Appl. Radiat. Isot. Vol. 43, No. 1/2, pp. 175–189, 1992
Int. J. Radiat. Appl. Instrum. Part A
Printed in Great Britain

0883-2889/92 $5.00 + 0.00
Pergamon Press plc

An International Radon-in-Air Measurement Intercomparison Using a New Transfer Standard

J.M.R. HUTCHINSON, J. CESSNA, R. COLLÉ AND P.A. HODGE

National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

A new secondary measuring system for ^{222}Rn-in-air that can be used as a very efficacious transfer calibration standard for measurement intercomparisons between laboratories has been developed and extensively tested. The system is based on measurements of the photon emission rate of radon samples contained in spherical 35-mL glass ampoules with a NaI(Tl) well counter. The system is calibrated against the NIST pulse-ionization-chamber (PIC) national radon measuring system, and has an overall uncertainty of approximately 2 percent. An international intercomparison of 11 laboratories, including NIST, using this system was performed.

Introduction

The National Institute of Standards and Technology (NIST) has recently developed a transfer radon measuring system and transfer calibration standard that is based on the measurement of radon-in-air samples in small, spherical glass ampoules with a calibrated NaI(Tl) well counter. This measuring system is used to intercompare quantities of total ^{222}Rn activity contained in sample bulbs by measuring their photon-emission rates with the NaI(Tl) scintillation detector. The counting method is very reproducible, fairly independent of geometry effects, and has a very linear and wide dynamic operating range for samples from a few bequerel to nearly 10^4 Bq. The relatively small total sample volumes are advantageous for insuring complete gas-sample transfers to other laboratories' measuring systems. This methodology also has the advantage of being able to directly and independently measure and verify the total activity contained in each sample prior to its shipment to other laboratories, unlike other intercomparisons [e.g., Fisenne, 1990] where often one must assume that comparable samples were filled homogeneously and identically.

This paper describes the completion of the development work for the radon measuring system and its application to measurement intercomparisons and as a transfer calibration standard, including : (i) calibration of the NIST national radon measuring system which utilizes pulse-ionization chambers in conjunction with the national ^{226}Ra solution standards; (ii) development and testing of the new sample-bulb and

NaI(Tl)-detector relative measuring system; (iii) cross calibration of this relative system against the NIST national radon standard measuring system; and (iv) an international intercomparison performed using this new system.

The measurement intercomparison was proposed at a previous International Committee for Radionuclide Metrology (ICRM) meeting in Braunschweig, Germany [Hutchinson and Collé, 1990]. The purpose of the intercomparison was to establish an international basis for radon calibrations among the various national metrology laboratories and principal laboratories within the U.S. that maintain an independent radon calibration capability based on radium solution standards. It was determined from the reports and subsequent discussion at that time that these laboratories by and large had calibration uncertainties of the order of ± 5 percent. For NIST, or any other laboratory, to serve as a reference laboratory, its calibration uncertainty should be not greater than the order of ± 2 percent.

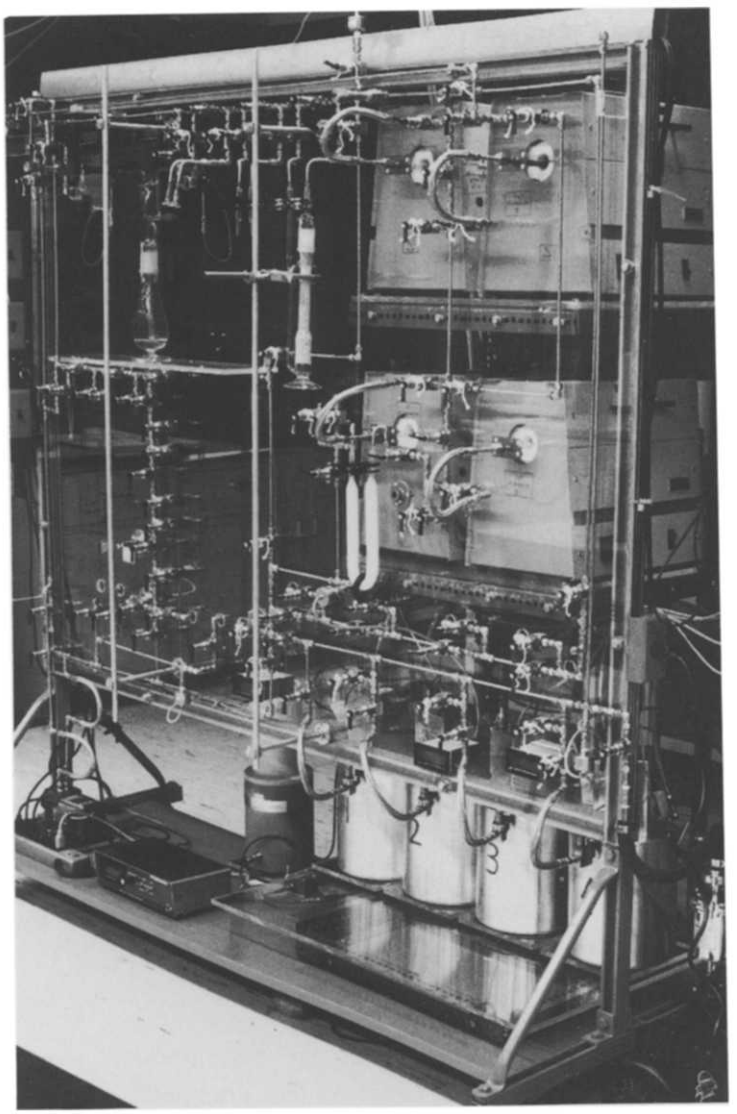

Fig. 1. The NIST radon measuring system showing the four pulse-ionization chambers and complete gas-handling and gas-purification manifold.

