdetermined and are very precise. Tables 3, 4, and 5 give the estimated relative standard deviations of the mean for f_4 , and these values of s_m are typical of those for f_3 and f_5 as well. In fact, even these values are somewhat misleading for the inherent flow rate precision in the middle of a standard addition. They are sometimes strongly influenced by abrupt changes in the flow rate that were made over the first 0.5 to 2 min in adjusting the dilution factor in going from one

standard addition to the next. Obviously, having a time delay between sequential additions would have obviated this shortcoming, but the rather costly nature of this intercomparison imposed time constraints. This kind of adjustment between standard additions is clearly shown in Figure 4 where flow rate f_3 was adjusted to vary the dilution factor from standard addition 10 to 11. Nevertheless, the data of Figures 3 through 6 nicely illustrate the typical variations in flow over the course of a standard addition. The flow rate data also often exhibited some slight, but gradual systematic drifts in flow rate over time. This effect is quite apparent in the data of f_3 and f_5 shown in Figures 4 and 5. This is not believed to be a result of any electrical or signal "drift" in the flow meters themselves at constant flow, but rather is believed to have arisen from gradual changes in the settings of the flow control valves in the manifold due to mechanical vibrations at the site.

In contrast to the flow rates f_4 , f_3 , and f_5 , the data for flow rate f_1 , shown in Figure 6, exhibit pronounced shifts. These marked changes arise as a result of the on and off cycling of the sampling pumps that were part of the measurement instruments for the three participating laboratories. The flow rate f_1 at any time was the sum of the flow rates from the three laboratories' pumps. Mean flow rates f_1 calculated for each individual standardized addition over the course of all the additions ranged from approximately 365 to 450 L min^{-1} , with estimated relative standard deviations of the mean of essentially the same magnitude as that for the dilution factors D (see Tables 3, 4, and 5). The variability in f_1 was the predominant contribution to the variability in the dilution factor D . The Lab E pump, which rapidly cycled on and off (over approximately 40 s) every hour, was dominant, contributing about 365–395 L min^{-1} of the total flow rate. The Lab D pump, with a flow rate of about 40–45 L min^{-1} , sampled for 2 hours but at irregular intervals of about every $4\frac{1}{2}$ hours. The Lab A pump ran continuously with a flow rate close to 40 L min^{-1} that increased to about 44 L min^{-1} for 20 s every 10 min. The four intervals labeled E11a through E11d in Figure 6 mark the pump sampling intervals for Lab E. The rapid drops in the flow rate as the Lab E pump shut down and then returned are very pronounced in the data but are barely perceptible in Figure 6 because each cycle affects only 3 or 4 out of the 1440 data values shown. The interval marked D11 in Figure 6 represents the sampling interval for Lab D.

The dilution factor D at each 10-s interval for the standard addition 11 flow data (Figures 3 through 6) is given in Figure 7. Of necessity, it exhibits the same marked discontinuities as the f_1 data. It is apparent, for example, that the dilution factor D (and hence C_0) is quite stable for the Lab E11a and E11c intervals and is somewhat less so for the Lab D11 interval because of the two disruptions by the Lab E pump. The intervals E11b and E11d exhibit pronounced step functions in the dilution factor as the Lab D pump went on and off. These evident and very different kinds of variations in the dilution factor are also manifested by the magnitude of their respective estimated relative standard deviations of the mean.

Consider the respective cases for the three laboratories.

Table 3 indicates that for the stable E11a and E11c intervals, s_m for dilution factor D is 0.02 and 0.06%, while for intervals E11b and E11d, with the step function in D , s_m is 0.26 and 0.25%, respectively. Intuitively, one might expect s_m for mean D for these cases with a drastic step function in D to be even larger than that given. This estimated s_m , however, is easily derived and verified from its component parts. In view of the

Table 3. NIST Standard Additions for Lab E

Standard Addition	Flow Rate f_4		^{222}Rn Concentration C_S , Bq L $^{-1}$	Dilution Factor D		^{222}Rn Concentration C_0 ^b , Bq L $^{-1}$
	Mean, L min $^{-1}$	s_m ^a , %		Mean, $\times 10^{-3}$	s_m ^a , %	
1	0.335	0.02	41.92	0.854	0.19	35.81
	0.333	0.02	42.15	0.796	0.03	33.55
	0.332	0.01	42.25	0.778	0.02	32.87
	0.328	0.01	42.83	0.865	0.04	37.07
2	1.200	0.01	9.968	2.919	0.18	29.09
	1.201	0.03	9.960	2.804	0.04	27.92
	1.194	0.01	10.03	2.874	0.14	27.82
	1.186	0.01	10.11	3.014	0.03	30.48
3	1.173	0.02	10.25	2.909	0.22	29.81
	1.175	0.02	10.24	2.792	0.04	28.59
	1.166	0.02	10.33	2.946	0.25	30.44
	1.175	0.11	10.23	3.052	0.31	31.23
5	0.985	0.04	12.67	0.422	0.04	5.349
	0.981	0.01	12.72	0.430	0.05	5.467
	0.979	0.01	12.75	0.454	0.05	5.787
	0.990	0.03	12.58	0.460	0.08	5.782
6	0.768	0.06	16.91	1.298	0.41	21.94
	0.770	0.02	16.87	1.211	0.04	20.43
	0.773	0.02	16.79	1.294	0.27	21.74
	0.772	0.03	16.82	1.300	0.04	21.87
7	0.645	0.41	20.60	0.243	3.0	5.013
	0.664	0.02	19.96	0.207	1.1	4.141
	0.668	0.01	19.82	0.199	0.06	3.946
	0.670	0.01	19.73	0.210	0.10	4.143
8	0.676	0.01	19.54	0.208	0.04	4.064
	0.669	0.02	19.78	0.201	0.14	3.978
	0.671	0.01	19.71	0.195	0.04	3.833
	0.671	0.01	19.70	0.198	0.15	3.898
9	1.051	0.12	11.72	0.627	0.63	7.350
	1.042	0.02	11.84	0.607	0.03	7.181
	1.019	0.05	12.16	0.619	0.19	7.524
	1.026	0.02	12.07	0.654	0.07	7.885
10	0.958	0.03	13.08	1.025	0.15	13.41
	0.944	0.01	13.32	0.930	0.03	12.39
	0.944	0.01	13.31	0.952	0.05	12.67
	0.953	0.02	13.17	1.041	0.11	13.70
11	0.710	0.02	18.49	1.961	0.02	36.25
	0.710	0.01	18.50	1.863	0.26	34.46
	0.713	0.02	18.40	1.764	0.06	32.47
	0.717	0.01	18.29	1.831	0.25	33.49
12	0.905	0.01	14.00	2.391	0.02	33.48
	0.909	0.01	13.92	2.278	0.12	31.71
	0.916	0.02	13.80	2.051	0.03	28.30
	0.907	0.01	13.95	2.124	0.03	29.64
13	0.916	0.10	13.80	1.072	0.16	14.79
	0.920	0.02	13.73	1.142	0.14	15.68
	0.922	0.01	13.69	1.144	0.02	15.66
	1.073	0.15	11.42	0.505	1.33	5.770
14	1.078	0.01	11.37	0.477	0.03	5.422
	1.079	0.01	11.36	0.499	0.21	5.671
	1.081	0.01	11.33	0.513	0.03	5.811
	1.146	0.03	10.56	0.242	0.58	2.556
15	1.145	0.01	10.56	0.225	0.06	2.371
	1.143	0.01	10.59	0.225	0.85	2.383
	1.138	0.01	10.65	0.232	0.10	2.465

^aStandard deviation of the mean.^bThe overall uncertainties ranged from 6.0 to 13.0% (see Table 8).

invariance within statistical variations for the three different calculational approaches to obtain a mean C_0 (section 3.3), it is clear that even with the step function in D (and thereby in C_0) the adopted treatment is adequate.

The mean dilution factor D for interval D11 has a s_m for D of 1.1% (Table 5). Although it is not as apparent in the illus-

trated data of Figure 7, its magnitude is strongly influenced by the two abrupt flow discontinuities when the Lab E pump went off and on.

Over the entire 4-hour interval of Figure 7, as applicable for calculation of the Lab A dilution factor mean D , s_m for D was 0.9% (Table 4).

Table 4. NIST Standard Additions for Lab A

Standard Addition	Flow Rate f_4		^{222}Rn Concentration C_S , Bq L $^{-1}$	Dilution Factor D		^{222}Rn Concentration C_0 , ^b Bq m $^{-3}$
	Mean, L min $^{-1}$	s_m , ^a %		Mean, $\times 10^{-3}$	s_m , ^a %	
1	0.332	0.02	42.30	0.825	0.21	34.91
2	1.195	0.02	10.02	2.915	0.20	29.20
3	1.172	0.03	10.26	2.935	0.21	30.11
5	0.984	0.02	12.68	0.480	1.9	6.09
6	0.771	0.02	16.84	1.338	2.0	22.53
7	0.662	0.11	20.02	0.217	1.0	4.35
8	0.672	0.01	19.68	0.206	1.2	4.06
9	1.035	0.05	11.94	0.643	0.89	7.68
10	0.950	0.02	13.22	1.003	0.57	13.27
11	0.713	0.01	18.42	1.900	0.88	35.01
12	0.909	0.01	13.92	2.232	0.33	31.06
13	0.919	0.03	13.74	1.149	1.1	15.78
14	1.078	0.04	11.37	0.510	0.86	5.80
15	1.143	0.01	10.59	0.238	1.9	2.52

^aStandard deviation of the mean.^bThe overall uncertainties ranged from 6.0 to 13.0% (see Table 8).

3.4. Confirmatory Measurements

The dimensionless dilution factors D , used to obtain the values of C_0 for the intercomparison, consist of flow rate ratios and therefore are more dependent on the relative flowmeter responses rather than on individual flowmeter calibrations per se. Although the matched flowmeters F_4 , F_3 , and F_5 in the NIST manifold were previously intercompared and also presumably based on similar and reliable calibrations by the manufacturer (Matheson), the design of the manifold (Figure 1) and the simultaneous flow rate measurements allowed a direct, in situ intercomparison of the flowmeters at the test site.

