

**THE DETERMINATION OF Rn PARTITION COEFFICIENTS FOR SEVERAL LIQUID SCINTILLATION COCKTAILS** M.G. Cantaloub<sup>1,2</sup>, J.F. Higginbotham<sup>1</sup>, & L. Semprini<sup>2</sup>. <sup>1</sup>Dept. of Nuclear Engineering, Oregon State University, Corvallis, OR 97331 (541)737-2341. <sup>2</sup>Dept. of Civil, Construction, and Environmental Engineering, Oregon State University, Corvallis, OR 97331-2302 (541)737-6895.

### ABSTRACT

One key to the measurement of Rn by liquid scintillation methods (LSC) is the high solubility of Rn in organic liquids and its preferential partitioning from an aqueous sample into an organic phase. Values of the partition coefficient for Rn distributed between a water sample and liquid scintillation cocktail have traditionally been estimated from a ratio of Rn Ostwald solubility coefficients for the solvent and water. Estimates in the literature of the Rn partition coefficient for LSC cocktails range from 30-50. A value of 50 based on Rn's solubility in toluene is typically cited as the Rn distribution coefficient for LSC cocktails. Use of a toluene based partition coefficient, however, may not be appropriate for mineral oil cocktails or the newer "environmentally safe" cocktails that are based on solvents significantly different from toluene. Confirmation of the actual Rn partition coefficient for these newer cocktails has been largely ignored or left for the researcher to perform. In the course of our research into Rn partitioning in subsurface fluids, we developed a multiple-equilibration method for quickly and accurately measuring organic-aqueous Rn partition coefficients. The method is fast and accurate, utilizing alpha counting on an LS analyzer with Pulse Shape Analysis (PSA). Using the multiple-equilibration method, we measured Rn partition coefficients for several solvents used in scintillation cocktails as well as partition values for the commercial cocktails of Ultima Gold F, Opti-Fluor O, and Insta-Fluor. The values measured for the commercial cocktails ranged between 32 and 39. Though within the 30-50 range, they are lower than the value of 50 typically cited for toluene based scintillation cocktails.

This paper describes the multiple-equilibration method used for measuring Rn partition coefficients as well as presenting measured Rn partition coefficients for a variety of organic solvents and commercial cocktails. In addition, the effect of Rn partitioning between water, solvent, and air phases is discussed. Understanding the relationship between the Rn partition coefficient and Rn partitioning within the sample, cocktail, and head space volumes is critical to developing the most efficient protocol for measuring Rn by LSC with PSA.

### INTRODUCTION

In their landmark article describing radon measurement by liquid scintillation methods (LSC), Prichard and Gesell (1977) refer to the ratio of the Ostwald coefficients for radon in toluene and radon in water as large and fairly constant, ranging from 50 at 20°C to 52 at 30°C. Parks (1979) also cites the ratio of "Ostwald distribution" coefficients for radon in various organic scintillators and radon in water as ranging between 30-50. In subsequent research, this Ostwald coefficient ratio has become identified as the radon partition or distribution coefficient. The Ostwald coefficient of solubility,  $L$  was defined by Ostwald as the "ratio of the volume of the absorbed gas to that of the absorbing liquid" (Markham and Kobe, 1963) and can be shown to be a ratio of the concentrations of gas in the liquid phase,  $C_l$  and the gaseous phase above the liquid,  $C_g$ . Taking the ratio of Ostwald coefficients for Rn in a given solvent,  $L_s$ , to the solubility coefficient for Rn in water,  $L_w$  gives a theoretical Rn partition coefficient,  $K$ : A dimensionless ratio of the Rn concentration in the solvent,  $C_s$ , to the Rn concentration in water,  $C_w$ .

$$K = \frac{L_s}{L_w} = \left( \frac{C_s}{C_g} \right) \left( \frac{C_g}{C_w} \right) = \frac{C_s}{C_w} \quad (1)$$