Calibration of the PIC System

The NIST national radon measuring system is shown in Figure 1 and has been discussed previously [Collé *et al.*, 1990]. It consists of four, approximately four-liter pulse-ionization chambers (PIC) which are calibrated against NIST radium solution standards contained in modified gas-washing bottles ("bubblers"). Calibrations are performed by quantitatively transferring known accumulated amounts of radon into the chambers by slowly bubbling a carrier stream of nitrogen-gas stream through the radium solution, and passing the gas stream through the ancillary gas purification system. The latter consists of a mixed bed of commercial desiccants (anhydrous $CaSO_4$ and NaOH on nonfibrous silicate carrier) to dry the gas and remove acid vapors, a copper furnace to remove the oxygen, and a bed of magnesium perchlorate for a final drying step. Typically 10 to 15 sequential, replicate measurements are made for each chamber filling. The data are collected in the form of a spectrum on a dedicated "personal" computer which has the capability for input multiplexing and multiple-channel energy analysis. Extrapolations are made to zero energy. Background is subtracted and the data are corrected for decay to the end of the gas transfer time. Dead-time corrections ($\tau_d \sim 10\ \mu s$) are negligible for the count rates used (typically less than 10 s^{-1}).

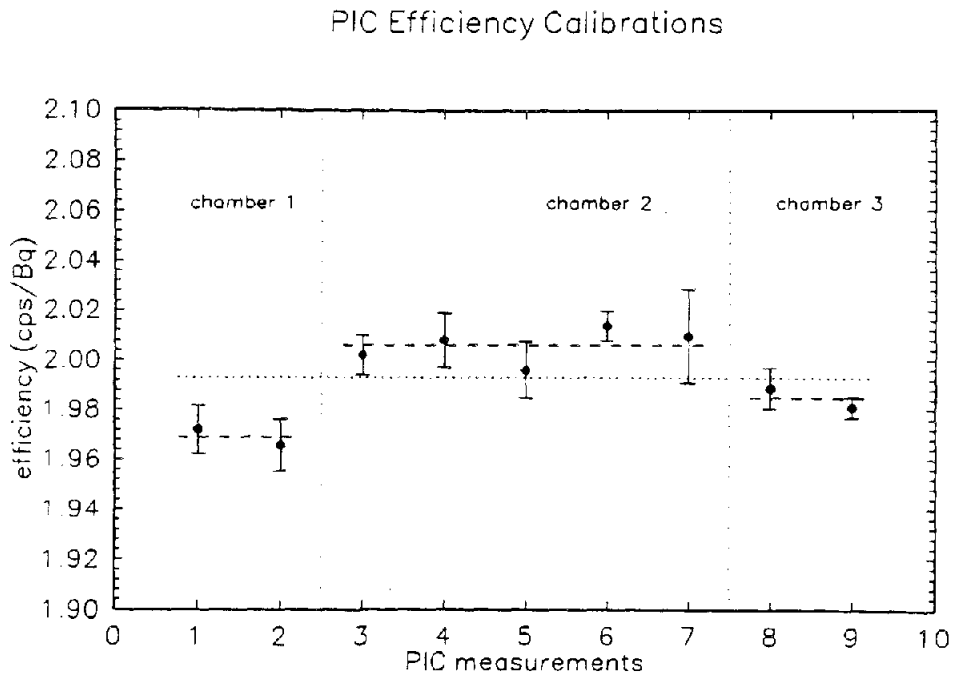

Fig. 2. Typical PIC efficiency calibrations for three chambers.

Typical PIC efficiency calibrations for three chambers are summarized in Figure 2. Although all the chambers have about the same efficiency (approximately 2.0), there are slight differences from each other by a few percent. The "error bars" on each individual point shown in Figure 2 represent the estimated standard deviation of the mean for about ten replicate counting measurements. The typical precision for these measurements is illustrated in Figure 3 for 27 different chamber fillings, each based on 9 to 16 replicate measurements. The distribution in Figure 3 roughly exhibits that expected for a standard

deviation sampling distribution for random samples selected from a normal population (i.e., the sample variance being χ^2 distributed). The estimated relative standard deviations, typically 0.4 to 0.6 percent, is about the same as the statistical expectation for the Poisson "counting error" based on the total number of counts for a measurement, indicating essentially that there are no significant additional sources of measurement variability between different chamber fillings.

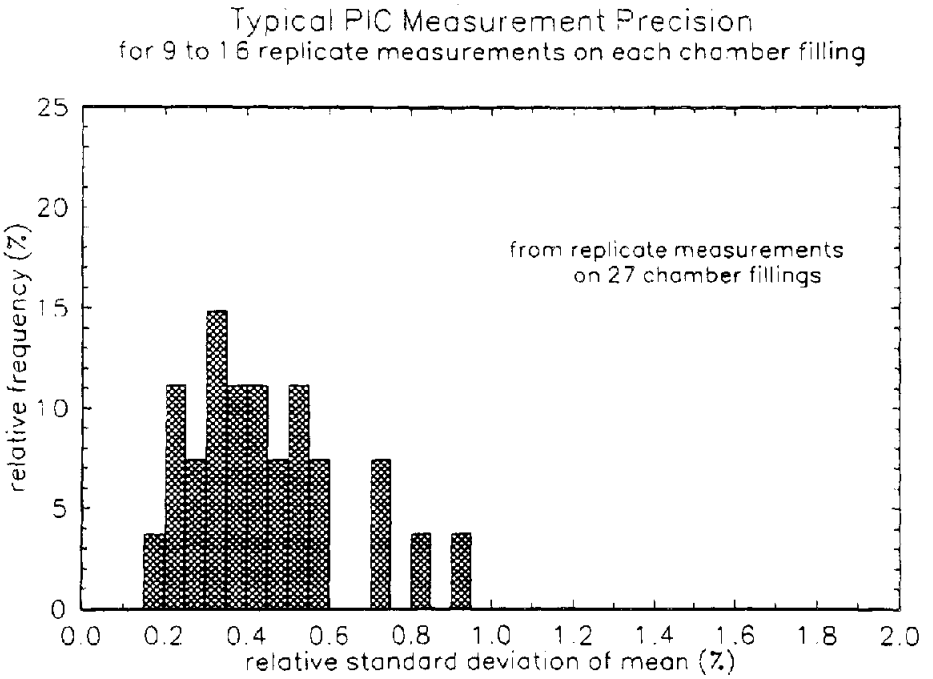

Fig. 3. Distribution of the relative estimated standard deviation of the mean for 9 to 16 replicate measurements showing the typical PIC measurement precision in 27 different chamber fillings.