Inspection of Figure 1 indicates that when $f_x = 0$, then in principle, $(f_4 + f_3) = f_5$. This provided the opportunity to intercompare the flowmeter responses for the following conditions: $(f_4/f_5) = 1$ with $f_3 = 0$; $(f_3/f_5) = 1$ with $f_4 = 0$; and $(f_4 + f_3)/f_5 = 1$. All three conditions were tested in Bermuda during the course of the intercomparison. The results are given

in Table 6. Mean values for the flow rates were obtained from the 10-s measurement data averaged over periods of from 20 to nearly 60 min. All of the estimated relative standard deviations of the mean for the flow rates were in the range 0.01 to 0.04%. As is indicated, all of the flow ratio intercomparisons are within $\pm 1\%$, which is well within the range of the expected statistical variations for meters with an assumed relative uncertainty of 0.5% (see section 3.2 discussion).

Regrettably, it was not possible to independently verify by intercomparison the relative response of flowmeter F_1 to the others. The repercussions of this shortcoming as it affects the results and conclusions of the intercomparison of standardized additions will be addressed later in the discussion of the intercomparison findings.

Two types of in situ confirmatory tests of the operation of the NIST manifold to deliver known ^{222}Rn activity concentrations at the site in Bermuda were performed. Both involved

Table 5. NIST Standard Additions for Lab D

Standard Addition	Flow Rate f_4		^{222}Rn Concentration C_S , Bq L $^{-1}$	Dilution Factor D		^{222}Rn Concentration C_0 , ^b Bq m $^{-3}$
	Mean, L min $^{-1}$	s_m , ^a %		Mean, $\times 10^{-3}$	s_m , ^a %	
1	0.332	0.02	42.21	0.792	0.27	33.43
2	1.198	0.02	9.99	2.844	0.26	28.41
3	1.174	0.02	10.25	2.823	0.26	28.93
5	0.983	0.02	12.70	0.490	3.2	6.22
6	0.771	0.02	16.85	1.291	3.0	21.76
7	0.666	0.01	19.88	0.205	0.81	4.08
8	0.671	0.01	19.72	0.202	2.3	3.98
9	1.040	0.04	11.88	0.619	0.94	7.35
10	0.944	0.01	13.32	0.964	0.94	12.84
11	0.714	0.02	18.39	1.814	1.09	33.36
12	0.912	0.02	13.88	2.104	0.31	29.20
13 ^c	0.917	0.09	13.78	0.612 ^c	1.2	8.43 ^c
14	1.079	0.01	11.36	0.488	0.91	5.54
15	1.143	0.01	10.58	0.234	3.6	2.48

^aStandard deviation of the mean.^bThe overall uncertainty ranged from 6.0 to 13.6% (see Table 8).

^cStandard addition 13 for Lab D was normalized by the ratio 0.5583 to account for a partial standard addition during the measurement interval. The standard addition was made for only the last 67 min of the 120-min. measurement interval.

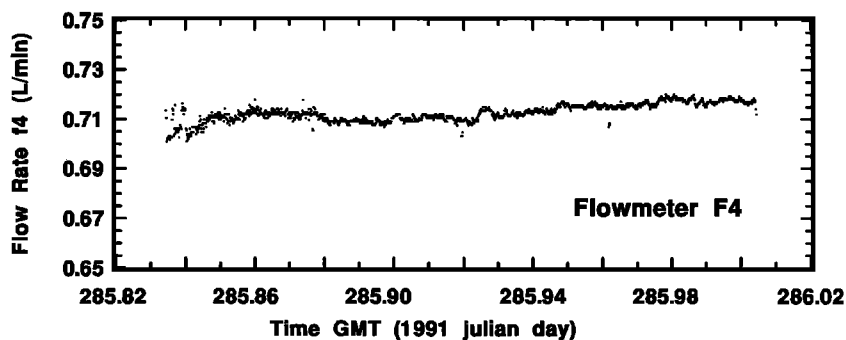


Figure 3. Typical flow rate f_4 data as measured by flowmeter F_4 approximately every 10 s over the 4-hour interval for standard addition 11.

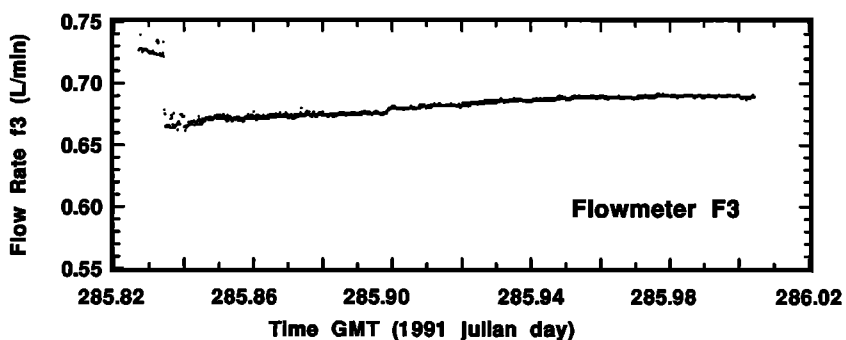


Figure 4. Typical flow rate f_3 data as measured by flowmeter F_3 approximately every 10 s over the 4-hour interval for standard addition 11. The discontinuity in flow at the outset (from about 0.73 to 0.67 L min^{-1}) was an adjustment in the flow rate to change the dilution factor from standard addition 10 to 11 (see text).

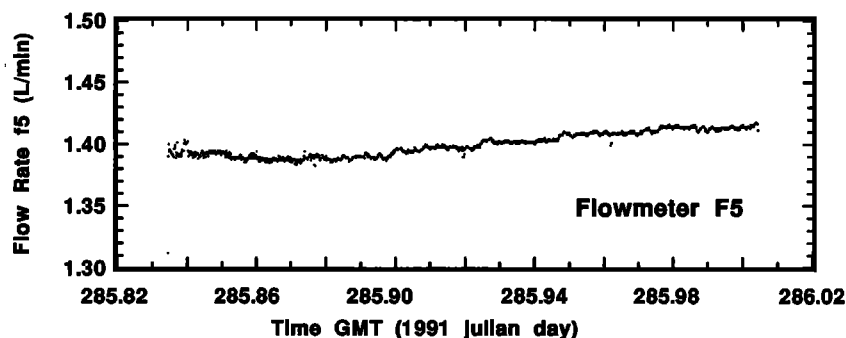


Figure 5. Typical flow rate f_5 data as measured by flowmeter F_5 approximately every 10 s over the 4-hour interval for standard addition 11.

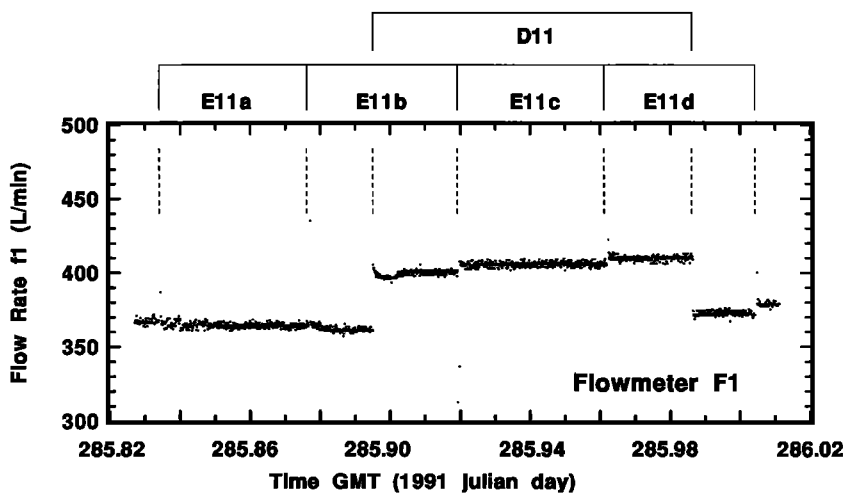


Figure 6. Typical flow rate f_1 data as measured by flowmeter F_1 approximately every 10 s over the 4-hour interval for standard addition 11. The discontinuities are discussed in the text.

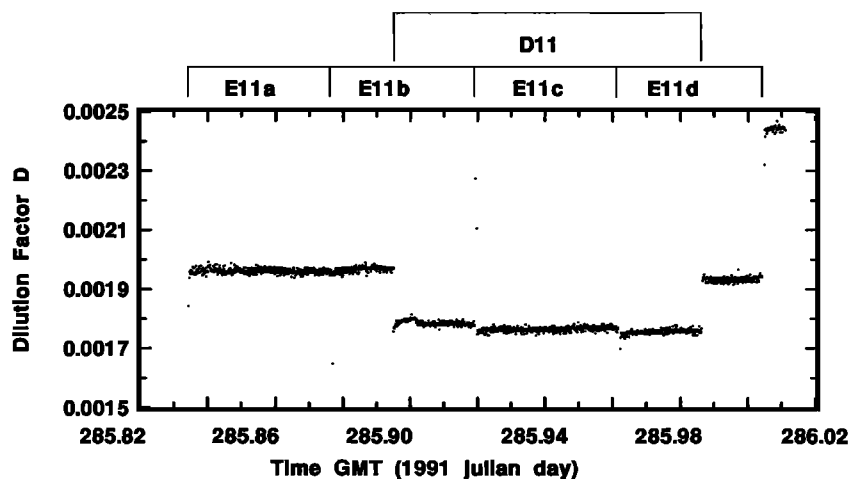


Figure 7. Dilution factor D as a function of time over the 4-hour interval for standard addition 11. The data values were calculated every 10 s using the flow rate data of Figures 3 through 6.

collecting grab samples from the manifold using glass sampling bulbs identical to those used to perform the ^{226}Ra source calibration. The samples were returned to NIST for assay, again using a PIC measurement procedure identical to that used in calibrating the radium source (see section 3.2). The assayed ^{222}Rn activity concentrations in the samples were decay corrected to the time of sample collection, and this corrected concentration C_T was compared to that concentration C_P predicted from the operation of the manifold.

