Optimization of Simultaneous Tritium-Radiocarbon Internal Gas Proportional Counting

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Abstract

Specific environmental applications can benefit from dual tritium and radiocarbon measurements in a single compound. Assuming typical environmental levels, it is often the low tritium activity relative to the higher radiocarbon activity that limits the dual measurement. In this paper, we explore the parameter space for a combined tritium and radiocarbon measurement using a natural methane sample mixed with an argon fill gas in low-background proportional counters of a specific design. We present an optimized methane percentage, detector fill pressure, and analysis energy windows to maximize measurement sensitivity while minimizing count time. The final optimized method uses a 9-atm fill of P35 (35% methane, 65% argon), and a tritium analysis window from 1.5 to 10.3 keV, which stops short of the tritium beta decay endpoint energy of 18.6 keV. This method optimizes tritium-counting efficiency while minimizing radiocarbon beta-decay interference.

Keywords

Tritium; radiocarbon; optimization; proportional counter; environmental methane;

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1. Introduction

Tritium and Radiocarbon Backgrounds

Both tritium (^3H) and radiocarbon (^{14}C) are extensively used for age dating in a wide variety of circumstances. These two standard radioisotopes span the period of 10's to 1000's of years: tritium with a half-life of 12.32 years and radiocarbon with a half-life of 5730 years. Both tritium and radiocarbon undergo beta decay; tritium is a low-energy beta emitter with an endpoint of 18.6 keV (Tilley *et al.* 1987) whereas radiocarbon has an endpoint energy of 156.5 keV (Ajzenberg-Selove 1991).

Tritium concentrations are typically reported in tritium units (TU) where 1 TU indicates one tritium atom per 10^{18} hydrogen atoms. This corresponds to 0.015 disintegrations per day per standard cubic centimeter of methane (Hackley *et al.* 1996). Before atmospheric nuclear testing began in 1945, tritium concentration levels in precipitation were around a few TUs from natural processes, e.g., cosmic bombardment of atmospheric nitrogen. Atmospheric tritium concentrations peaked in 1963 at thousands of TU, depending on the geographic location (the majority was injected into the northern stratosphere). After the last atmospheric nuclear test in 1980, atmospheric tritium concentrations have been steadily decreasing and have now returned to nearly pre-test levels (Rozanski *et al.* 1991, Zhang *et al.* 2011).

Radiocarbon concentrations are typically (Stenström *et al.* 2011) reported in *percent Modern Carbon* (pMC), defined relative to an oxalic acid standard with a reference value of 95 percent of the activity in AD 1950, such that 100 pMC is 10.5 disintegrations per day per standard cc of methane (Stuiver and Polach 1977, Olsson 1991). Before 1945, biosphere radiocarbon fluctuated around 100 pMC. At the peak of atmospheric nuclear testing, the atmospheric ^{14}C concentration was roughly double (200 pMC) that of pre-nuclear test years (Lehmann *et al.* 1993). After the end of above-ground testing, radiocarbon concentrations have fallen to nearly pre-nuclear-age levels (Naegler and Levin 2006).

Tritium and Radiocarbon Measurement Techniques

There are multiple measurement techniques to count tritium including liquid scintillation counting (LSC), gas proportional counting (PC), or mass spectrometry; each method offers its own advantages (Theodorsson 1996). This paper focuses on gas proportional counting to measure tritium, which offers the main advantages of high counting efficiency and low backgrounds. This method lends itself best to samples that are small in size (mL) or contain low concentrations of tritium. Given the high efficiency of this counting method, nearly every decaying atom of tritium can be counted in the active gas volume, so even very small samples can be measured. Natural methane samples are the most simple to count via PC since they can be loaded directly into counters with minimal chemistry or sample preparation.

There are similar techniques used to measure radiocarbon: LSC, gas PC, and accelerator mass spectrometry (AMS). For radiocarbon analysis, AMS is the acknowledged leader in ^{14}C -dating (Fifield 1999). However, proportional counters and LSC are also able to do ^{14}C measurements with less precision.

There exists a class of samples where the dual isotope measurement for $^{14}\text{C}/\text{T}$ is more desirable than preparing the sample for alternative methods. Specifically, natural methane samples that are easily loaded into a proportional counter without complex sample preparation chemistry. This class of samples could include swamp or marsh gases, dissolved methane from freshwater lakes, and atmospheric methane.