NIST NaI(Tl)-Glass Bulb Relative Measuring System for ^{222}Rn

The new measuring system is schematically illustrated in Figure 4, and includes a shielded 13-cm NaI(Tl) detector with a 6.4-cm-diameter well. The approximately 4.2-cm-diameter bulb has 1-mm capillary inlet tubing with O-ring type valves that are located just outside the detector well when the bulb is in the measuring position. The contained volume in the capillary and valves is approximately 1 percent of the volume of the bulb itself. The valves have been examined extensively for leakage as shown by the typical results given in Figure 5 which shows the NaI(Tl) count rate, corrected for radon decay, for a given bulb as a function of time elapsed after filling. No systematic slow-leakage losses were observed in any of the evaluations.

Because the radon samples were to be sent by air freight, possibly in low-pressure compartments, a study was made to assess the reliability of the valves during transport. The procedure for testing was to fill the bulbs, follow the response in the NaI(Tl) detector for a few days, and to send them to the Environmental Measurements Laboratory,

New York, by air express. They were sent back to us immediately, unopened, also by air. They were then recounted to assess whether there had been any loss of radon. This and other measurements gave no indication of radon loss for any of the bulbs tested.

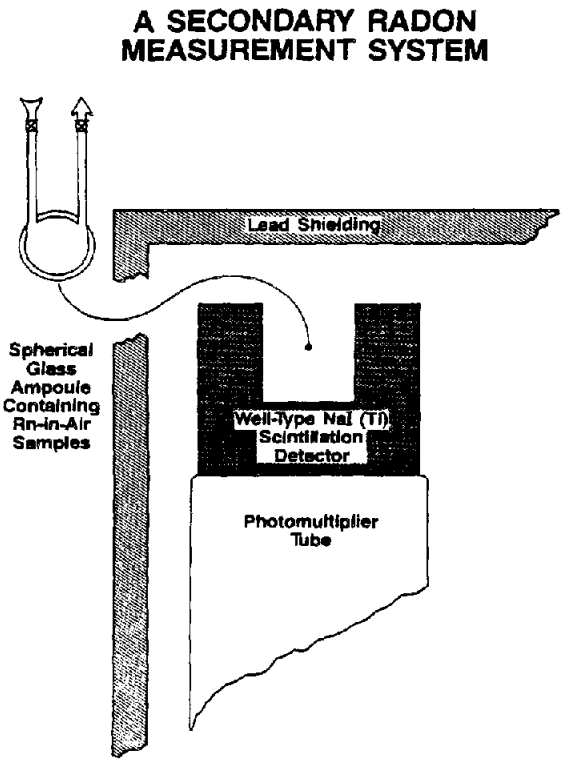

Fig. 4. Schematic of the new NIST radon transfer standard measuring system based on NaI(Tl) measurements of spherical glass ampoules containing radon-in-air samples.

A check on the stability of the NaI(Tl) counting system was performed. An encapsulated solid ^{226}Ra reference source was measured twice a week over a 7-month period and the results are shown in Figure 6. As indicated, the variability in the detector response (as measured by the residual from the mean count rate) is random and scatters with a range of about ± 0.1 percent over the period.

The typical NaI(Tl) measurement precision based on 2 to 6 replicate measurements on each sample bulb for 85 different sample bulb fillings is shown in Figure 7. The estimated relative standard deviation of the mean is typically 0.1 percent, and the sampling distribution of Figure 7 again suggests that expected from random sampling from a normal population. There are no indications of any non-random, systematic effects introduced as a function of time or as a result of the samples being taken out and reinserted into the NaI(Tl) well detector.

Calibration of the New Transfer System

The NaI(Tl) transfer-standard system was cross calibrated against the basic NIST PIC radon calibration system by filling the sample bulbs, measuring the bulbs with the NaI(Tl)