The literature contains few Rn partition coefficients. In addition, few Rn Ostwald solubility coefficients exist in the literature for use in estimating a theoretical partition coefficient. The most comprehensive data set was compiled by Clever (1979). The compilation gives Rn Ostwald coefficients for water, various ionic solutions, and for a number of organic compounds. Several researchers have measured Ostwald solubilities specifically related to Rn in scintillation solutions. Horrocks and Studier (1964) determined a value of 32 for a toluene based liquid scintillator at -15°C. Parks and Tsuboi (1978) determined a Rn gas distribution coefficient for a p-xylene based emulsion scintillator (Insta-Gel) of 10.88 at 8°C and estimated a value of 18.87 for toluene scintillator at 8°C based on Horrocks' and Studier's data. Prichard and Gessell (1977) cite 12.7 for Rn's solubility in toluene and 0.255 for Rn in water at 20°C. Finally, Lowery (1991) determined 23 as the partition coefficient for Rn distributed between a high efficiency mineral oil based scintillation cocktail and well water samples. The past five years have seen the introduction of scintillation cocktails based on less environmentally sensitive solvents such as diisopropylnaphthalene (DIN) and phenylorthoxyleneethane (PXE). High efficiency mineral oil cocktail (HEMO) is

still widely used for Rn analysis by LSC, though alpha/beta discrimination by pulse shape analysis (PSA) has shifted Rn analysis by LSC methods towards the use of DIN and PXE cocktails because of their superior performance with respect to PSA. The limited data on direct partitioning of Rn from the water sample directly into a particular cocktail, coupled with the uncertainty of using partition coefficient estimates based on toluene for DIN and long-chain linear alkylbenzene based cocktails, prompted us to investigate and measure the Rn partition coefficients for several commercial liquid scintillation cocktails. The partition coefficients were measured using a method developed as part of our current investigations into utilizing naturally occurring radon gas as an indicator of organic contamination in the saturated zone of the subsurface (Semprini et al., 1993).

## MATERIALS and METHODS

The method used for measuring the Rn partition coefficients is a modification of McAuliffe's (1972) technique for determining Henry's Law constants. It is based on multiple extractions of dissolved Rn gas from an aqueous Ra-226 solution whereby each extraction removes a fixed fraction of the Rn from solution. For a series of equilibrations, the concentration of Rn in the organic solvent after the "nth" extraction,  $C_{o,n}$ , can be expressed as

$$C_{o,n} = K \left[ \frac{V_w}{KV_o + V_w} \right]^n C_{w,0} \quad (2)$$

where K is the dimensionless Rn partition coefficient,  $C_{w,0}$  the initial Rn concentration in solution (cpm/ml) and V the volume (ml) of the organic and water phases respectively. Taking the natural log of eqn (2) yields a linear relationship between  $C_{o,n}$  and the "nth" extraction.

$$\ln[C_{o,n}] = n \cdot \ln \left[ \frac{V_w}{KV_o + V_w} \right] + \ln[C_{w,0} \cdot K] \quad (3)$$

Plotting the natural log of the Rn activity in the organic extraction versus the extraction number yields a straight line with slope  $\ln[V_w/(KV_o + V_w)]$ ; a function solely of the aqueous and organic volumes, and the Rn partition coefficient. The slope is independent of the absolute Rn activity, initial dissolved Rn activity concentration, or related parameters such as counting efficiency or quench correction.

