National Institute of Standards & Technology

Certificate

Standard Reference Material 4972
Radon-222 Emanation Standard

This Standard Reference Material (SRM) consists of a heat-sealed polyethylene capsule that contains a solution of radioactive radium-226 chloride (and its radioactive decay products), non-radioactive barium chloride and hydrochloric acid dissolved in approximately 0.2 mL of distilled water. The SRM is intended for the calibration of radon-222 measurement systems.

Radiological Hazard: The SRM capsule contains radium-226 with an activity of approximately 50 Bq. Radium-226 decays by alpha-particle emission. The progeny of radium-226 inside the capsule have a total activity of approximately 150 Bq and decay by alpha- and beta-particle emission. None of the alpha or beta particles escape from the SRM capsule. During the decay process, X-rays and gamma rays with energies from 11 keV to 2.5 MeV are also emitted. Some of these photons escape from the SRM capsule, but do not represent a radiation hazard. The capsule is shipped and is intended to be stored in a closed screw-cap vial. Gaseous radon-222 will escape from the capsule through diffusion so the capsule, when not in use, should be kept in the vial. None of alpha or beta particles from decay of radon-222 and its progeny escape from the closed glass vial. The total activity of radon-222 and its progeny inside the vial is approximately 220 Bq. High energy gamma rays may escape, but do not represent a radiation hazard. The SRM should be used only by persons qualified to handle radioactive material.

Chemical Hazard: The SRM capsule contains hydrochloric acid (HCl) with a concentration of 1.0 mole per liter of water. The solution is corrosive and represents a health hazard if it comes in contact with eyes or skin if the capsule is damaged. This SRM should be used only by persons qualified to handle both radioactive and chemical hazardous materials.

Storage and Handling: The SRM should be stored and used at temperatures between 5 °C and 45 °C. The certified emanation parameters should be valid until at least December 2013. The capsule should be kept in a closed glass vial with humidity inside close to 100%. The vial should always be clearly marked as containing radioactive material. If the capsule is transported, it should be packed, marked, labeled, and shipped in accordance with the applicable national, international, and carrier regulations. The solution in the capsule is a hazardous material because of both the radioactivity and the strong acid. Refer to the attached Annex (Information for Users) for details on appropriate applications and restrictions for use and storage the capsules.

Preparation: This Standard Reference Material was prepared in the Physics Laboratory, Ionizing Radiation Division, Radioactivity Group, M. Unterweger, Acting Group Leader. The overall technical direction and physical measurements leading to certification were provided by P. Volkovitsky of the Radioactivity Group.

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PROPERTIES OF SRM 4972
Certified values

Radionuclide	**Radium-226 (Radon-222)**
Capsule identification	**SRM 4972 - 1**
Reference time	**12:00 EST, 1 September 2003**
Capsule mass	**(0.3962 ± 0.0024) g** [a], [b]*
Radium-226 activity of the solution at the reference time, A^0_{Ra}	**(49.55 ± 0.59) Bq**[a]
Radon-222 emanation fraction at equilibrium, f_0 [c], [d]	**(0.867 ± 0.014) at 21 °C** [a]
Radon-222 fraction contained in the polyethylene, a [d], [e]	**(0.039 ± 0.016) at 21 °C** [a]

Uncertified values

Physical Properties:			
Source description	Liquid in heat-sealed polyethylene capsule		
Solution density	(1.017 ± 0.002) $g \cdot mL^{-1}$ at 21ºC [a]		
Capsule specifications (refer to Annex for Description)	Outside diameter	4.4 mm	
	Overall length	26 mm	
	Effective length	20 mm	
	Wall thickness	0.5 mm	
Chemical Properties:			
Solution composition	Chemical Formula	Concentration ($mol \cdot L^{-1}$)	Mass Fraction ($g \cdot g^{-1}$)
	H_2O	54	0.96
	HCl	1.0	0.04
	$BaCl_2$	4×10^{-4}	8×10^{-5}
	$^{226}RaCl_2$	3×10^{-8}	9×10^{-9}
Radiological Properties:			
Half lives used	Radium-226: (1600 ± 7) a [3], [f] Radon-222: (3.8235 ± 0.0003) d [3], [f]		
Calibration method and measuring instrument(s) for A_{Ra}	Gravimetric dilution and dispensing of SRM 4967A [4,5] with certified massic activity		
Calibration method and measuring instrument(s) for f_0	Derived as a parameter of regression fit [e] of radon emanation fraction measurements by Pulse Ionization Chambers (PIC) with the NIST primary radon measurement system [6]		
Calibration method and measuring instrument(s) for a	Derived as a parameter of regression fit [e] of radon emanation fraction measurements by Pulse Ionization Chambers (PIC) with the NIST primary radon measurement system [6]		