The first kind of test involved samples collected at the sampling port directly downstream from the radium source (see Figure 1). The activity concentrations in these samples are expected to be that given by the source calibration term C_S as a function of the flow rate f_4 . Three such samples were collected during standard additions 7, 10, and 14, with the results summarized in Table 7. An additional two samples were collected but were unfortunately destroyed in transit to NIST.

The second kind of test was performed at the conclusion of the standardized additions when the NIST manifold was disconnected from the main sampling line. Two samples were collected directly at the outlet of the manifold (see Figure 1) after flowmeter F_5 and just as it would have entered the main line before flowmeter F_1 . This confirmatory test was made to demonstrate the efficacy of mixing the f_4 and f_3 flows, and the $(f_4 + f_3)$ dilution calculation. In this case, the predicted concentration C_P is given by a C_S which is diluted by the factor

$f_4/(f_4 + f_3)$. The results for these two samples, labeled ND and NF, are also presented in Table 7.

The mean flow rates for f_4 and f_3 used to obtain the predicted concentration C_S and diluting factor $f_4/(f_4 + f_3)$ were obtained from the 10-s flow rate data averaged over approximately 10-min intervals that immediately preceded the closing of the sample bulbs. The estimated s_m for f_4 and f_3 were, in all cases, less than 0.01%. The mean values averaged over shorter intervals (down to 3 min) and longer intervals (up to 20 min) were invariant.

Comparison of the assayed concentrations C_T and predicted values C_P in Table 7 indicates an overall agreement to slightly over 1%, with no significant differences between the two kinds of samples. The mean value of $C_P/C_T = 0.987$ has an estimated s_m of 0.49%. This uncertainty is roughly the same magnitude as that expected for the derived uncertainty in C_S as given earlier (section 3.2). It should be noted that the C_P/C_T comparison given in Table 6 neglected any contribution of radon activity from ambient air. In actuality, a comparison of $(C_P + C_A)/C_T$ (where C_A is the ambient ^{222}Rn activity concentration at the time of sample collection) would be more valid. However, C_A is believed to be $\leq 0.003 \text{ Bq L}^{-1}$ (3 Bq m^{-3}) for any of the samples and should therefore have a negligible effect ($\leq 0.03\%$ of C_T) on the results. This limit is based on the maximum ambient concentration that was measured by any of the participating laboratories at any time during the intercomparison.

Table 6. In Situ Intercomparison of the Flowmeters F_4 , F_3 , and F_5

Test Conditions	Flow Rates, L min ⁻¹						Flow Ratio
	<i>f</i> ₃		<i>f</i> ₄		<i>f</i> ₅		
	Mean	<i>s_m</i> , ^a %	Mean	<i>s_m</i> , ^a %	Mean	<i>s_m</i> , ^a %	
<i>f</i> ₄ = 0, <i>f</i> ₃ ≈ <i>f</i> ₅	0.770	0.02	0.766	0.03	<i>f</i> ₃ / <i>f</i> ₅ = 1.005
<i>f</i> ₃ = 0, <i>f</i> ₄ ≈ <i>f</i> ₅	0.793	0.01	0.797	0.03	<i>f</i> ₄ / <i>f</i> ₅ = 0.995
			0.919	0.01	0.927	0.01	<i>f</i> ₄ / <i>f</i> ₅ = 0.991
			1.078	0.04	1.076	0.02	<i>f</i> ₄ / <i>f</i> ₅ = 1.002
<i>f</i> ₃ + <i>f</i> ₄ ≈ <i>f</i> ₅	0.681	0.03	0.713	0.01	1.400	0.02	(<i>f</i> ₃ + <i>f</i> ₄)/ <i>f</i> ₅ = 0.996

^aEstimated relative standard deviation of the mean.

Table 7. Results of the Confirmatory Measurements for ^{222}Rn Activity Concentration Collected in Situ at Bermuda and Assayed at NIST

Sample	f_4 , L min^{-1}	C_S^a , Bq L^{-1}	f_3 , L min^{-1}	$f_4/(f_4 + f_3)$	C_P^b , Bq L^{-1}	C_T^c , Bq L^{-1}	C_P/C_T
N10	0.9572	13.10	0	1	13.10	13.27	0.9873
N14	1.0840	11.29	0	1	11.29	11.43	0.9878
N7(b)	0.6924	19.03	0	1	19.03	19.43	0.9792
ND	0.4715	29.06	0.6948	0.4043	11.75	11.69	1.0049
NF	0.3932	35.32	0.6983	0.3602	12.72	13.01	0.9779

Number of samples is 5; C_P/C_T mean is 0.9874; relative standard deviation of mean (s_m) is 0.49%.

^aSee section 3.2.

^b C_P is the predicted ^{222}Rn activity concentration given by $C_P = [f_4/(f_4 + f_3)]C_S$.

^c C_T is the assayed, decay-corrected ^{222}Rn activity concentration at the grab sample time of collection, corresponding to that expected for C_P . Refer to text for details.

3.5. Uncertainty Analysis

A complete analysis of the measurement uncertainties for the ^{226}Ra source calibration and ^{222}Rn activity concentrations in the standardized sample additions is outlined in extenso in Table 8.

4. Results for the Intercomparison

4.1. Reported Measurements

The measurement results of the participating laboratories, as reported by them, over the intercomparison period October 5–17, 1991, are summarized in Figures 8 through 10. The figures provide reported values of the mean ^{222}Rn activity concentrations over their individual sampling-measurement intervals for both the standardized sample additions (C_I) and for the ambient air measurements (C_A). The times, given in the figures as Greenwich Mean Time (GMT) in units of 1991 Julian date, correspond to approximate midpoint times for each sampling-measurement interval. The concentrations reported by each laboratory were converted to common units of becquerels per cubic meter for comparison. Figure 8 provides the first 4 days of ambient air measurements, Figure 9 gives the reported concentrations over the course of the 15 standard additions, and Figure 10 shows the results of 4 days of ambient measurements following the standard addition period.

A complete tabulation of the reported values for all four laboratories is available from either NIST or from the principals at any of the four participating laboratories. The tabulation is archived in Report of Test data files of the NIST Radioactivity Group.

As was indicated previously, the results for Lab F represent only measurements of C_A . Lab F reported both mean activity concentrations for the measured ^{212}Pb daughter activity and the inferred ^{222}Rn activity for 2-hour intervals. Only the reported ^{222}Rn concentration values are reported and treated here. Lab F separately noted two conditionals: ^{222}Rn concentration values that corresponded to ^{212}Pb concentrations having what were considered by Lab F to be abnormally high values due to local land influences, and values suspected to have been influenced by rainfall. These conditions affected only a small fraction of the data values: 13 and 5, respectively, out of a total of 142 reported values. No effort was made to treat these conditional values separately. The uncertainties associated with the ^{222}Rn concentrations in the range of about 0.07 to 0.2 Bq m^{-3} was estimated and reported to be approximately plus or minus 20%. This uncertainty was reported to correspond to 2 standard deviations for an assumed Poisson-

distributed statistical “counting error” (based on the square root of the total number of detected counts) as well as contributions due to the uncertainties in detection efficiency and flow rate measurements.

The results in Figures 8 through 10 reported by Lab E are for 1-hour sampling-measurement intervals. The uncertainties for these values, which were reported to correspond to a 1 standard deviation interval for the assumed Poisson-distributed statistical “counting error,” range from well over 100% at concentrations of a few hundredths of 1 Bq m^{-3} to less than 1% at about 30 Bq m^{-3} . These uncertainties do not necessarily represent the inherent or minimum obtainable precision of the two-filter technique. Those reported here are significantly influenced by the count rate arising from a thoron (^{220}Rn) contamination that is due to trace quantities of thorium in the materials used to construct their decay chamber. This thoron background is treated as part of the overall counting system background. The magnitude of this contribution may be appreciated by considering that the 39% relative uncertainty at a concentration of 0.1 Bq m^{-3} would decrease to 19% in the absence of the thoron. This contamination problem can be eliminated, as is done by Lab A, by using a plastic or fiberglass decay chamber with a conducting inner surface. It has been reported that Lab E has subsequently eliminated the thoron contamination problem by coating the welds in the decay chamber with a white epoxy (R. L. Larsen, private communication, 1994).

The results in Figures 8 through 10 for Lab A are also for 1-hour intervals. As was indicated previously, however, their instrument recorded continuously and gave averaged results that were “smoothed” by a time constant of approximately 90 min. As a result of the smoothing, the evaluation of their results could not be as direct, or as subjectively unequivocal, as with that of other laboratories. The measurement uncertainties reported by Lab A were stated to correspond to a 1 standard deviation statistical “counting error” combined with the estimated uncertainty in correcting for detection efficiency variations that arise because of changes in particulate concentrations in their delay tank. Over the course of the intercomparison, the radon concentration ranged mainly between 0.2 and 40 Bq m^{-3} . The uncertainties for Lab A in this concentration range varied from 12% to 0.7%, which is comparable with those of Lab E (20% to 0.7%). However, the uncertainties at lower concentrations were markedly less for Lab A, presumably because of the thoron contamination in the Lab E decay chamber. For example, at a concentration of 0.1

Table 8. Analysis of Uncertainties for the ²²⁶Ra Source Calibration and ²²²Rn Concentrations in the Standardized Additions

Source of Uncertainty	Component Uncertainty ^a	Propagated Uncertainty ^a	Typical Overall Uncertainty ^b
Precision of radon measurement in sample bulbs by PIC (δ_i)	0.05–0.2
PIC calibration (δ_i)	0.7 ^(c)
Volume sample bulbs (δ_i)	0.2–0.5
Radium and radon decay corrections (δ_i)	<0.01
Radon concentration in sample ($\delta_S = (\sum \delta_i^2)^{1/2}$)	...	0.73–0.88	2.2–2.6
Precision flow rate during sampling (δ_f)	0.02
Flow meter calibration (δ_f)	0.5 ^d
Flow rate ($\delta_F = (\sum \delta_f^2)^{1/2}$)	...	0.5	...
Fit (regression) of radon concentration as a function of flow rate (δ_R)	0.77–2.4
Radon concentration C_S from source at given flow rate f_4 ($\delta_{C_S} = (\delta_S^2 + \delta_F^2 + \delta_R^2)^{1/2}$)	...	1.2–2.6	3.5–7.8
Timing errors for standardized addition (δ_k)	0.1–0.3
Overall precision in dilution factor from flow rate measurement (δ_k)	0.2–3.0
Calibration flowmeters F_3 , F_4 , and F_5 (δ_k)	0.5 ^d
Calibration flowmeter F_1 (δ_k)	1.4 ^e
Dilution factor ($\delta_D = (\sum \delta_k^2)^{1/2}$)	...	1.6–3.5	...
Precision flow rate f_4 for standard addition (δ_{f_4})	0.01–0.4
Radon concentration (C_0) in standard addition, excluding ambient concentration ($\delta_{C_0} = (\delta_{C_S}^2 + \delta_D^2 + \delta_{f_4}^2)^{1/2}$)	...	2.0–4.4	6.0–13
Radon concentration C_A for ambient air (δ_{C_A})	assumed 50
Radon concentration C_1 for standard addition, including ambient concentration ($\delta_{C_1} = [(C_A/C_1)^2 \delta_{C_0}^2 + (C_0/C_1)^2 \delta_{C_0}^2]^{1/2}$)
For $C_0/C_A = 100$...	2.0–4.4	6.1–13
For $C_0/C_A = 25$...	2.7–4.6	8.2–14
For $C_0/C_A = 10$...	4.9–6.1	15–18

PIC, pulse ionization chamber.

