INTERACTION OF SAMPLE, COCKTAIL, AND HEADSPACE VOLUME WHEN MEASURING AQUEOUS RN IN SMALL VOLUME SAMPLES

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ABSTRACT

Techniques for measuring aqueous ^{222}Rn (Rn) by liquid scintillation methods (LSC) are well established, including those incorporating alpha counting by pulse shape discrimination or analysis (PSD or PSA). The most widely used method involves injection of a 10 ml aqueous sample directly into a standard LSC vial preloaded with 10 ml of LSC cocktail. When desirable, the Rn can be pre-concentrated by direct extraction of the Rn from the water sample. This allows Rn measurement from sample volumes of up to 1.0 L, and is particularly useful when very low Rn concentrations are anticipated. There are instances, however, when sample volumes of even 10 ml are not feasible. This is often encountered in bench-scale work where the physical size of the experimental apparatus is limited, or where large sample volumes would disrupt other analytical measurements. In those instances where sample volume is limited, it is important that the measurement protocol makes the most efficient use of the Rn within the small sample volume. With respect to LSC methods, Rn is unique in that it distributes itself between the aqueous, organic (cocktail) and gas (headspace) phases within the LSC vial. When small sample sizes are involved (≤ 5 ml), serious consideration must be given to the volume of cocktail used and the resulting vial headspace. If too little cocktail is utilized, the vial headspace can be a significant Rn sink, reducing the amount of Rn extracted into the cocktail and thus available for counting. Adding more cocktail to the system minimizes the Rn lost to the vial headspace, however, the benefit of the increased Rn extraction efficiency comes at the expense of a larger instrument background. The situation is further complicated when counting Rn and its alpha emitting daughters by employing PSD or PSA to separate the alpha and beta spectra. Both the optimum pulse decay discriminator setting and the overall detection efficiency are dependent, in part, on the cocktail-sample volumes and the position of the cocktail-air meniscus relative to the instrument PMTs. This paper examines the interaction between the cocktail and headspace volumes within a standard LSC vial and their effect on Rn distribution, counting efficiency, background, and alpha/beta separation when measuring Rn in small volume (≤ 5 ml) samples. Understanding the interaction of the three separate phases within an LSC vial is crucial to developing the most efficient sample measurement protocol and obtaining the highest Figure of Merit (FOM) when analyzing for Rn in a small sample volume.

INTRODUCTION

Aqueous Rn measurement is often associated with drinking water and the health concerns associated with ingested Rn, or with waterborne Rn's contribution to indoor Rn levels. Radon, however, is frequently used as an environmental radio-tracer. Radon's unique properties make it an excellent tracer of natural processes, including monitoring surface water infiltration rates, water body mixing, the tracing of flow paths, and most recently, monitoring the remediation of

subsurface NAPL contamination (Semprini et al, 1998). In nearly all instances the sampling volume is not limited by the size of the field sample, but by the size of the standard 20 ml LSC vial. The most frequently used Rn LSC method incorporates 10 ml of aqueous sample sitting below 10 ml of aqueous immiscible LS cocktail.

There are instances, however, when aqueous sample volumes of even 10 ml are not feasible. This is often encountered in bench-scale work where the physical size of the experimental apparatus is limited, or where sample volumes greater than several ml would disrupt other analytical measurements. In those instances where sample volume is limited, it is important that the analysis protocol makes the most efficient use of the available Rn. With respect to LSC, Rn is unique in that it distributes itself between the aqueous, organic (cocktail) and gas (headspace) phases within the LSC vial. When small sample sizes are involved (≤ 5 ml), consideration must be given to the volume of cocktail used and the resulting vial headspace. If too little cocktail is utilized, the vial headspace can be a significant Rn sink, reducing the amount of Rn extracted into the cocktail and thus available for counting. While more cocktail in the vial minimizes the Rn lost to the vial headspace, the benefit of the increased Rn extraction efficiency may come at the expense of a larger sample background due to the increased cocktail volume.