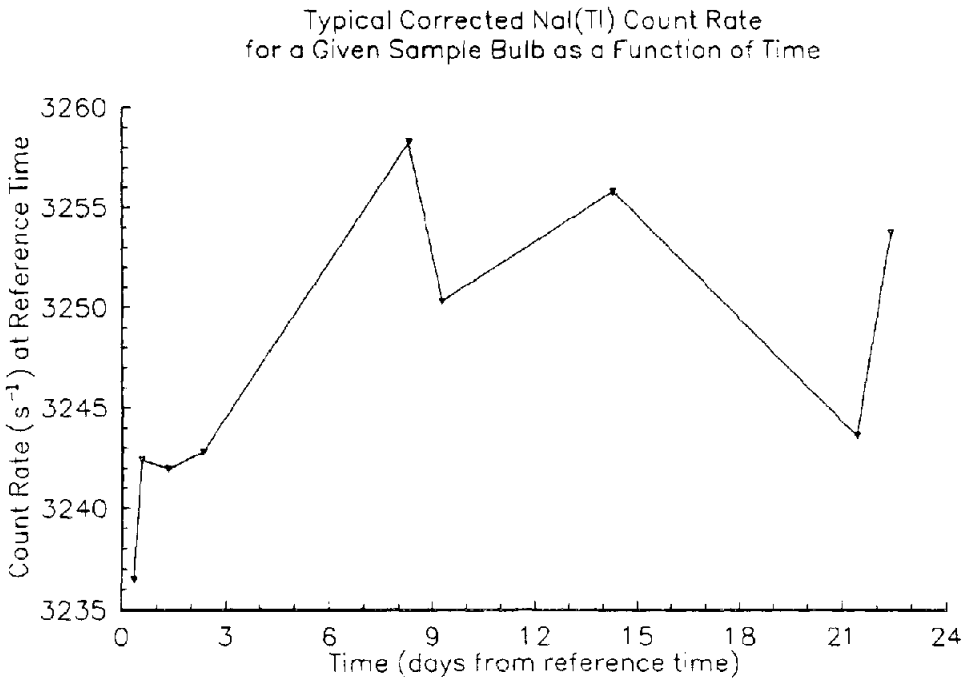

Fig. 5. Typical NaI(Tl) counting results, in terms of emission rate corrected for deadtime, decay, and background as a function of time, illustrating the integrity and stability of the radon-in-air sample bulbs. The sample decayed over a factor of 250 during the time of these measurements.

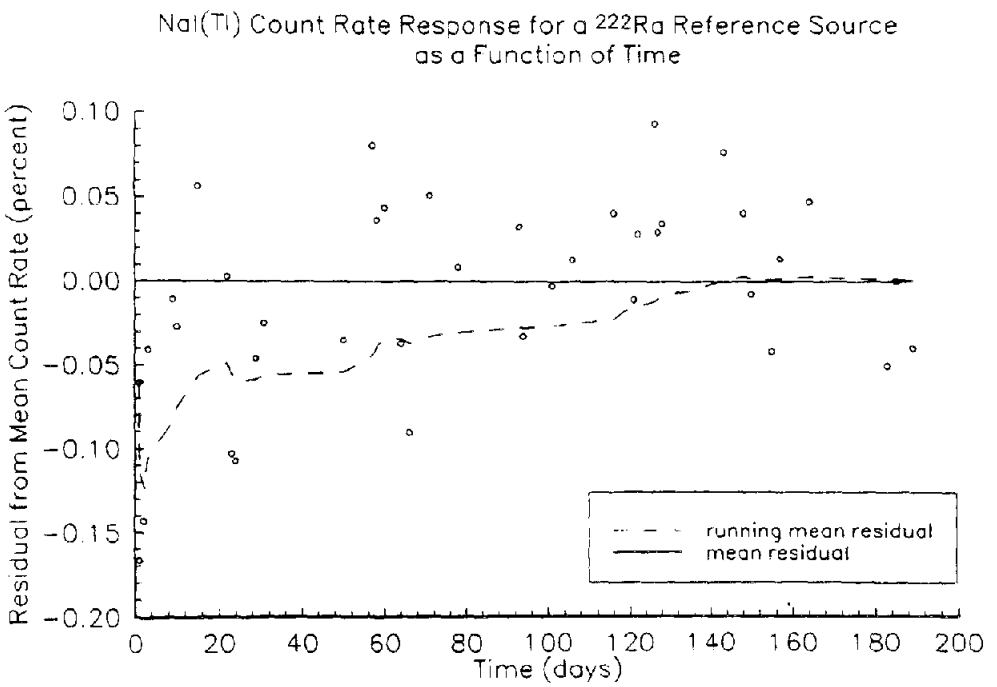

Fig. 6. Stability of the NaI(Tl) counting system based on measurements with a solid encapsulated radium reference source over a 7-month time period.

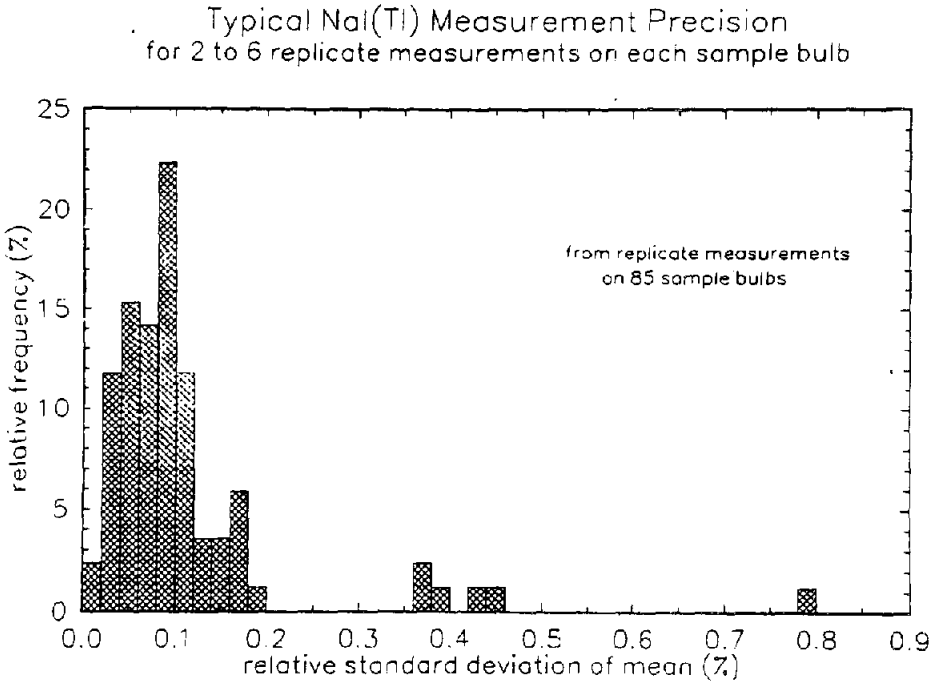

Fig. 7. Distribution of the relative estimated standard deviation of the mean for 2 to 6 replicate measurements showing the typical NIST NaI(Tl) measurement uncertainties on 85 sample bulbs.

system, and subsequently measuring the samples with the PIC system. Initial (end of filling) sample activities ranged from a few hundred to nearly 10,000 Bq. Samples could be followed by the NaI(Tl) detector over a very wide dynamic range. Decay corrections over a range of even 5 to 6 half lives were reproducible and consistent. A half life of 3.825 d was used.