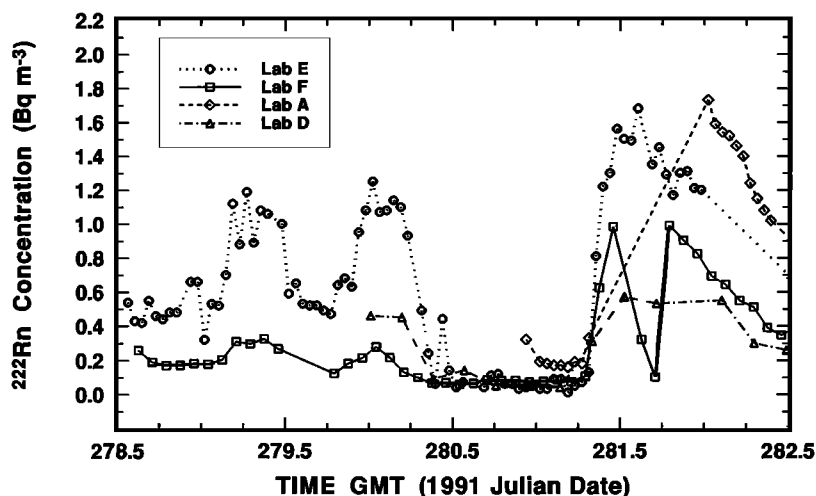
^aThe estimated component and propagated uncertainties are assumed to correspond to an approximate relative standard deviation (or standard deviation of the mean) expressed in percent.

^bThe overall uncertainty is taken to be 3 times the propagated uncertainty in percent.

^cSee Collé *et al.* [1990] and Hutchinson *et al.* [1992].

^dCorresponds to one-half the vendor's (Matheson) stated calibration accuracy.

^eCorresponds to one-half the vendor's (TSI, Inc.) stated calibration "tolerance."

**Figure 8.** Mean ²²²Rn concentrations C_0 for ambient Bermudian air reported by the four participating laboratories over the course of 4 days prior to the standardized additions.

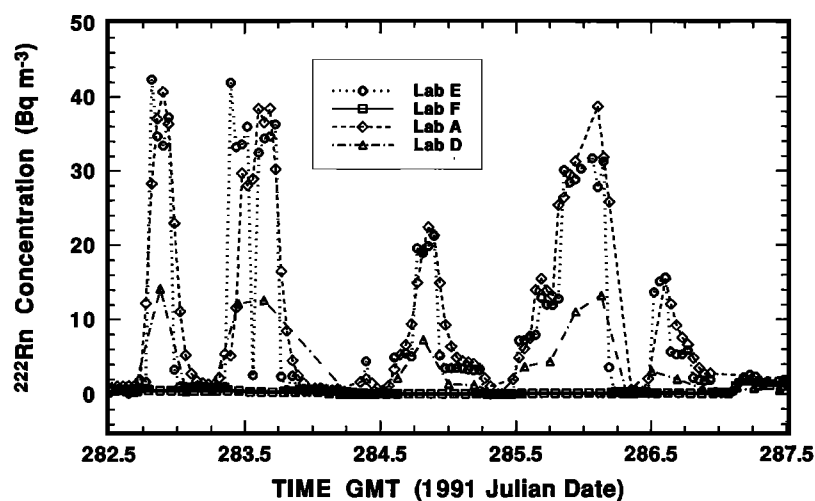


Figure 9. Mean ^{222}Rn concentrations $C_0 + C_A$ reported by the four participating laboratories during the course of the standardized additions.

Bq m^{-3} the uncertainty for Lab A was 8%, whereas that for Lab E was 40%.

The reported measurement results for Lab D given in Figures 8 through 10 are mean concentrations averaged over 2-hour sampling intervals. Associated relative uncertainties at a 1 standard deviation interval were reported to range from ± 3.4 to 3.9% for the entire data set and include contributions from (1) the measurement precision, which has a relative magnitude of about 2.8% across the range of observed activity concentrations, (2) the uncertainty associated with a $^{226}\text{Ra}/^{222}\text{Rn}$ reference standard used for calibration, and (3) the flowmeter uncertainty over the range of flow rates used.

4.2. Intercomparison of Standardized Sample Additions

The activity concentrations C_0 for the standard additions were derived independently, as was noted previously, from well-known dilution factors that were in turn obtained from simultaneous flow rate measurements for each sampling-measurement interval (from some given start time t_a to a stop time t_z) for each participating laboratory. Thus over the course of the 14 valid additions, Lab E, with well-defined 1-hour t_a to

t_z sampling intervals, received 53 standardized samples for comparison. The Lab A additions, because of the averaged “smoothed” measurement results, utilized the mean C_0 for the entire 4- or 3-hour t_a to t_z sample interval. Lab D, which had only one 2-hour t_a to t_z sampling-measurement interval enveloped within each 4- or 3-hour sample interval, therefore also received 14 standardized samples for comparison. Out of experimental necessity, the comparison of each laboratory’s reported values with the derived mean C_0 values provided by NIST required somewhat different and individual treatments (and in all cases invoked some conditional provisos).

Tables 9 through 11 summarize the findings for the three laboratories.

For the Lab E reported values (Table 9), direct comparisons were made between C_0 and the mean concentration $C_{1(E)}$ in the main sampling stream line. The results for $C_{1(E)}$ and C_0 over the entire course of the standardized sample additions are illustrated in Figure 11. Comparisons were also made between $C_{1(E)} - C_{A(E)}$ and C_0 using conservatively estimated values of the ambient concentrations $C_{A(E)}$. These $C_{A(E)}$ values were

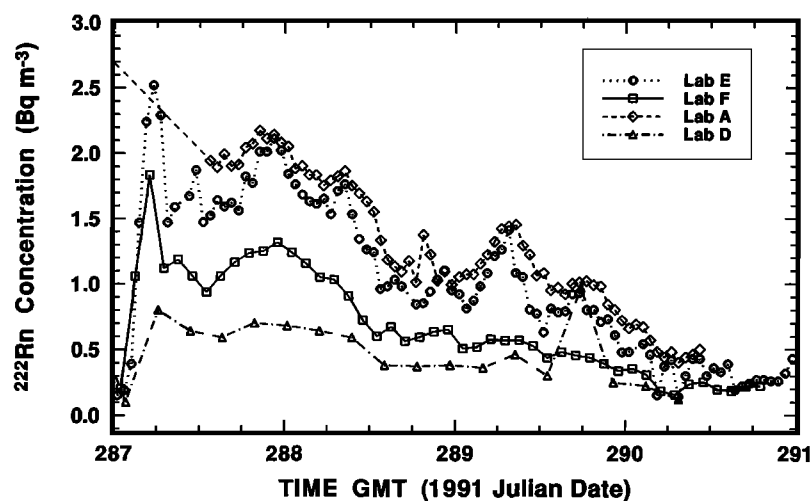


Figure 10. Mean ^{222}Rn concentrations C_0 for ambient Bermudian air reported by the four participating laboratories over the course of 4 days following the standardized additions.

Table 9. Lab E Reported Results for the Standardized Additions

	²²² Rn Concentration, Bq m ⁻³				
	Lab E		NIST Standard Addition C ₀	Concentration Ratio	
	C _{1(E)}	Assumed C _{A(E)}		C _{1(E)} /C ₀	C _{1(E)} - C _{A(E)} /C ₀
1	42.35	1.4	35.81	1.183	1.144
	34.70		33.55	1.034	0.993
	33.45		32.87	1.018	0.975
	37.29		37.07	1.006	0.968
2	41.87	1.5	29.09	1.439	1.388
	33.20		27.92	1.189	1.135
	33.55		28.82	1.162	1.112
	35.96		30.48	1.180	1.131
3	32.46	1.5	29.81	1.089	1.039
	34.39		28.59	1.200	1.150
	34.66		30.44	1.139	1.089
	36.26		31.23	1.161	1.113
5	4.90	0.07	5.349	0.916	0.903
	...		5.467
	5.39		5.787	0.931	0.919
	4.98		5.782	0.861	0.849
6	19.52	0.07	21.94	0.890	0.887
	18.88		20.43	0.924	0.921
	19.83		21.74	0.912	0.909
	21.22		21.87	0.970	0.967
7	5.13	0.07	5.013	1.023	1.009
	3.40		4.141	0.821	0.804
	3.43		3.946	0.869	0.852
	3.46		4.143	0.835	0.818
8	3.41	0.07	4.046	0.843	0.826
	3.23		3.978	0.812	0.794
	3.14		3.833	0.819	0.801
	3.20		3.898	0.821	0.803
9	7.12	0.15	7.350	0.969	0.948
	7.18		7.181	1.000	0.979
	7.75		7.524	1.030	1.010
	7.90		7.885	1.002	0.983
10	12.91	0.15	13.41	0.963	0.952
	11.98		12.39	0.967	0.955
	11.92		12.67	0.941	0.929
	12.78		13.70	0.933	0.922
11	30.41	0.15	36.25	0.839	0.835
	28.42		34.46	0.825	0.820
	28.84		32.47	0.888	0.884
	30.29		33.49	0.904	0.900
12	...	0.15	33.48
	31.69		31.71	0.999	0.995
	27.80		28.30	0.982	0.977
	31.28		29.64	1.055	1.050
13	13.64	0.17	14.79	0.922	0.911
	15.09		15.68	0.962	0.952
	15.63		15.66	0.998	0.987
14	5.62	0.17	5.770	0.974	0.945
	5.28		5.422	0.974	0.942
	5.29		5.671	0.933	0.903
	5.87		5.811	1.010	0.981
15	2.18	0.17	2.556	0.853	0.786
	1.91		2.371	0.806	0.734
	1.79		2.383	0.751	0.680
	1.92		2.465	0.779	0.710
<i>n</i>				53	53
<i>m</i>				0.968	0.943
<i>s_m</i> , %				1.9	1.8
<i>r</i>				0.976	0.980