The distribution of Rn between the three phases within a LSC vial can be calculated using an activity balance and the known volumes of the three phases. Assuming all the Rn enters via the aqueous phase, the fraction of Rn in the cocktail phase once chemical equilibrium has been achieved, can be expressed as:

$$F_c = \frac{K}{\left[K + \left(V_s/V_c\right) + \left(V_v/V_c\right)H\right]} \quad (1)$$

where F_c is the fraction of Rn in the cocktail phase, K is the sample:cocktail Rn partition coefficient (dimensionless), H the air:water Rn partition coefficient (dimensionless), and V_s, V_c, and V_v are the sample, cocktail, and vial void (gas) phase volume (ml) respectively. In a similar manner, the fraction of Rn in the vial void or headspace, F_v, can be expressed as:

$$F_v = \frac{H}{\left[H + \left(V_s/V_v\right) + \left(V_c/V_v\right)K\right]} \quad (2)$$

The magnitude of the sample:cocktail Rn partition coefficient is dependent on the base solvent of the cocktail. For a DIN based cocktail such as Ultima Gold F, a value of 32.4 ± 1.7 measured at 20^{o}C, has been reported (Cantaloub et al, 1997). Values of H range from 3.5 to 4.0 (Cleaver, 1981). Using equations (1) and (2), a fixed aqueous sample of 5.0 ml, a standard LS vial volume (polycone top) of 23.5 ml, and values of 32 and 4 for K and H respectively, the fraction of Rn in each of the phases as a function of cocktail volume can be calculated. Fig. 1. shows the effect of the cocktail volume on the Rn fraction in the cocktail and gas phase for cocktail volumes of 5 to 15 ml. With 5.0 ml of cocktail, nearly 25% of the Rn is expected to occur within the 13.5 ml void space above the cocktail. As cocktail volume increases (smaller void space), more Rn resides within the cocktail until at a cocktail volume of 15 ml, more than 95% of the Rn is expected in the cocktail phase. No more than 2% of the Rn is expected to remain in the aqueous phase for any cocktail-headspace combination. This is due to the aqueous phase being the least preferred phase for Rn, coupled with the relatively small 5 ml aqueous volume.

METHODS & MATERIALS

Standard and background vials were prepared with cocktail volumes of 5.0, 7.5, 10.0, 12.5 and 15.0 ml floating on top of a 5.0 ml aqueous sample. The LS cocktail used was Ultima Gold F, a DIN based cocktail manufactured by Packard Instruments. Radioactive standards were prepared by transferring 5.0 ml of a NIST traceable aqueous $RaCl_2$ solution into pre-weighed 20 ml glass scintillation vials. The Ra activity was 100.2 ± 1.2 dpm/ml and contained 20 ppm $BaNO_3$ carrier and 0.5 M HCl. Background vials were prepared from a DI solution of similar ionic and acidic strength. Five standards with matching background vials were prepared for the 5 cocktail volumes. Auto-pipettes were used for all liquid transfers, but the sample and cocktail volumes were determined by mass difference using an analytical balance and the appropriate density. The average aqueous and cocktail volume, along with the theoretical alpha activity for the sample sets is shown in Table 1. Prior to counting, the vials were placed in a laboratory refrigerator for over 30 days to reach chemical and radioactive equilibrium. The sample vials were never shaken.

Table 1. Average (n=5) aqueous volume and cocktail volume for the five cocktail sets. Activity is maximum alpha activity for supported ^{222}Rn in equilibrium with ^{218}Po and ^{214}Po daughters.

Sample Set	Aqueous Volume (ml ± 2σ)	Cocktail Volume (ml ± 2σ)	Sample Activity (dpm α ± 2σ)
5-5.0	5.07 ± 0.01	4.94 ± 0.11	1523 ± 2
bkgd	5.04 ± 0.03	4.99 ± 0.09	
5-7.5	5.06 ± 0.01	7.44 ± 0.04	1521 ± 1
bkgd	5.03 ± 0.02	7.43 ± 0.03	
5-10.0	5.06 ± 0.02	9.94 ± 0.03	1521 ± 3
bkgd	5.03 ± 0.01	9.94 ± 0.04	
5-12.0	5.06 ± 0.02	12.43 ± 0.04	1523 ± 4
bkgd	5.02 ± 0.01	12.44 ± 0.04	
5-15.0	5.06 ± 0.01	14.89 ± 0.06	1520 ± 1
bkgd	5.02 ± 0.02	14.88 ± 0.04	