Following the NaI(Tl) measurements, the samples were allowed in all cases to decay to levels, typically < 10 Bq, that could be measured by the PIC. The samples were transferred to the PIC system using a method as nearly identical as possible to that used for calibrations with the radium solution standards. The samples are introduced at three inlet ports on the gas manifold located immediately after the radium standard assembly (see Figure 1). Of course, when it is used in this mode the system is set to bypass the radium standard.

The data of Figure 8 clearly demonstrate that in regard to the PIC measurement precision, there is no difference when the chamber is filled from sample bulbs or from the radium solution standard. Based on past experience there is an appreciable deterioration in both PIC detection efficiency and in measurement precision if there is incomplete oxygen or water removal.

The linearity between the transfer system count rates and PIC calibration activities over a wide activity range is clearly shown in Figure 9. An additional data point at about 7000 Bq also falls on the linear plot, but is not shown in the figure. The slope of the line,

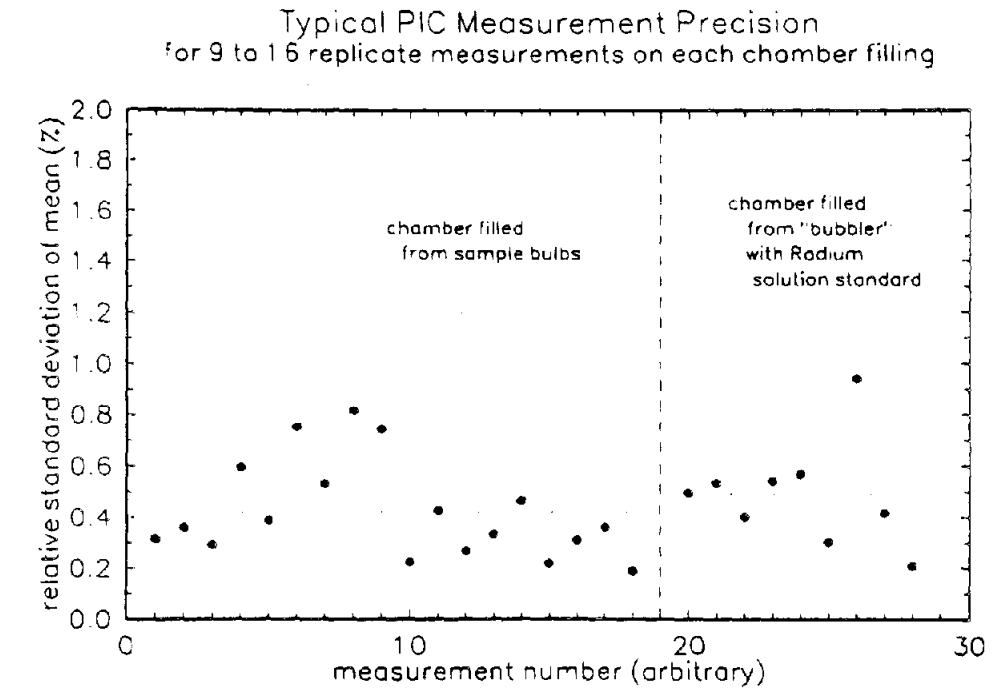

Fig. 8. Typical PIC measurement precision (data of Fig. 3) showing the comparability in measuring precision with the chamber filled from sample bulbs and from a radium solution standard "bubbler".

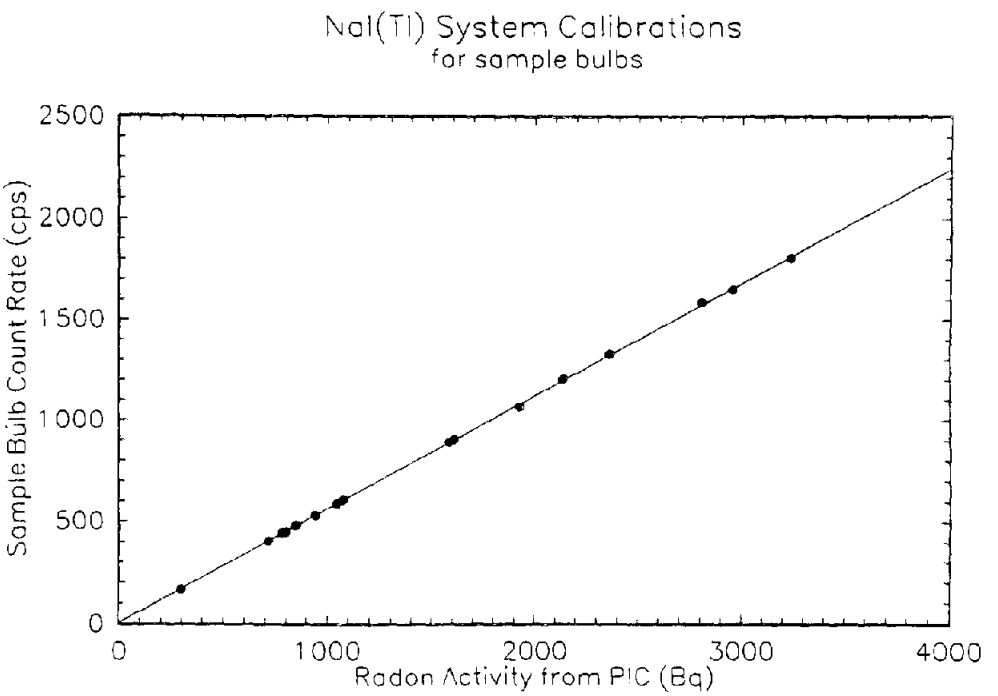

Fig. 9. Linearity in the NaI(Tl) measurement system and calibration against the PIC. An additional data point at nearly 7000 Bq is also linear, but was not shown to avoid compression of the axes.

of course, corresponds to a system calibration factor in terms of the NaI(Tl) count rate per bequerel.

