



A novel application for ^{222}Rn emanation standards: Radon–cryptophane host chemistry

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ABSTRACT

In collaboration with the University of Pennsylvania, a ^{222}Rn emanation source was used for the determination of the binding affinity of radon to a cryptophane molecular host. This source was similar to a ^{222}Rn emanation standard that was developed and disseminated by the National Institute of Standards and Technology (NIST). The novel experimental design involved performing the reactions at femtomole levels, developing exacting gravimetric sampling methods and making precise ^{222}Rn assays by liquid scintillation counting. A cryptophane–radon association constant was determined, $K_A = (49,000 \pm 12,000) \text{ L mol}^{-1}$ at 293 K, which was the first measurement of radon binding to a molecular host.

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1. Introduction

The first polyethylene-encapsulated ^{226}Ra solution standards were developed in the 1980s by NIST for use in a radon-in-water standard generator (Hutchinson et al., 1984, 1986; Collé and Kishore, 1997). This standard generator provided dispensed aliquots of radium-free water solutions having known ^{222}Rn activity concentrations, and was primarily intended to calibrate radon-in-water measurement systems and for quality control of the US Environmental Protection Agency drinking water national survey (Hutchinson et al., 1984). The use of such of a polyethylene-encapsulated source was further extended as an emanation standard for radon-in-air measurements. Years of research in developing a radon emanation standard led to production of SRM 4968, (NIST, National Institute of Standards and Technology, 1996). This standard emanates a well-characterized and known quantity of ^{222}Rn when employed in accumulation mode in either air or water. The encapsulated standards are sufficiently accurate and efficacious for calibrating instruments used in a variety of measurement applications when suitable protocols are followed. These standards have been used for calibrating radon detection monitors (Collé and Kotrappa, 1995; Kotrappa and Stieff, 1994), and other measurement methods (NIST, National Institute of Standards and Technology, 1996).

In this work, done in collaboration with University of Pennsylvania (UPenn), the encapsulated sources were used to radio-metrically determine the partitioning of radon between air and aqueous cryptophane solutions of varying concentrations. Cryptophanes are a class of organic supramolecular compounds studied and synthesized primarily for molecular encapsulation and recognition. Due to their unique molecular recognition properties, cryptophanes hold great promise as a potentially new way to study the binding of organic molecules with substrates, particularly as pertaining to biological and biochemical applications (Brotin and Dutasta, 2009). In this work we used a cryptophane-A derivative, tris-(triazole ethylamine) cryptophane (TTEC) (see Fig. 1) that was synthesized and purified by the UPenn researchers (Jacobson et al., 2011).

2. Experiment and methodology

In order to obtain aqueous radon solutions for this work, a simple radon-in-water generator was assembled. The generator consisted of a nominal 10 mL dose vial containing four emanation capsules that was filled with pure water and crimp sealed with an aluminum-lined rubber septum. The generator was filled with water in such a way as to minimize air space in the bottle and hence minimize the amount of radon that would partition between the air and water volumes. Each capsule consisted of a heat-sealed circular cylinder of low density polyethylene with a nominal 1.7 cm effective length along the emanating surface. Each capsule was gravimetrically filled with approximately 0.22 g of a calibrated ^{226}Ra solution (SRM 4961). The ^{226}Ra

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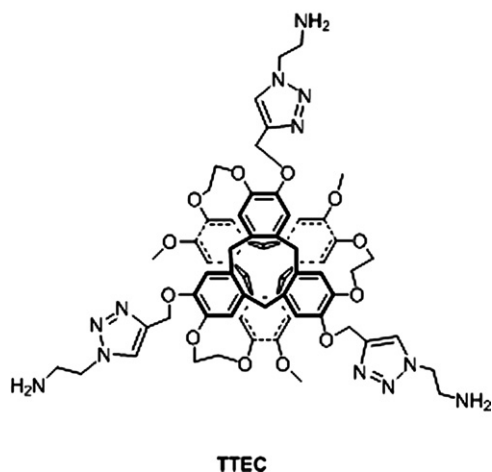