Here, *n* is number of standardized samples, *m* is mean, *s_m* is standard deviation of the mean, and *r* is correlation coefficient.

very approximated values selected from the Lab E data set from adjacent measurement intervals that were believed not to be influenced by the standard sample additions. The large intervals between ambient concentration measurements, which

might otherwise have very suspect assumed *C_{A(E)}* values, could be somewhat verified by normalizing the Lab E results to the uninfluenced Lab F results. Figure 12 shows the results of the reported measurements of *C_{A(F)}* by Lab F (solid line) over the

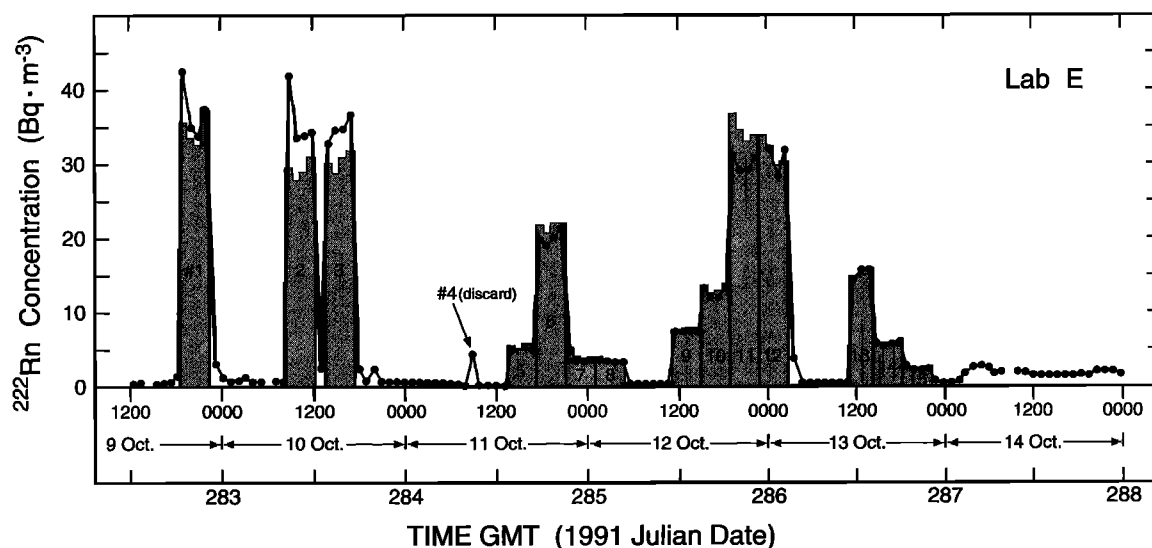


Figure 11. Lab E measurement results for the mean ^{222}Rn activity concentration C_1 (plotted data points) compared with the standardized sample concentrations C_0 provided by NIST (shaded areas). The comparisons exclude contributions from the ambient concentrations C_A (refer to text).

course of the standardized sample additions, along with the reported Lab E values (crossed circles) in the intervals not influenced by the additions. As is indicated in the figure, there appears to be scant cause to suspect that there were any masked irregularities in C_A during the standardized sample additions, and it seems reasonable that assumed values of C_A could be obtained from interpolations.

Subsequent to the analysis by NIST shown in Table 9, Lab E independently reevaluated the background ambient concentrations using a less conservative approach of excluding the first

ambient values following a standard addition. The effect of these background choices on the $(C_{1(E)} - C_{A(E)})/C_0$ results was negligible. The change in $(C_{1(E)} - C_{A(E)})/C_0$ for any standard addition was typically less than 1% and ranged to 2.3% in the worst case.

The comparisons of Table 3 indicate a remarkably excellent agreement between Lab E and NIST. In addition, no significant systematic trends as a function of ^{222}Rn concentration were evident. As can be seen in Figure 11, the comparative concentrations scale in good agreement over the entire range.

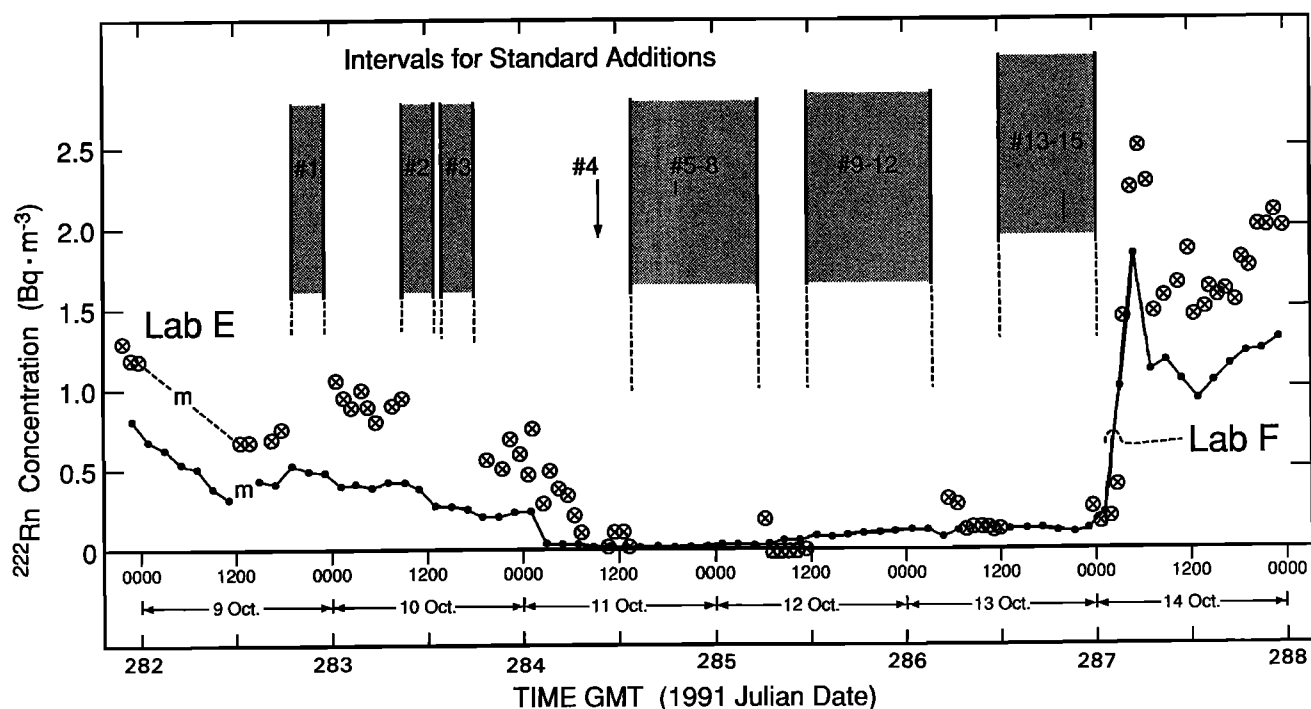


Figure 12. Measurement results by Lab F (solid line) and Lab E (crossed circles) for the natural Bermudian ambient air ^{222}Rn activity concentrations C_A during the time of the standardized sample addition intercomparison. The time intervals for the additions are shown. Refer to text for details and discussion.

Several observations may be noted in regard to Figures 11 and 12. First, in Figure 12, the first measurements of $C_{1(\text{E})}$ for additions 1 and 2 appear to be abnormally high compared with the following three in each series. A question has arisen as to whether the NIST manifold was completely flushed of accumulated radon prior to the commencement of these additions. This could possibly account for the large initial values. Although the incomplete removal of previously accumulated radon can not be absolutely excluded as a possibility (particularly in the first few standard additions, for example, additions e.g., 1, 2, and 3, when the NIST persona grata was somewhat unfamiliar with the test site's experimental layout), it is not believed to have occurred. Also, these large positive deviations in additions 1 and 2 appear to be somewhat matched by the negative deviations of almost comparable magnitude of addition 11, for example, thereby suggesting that the exhibited deviations are statistical in nature. Second the first ambient measurement result $C_{\text{A(E)}}$ by Lab E following a standardized sample addition was invariably elevated above subsequent $C_{\text{A(E)}}$ measurements. This effect is due to the continuous dilution in the decay chamber from one sampling cycle to the next. This incomplete removal of previously introduced activity is most pronounced in changes from very high standard addition concentrations to ambient levels. On the basis of the decay chamber volume (500 L) and flow rate (400 L m^{-1}), the removal is virtually complete within a few minutes. Finally, in Figure 12, the abrupt and large increase in the Bermudian ambient concentration following addition 15 was similarly exhibited in both the Lab F and Lab E data. The same trend is also seen in the data of Lab A and Lab D (Figure 10). The introduced ^{222}Rn activity concentration C_0 for addition 15 was approximately 2.5 Bq m^{-3} . The observed increase in the natural ambient concentration following addition 15 went to experimentally determined C_{A} levels of roughly 1 to 2 Bq m^{-3} . This was a surprisingly unexpected result (based on what the organizers led NIST to believe would be typical ambient concentrations). It was fortuitous in that it occurred at the conclusion of the standardized sample additions; and fortunate in that it provided an almost complete overlap in the ^{222}Rn activity concentrations covered in the intercomparison of Bermudian natural ambient air concentration levels C_{A} (<0.01 to 2 Bq m^{-3}) and in the intercomparison of introduced C_0 concentrations (≈ 2.5 to 35 Bq m^{-3}).