The samples were counted on a Packard Tri-Carb 2500 TR/AB liquid scintillation analyzer having an attached chill unit operating at 12°C. Samples were allowed a minimum of 3 days temperature equilibration on the detector deck following transfer from the refrigerator. The ten vials in a set (5 supported Rn, 5 background) were counted in a single rack in alternating positions (odd-background; even-standards) to better estimate the background during the sampling interval. All samples were dark adapted for 5 minutes then monitored for quench for 60 seconds using the instrument's external standard tSIE quench parameter. Settings for all parameters were the default values, except for enabling of luminescence correction. The cocktail sets were counted in the "alpha-beta" mode over a pulse decay discriminator (PDD) range of 100 to 200. Counting terminated at 60 minutes or when a 2σ of 1% was reached in the alpha MCA.

RESULTS & CONCLUSIONS

Spectra from 1 - 2000 channels were saved for each sample and transferred to a personal computer for analysis. The spectra were converted to cpm/channel and then an average spectrum was created from the five background vials and from the 5 sample vials of each cocktail set. This was done for both the alpha and beta MCA spectra. Alpha background, efficiency, FOM and the total sample efficiency (net alpha & net beta count rate) at each PDD setting, were calculated using all 2000 channels. If alpha and beta counting efficiency are near 100%, then the total sample efficiency values should reflect the partitioning of Rn into the vial headspace. The total sample efficiency for each cocktail set is plotted along with the theoretical Rn partition curve in Fig. 1.

The data shows good agreement for the 15.0 and 12.5 cocktail volume samples, however, the 10.0, 7.5, and 5.0 ml efficiencies are greater than predicted. More Rn is being counted in the cocktail phase than is expected. One possible explanation for this is interaction of the gas phase Rn with the LS cocktail. Prichard and Gesell (1977) assumed that 25% of the gas phase Rn contributed to the observed count rate. The curve (Eqs. 1 & 2) neglect this effect. A second possibility is the magnitude of the Rn partition coefficient. A larger value of K (50) fits the 5.0, 7.5, and 10.0 data better, but would result in the measured Rn in the 15.0 and 12.5 ml sets falling below predicted values. Results below the predicted distribution, due to decreased counting efficiency, could be justified by quench as the tSIE parameter was lower (more quench) for the larger cocktail volume sets. (A partition coefficient of 50 for UGF, however, is not consistent with previous and current research.) Despite the increased quench of the larger volume samples, both the alpha and total counting efficiency are larger for the samples having more cocktail volume. The higher counting efficiency, however, does not always result in the most efficient analysis protocol. Table 2 shows the full spectrum and window optimized FOM for each cocktail set at several PDD values. For the range of PDD settings, the optimum FOM decreases as the cocktail volume increases despite the consistently higher counting efficiencies for the larger cocktail volume samples (data not shown). The increase in counting efficiency gained by filling the vial headspace with cocktail comes at the expense of a higher alpha background. The maximum FOM is consistently achieved for the 5.0 ml samples over the range of PDDs. The effect of cocktail volume on background is shown in Fig. 2. which gives alpha MCA backgrounds as a function of cocktail volume. The relationship between cocktail volume and alpha background is linear at a specific PDD, but it does not remain constant over the PDD range (100-200). At a PDD of 100, the background for the 15.0 ml set is nearly

Fig. 1. Theoretical and measured Rn distributed in the LS cocktail and headspace for a 5.0 ml aqueous sample. Data points are the average total sample (alpha & beta) efficiency for each set (n = 15; 2s < 1%)