*Notes and references are on pages 5 and 6

EVALUATION OF THE UNCERTAINTY OF THE RADIUM-226 ACTIVITY, A^{0}_{Ra} [g]*, AT THE REFERENCE TIME,

Input quantity x_i, the source of uncertainty (and individual uncertainty components where appropriate)	Method used to evaluate $u(x_i)$, the standard uncertainty of x_i (A) denotes evaluation by statistical methods (B) denotes evaluation by other methods	Relative uncertainty of input quantity, $u(x_i)/x_i$, (%) [h]	Relative sensitivity factor, $\lvert \partial y/\partial x_i \rvert \cdot (x_i/y)$ [j]	Relative uncertainty of output quantity, $u_i(y)/y$, (%) [k]
Calibration of SRM 4967A radium-226 standards	Estimated (B)	0.60	1.0	0.60
Uncertainty of gravimetric dilutions and dispensing	Estimated (B)	0.10	1.0	0.10
Corrections for decay of radium-226	Standard uncertainty of the radium-226 half-life (B)	0.44	0.015	0.007
Combined Relative Standard Uncertainty of the Evaluation				**0.61**
Coverage factor, *k*				x 2
Relative Expanded Uncertainty of the Evaluation				**1.2**

EVALUATION OF THE UNCERTAINTY OF THE RADON-222 EMANATION FRACTION IN EQUILIBRIUM, f_0 [e]

Input quantity x_i, the source of uncertainty (and individual uncertainty components where appropriate)	Method used to evaluate $u(x_i)$, the standard uncertainty of x_i (A) denotes evaluation by statistical methods (B) denotes evaluation by other methods	Relative uncertainty of input quantity, $u(x_i)/x_i$, (%) [h]	Relative sensitivity factor, $\lvert \partial y/\partial x_i \rvert \cdot (x_i/y)$ [j]	Relative uncertainty of output quantity, $u_i(y)/y$, (%) [k]
Standard deviation of regression fit parameter based on 20 measurements [m]	Statistical (A)	0.58	1.0	0.58
Standard deviation of the mean on the detection efficiency for 8 PIC calibrations [n]	Statistical (A)	0.530	1.0	0.53
Combined Relative Standard Uncertainty of the Evaluation				**0.79**
Coverage factor, *k*				x 2
Relative Expanded Uncertainty of the Evaluation				**1.6**

*Notes and references are on pages 5 and 6

EVALUATION OF THE UNCERTAINTY OF THE RADON-222 FRACTION CONTAINED IN THE POLYETHYLENE, a [e]*

Input quantity x_i , the source of uncertainty (and individual uncertainty components where appropriate)	Method used to evaluate $u(x_i)$, the standard uncertainty of x_i (A) denotes evaluation by statistical methods (B) denotes evaluation by other methods	Relative uncertainty of input quantity, $u(x_i)/x_i$, (%) [h]	Relative sensitivity factor, $\lvert \partial y/\partial x_i \rvert \cdot (x_i/y)$ [j]	Relative uncertainty of output quantity, $u_i(y)/y$, (%) [k]
Standard deviation of regression fit parameter based on 20 measurements [m]	Statistical (A)	20.5	1.0	20.5
Standard deviation of the mean on the detection efficiency for 8 PIC calibrations [n]	Statistical (A)	0.53	1.0	0.53
Combined Relative Standard Uncertainty of the Evaluation				**20.5**
Coverage factor, *k*				x 2
Relative Expanded Uncertainty of the Evaluation				**41**

*Notes and references are on pages 5 and 6

NOTES

[a] The stated uncertainty is two times the standard uncertainty.

[b] The standard should not be used if the total mass of the capsule decreases by more than 15 % from its certified value. Refer to Annex.