The Ra solutions are prepared in 100 ml volumetric flasks. The flask is filled completely with double distilled water and spiked with a radium standard. The sample is capped with a rubber septum and set aside for Rn buildup. After sufficient time, roughly 5 ml of aqueous solution is removed and replaced with approximately 4 ml of solvent, leaving a 1 ml air bubble to facilitate mixing. The flask is inverted, briefly shaken to disperse the solvent throughout the bulk solution, then placed on a rotary mixer. After mixing 15 minutes, the phases are allowed to separate and the solvent is transferred from the flask to a scintillation vial containing 10 ml of cocktail. A second organic aliquot is immediately injected into the Ra solution and the process is repeated for a total of four extractions collected in 4 vials. The sample extractions are counted on a Packard Tri-Carb 2500 TR A/B operating in the alpha/beta mode. The pulse decay discriminator (PDD) is set high (170) to obtain a near "beta-less" alpha spectrum which is more stable to minor variations in solvent and cocktail volumes between the chemically "identical" samples. Additionally, the high alpha counting efficiency possible with quenched samples allows measurement of partition coefficients for a wide range of organic solvents possibly even chlorinated solvents. The net alpha activity concentration in each extraction sample is determined using backgrounds performed and counted in an identical manner on identical Ra solutions which have been stripped of Rn. Plotting the natural log of the net alpha activity concentration ( $^{222}\text{Rn}$ ,  $^{218}\text{Po}$ , and  $^{214}\text{Po}$ ) in each sample versus the extraction number, eqn (3), yields a straight line. The Rn partition coefficient is determined from the slope of the data regression line, the aqueous Ra volume, and the average solvent volume used in the series of four extractions. All volume determinations are done by mass difference and replicate extractions are performed for each solvent. The method was evaluated with four organic solvents. Table 1 shows the solvents, the Ostwald solubility coefficients, and the estimated and experimentally measured partition coefficients. The experimental values agree well with the estimated values. Regression analysis of the measured partition coefficients and theoretically estimated values yielded an  $R^2$  of 0.95; strong evidence for the method's validity in determining Rn partition coefficients.

## DATA AND RESULTS

Using the multiple extraction method described above, Rn partition coefficients were measured for three commercially prepared LSC cocktails: Ultima Gold F (DIN), Opti-Fluor O (linear alkylbenzene), and Insta-Fluor (o-xylene). The measurements were performed in triplicate for the UGF and duplicate for the Opti-Fluor O and Insta-Fluor. Table 2 shows the average Rn partition coefficient value for the replicate measurements of each cocktail along with the standard deviation. The Rn partition coefficient measured for a HEMO cocktail is included (Lowery, 1991) as a comparison as are partition coefficients measured for pure (>99%) toluene and o-xylene which are often used a cocktail solvents. With the exception of the HEMO, all the measured Rn partition coefficients fall within the range of 30-50. The partition coefficients for the LSC cocktails ranged from a low of  $32.4 \pm 1.7$  for UGF up to a high of  $38.6 \pm 2.6$  for Insta-Fluor. Of note is the agreement between the measured K for Insta-Fluor (o-xylene with some pentanol) and that measured for pure o-xylene. The close agreement between the two suggests that the additives (scintillators etc.) have little effect on the magnitude of the partition coefficient.

## DISCUSSION

The measured cocktail:water Rn partition coefficients ranged between 32 and 39 for the three cocktails. The effect of the Rn partition coefficient on the fraction of Rn extracted from a water sample into the cocktail can be analyzed by using an activity balance to account for Rn distributed between the three phases (water, cocktail, air/headspace) within a LSC vial. Eqn (4) expresses the fraction of Rn in the cocktail,  $F_c$

$$F_c = \frac{K}{[(V_s/V_c) + K + (V_g/V_c)(1/L_w)]} \quad (4)$$

as a function of the cocktail:water Rn partition coefficient, K, the Ostwald solubility coefficient for water,  $L_w$  (0.285) and the sample ( $V_s$ ), cocktail ( $V_c$ ), and vial headspace ( $V_g$ ) volumes. Table 3 shows the extraction efficiency determined for several sample:cocktail volumes using the measured cocktail partition coefficients. As shown for the 10:10 systems, the magnitude of the partition coefficient does not have an appreciable effect on Rn extraction. Comparing the UGF with the HEMO, a 28% increase in the magnitude of the partition coefficient results in only a 2% increase in the fraction of Rn extracted. A slightly larger increase of 6% is obtained when comparing the UGF and HEMO data for 10 ml of sample and 5 ml of cocktail. In this system, the 8 ml of headspace provides significant competition with the 5 ml of cocktail and a larger Rn partition coefficient (i.e. toluene) would increase the Rn extracted into the cocktail layer. The values in Table 3 indicate that as the magnitude of K increases the benefit to Rn extraction by increasing the cocktail volume from 5 to 10 ml lessens. Again using the UGF data, for a 10 ml sample, increasing the cocktail volume from 5 to 10 ml (a 100% increase) yields a 16% increase in the fraction of Rn extracted into the cocktail and available for counting. For HEMO the increase is 22%, while for the Insta-Fluor a 14% gain in Rn extraction efficiency is achieved by doubling the cocktail volume while holding the sample volume constant at 10 ml.