The results of Lab A are summarized in Table 10. Figure 13, which will greatly assist in the understanding of the analysis and interpretation of the comparisons, illustrates these data. The experimental design and protocol used for the standardized additions inherently were very inappropriate for evaluating the Lab A performance. The continuous and slow response of the Lab A instrument is highly suitable for continuous monitoring of slowly varying ambient concentrations. The artificially imposed ^{222}Rn concentration step functions of the standard additions place the evaluation of Lab A at a serious disadvantage compared with automated instruments that operate with finite sample collection and measurement time intervals.

Analysis of the Lab A data was complicated in that the results C_1 are hourly averages of continuously accumulated data "smoothed" by a time constant of 90 min. In effect, the average $C_1(t_i)$ reported during some arbitrary time interval period t_i is influenced not only by the current concentration $C_0(t_i)$ in the sampling stream line as it enters the Lab A delay tank, but also by the concentration $C_0(t_i - j)$ that entered the

Table 10. Lab A Reported Results for the Standard Additions

	^{222}Rn Concentration, Bq m^{-3}				
	Lab A		NIST Std.	Concentration Ratio	
	$C_{1(\text{A}3)}^{\text{a}}$	$C_{1(\text{A}4)}^{\text{a}}$		$C_{1(\text{A}3)}/C_0$	$C_{1(\text{A}4)}/C_0$
1	40.66	36.38	34.91	1.17	1.04
2	29.66	28.02	29.20	1.02	0.96
3	38.43	30.21	30.11	1.28	1.00
5	6.52	9.32	6.09	1.07	1.53 ^b
6	22.36	21.3	22.53	0.99	0.95
7	6.34	4.85	4.35	1.46	1.12
8	4.02	3.39	4.06	0.99	0.83
9	7.46	13.95	7.68	0.97	1.82 ^b
10	13.17	25.39	13.27	0.99	1.91 ^b
11	31.29	...	35.01	0.89	...
12	38.69	31.83	31.06	1.25	1.02
13	15.47	...	15.78	0.98	...
14	7.58	6.62	5.80	1.31	1.14
15	2.67	2.77	2.52	1.06	1.10
<i>n</i>				14	9
<i>m</i>				1.101	1.018
<i>s_m</i> , %				4.0	3.2
<i>r</i>				0.975	0.998

Here *n* is number of standardized samples, *m* is mean, *s_m* is standard deviation of the mean in percent, and *r* is correlation coefficient.

^aThe reported concentrations for the third [$C_{1(\text{A}3)}$] and fourth [$C_{1(\text{A}4)}$] hourly sampling/measurement intervals after the start of the standardized sample additions.

^bSee text.

delay tank in previous periods $t_i - j$ (where $j = 1, 2, 3, \dots$). Thus to obtain any given concentration $C_1(t_i)$, the averaged measured response at a given time must be unfolded from all previous measurements of C_1 during the influencing period. Attempts were made to "unfold" the data set, but without success. Instead, comparisons with C_0 were made, on consideration of the simple physics involved, with the third hourly averaged value $C_{1(\text{A}3)}$ and fourth hourly-averaged value $C_{1(\text{A}4)}$. It could be argued that this approach is somewhat subjective; but, given the limitations of the adopted standard addition procedure for comparisons with this continuous measurement method, no other analysis procedure was found to be feasible.

Even this simple and reasonable approach is only partially applicable in the cases of adjoining standard sample addition intervals when the mean C_0 is adjusted dramatically from one interval to the next. Influences from preceding concentrations C_0 require the passage of at least approximately 4- to 5-hourly intervals as can be clearly seen in the return to ambient concentrations after additions 1 and 3 in Figure 13. This is clearly affecting the results of addition 7 after the abrupt change from 6, and that of 14 following 13. This is the situation for decreasing step changes in C_0 . There is yet one more complicating feature in the data set of Lab A. It is apparent that the values of $C_{1(\text{A}4)}$ for additions 5, 9, and 10, in which the following additions (6, 10, and 11) are increasing step changes, are abnormally high. This strongly suggests a slight difference in timing between that reported for the Lab A data and that for the standard additions in which the onset of activity concentration C_0 for addition *N* is reflected in the reported result $C_{1(\text{A}4)}$ for addition (*N* - 1). This then calls into question the results of the comparison $C_{1(\text{A}4)}/C_0$ for additions 5, 9, and 10

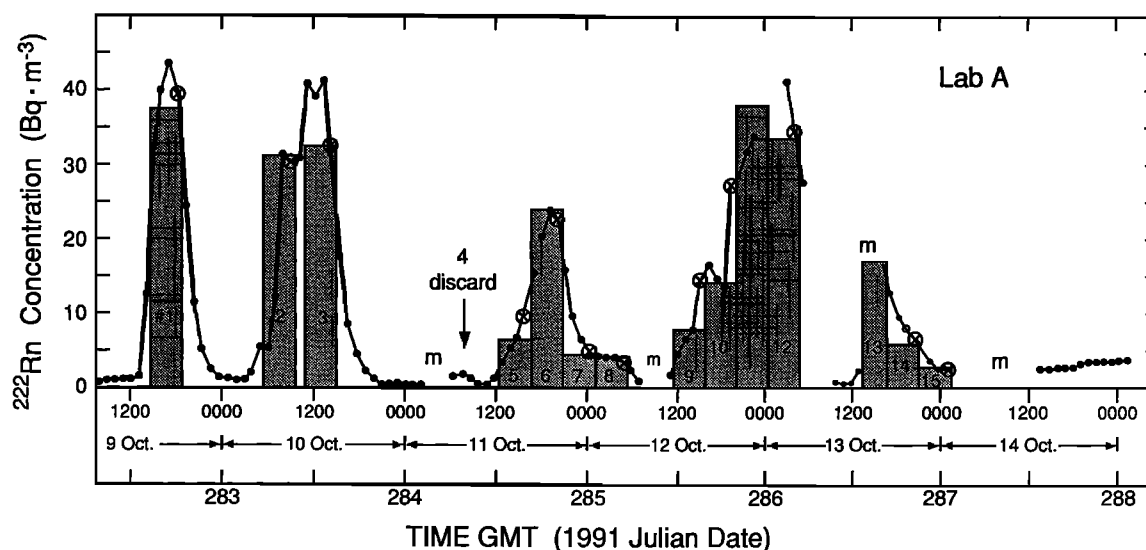


Figure 13. Lab A measurement results for the “smoothed,” hourly-averaged, mean ^{222}Rn concentration C_1 (plotted data points) compared with the standardized sample concentrations C_0 provided by NIST (shaded areas). Comparisons with C_0 were made using the fourth $C_{1(A4)}$ (enlarged crossed circles and third $C_{1(A3)}$ hourly averaged concentrations that followed the introduction of the standardized sample. Refer to the text for discussion.

in Table 4. Figure 13 indicates that the effect of the previous concentration on $C_{1(A3)}$ is not severe for an increasing step change. However, for a decreasing step, the peak contribution remaining at $C_{1(A3)}$ after a decreasing step can cause a substantial overestimate of C_0 . This is readily apparent for additions 7, 14, and 15. The relative magnitude of this overresponse at $C_{1(A3)}$ is roughly 10%.

Nonetheless, even with these inherent limitations, the results of Table 10 indicate a reasonably good agreement between Lab A and NIST, and Figure 13 clearly illustrates the general tracking and reasonably good agreement of their “smoothed” C_1 data with C_0 . Considering the limitations of the experimental design for comparing the Lab A data with the standard additions, NIST felt that the quality of the data comparisons did not warrant attempts to account for contributions from ambient concentrations C_A .

Lab A, following the original NIST analyses and report of the comparisons, suggested that the data set indeed warrants reconsideration. Their independent reanalysis involved using only $C_{1(A3)}$ values, making background corrections using the assumed $C_{A(E)}$ values of Table 9, and correcting these ($C_{1(A3)} - C_{A(E)}$) values by “subtracting 10% of the difference between the current and previous value when the previous value was larger, in order to account for the slow response of the detector” (S. Whittlestone, private communication, 1993). Lab A thereby concluded that with the background subtraction and the correction on the basis of 10% of the concentration change, comparison to NIST “substantially improves,” resulting in a mean corrected $C_{1(A3)}/C_0$ ratio of 1.027 with a relative standard deviation of the mean of 3.3 percent based on 14 comparisons and with a correlation coefficient of 0.978. This may be compared with the NIST analyses of Table 10. It must be emphasized, however, that the 10% corrections suggested by Lab A were not known prior to the intercomparison, and were derived only as a result of the Lab A to NIST standard addition comparisons.

The reported results for Lab D are summarized in Table 11,

which contains the reported values of $C_{1(D)}$ and estimated $C_{0(D)}$ that were derived from their own assumed values for C_A . Comparisons of both $C_{1(D)}/C_0$ and $C_{0(D)}/C_0$ indicate a substantial systematic difference between the results of Lab D and

Table 11. Lab D Reported Results for the Standard Additions

	^{222}Rn Concentration, Bq m^{-3}			Concentration Ratio	
	Lab D		NIST Standard Addition C_0		
	$C_{1(D)}^a$	$C_{1(D)}^b$		$C_{1(D)}/C_0$	$C_{0(D)}/C_0$
1	14.15	13.83	33.43	0.423	0.414
2	12.12	11.67	28.41	0.426	0.411
3	12.57	12.11	28.93	0.434	0.419
5	2.13	2.10	6.22	0.343	0.337
6	7.22	7.18	21.76	0.332	0.330
7	1.31	1.27	4.08	0.320	0.312
8	1.20	1.16	3.98	0.301	0.292
9	3.64	3.59	7.35	0.496	0.488
10	4.34	4.28	12.84	0.338	0.334
11	10.99	10.93	33.36	0.329	0.328
12	13.22	13.16	29.20	0.453	0.451
13	3.02	2.93	8.43 ^c	0.358 ^c	0.347 ^c
14	2.00	1.91	5.54	0.362	0.345
15	0.72	0.63	2.48	0.289	0.254
<i>n</i>				14	14
<i>m</i>				0.372	0.361
<i>s_m</i> , %				4.5	4.8
<i>r</i>				0.980	0.982

^aThe reported total concentration (as observed) due to both the ambient air and standard addition contributions. The reported uncertainties ranged from 3.4 to 3.9%.