[c] Emanation fraction in equilibrium f_0 is determined as the ratio of radon-222 activity outside the capsule, A_{Rn}, over the activity of radium-226, A_{Ra}, inside the capsule in secular equilibrium. See details in attached Annex (Information for Users). The reported value, $y = f_0$, of emanation fraction in equilibrium was not measured directly but was derived from measurements and calculations of other quantities. This can be expressed as $y = f(x_1, x_2, x_3, \ldots x_n)$, where f is a mathematical function derived from the assumed model of the measurement process. The value, x_i , used for each input quantity i has a standard uncertainty, $u(x_i)$, associated with a corresponding uncertainty in y, $u_i(y) \equiv \left|\partial y/\partial x_i\right| \cdot u(x_i)$, called a component of combined standard uncertainty of y. The combined standard uncertainty of y, $u_c(y)$, is the positive square root of the sum of the squares of the components of combined standard uncertainty.

The combined standard uncertainty is multiplied by a coverage factor of $k = 2$ to obtain U, the expanded uncertainty of y. The unknown value of the massic activity is believed to lie in the interval $y \pm U$ with a level of confidence of approximately 95 percent.

For further information on the expression of uncertainties, see references [1] and [2].

[d] The emanation fraction in equilibrium, f_0, and contained fraction in polyethylene, a, exhibit temperature dependence. Refer to Annex.

[e] Measured emanation fraction as a function of time, f, is determined as $f = A_{Rn}/A_{Ra}$, where A_{Rn} is the radon-222 activity outside of a capsule and A_{Ra} is the activity of the radium solution inside the capsule at the time of measurement. As it is described below (see Annex), $f(x) = f_0 \cdot [x + a(1 - x)]$, where f_0 is the emanation fraction in equilibrium, a is a radon-222 fraction contained in the polyethylene of the capsule, and x is a time-dependent variable, $x = 1 - \exp(-\lambda_{Rn} \cdot t_A)$, where t_A is an accumulation time and λ_{Rn} is radon-222 decay constant.

[f] The stated uncertainty is the standard uncertainty.

[g] The value of each standard uncertainty component, and hence the value of the expanded uncertainty itself, is a best estimate based upon all available information, but is only approximately known. That is to say, the "uncertainty of the uncertainty" is not well known. This is true for uncertainties evaluated by statistical methods (e.g., the relative standard deviation of the standard deviation of the mean for the massic count rate is approximately 50%) and for uncertainties evaluated by other methods (which could easily be over or under estimated).

[h] Relative standard uncertainty of the input quantity x_i.

[j] The relative change in the output quantity y divided by the relative change in the input quantity x_i. If $\left|\partial y/\partial x_i\right| \cdot (x_i/y) = 1.0$, then a 1% change in x_i results in a 1% change in y. If $\left|\partial y/\partial x_i\right| \cdot (x_i/y) = 0.05$, then a 1% change in x_i results in a 0.05% change in y.

[k] Relative component of combined standard uncertainty of output quantity y, rounded to two significant figures or less. The relative component of combined standard uncertainty of y is given by $u_i(y)/y \equiv \left|\partial y/\partial x_i\right| \cdot u(x_i)/y = \left|\partial y/\partial x_i\right| \cdot (x_i/y) \cdot u(x_i)/x_i$. The numerical values of $u(x_i)/x_i$, $\left|\partial y/\partial x_i\right| \cdot (x_i/y)$, and $u_i(y)/y$, all dimensionless quantities, are listed in columns 3, 4, and 5, respectively. Thus, the value in column 5 is equal to the value in column 4 multiplied by the value in column 3. The input quantities are independent, or very nearly so. Hence the covariances are zero or negligible.

[m] The uncertainties of the regression fit parameters are determined as follows [7]: if emanation fractions $f_i = Y_i$, are measured at points $x_i = X_i$ (i = 1,.., n), than the standard deviations of regression fit parameters a and f_0 are given by the following formulas:

$$\text{s.d.}(a) = s\left(\frac{1}{n} + \frac{\overline{X}^2}{S_{XX}}\right)^{1/2}$$

$$\text{s.d.}(f_0) = s\left(\frac{1}{n} + \frac{(1-\overline{X})^2}{S_{XX}}\right)^{1/2},$$

where $s = \left(\frac{S_{YY}}{n-2}\right)^{1/2}$, $S_{YY} = \sum_{i=1}^{n}(Y_i - \overline{Y})^2$, $S_{XX} = \sum_{i=1}^{n}(X_i - \overline{X})^2$, $\overline{X} = \frac{1}{n}\sum_{i=1}^{n} X_i$, and $\overline{Y} = \frac{1}{n}\sum_{i=1}^{n} Y_i$

[n] This uncertainty excludes the common and correlated uncertainty components for the radium standards used to perform the PIC calibrations. Those components were included in the uncertainty of A^0_{Ra}.