Fig. 1. Molecular structure of the cryptophane host (TTEC) used in this work. The formula for the deprotonated molecule (TTEC) is $C_{66}H_{72}N_{12}O_{12}$ and its molecular mass is $1225.36 \text{ g mol}^{-1}$. See Jacobson et al., 2011 for the method of synthesis.

solution in the four capsules had a total ^{226}Ra activity of 21.7 kBq as of 25 June 2010. For the final experiment used to determine the association constant, K_A , radon was accumulated in the generator (from decay of ^{226}Ra in the capsules) for 8 days. No ^{226}Ra was present in the generator's water volume because the polyethylene capsule only allows diffusion of ^{222}Rn . The absence of radium was subsequently confirmed by following the decay of radon and observing its well-known half-life, $(3.8235 \pm 0.0003) \text{ d}$, (Chisté and Bé, 2011a, b) and by long-term background measurements after several weeks.

The ^{222}Rn activity (A_{Rn}) contained in the generator at the end of an accumulation period from $t=0$ to $t=T_A$ may be given in approximate form as:

$$A_{\text{Rn}} = f A_{\text{Ra}} e^{-\lambda_{\text{Ra}} T_D} (1 - e^{-\lambda_{\text{Rn}} T_A}) \quad (1)$$

where A_{Rn} is the ^{222}Rn activity accumulated in the generator at the end of an accumulation time interval (of duration T_A); f is the ^{222}Rn emanation fraction (i.e., the fraction of the total ^{222}Rn generated by decay of ^{226}Ra that is released from the capsule and contained within the volume of the accumulation vessel); A_{Ra} is the total ^{226}Ra activity in the capsule at reference time t_r ; λ_{Ra} is the ^{226}Ra decay constant (given by $\lambda_{\text{Ra}} = \ln(2)/(1600 \pm 7) \text{ a}^{-1}$ (Chisté and Bé, 2011a, b) T_D is the time interval from the certified ^{226}Ra activity reference time t_r to the start $t=0$ of the accumulation period ($T_D = t_0 - t_r$); λ_{Rn} is the ^{222}Rn decay constant (given by $\lambda_{\text{Rn}} = \ln(2)/(3.8235 \pm 0.0003) \text{ d}^{-1}$ (Chisté and Bé, 2011a, b) T_A is the time interval for the total duration of the accumulation

Eq. (1) assumes that there is no ^{222}Rn activity initially present.

After 8 days of accumulation, a 10 mL gas-tight syringe was used to transfer aliquots of the accumulated radon solution to a set of twelve reaction vessels with a cryptophane solution mass from 0.009 to 0.1 g (which corresponded to a cryptophane concentration of 0.7 to $10 \mu\text{mol L}^{-1}$), to three blank reaction vessels (not containing cryptophane), and directly into three LS vials (used to assay the generator's radon content). The reaction vessels used were cone-shaped glass vials with screw caps having Al-lined teflon septa and internal volumes of $(1.248 \pm 0.004) \text{ mL}$. The transfers were effected by inserting the syringe needle through the generator's septum and dispensing. After transfer the reaction vessels were intermittently mixed and kept at a constant temperature of 293 K using a water bath for 30 min. After the designated time, each reaction vessel was sampled using a 2-mL gas tight syringe. The syringe needle was inserted through the reaction vessel's septum and approximately 0.6 mL of the

solution from each reaction vessel drawn up. The solution in the syringe was dispensed below the surface of approximately 19 mL of LS cocktail that consisted of Ultima Gold AB² (Perkin Elmer, Waltham MA, USA) with a 5% water fraction in a 22-mL glass LS vial with aluminum foil lined caps. The syringe between each transfer of the aliquots to the LS vials was rinsed three times with blank water.