Table 3. Theoretical fraction of Rn extracted from water sample into LSC cocktail for several sample to cocktail volume ratios and experimentally determined Rn partition coefficients. Total vial volume of 23 ml.

$V_{\text{sample}}:$ $V_{\text{cocktail}}$	Rn Extraction Efficiency (%)			
	UGF K = 32	Opti-Fluor O K = 36	Insta-Fluor K = 38	HEMO K = 23
10:10	94.0	94.6	94.9	94.8
10:5	86.2	82.5	82.7	75.0
5:10	86.2	87.9	88.2	81.8

Table 1. Comparison of measured and estimated theoretical Rn partition coefficients. Measured results are an average of three measurements. The Ostwald solubility coefficient for water at 20°C is 0.285 (Clever, 1979).

Solvent	Ostwald solubility coefficient	Theoretical partition coefficient	Measured partition coefficient
cyclohexane	18.04	63.3	$61.0 \pm 4.0$
n-hexane	16.56	58.1	$56.5 \pm 2.8$
toluene	13.24	46.5	$43.6 \pm 1.5$
benzene	12.82	45.0	$42.9 \pm 2.9$

Table 2. Measured Rn partition coefficients for commercial LSC cocktails and several LSC solvents.

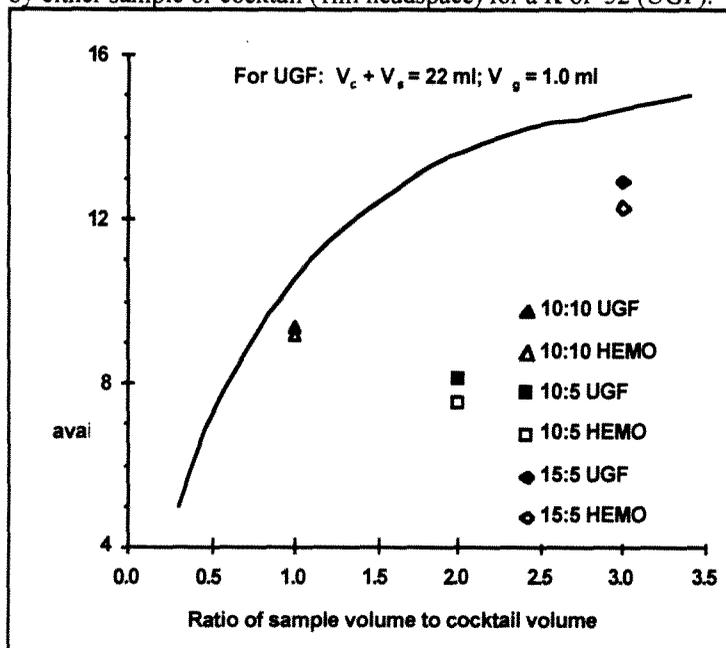
Cocktail or solvent	Measured Rn partition coefficient
Ultima Gold F	$32.4 \pm 1.7$
Opti-Fluor O	$35.3 \pm 1.6$
Insta-Fluor	$38.6 \pm 2.6$
H.E.M.O.	23
toluene	$43.6 \pm 1.5$
o-xylene	$37.0 \pm 0.5$

Table 4. Comparison of total Rn extracted from a 1.0 pCi/ml water sample for various sample:water:headspace ratios. Rn partition coefficient is 32 (UGF). Increase is compared with 10:10:3 ratio.