^bThe reported net concentration for the contribution due only to the standard addition. It was calculated by subtracting the ambient concentration (as assumed by Lab D) obtained from adjacent measurement intervals. The reported uncertainties ranged from 3.4 to 4.1%.

Here, *n* is number of standardized samples, *m* is mean, *s_m* is standard deviation of the mean, and *r* is correlation coefficient.

^cSee Table 5.

Table 12. Results for the Intercomparison of ^{222}Rn Activity Concentrations in Ambient Bermudian Air (October 5–17, 1991) Among the Participating Laboratories (Normalized to Lab E)

Comparison Estimator	^{222}Rn Ambient Concentration Ratio			
	$C_{A(F)}/C_{A(E)}$	$C_{A(A)}/C_{A(E)}$	$C_{A(D)}/C_{A(E)}$	"Ideal"
Number of comparisons	202	104	72	...
Minimum	0.063	0.898	0.256	1
Maximum	2.72	16.0	3.50	1
Median	0.600	1.251	0.399	1
Mean	0.649	1.908	0.628	1
s_m , %	4.7	10.3	11.5	...
r^a	0.877	0.931	0.878	1
Linear regression ^a intercept α	-0.037	0.270	0.076	0
s_α , %	61.	14.	30.	...
Linear regression ^a slope β	0.592	0.974	0.331	1
s_β , %	3.9	3.9	6.5	...

Here s_m is standard deviation of the mean; r is the correlation coefficient for the relative mutual dependence of variables $C_{A(\text{LAB})}$ and $C_{A(E)}$, where LAB = F, A, D; and s_α and s_β are the standard deviation of the mean for the regression coefficients α and β .

^aFor the regression function $C_{A(\text{LAB})} = \alpha + \beta C_{A(E)}$, where LAB = F, A, D.

that of NIST. The systematic proportional bias of approximately 0.37 in the concentration ratios was invariant over the range of concentrations. This effect was attributed by Lab D to a calibration error introduced by using the assumed calibration factors provided by the manufacturer of a commercially available, flow-through ^{226}Ra calibration source that was used by Lab D for their calibrations.

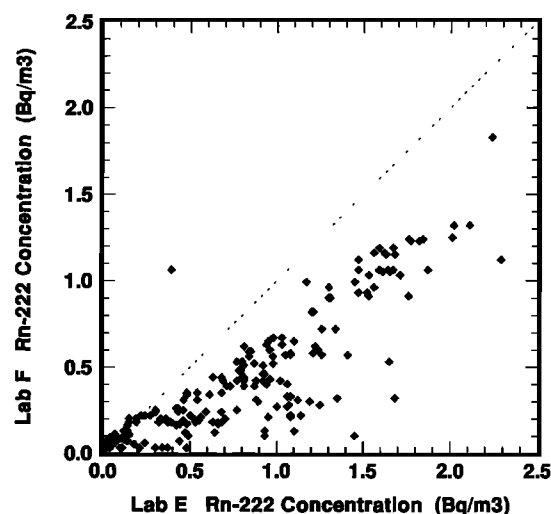
4.3. Intercomparison of Ambient Air Concentrations

For the intercomparison of mean ^{222}Rn activity concentrations C_A in ambient Bermudian air among all four participating laboratories, the data set of Lab E was selected to provide the necessary normalization. It was chosen because it not only was the largest and most complete data set available, but also seemed to be the data set whose C_A values were most in the midrange of all reported C_A values.

The comparisons were made by selecting pairs of the nearest adjacent values of C_A , in terms of their reported midpoint times, for Lab E and for the other participating laboratory. The paired values [$C_{A(E)}$ and $C_{A(\text{LAB})}$ where LAB = F, A, D] could then be used to form a set of comparison ratios $C_{A(\text{LAB})}/C_{A(E)}$. For example, a $C_{A(F)}$ value for Lab F whose midpoint time was 1700 would be compared to the $C_{A(E)}$ values at both 1630 and 1730 for Lab E. The Lab A $C_{A(A)}$ and Lab E $C_{A(E)}$ values typically had the same midpoint times and could be compared directly. No attempt was made to try to account for the "smoothing" effect in the Lab A data. The $C_{A(D)}$ results of Lab D similarly were compared to the nearest $C_{A(E)}$ values that were reported both before and after the midpoint time for the $C_{A(D)}$ results. In no cases were any comparisons made for values whose midpoints were separated by more than 1.5 hours. Also, every effort was made to avoid the selection of paired $C_{A(E)}$ and $C_{A(\text{LAB})}$ values that might have been influenced by the introduced activity of the standardized sample additions. This pairwise selection of reported values then comprised the data sets that were analyzed over the course of the entire 2-week intercomparison period (excluding the intervals for the standardized sample additions). Similar independent evaluations were also performed by making direct comparisons of $C_{A(A)}$ to $C_{A(F)}$, $C_{A(D)}$ to $C_{A(F)}$, and $C_{A(D)}$ to $C_{A(A)}$. In all cases, the results of the various comparison estimators (see

Table 12) were statistically consistent and redundant with the results that follow.

Table 12 summarizes the results of these $C_{A(F)}/C_{A(E)}$, $C_{A(A)}/C_{A(E)}$, and $C_{A(D)}/C_{A(E)}$ ratios in terms of various statistical estimators (median and mean values, etc.). The scatter diagrams of Figures 14 through 16 illustrate the data. The dotted line in each figure is the "helping line" for when the comparison ratios are equal to unity, i.e., for the "ideal" of exactly equal reported concentrations C_A . The regression estimators α and β are included in Table 12, since the results of a linear regression on sets of two measurement results which are estimates of the same quantity (e.g., for the case $C_{A(F)} = \alpha + \beta C_{A(E)}$ for the variables $C_{A(F)}$ and $C_{A(E)}$ that are estimating the "true" C_A) are informative. The slope β (for intercept $\alpha \approx 0$) is often a better comparison estimator of the agreement between the two variables than is an estimator of central tendency (e.g., the mean or median) alone. This is

**Figure 14.** A scatter diagram of 202 paired values of $C_{A(F)}$ and $C_{A(E)}$ for the ^{222}Rn activity concentration in ambient Bermudian air measured by Lab F and Lab E during the intercomparison.

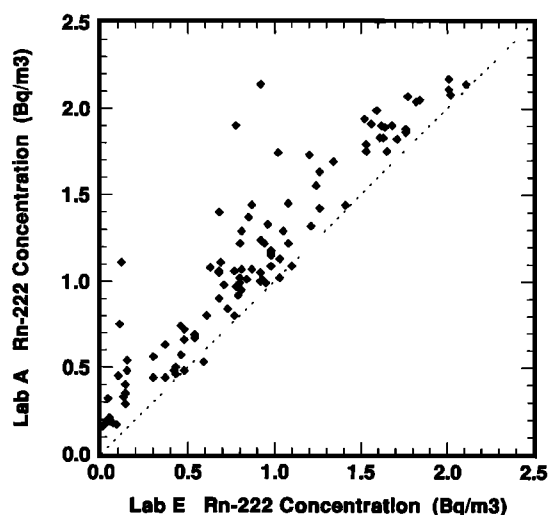


Figure 15. A scatter diagram of 104 paired values of $C_{A(A)}$ and $C_{A(E)}$ for the ^{222}Rn activity concentration in ambient Bermudian air measured by Lab A and Lab E during the intercomparison.

particularly true when the variables have large statistical variability. Means of ratios (e.g., $C_{A(F)}/C_{A(E)}$) can be substantially influenced by even a few exceedingly high or exceedingly low values, and their exclusive use in comparisons can lead to seriously misleading or distorting results.

4.4. Discussion of Findings

The results of the intercomparison itself are nearly self-evident on examination of the summaries in Tables 9, 10, and 11 for standardized sample additions and Table 12 for the ambient concentrations.

Lab E and Lab A were in excellent agreement with the NIST additions. The vast majority of reported values for both laboratories, over the entire 2.5 to 35 Bq m^{-3} concentration range, were within the 6 to 13% relative 3 standard deviation uncertainty interval associated with the NIST additions. The Lab D results for the standardized additions were obviously proportionately biased by a mean factor of about 0.36, which may be attributable to an instrument calibration error. The Lab D reported concentrations, after correction of all of its values by this common factor, are then in good agreement with both Lab E and Lab A. Further, the Lab E data, Lab A data, and corrected Lab D data track the fluctuations of radon concentrations very well over the entire range of concentrations even though the numbers of data values from the three laboratories were substantially different.

The intercomparison of reported ambient concentration values were performed by normalizations to the Lab E data. The results were statistically invariant of this arbitrary choice; normalizing to any other laboratory set results in redundant and statistically equivalent comparison estimators (means, linear regression slopes, etc.) (see Table 12). These ambient concentration results were wholly compatible with and reinforced the findings of that found for the standardized sample additions. The slope β of a linear regression of the reported ambient concentrations from the two laboratories under comparison was considered the best available comparison estimator. Concentration pairs selected for the comparison regressions were nearest measurement values in terms of their midpoint times.