See Fig. 2 for an overview of the experimental design. A total of 20 LS vials were measured for three cycles on two separate occasions in two different LS counters. The 20 vials were composed of cocktails containing the sampled aliquots from the 12 reaction vessels (R1a through R6a and R1b through R6b) and from the two reaction vessel blanks (RB_1 and RB_2), as well as the three generator assay vials (A_1 , A_2 and A_3) and two LS background blanks (B_1 and B_2). The LS counters used were; (i) Wallac 1414 Winspectral[®] (Perkin-Elmer, Wesley, MA) and (ii) Beckman LS 6500[®] (Beckman Colter, Fullerton, CA). They have considerably different operating conditions characteristics (e.g., low-energy threshold, deadtime, linear vs. logarithmic energy binning, etc.), which helps to ensure variation in measurement conditions. A more detailed description on the counters is presented elsewhere (Laureano-Perez et al., 2007).

This experimental design allowed determination for the radon-cryptophane association constant, K_A , by making only relative LS measurements without the need for absolute ^{222}Rn sub-chain detection efficiencies. This K_A could be obtained from measured water-to-air partition coefficients in the presence of cryptophane. To do this, the ^{222}Rn solution from the generator was transferred to reaction vessels containing varying amounts of TTEC solutions. The radon would partition between the reaction vessels air space and the solution. With binding of the radon to the cryptophane in solution, more ^{222}Rn activity in the solution would be present on sampling the reaction vessels, thereby exhibiting a larger water-to-air partitioning coefficient.

3. Results and discussion

A radon generator was assembled and radon accumulated for 8 days, which corresponds to a ^{222}Rn activity that is in 77% of equilibrium with ^{226}Ra . The emanation fraction (i.e., the ratio of accumulated ^{222}Rn to the total generated from ^{226}Ra decay) for this generator was determined to be about 30%. This was the same value found in preliminary trials.

Raw LS data were corrected for background ($< 0.3\%$ correction), for the radon content in the airspace above the cocktail in the LS vials (approx. 0.7% correction), and for radioactive decay to a common reference time. The volume corrections were empirical and were obtained from separate experiments where the partition of radon between the LS cocktail and air was measured as a function of cocktail volume. Counting was in all cases initiated after a minimum of 4 h to ensure that the radon daughters were in radioactive equilibrium with the ^{222}Rn parent. The corrected net counting rates were observed to decay with the radon half-life, indicating that there was no radium leakage from the capsules.

Initial experimental trials, prior to the final K_A experiment, demonstrated excellent agreement (within the LS measurement precision) in dividing the sample aliquot into two LS vials. Therefore, duplicate LS vials were not used for the final experiment.

Previous to the final experiment, a leak test experiment was performed. In this experiment a similar schema as the final

² Certain commercial equipment, instruments and materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials and/or equipment are the best available for the purpose.