$V_s/V_c$	$V_s:V_c:V_g$ (ml)	Total Rn in cocktail (pCi)	Increase (%)
1.00	10:10:3	9.4	-
3.00	15:5:3	12.9	37
1.00	11:11:1	10.6	16
1.44	13:9:1	12.3	30
2.14	15:7:1	13.9	48
2.67	16:6:1	14.5	54
3.40	17:5:1	15.1	61

15:5 sample:cocktail system is more than made up by the 33% increase in the total Rn available for extraction in the 15 ml of aqueous sample. The smooth curve shows the Rn expected in the cocktail assuming a K equal to 32 (UGF) and that 22 ml of the vial volume is occupied by either sample or cocktail, leaving a 1.0 ml headspace. Based on total Rn extracted, the figure suggests that limiting the vial headspace to 1.0 ml is the more efficient setup. Table 4 gives values from Fig. 1 along with the percent increase in the total Rn extracted into the cocktail compared to using 10 ml of sample with 10 ml of cocktail. The results are similar to those of Lowery (1991) who suggested a 17:5:1 ratio would lead to greater sensitivity for a given sample measurement. Lowery's work was performed with HEMO cocktail and Rn measurements using a conventional LS counter. Similar optimization utilizing an LS analyzer with alpha/beta discrimination has not been performed. Pritchard et al. (1992), using an instrument with alpha/beta discrimination, suggested that the volume of cocktail can be reduced to accommodate a larger water sample, but cautioned against using scintillation volumes less than 5 ml because the top meniscus of

Fig. 1. Total Rn available in LSC cocktail layer for some sample:cocktail volumes. Smooth curve represents 22 ml of vial occupied by either sample or cocktail (1ml headspace) for a K of 32 (UGF).



the organic layer must not be masked by the vial cap. What is not stated is how much of an effect the decreased counting efficiency would have on the overall sensitivity of the method. From Table 4, a sample to cocktail ratio of 16:6 or 17:5 results in at least a 50% increase in the total Rn available in the cocktail for counting. However the same ratio brings the air:cocktail meniscus very close to the cap, prompting the question of whether the 50% increase in the total Rn available for counting might be offset by reduced alpha counting efficiency? The potential effects of counting efficiency and sample volume can be investigated from a theoretical standpoint by evaluating a frequently used expression for the minimum detectable activity (MDA). Spaulding and Noakes (1993) give an expression for determining the MDA at the 95% confidence interval (Bq/L) as

$$MDA(95\%) = \frac{4.65\sqrt{C/t + 271/t}}{K\epsilon V} \quad (5)$$

where C is the background count rate (cpm), t the sample count time (min), K a conversion factor,  $\epsilon$  the counting efficiency, and V the

sample volume (liter). Assuming for that background and counting efficiency are constant at 1 cpm and 100% respectively the time required to achieve a particular MDA can be evaluated as a function of sample volume. An increase in sample volume from 10 ml to 17 ml reduces the required counting time by over one-half to achieve an MDA of 1 Bq/L. The effect is even greater as the MDA is lowered. This assumes that counting efficiency for the two samples is identical. From eqn (5) it can be shown that for the 17:5 sample, the alpha counting efficiency would have to decrease to roughly 58% to yield the same MDA in the same count time as the 10:10 sample.

Though the alpha counting efficiency is likely to decrease as the sample:cocktail meniscus and cocktail:air meniscus shift to the upper reaches of the vial, a 58% decrease has not been reported.

## CONCLUSIONS

The partitioning of dissolved Rn gas from the water sample to the scintillation cocktail is the basis for Rn measurement by LSC methods. Literature values for Rn partition coefficients have been based on the Ostwald solubility coefficient for Rn in toluene. Estimates for Rn partitioning range from 30-50, but few experimentally determined partition values exist especially for the newer environmentally safer cocktails. Using a multiple equilibration and extraction method, Rn partition coefficients were measured for several organic solvents and three commercial liquid scintillation cocktails. The partition coefficients for the cocktails were 32 for UGF, 36 for Opti-Fluor O, and 39 for Insta-Fluor. While the magnitude of the partition coefficients are similar, the interaction of the Rn partition coefficient, sample volume, and cocktail volume must be considered in developing the most efficient means for measuring Rn by LSC methods.

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