REFERENCES

[1] B. N. Taylor and C. E. Kuyatt, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Technical Note **1297**, 1994. Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20407, U.S.A.

[2] International Organization for Standardization (ISO), *Guide to the Expression of Uncertainty in Measurement*, 1993. Available from the American National Standards Institute, 11 West 42nd Street, New York, NY 10036, U.S.A. 1-212-642-4900. (Listed under ISO miscellaneous publications as "ISO Guide to the Expression 1993").

[3] Evaluated Nuclear Structure Data File (ENSDF), October 2005.

[4] Certificate for Standard Reference Material 4967A, Radium-226 Radioactivity Standard, National Institute of Standards and Technology, December 2004.

[5] P. Volkovitsky, *Preparation of a Radium-226 Standard and Determination of its Activity by Different Methods*, to be submitted to J. Res. Natl. Inst. Stand. Technol., 2005.

[6] R. Collé, J.M.R.Hutchinson, and M.P. Unterweger, *The NIST Primary Radon-222 Measurement System*, J. Res. Natl. Inst. Stand. Technol., **95**, 155-165, 1990.

[7] Draper, N.R. and Smith H., *Applied Regression Analysis*, John Wiley & Sons, 2nd Ed., pp 27-31, 1981.

[8] P. Volkovitsky, *Radon Diffusion and Emanation Fraction for NIST Polyethylene Capsules with Radium Solution*, submitted to Appl. Radiat. Isot., 2005.

ANNEX. INFORMATION FOR USERS

Contents:

1. DESCRIPTION

The emanation standard SRM4972 consists of a heat-sealed right circular cylinder of a low-density polyethylene having a 4.4-mm outside diameter and an overall length of 26 mm. The effective length along the emanating surface is 20 mm. The polyethylene capsule was filled with a calibrated ^{226}Ra solution having a known massic activity. The total mass of a capsule is about 0.4 g, while the total mass of solution is about 0.2 g. ^{226}Ra solution emanates a known amount of ^{222}Rn activity in an "accumulation mode" as a function of accumulation time.

Each standard is certified in terms of three parameters: the ^{226}Ra activity content at the reference time, A^0_{Ra}, the ^{222}Rn emanation fraction in equilibrium, f_0, and the fraction of ^{222}Rn contained in polyethylene, a. This standard, therefore, has a larger overall calibration uncertainty than that of the currently available ^{226}Ra solution standards (SRM 4965, 4966, and 4967A), which are certified only for ^{226}Ra activity at the reference time.

The certified parameters A^0_{Ra}, f_0, and a allow calculation of ^{222}Rn activity in a suitable vessel after a given accumulation time.

2. PACKAGING FOR SHIPMENT

The encapsulated standard is packaged for shipment in a nominal 22 mL glass screw-capped vial containing moist absorbent cotton and the capsule. Any observed liquid in the vial or on the capsule itself is condensed water, and contains only minimally accumulated quantities of ^{222}Rn daughter radionuclides.

3. STORAGE

The standard should be stored when not in use (and when in use, if possible; see section 4) at all times in water-saturated air. This may be achieved by storing the capsule in the original shipping vial (see section 2) or in any other suitable closed container, with volume larger than 20 mL, in which the capsule is suspended above water.

4. USE FOR ACCUMULATED ^{222}RN ACTIVITY APPLICATIONS

The standard should be employed in a suitable closed accumulation vessel with a volume larger than 20 mL to allow the quantitative transfer of accumulated ^{222}Rn activity, such as conventional bubblers or gas-washing bottles used with radium solution standards. The capsule should be employed under similar (or as nearly as possible identical) conditions to the bubbler/emanation procedure routinely used in the laboratory.

The capsule should be suspended above the water level in the bubbler during accumulation, and not immersed into the water.