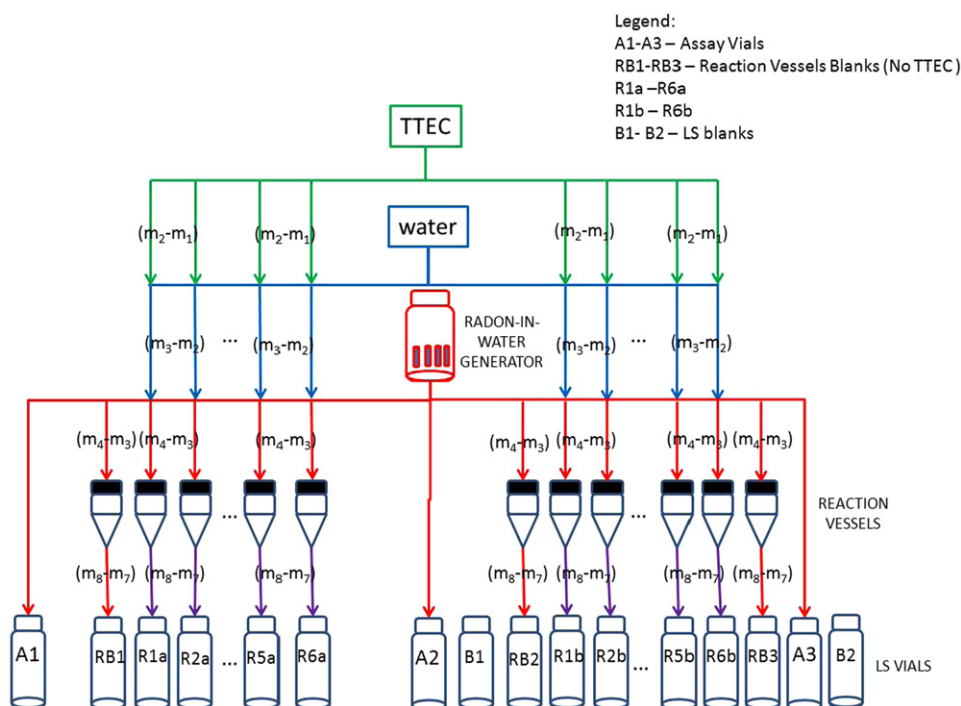


Fig. 2. Overview of the experimental design. Refer to text for symbol definitions.

experiment was used, however, TTEC was not used. This trial was intended to test the effect of possible radon leakage from the reaction vessels as a function of volume and sampling time, and in addition to test for radium leakage from the capsules. The generator aliquots were dispensed into these two sets of reaction vessels for these tests. The first set consisted of 10 reaction vessels (five different volumes in duplicate) and the aliquot size ranged from 0.2 to 1.0 g. The aliquots in this first set were kept at a constant temperature without agitation and sampled after approximately 30 min. The second set consisted of eight reaction vessels (four varied times in duplicate). A 0.4 g aliquot was added to each reaction vessel. The reaction vessels were then sampled at various time intervals from 30 to 260 min. No correlation was found between sampling time and partition coefficient; hence, sampling after 30 min was adequate. This trial also showed excellent between measurement cycle replication and no radium leakage from the capsules.

Although the experimental design (relying upon relative measurements with blank reaction vessels and assay vials) obviated the need for absolute radon determinations, all results were consistent with a ^{222}Rn sub-chain detection efficiency of 4.98 ± 0.04 with all daughters in radiological equilibrium.

The experimental design utilized careful and exhausting gravimetric determinations of all reaction components and sampling aliquots (Fig. 2). The TTEC concentrations and total solution volume in each reaction vessel were determined from four mass measurements;

m_1	empty reaction vessel,
m_2	$m_1 + \text{TTEC stock solution,}$
m_3	$m_2 + \text{additional water,}$
m_4	$m_3 + \text{radon-in-water aliquot}$

The total solution volume was obtained from the mass difference $(m_4 - m_1)$. The radon activity concentration was obtained from the ratio of $[(m_4 - m_3)/(m_4 - m_1)]$ and the TTEC concentration was obtained from the ratio $[(m_2 - m_1)/(m_4 - m_1)]$.

Sampling of the reaction vessels were also performed gravimetrically with transfers done with gas-tight syringes. In this case the determined masses were;

m_6	empty LS vials
m_7	$m_6 + \text{LS cocktail}$
m_8	$m_7 + \text{reaction vessel aliquot}$

The total LS vial volume was given by $(m_8 - m_7)/\rho_1 + (m_7 - m_6)/\rho_2$; where ρ_1 and ρ_2 are the specific gravities of the aliquot and LS cocktail, respectively. The volume range for all 20 LS vials was (18.6–20.3) mL, which corresponds to an average volume correction of 0.993 ± 0.002 ($k=2$). The sampled reaction vessel volume was given by $(m_8 - m_7)/\rho_1$. The sampling aliquots were approximately confirmed by re-measurements of the reaction vessel mass m_5 after sampling such that $(m_5 - m_4)$ could confirm $(m_8 - m_7)$ excepting small transfer losses.