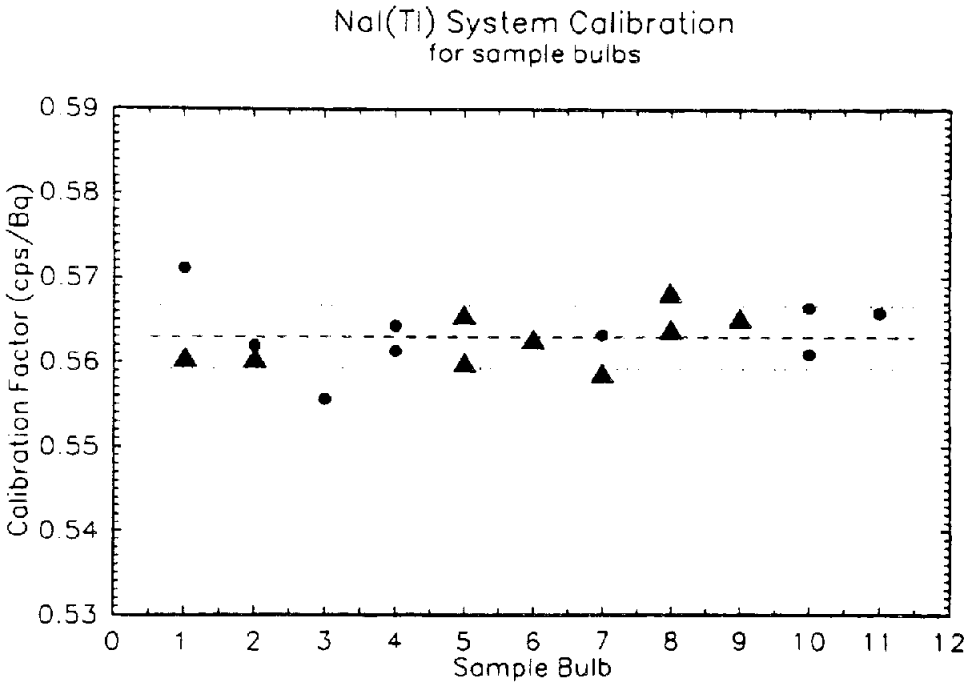

Fig. 10. Calibration factor for the NaI(Tl) system, in terms of the NaI(Tl) count rate per unit activity (as measured with PIC), for 18 measurements on 11 different sample bulbs. The circles and triangles represent measurements obtained with PIC chambers 2 and 3, respectively.

The same data are exhibited in Figure 10 as a function of sample bulb number for 18 different sample fillings using 11 different bulbs. As indicated in the figure, two different chambers were used for the activity determinations. Based on replicate measurements, the precision on the between-bulb variability was in all cases comparable to that for within-bulb reproducibility suggesting that there is not a significant additional component of variance due to differences in the sample bulbs. Similarly, the results of measurements with each of the two different chambers were not statistically different than that within a given chamber. The calibration factors obtained were:

for bulbs with chamber 2	0.5634	(± 0.25%)
for bulbs with chamber 3	0.5624	(± 0.13%)
for all bulbs	0.5629	(± 0.22%)

where the quoted uncertainty percentages are calculated relative standard deviations of the mean with 8, 8, and 17 degrees of freedom, respectively, and includes the measurement variability in both the NaI(Tl) counting and in the PIC measurements.

The overall uncertainty of the calibration was estimated to be approximately ± 2.1 percent. The additional sources of uncertainty comprising this estimate are tabulated in Table 1.

Table 1: Estimated uncertainties in the calibration of NaI(Tl) - Glass bulb transfer standard measuring system

Source of uncertainty	Estimated Uncertainty δ_i (%)
Measurement uncertainty (both NaI and PIC)	0.2
Radium standard (including calibration, decay correction, and accumulation time)	0.6
Sample transfer efficiency	0.1
Dead-time corrections (both NaI and PIC)	0.1
Radon decay corrections	negligible
Zero-energy extrapolation (PIC)	0.3
$\sqrt{\Sigma \delta_i^2}$	0.71
$3\sqrt{\Sigma \delta_i^2}$	2.1

International Intercomparison

Ten laboratories were invited to participate in the intercomparison of measurements of total radon activity in sample bulbs using the new NaI(Tl) secondary measurement system as the transfer standard. The laboratories were:

Argonne National Laboratory, Chicago, IL, USA (F. Markum and H. Lucas)

Australian Radiation Laboratory, Melbourne, Australia (Stephen Soloman)

U.S. Bureau of Mines, Denver, CO, USA (Robert F. Holub)

Environmental Measurements Laboratory, New York, NY, USA (Isabel M. Fisenne)

U.S. Environmental Protection Agency, Las Vegas, NV, USA (Richard D. Hopper)

U.S. Environmental Protection Agency, Montgomery, AL, USA (Edward Sensintaffar)

Chem Nuclear Geotech, Grand Junction, CO, USA (Harold Langner and Joan George)

National Institute of Radiation Protection, Stockholm, Sweden (Rolf Falk)

National Physical Laboratory, Teddington, U.K. (Julian Dean)

National Radiation Protection Board, Chilton, U.K. (Keith D. Cliff and John Miles)

The laboratories were selected on the basis of their being principal U.S. laboratories and international metrological laboratories that maintain independent radon calibration capabilities. All of the laboratories use NIST radium solution standards in conventional "bubbler" arrangements directly for their basic calibration reference. None relied on calibrations derived from secondary measurements or intercomparisons. The purpose was to give each laboratory a measure of its calibration value compared to the NIST standard, essentially as a service from NIST and to form an international basis for radon measurements. At the same time, it served as a valuable test of the effectiveness of the NIST transfer standard. The results also could be compared with those from previous international comparisons.