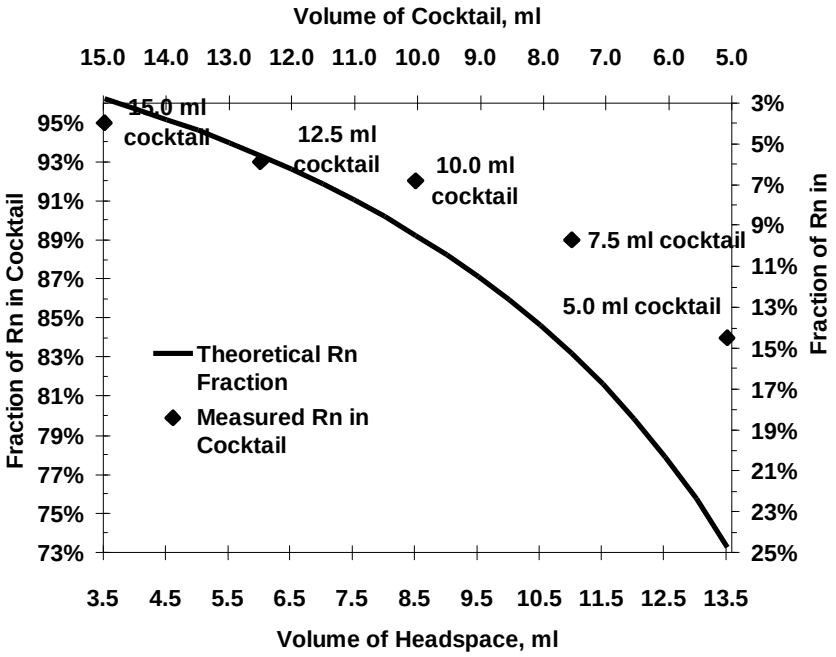
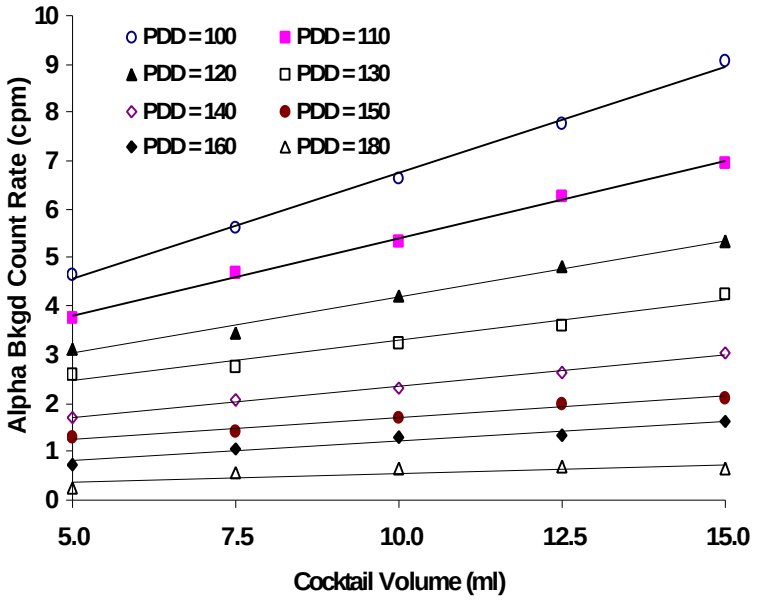


Table 2. Average (n=5) FOM for cocktail sets at selected PDD.

	PDD - 140		PDD - 160		PDD - 180	
Set	Open	Optimum	Open	Optimum	Open	Optimum
5.0	3567	21080	6602	50412	10062	75572
7.5	3525	17444	5662	28150	5270	42624
10.0	3469	16025	4843	22757	4603	26306
12.5	3099	14270	4611	18604	3999	22304
15.0	2816	11756	3741	15189	3803	16723

twice the background of the 5.0 ml cocktail set (9.1 vs 4.7 cpm). At a PDD of 180, however, alpha background for the 15.0 ml set is nearly 3 times that of the 5.0 ml set (0.67 vs 0.24 cpm).

Fig. 2. Alpha background as a function of cocktail volume and PDD (full open window of 1 - 2000 channels).



A final comment regards sample quench. As noted earlier, the measured tSIE parameter decreased (more quench) as the cocktail volume was increased. With increased quench, one expects that the optimum counting window shifts to lower channels as the alpha spectrum shifts to lower energies. Indeed, the average interval for the optimum FOM was 200–650 channels for the 5.0 ml set and 150–550 channels for the 15.0 ml set. An expected, and as yet unexplained observation, was the relationship between PDD and tSIE. For each of the sets, the magnitude of tSIE decreased with increasing PDD. Overall, the relationship between tSIE and cocktail volume, for a fixed sample volume, suggests that in this experiment quenching was a result of the cocktail rather than the sample ionic or acidic strength.

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