A cryptophane–radon association constant was determined to be $K_A = (49,000 \pm 12,000) \text{ L mol}^{-1}$ at 293 K, which was the first measurement of radon binding to a molecular host (Jacobson et al., 2011). This association constant was extracted from a plot of an observed partition coefficient, L , in the reaction vessel as a function of TTEC concentration. This is given by

$$L = L_0(1 + K_A[\text{TTEC}]) \quad (2)$$

where L_0 is the pure water-to-air partition coefficient (without cryptophane) and K_A is the radon–cryptophane association constant and where $[\text{TTEC}]$ is the cryptophane concentration in mol L^{-1} . The model assumptions used to obtain Eq. (2) are described in Jacobson et al., 2011. The value of L for each vessel was obtained from;

$$L = \frac{(A_w/V_w)}{(A_A/V_A)} \quad (3)$$

where $(V_w + V_A)$ was the total reaction vessel volume (each independently measured at UPenn by gravimetrically filling prior to experiments) and where $V_w = (m_4 - m_1)$. The radon activity in the water

volume, A_w , and air volume, A_A , was obtained from the dispensed and sampling mass aliquots and the LS measurements. The total radon activity in each reaction vessel was given by $A_w + A_A = (m_4 - m_3) A$ where; A is the massic radon activity accumulated in the radon generator as obtained from direct LS measurements of the assay vials. The activity in the water volume A_w was obtained from the LS measurements of the aliquot samples taken from the reaction vessels and A_A is obtained from the difference ($A - A_w$).

Table 1 summarizes the data obtained from this experiment. As indicated, the average difference between counters across all 20 vials was 0.27%. The estimated uncertainty in the ^{222}Rn massic activity for any one LS vial was 1.7% ($k=2$). Agreement for the assay vials (A_1 – A_3), reaction blanks (RB_1 – RB_3), and reaction vessel duplicates was very good. The relative standard deviation of the mean for the three assay vials was 0.8% and 0.9% for the two counters, respectively. The three reaction vessel blanks could be used to obtain L_0 (see Eq. (2)), which were found to be 0.297 for the Beckman data and 0.299 for the Wallac data. Both of these values had relative standard deviations of the mean of 3%. The fit of the observed partition coefficients L as a function of [TTEC], as used to obtain the association constant K_A , is shown in Fig. 3. The value [TTEC] was obtained from the mass fraction $[(m_2 - m_1)/(m_4 - m_1)]$ multiplied by the stock TTEC solution concentration ($48.3 \mu\text{mol L}^{-1}$). The horizontal line at $L=0.298$ is that obtained with the blank reaction vials. The fitted line does not intercept at the blank, $L=0.298$, because of the model (Eq. (2)) assumptions as [TTEC] approaches zero. The model is valid in the fitted region when [TTEC] is much greater than the radon concentration at equilibrium and when [TTEC] > 0.

The cryptophane–xenon association constant was determined by Jacobson et al., 2011 to be $K_A = (42,000 \pm 2,000) \text{ L mol}^{-1}$ at 293 K, which represents the highest measured xenon affinity for a host molecule. The bigger cryptophane–radon association constant [$K_A = (49,000 \pm 12,000) \text{ L mol}^{-1}$ at 293 K] implies that radon has higher affinity than xenon which is explained because the higher polarizability of radon as compared to xenon promotes binding to void spaces.

This work may have an important metrological application. Ion chamber and gamma spectrometry measurements of radium solutions in ampoules are compromised by radon partitioning

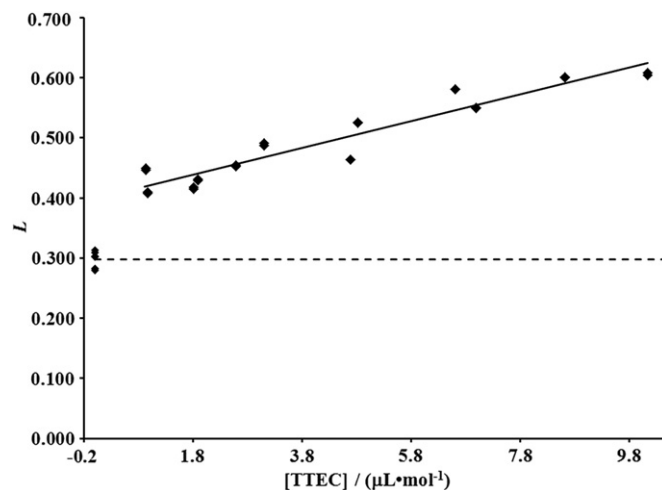


Fig. 3. Fit of the observed partition coefficient L as a function of [TTEC].

between the solution and airspace. The use of cryptophane as a binding agent may keep radon in solution, making measurements more reliable. However, further investigation is required to assess the effect that this would have on the solution density.