For comparison of Lab A to Lab E, $\beta = 0.97 \pm 0.11$, which again is indicative of the generally good agreement between these two laboratories' results. (All of the uncertainty intervals that follow are assumed to correspond to 3 standard deviations and are assumed to provide an uncertainty interval having a high level of confidence of roughly 95 to 99%.) The median and mean values, however, are 1.3 and 1.9, respectively, indicating that the Lab A values are, in general, systematically high with respect to Lab E. Examination of Figure 15 reinforces this and confirms the generality. The difference may be explained by noting that although the slope β is very nearly equal to unity, which in itself would indicate good agreement with Lab E (and NIST by inference), the intercept of the regression, however, is substantial: $\alpha = 0.27$, which implies a uniformly offsetting bias of about 0.3 Bq m^{-3} that is more significant at low concentrations (e.g., ambient air) than at higher concentrations (e.g., in the standardized sample additions). Possible reasons for this nonzero offset in terms of the Lab A and Lab E instrumentation are unknown. Both the generally higher results of Lab A and the nonzero offset in comparison with Lab E may, of course, be due to unaccounted thoron (^{220}Rn) background contributions with the Lab A results. Equally possible, the apparent offset may not necessarily be attributable to an offset by the Lab A results but rather may be due to a negative offset in the Lab E results due to an oversubtraction of background by Lab E. The latter possibility is supported in part by comparisons of the Lab E to Lab D results (after invoking a 65 to 70% correction to the Lab D results as concluded from the comparisons with standardized additions).

For the Lab D to Lab E comparison, $\beta = 0.33 \pm 0.06$, which exhibits the same magnitude proportional bias found in the comparison to standardized sample additions. If one evaluates the Lab A data, Lab E data, and corrected Lab D data (after correcting all of the Lab D values by a common reciprocal correction factor of 0.36), all three laboratories were in good agreement in tracking changes in the ambient concentrations from the relatively high 2 Bq m^{-3} ambient levels down to concentrations of a few hundredths of 1 Bq m^{-3} . Differences were greatest at the very lowest ambient concentrations be-

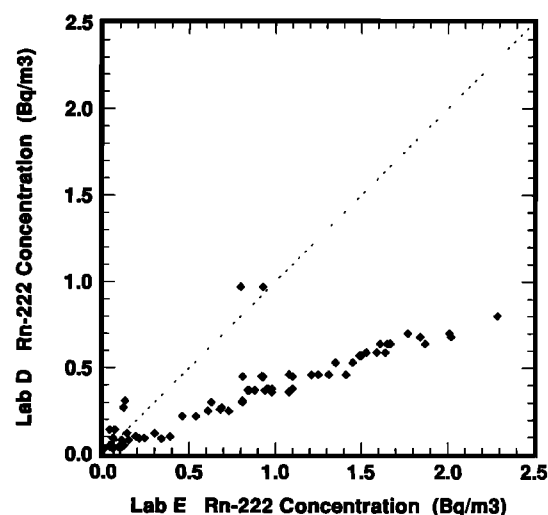


Figure 16. A scatter diagram of 72 paired values of $C_{A(D)}$ and $C_{A(E)}$ for the ^{222}Rn activity concentration in ambient Bermudian air measured by Lab D and Lab E during the intercomparison.

cause of the apparent offset in the Lab A/Lab E regression. The offset between Lab D and Lab E was nearly negligible, $\alpha = 0.076 \pm 0.068 \text{ Bq m}^{-3}$. However, if one invokes the same correction as before to the Lab D data, then the corrected intercept $\alpha = 0.23 \pm 0.22 \text{ Bq m}^{-3}$ would seem to support the latter overcorrected background argument. The magnitude of the uncertainty intervals for the intercept values, however, does not make the argument compelling.

For the Lab F to Lab E comparison, $\beta = 0.59 \pm 0.07$ indicating an approximate 40% disagreement which is also consistent with the $C_{A(F)}/C_{A(E)}$ mean. This difference is equally manifest in direct comparisons between the Lab F and Lab A measurement data and in direct comparisons between Lab F and corrected Lab D data. The Lab F to Lab E intercept $\alpha = -0.04 \pm 0.07 \text{ Bq m}^{-3}$ is truly negligible. This result does not support the previously observed offset between Lab A and Lab E even if the Lab F data are renormalized (i.e., "corrected") by the reciprocal of the observed β between Lab F and Lab E. Throughout the course of the ambient concentration intercomparison period, over all concentration ranges, the Lab F data appropriately scaled (by a factor of roughly 0.6) over all concentration ranges with the Lab E data along with the Lab A data and similarly scaled (by a factor of roughly 1.8) with the Lab D data. The Lab F results might suggest that ^{222}Rn was not, as was assumed, in secular equilibrium with its daughters and that the equilibrium ratios substantially differed from unity as a result of unexpectedly large condensation nuclei concentrations in the sampled Bermuda atmosphere.

A considerable number of additional statistical analyses beyond those reported here were performed on the data sets. These, noted for completeness, included (1) sequential time analyses to determine if there were any time dependencies or correlations in the observed measurement differences between the participating laboratories or with the NIST standardized sample additions, (2) regression analyses between the results of each participating laboratory and the NIST additions, (3) regression analyses between every combination of participating laboratory pair; (4) χ^2 tests for all regressions and comparison frequency distributions, (5) divisions of the ambient concentration comparison data for the participating laboratory pairs (first into halves and then into thirds), and testing of the resulting data subsets for differences in the various means using t tests and for homogeneity in the various subset sample means and variances using χ^2 and F tests, and (6) sequential two-variable analysis of variance (ANOVA) techniques for differences in similarly constructed subset means and variances. The results of these analyses were not reported, since they added nothing to the analyses that were reported or to the findings and conclusions.

In order to maintain the integrity of the intercomparison, R. Collé, representing NIST, retained overriding authority among the coauthors with regard to the statements of the results and the conclusions as reported herein. The data interpretations, design of the evaluation procedures, and statistical analyses are his and his alone. Each of the participating laboratories provided supplemental information, such as descriptions of their respective instruments and measurement methodologies, contributed to the discussion, and had an opportunity to comment on the NIST analyses.

The design of the intercomparison was as near as the investigators could come to conducting a "blind" comparative exercise. The exercise was "blind" in several regards: (1) the standard sample additions provided by NIST were introduced

with undisclosed ^{222}Rn activity concentrations, and the NIST results were not disclosed and released until all of the participating laboratories had provided their respective measurement data. (2) The timing and duration of the NIST standard sample additions were also largely unknown to the participating laboratories. (3) NIST participation required that once the participating laboratories reported their measurement values, the data would be analyzed and reported without subsequent modifications or corrections to the originally reported values. (4) Although NIST knew the approximate activity concentrations at the time of the introduction of the standardized sample additions, the final mean activity concentrations provided to each participating laboratory during their respective sampling intervals were not known by NIST until after reduction of the extensive flow rate data base. (5) NIST provided the standardized sample additions largely in complete ignorance of the underlying ^{222}Rn ambient concentration at the time of the additions.

This intercomparison was not without imposed limitations. Although all of the principal measurement methodologies used to continuously monitor marine air masses (where typical concentrations are much lower than found in continental air masses and where humidity levels vary) were represented by the participating laboratories, funding and space limitations of the experimental site could not accommodate other groups making atmospheric radon measurements. It is arguable that the intercomparison exercise was too short in duration. Excluding the period for the intercomparison of standardized sample additions, the time for intercomparison of ambient air concentrations was of the order of 2 weeks, and even this period was not continuous. Without question, continuous intercomparison measurements over longer time intervals, two or more uninterrupted weeks or even months, would have been much better. Equally, it would have been more useful to conduct correlations with meteorological data and with ^{222}Rn progeny measurements and equilibrium ratios. These correlations would have been useful in discriminating the air masses' origin, to know if they are of direct continental origin, or marine origin, or mixed. In this way it might have been possible to discern if the apparent discrepancies among some of the participating laboratories were different in relation to differing meteorological situations or condensation nuclei concentrations (e.g., to account for differences between Lab F and Lab E). The differences between the measurements of Lab A and Lab E, for example, were not apparent in previous intercomparisons (S. Whittlestone, private communication, 1993). These kinds of efforts, however, were beyond the scope of this work.

This intercomparison was not intended to critique or evaluate the various instruments or measurement methodologies in terms of their advantages, disadvantages, or suitability for performing continuous ^{222}Rn monitoring in marine atmospheres. The sole intent was, as stated, to provide an unbiased and refereed intercomparison of ^{222}Rn activity concentration measurements made by four laboratories and to provide three of these laboratories, under somewhat inappropriate and limiting experimental test conditions for at least one laboratory, with introduced samples containing known, but undisclosed (i.e., "blind") ^{222}Rn activity concentrations that could be referenced to U.S. national standards. To wit, for the purposes of this intercomparison exercise, the various instruments and measurement methodologies were viewed much as the diversity of prevailing religious modes of worship was regarded in

the late Roman empire: all equally true; all equally false; all equally useful [Gibbon, 1776].

5. Conclusions

This exercise was unique among other environmental inter-comparisons, and it fulfilled two major objectives.

First, this work provided an unbiased, refereed basis for comparing the measurement results and performance of four principal instruments (as employed by four different laboratories) that are used to measure ^{222}Rn activity concentrations for marine atmospheric studies. Collectively, these instruments and laboratories represent those responsible for a significant fraction of the atmospheric ^{222}Rn measurements made over the past decade. The intercomparison utilized a common standardized, in situ, reference basis that could be directly related to U.S. national, and internationally recognized, ^{226}Ra and ^{222}Rn standards. The findings of the intercomparison may assist various users (e.g., those in the global modeling community) in applying the available and future ^{222}Rn measurement data bases in a more reliable and effective manner.

Second, the work went beyond serving the needs of this particular intercomparison. It also demonstrated the broader utility of the calibration protocol and the methodology for the standardized sample additions that were developed for it. Most environmental measurement intercomparisons of field instruments in actual use merely rely on evaluating the relative performance of the participants, or some comparison to the pooled results. This exercise demonstrated, for the very first time, the capability of providing a standardized reference basis even for such low-level, field-measurement intercomparisons. The developed methodologies presented here could, of course, be adopted with slight modifications to cover other ^{222}Rn concentration ranges and other applications and could be employed in many other types of ^{222}Rn environmental, field measurement intercomparisons.

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for the intercomparison, as well as providing the detailed meteorological records; and for the services provided by the Bermuda Biological Station for Research, especially those of Anne Glasspool, without whose cooperation and help this exercise would not have been possible. The National Institute of Standards and Technology (NIST) is an agency of the Technology Administration, U.S. Department of Commerce. The mention of commercial products does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

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