For the intercomparison 85 bulbs were filled and measured in the NaI(Tl) system and five were sent to each of the participating laboratories. Gas transfer of the samples to their measuring systems was similar to that employed with their radium standards. They then measured the total radon activity in each of the samples and sent the results back to NIST.

Table 2: Summary of the intercomparison results.

Laboratory	Number of sample bulbs	Mean (Ratio to NIST)	Range (%)	2 s^a (%)	2 $s_m{}^b$ (%)
A	5	1.011	8.2	6.4	2.8
B	5	1.036	3.7	2.9	1.3
C	5	0.999	3.6	2.6	1.2
D	5	1.033[c]	7.8	6.3	2.8
E	5	0.995	2.1	2.0	0.9
F	5	1.014	2.9	2.3	1.0
G	5	1.001	5.3	5.4	2.4
H	4	1.006	7.3	6.8	3.4
I	5	0.995	2.4	1.8	0.8
J	5	1.068	4.4	3.3	1.5
NIST	18	(1)	4.5	1.9	0.4

[a]Estimated Standard deviation

[b]Estimated Standard deviation of the mean

[c]Laboratory's quoted weighted average: 1.012.

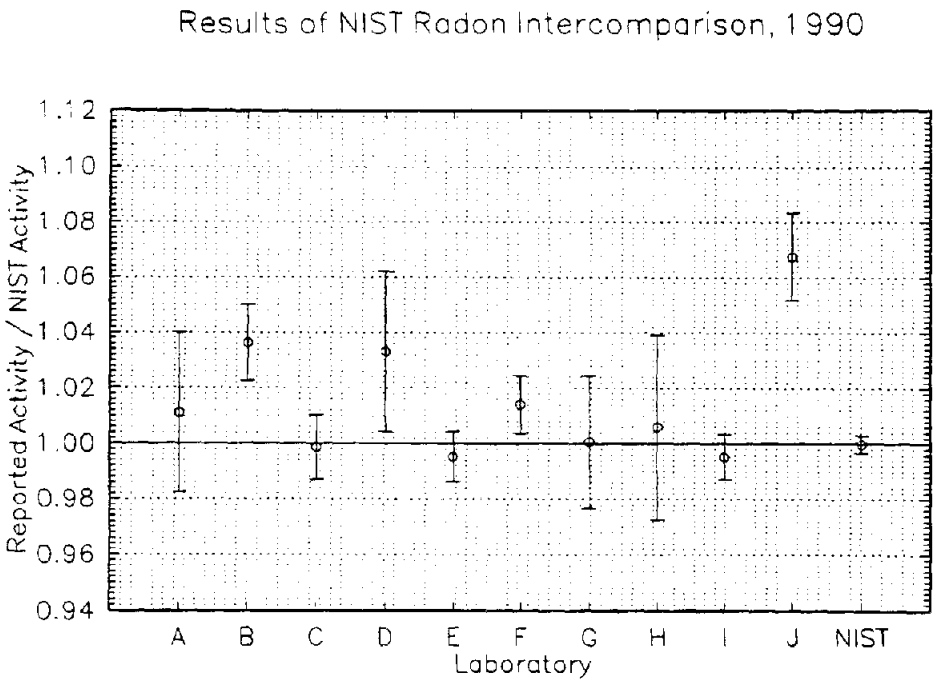

Fig. 11. Averaged reported results for the radon measurement intercomparison normalized to the NIST value. The "error bars" correspond to the standard deviation of the mean for 4 or 5 sample bulbs (with the exception of the NIST value). Table 2 contains the summarized results.

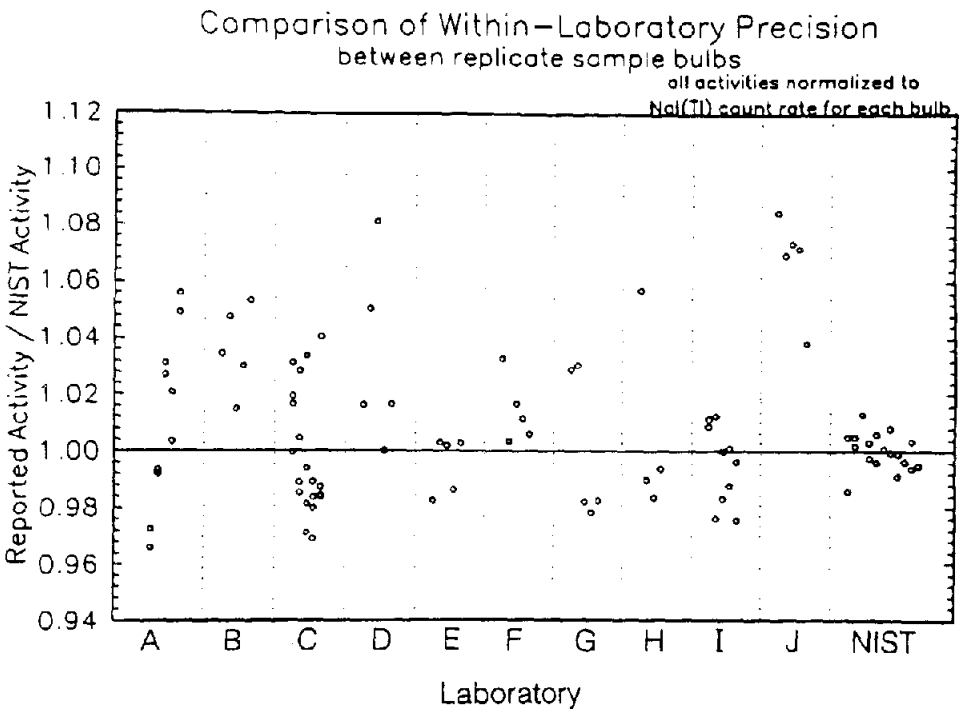

Fig. 12. Reported results for the radon measurement intercomparison. Each individual measurement value for all 11 laboratories are shown which illustrates the within- laboratory and between laboratory performance.