Using a value for the association constant, $K_A = 49,000 \text{ L mol}^{-1}$, the cryptophane concentration needed to keep 99% of radon in solution was calculated, assuming equal air and water volumes and for air–water in the presence of TTEC to be $5 \times 10^{-3} \text{ mol L}^{-1}$.

4. Summary

Radon emanation sources similar to the NIST ^{222}Rn emanation standard (SRM 4968, NIST, National Institute of Standards and Technology, 1996) were found to have a unique and novel application in a radon-in-water generator. They were used for the first measurement of radon binding to a molecular host. A cryptophane (TTEC)–radon association constant was determined to be $K_A = (49,000 \pm 12,000) \text{ L mol}^{-1}$ at 293 K (Jacobson et al., 2011). The experimental design relied upon relative measurements with blank reaction vessels and assay vials, obviating the need for absolute radon determinations. The experimental design utilized careful and exhausting gravimetric determinations of all reaction components and sampling aliquots. LS measurements showed excellent between measurement cycle replication. The average difference between LS counters across all 20 vials was 0.27%. The estimated uncertainty in the ^{222}Rn massic activity for any vial was 1.7% ($k=2$).

The use of cryptophane as a binding agent in ^{226}Ra solution ampoules may keep radon in solution, which would make ion chamber and gamma-ray spectrometry of these ampoules decidedly more reliable and accurate. However, further investigation is required to assess the effect that the addition of millimolar cryptophane concentrations would have on the solution density and photon attenuation.

Acknowledgments

This work was a collaboration between the University of Pennsylvania (UPenn), whose effort was led by I.J. Dmochowski, and NIST, under the direction of R. Collé. Support to UPenn was provided by the Department of Defense, National Institute of Health, and the National Science Foundation. The TTEC stock solution was prepared by N.S. Khan at UPenn. The experimental design and protocol was developed by R. Collé, D.R. Jacobson,

Table 1

Experimental data for the determination of the ^{222}Rn activity concentration, A_w , as sampled from the reaction vessels and the observed partition coefficient, L , as a function of [TTEC]. Refer to text and Fig. 2.

	A_w^a (Bq g $^{-1}$)		L		[TTEC] ($\mu\text{L mol}^{-1}$)
	Beckman	Wallac	Beckman	Wallac	
A1	1253	1258	–	–	
A2	1285	1291	–	–	
A3	1253	1255	–	–	
RB1	190.6	192.3	0.280	0.283	0
RB2	173.9	176.0	0.309	0.313	0
RB3	219.8	220.0	0.302	0.303	0
R1a	310.5	312.2	0.446	0.449	0.9322
R1b	292.5	291.4	0.410	0.408	0.9708
R2a	335.9	337.6	0.415	0.418	1.8113
R2b	310.2	309.2	0.431	0.429	1.8885
R3a	240.8	243.3	0.487	0.491	3.1009
R3b	346.5	345.9	0.455	0.453	2.5841
R4a	326.6	326.9	0.525	0.526	4.8155
R4b	337.0	336.9	0.464	0.464	4.6899
R5a	303.0	303.8	0.549	0.550	6.9842
R5b	362.2	362.5	0.581	0.581	6.6074
R6a	388.9	390.5	0.604	0.608	10.1382
R6b	342.5	342.8	0.600	0.601	8.6216

^a The standard deviation of the mean for 3–7 replicate measurements of each LS vial ranged from 0.03 to 0.26%.

R. Fitzgerald, L. Laureano-Pérez, and I.J. Dmochowski. The analysis protocol was developed and data reduction performed by R. Collé, D.R. Jacobson and R. Fitzgerald. The experimental work, including all LS counting was performed by R. Collé, L. Laureano-Pérez, and D.R. Jacobson. P. Volkovitsky is thanked for preparing some of the emanation standards used in this work.

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