For the case of a typical bubbler/accumulation application, the ^{222}Rn activity A_{Rn} at the end of an accumulation period t_A from $t = t_0$ to $t = t_F$, $t_A = t_F - t_0$, may be written [8]* in a form as:

$$A_{Rn} = A^0_{Ra} \cdot \exp(-\lambda_{Ra} t_D) \cdot f_0 \cdot [x + a \cdot (1 - x)],$$

*Notes and references are on pages 5 and 6

Here f_0 is the ^{222}Rn emanation fraction,

A^0_{Ra} is the total ^{226}Ra activity in the capsule at reference time t_R,

λ_{Ra} is the ^{226}Ra decay constant, $\lambda_{Ra} = (4.332 \pm 0.019)\cdot 10^{-4}\ \text{y}^{-1}$ [3]*,

t_D is the time interval from $t = t_R$ (t_R is the reference time , 12:00 EST September 1, 2003) to $t = t_0$, $t_D = t_0 - t_R$,

$x = 1 - \exp(-\lambda_{Rn} \cdot t_A)$, where $\lambda_{Rn} = (2.09822 \pm 0.00016)\cdot 10^{-6}\ \text{s}^{-1}$ [3],

a is the ^{222}Rn fraction contained in the polyethylene.

Three parameters, A^0_{Ra}, f_0, and a, are certified with corresponding standard uncertainties $u_{A_{Ra}}$, u_{f_0}, and u_a. The relative uncertainty of A_{Rn}, $u_{A_{Rn}} / A_{Rn}$, should be calculated using the formula:

$$u_{A_{Rn}} \Big/ A_{Rn} = \sqrt{w_{f_0}^2 + w_{A_{Ra}}^2 + w_{\lambda_{Ra}}^2 + w_{\lambda_{Rn}}^2 + w_a^2}$$

Here $w_{f_0} = u_{f_0} / f_0 = 0.0079$, $w_{A_{Ra}} = u_{A_{Ra}} / A_{Ra} = 0.006$, $w_{\lambda_{Rn}} = \dfrac{u_{\lambda_{Rn}} t_A (1-a)}{\exp(\lambda_{Rn} t_A) + a - 1} = \dfrac{7.8 \cdot 10^{-5}\, \lambda_{Rn} t_A (1-a)}{\exp(\lambda_{Rn} t_A) + a - 1}$,

$w_a = \dfrac{u_a}{\exp(\lambda_{Rn} t_A) + a - 1} = \dfrac{0.21a}{\exp(\lambda_{Rn} t_A) + a - 1}$, $w_{\lambda_{Ra}} = u_{\lambda_{Ra}} t_D = 0.0044 \lambda_{Ra} t_D$ (see note [k] above for definition of u_i).

For $t_D \leq 10$ years $u_{\lambda_{Ra}} \leq 2.75 \cdot 10^{-5} \lambda_{Ra}$ and can be neglected. For accumulation time $t_A \geq 1$ day, $u_{\lambda_{Rn}} \leq 2.2 \cdot 10^{-5} \lambda_{Rn}$ and also can be neglected. However, because of large uncertainty in parameter a, u_a can not be neglected unless $t_A < 4$ days.

5. OTHER RESTRICTIONS AND CONDITIONS

The standard should not be used if the total mass of the capsule decreases by ≈ 60 mg. The mass (and visibly apparent volume) of the encapsulated solution will gradually decrease with time because of transpiration/evaporation losses of radium solution through the polyethylene. The rate of these losses depends on usage; but extensive tests over more than ten years show that under normal humidity usage and storage conditions, the capsules should not approach a 60 mg mass lost for at least a decade. Alternatively, the apparent solution volume inside the polyethylene capsule can be visibly observed and monitored at each use for any appreciable transpiration losses.

The emanation fraction in equilibrium, f_0, and the contained fraction in polyethylene, a, exhibit a temperature dependence. In the region of about 21° C, the emanation fraction varies by approximately 0.7% per degree Celsius. The certified values of f_0 and a (within its reported uncertainty) are applicable for a temperature range of approximately 19 to 23° C.

The certified parameters were obtained for radon accumulation in bubbler at pressure within the interval (70 – 100) % of normal atmospheric pressure.

Questions regarding this standard should be addressed to Dr. Peter Volkovitsky of the NIST Radioactivity Group at +1 301 975 5527 or peter.volkovitsky@nist.gov.

*Notes and references are on pages 5 and 6