Eight of the ten participating laboratories used scintillation counting (SC) with ZnS (Ag) cells as their measurement method. Another used pulse ionization chambers (PIC) similar to that employed in the NIST primary measurement system. And one used an independently calibrated NaI(Tl)-PIC system similar to the NIST secondary measurement system described here.

The reported result for each sample bulb was normalized to the NaI(Tl) emission rate measured by NIST prior to shipment. A summary of the averaged reported results are tabulated in Table 2 and shown in Figure 11. Figure 12 provides a better indication of the within-laboratory performance by showing the reported results for each sample bulb. In some cases, laboratories reported results of multiple measurement on a single bulb. These results are also included in the figure.

Because uncertainties were not quoted uniformly from laboratory to laboratory (see Table 3), comparisons were made by taking 2 standard deviations of the mean of the 5 measurements. Typically 2 s_m was in the range 1 to 3 percent. Overall, the agreement between the laboratories was within 5 percent with one exception.

In two cases Laboratories I and J where the reported results appeared to be greatly discrepant from results of previous published intercomparisons, the laboratory was asked to repeat the comparison with a new set of bulbs. Thus, problems such as, for example, simple errors in numerical calculations were not of interest and changes were permitted in reported numbers if simple calculational errors were discovered in the reporting of the first results which occurred on two occasions with one laboratory.

No systematic differences were observed between results of PIC and scintillation counting (SC) measurements (PIC average: 1.026 and SC average: 1.013 relative to NIST). There were no observed correlations between the length of time the radon was in the bulbs, including transportation time and time to decay to suitable levels, and the magnitude of the reported values (high or low) of the measurements.

Conclusions

A system has been developed that is capable of transferring radon calibrations from NIST to other laboratories with overall uncertainties of less than the order of 2 percent at one estimated standard deviation. The system comprises spherical bulbs which are measured in a NaI(Tl) well detector that has been calibrated by means of the NIST PIC radon measuring system for total contained radon activity.

The system was used in an international intercomparison of principal laboratories that maintain an independent calibration capability, i.e., that calibrate their systems directly with radium standards rather than by intercomparison with quality control laboratories. Five sample bulbs were sent to each of 10 laboratories which used one of two basic methods, scintillation cells or ionization chambers, to perform the measurements.

Table 3: Uncertainties[a] reported by the participating laboratories

Laboratory	Overall or total uncertainty	Measurement precision (random or statistical)	Other uncertainties	
A	3.2	0.2 (overall)	timing/decay	0.5
			sample transfer	0.1
			sample volume	1.0
			calibration (Ra standard)	3.0
B	1.4	1.2	Ra standard	0.4
			Rn decay correction	0.1
			Ra decay correction	0.44
			gravimetric measurement	0.25
C	2.0 - 2.1	0.5 to 0.7 each bulb	volume gas emanated	0.3
			mixing in bag	0.02
			timing	0.3
			SC calibration	0.6
			Ra standard	0.4
D	1.4	0.4	reference source	0.5
			reference volume	0.17
			temperature, pressure, etc.	0.33
			calibration factor	0.2
			sample transfer	0.17
E	1.5	0.4	reference source	0.5
			reference volume	0.2
			temperature, pressure, etc.	0.3
			calibration factor	0.2
			sample transfer	0.2
F	2.4	1.9 (overall)	gravimetric measurement	0.03
			PIC volume	0.5
			sample volume	0.01
			dead volume in system	0.15
			NaI stability	0.7
			Ra standard	1.2
G	0.52	0.12 to 1.1	not given	
H	2.0 - 2.1	0.5 to 0.7 each bulb	volume gas emanated	0.3
			mixing in bag	0.02
			timing	0.3
			SC calibration	0.6
			Ra standard	0.4
I	1.5	0.9 (overall)	sample transfer	0.2
		0.18 to 0.74 each bulb	cylinder volume	0.1
			cell calibration	1.2
			counting instability	0.2
J	3.6	1.8 calibration	timing	<0.5
		<0.5 counting	cell calibration	2.0
		(1.9 overall)	transfer	<0.5
			dilution correction	0.8
			20 L container	2.0
			(overall 3.0)	

[a]The uncertainty components are assumed to correspond to an approximate relative standard deviation in percent.

In general, the measurements are in good agreement at the desired level of ± 5 percent all reported values except one are within that deviation from the NIST value. Estimates of the measurement precision for 5 bulbs shows that differences from the NIST value are mostly within 2 s_m (the estimated standard deviation of the mean of 4 or 5 bulb measurements).

Acknowledgment

The authors wish to thank Jeff Anderson for performing extensive work in carefully preparing many odd glass configurations which contributed importantly to the success of this project.

References

Collé R., Hutchinson J.M.R., and Unterweger M. (1990) The NIST Primary Radon-222 Measurement System, J. Res. NIST, **95**, No. 2, 155.

Fisenne I.M., George A.C., and Keller H.W. (1990) The August 1988 and June 1989 Radon Intercomparisons at EML, U.S. DoE Report EML-528, New York, NY.

Hutchinson J.M.R. and Collé R. (1990) Preface: Radon Measurement Standards and Calibration, J. Res. NIST, **95**, No. 2.