This paper concerns a dual tritium-radiocarbon measurement using ultra-low-background gas proportional counters that were developed at Pacific Northwest National Laboratory (PNNL) (Aalseth *et al.* 2009). These proportional counters have a design volume of 100 cm^3 (STP) and are operable up to a pressure of 10 atm. Low backgrounds are achieved with a combination of ultra-pure materials (Hoppe *et al.* 2008), active and passive shielding (Seifert 2011), and operation in a shallow underground laboratory (Aalseth *et al.* 2012a). In this study, candidate gas fills are restricted to mixtures of argon and methane. PXX denotes such a mixture with XX% methane, e.g., P10 is 10% methane with the balance (90%) being argon. The methane component (i.e. the sample) could come from a natural methane source (most simple option) or could be prepared from an organic or water precursor, which requires a greater level of effort (Povinec 1972).

The simultaneous measurement of tritium and radiocarbon has been previously demonstrated (Povinec 1980), but this work was performed during a time of much higher atmospheric tritium content. We revisit this topic in light of the challenges now associated with a dual measurement decades after atmospheric nuclear testing has ceased and tritium and radiocarbon components are significantly diminished. It is necessary to optimize detector parameters in order to successfully measure these natural backgrounds. The assumed activity level for natural levels of tritium in water is 6 TU and the assumed natural level for carbon is 120 pMC. Thus, the tritium measurement dominates considerations since a portion of the few counts from tritium will fall into the overlapping region with carbon (note: 6 TU is equivalent to ~ 0.1 count per day per cm^3).

2. Theory

As discussed above, the overlapping emission energies for tritium and radiocarbon decay combined with the lower tritium decay rate in typical samples presents the primary challenge in the dual tritium-radiocarbon measurement. Therefore, this section focuses on discussion of the appropriate expression for the uncertainty in the tritium specific activity. The principal data consists of an energy spectrum (number of events vs. energy) recorded by the proportional counter system where it is assumed that the detector's background spectrum has already been well characterized. It is important to remember that the energy value corresponding to a particular event represents the energy deposited in the detector

and not necessarily the full energy of the ionizing particle itself. The deposited energy depends not only on the initial energy of the particle, but also on its initial location and direction, as well as the stopping power of the fill gas.

To calculate radioisotope activities from these data, one must understand the detector's response to the isotopes of interest. To this end, the EGS4 software package (Nelson and Namito 1990) was used to generate representative tritium and radiocarbon spectra for the gas fills under consideration. The EGS4 code is a Monte Carlo package for the transport of electrons and photons that takes as user input the detector's geometry and composition, along with the desired events and their initial locations, e.g., tritium beta decays placed uniformly throughout the gas volume. However, the smearing effect corresponding to the detector's non-ideal energy resolution is unaccounted for, as charge transport processes after energy deposition (ionization) in the detector are not modeled. This simplification is acceptable since the slight changes in the spectra do not significantly affect the optimization as discussed in section 4. All the presented Monte Carlo simulations consist of 10^7 events.

Figure 1 shows the EGS4 results for two different gas fills in the PNNL proportional counter geometry: P10 at a pressure of 3 atm and P35 at 9 atm. The tritium spectra (Figure 1a) are almost identical for the two fills as both gases have enough stopping power to predominantly cause full energy deposition for the range of tritium energies. On the other hand, the radiocarbon spectra differ significantly since the higher energy radiocarbon decays deposit proportionately less of their energy in the 3-atm P10 gas due to its lower stopping power. Consequently, as can be seen in Figure 1b, there are more counts at lower energies for the P10 fill compared to P35.

Insert Figure 1a and Figure 1b here.

To translate the spectral data into a radioisotope concentration, one can define an analysis energy window for the given isotope, and compare the net number of counts in this window (after correcting for expected backgrounds) with the number predicted by the EGS4 simulation. When multiplied by the appropriate factors, the ratio of these two numbers generates an estimate for the specific activity/concentration of the radioisotope. Analysis of this sort for the tritium-radiocarbon content of a methane landfill sample is shown in Figure 2. These data were acquired by a PNNL proportional counter filled with 3 atm of P10 where the sample was the landfill methane, which was then mixed with argon to blend to P10. The analysis uses a tritium window of 3 to 19 keV and a radiocarbon window of 19 to 157 keV. Due to the sample's relatively large tritium concentration (over three orders-of-magnitude greater than the level assumed by this article), no optimization for fill type or analysis windows was necessary and the authors (Aalseth *et al.* 2012b) reported agreement between measurements made via proportional counting and an AMS result from a commercial vendor.

Insert Figure 2 here.

A consistency check can be made with the above data for the applicable EGS4 results, namely the response of P10 at a pressure of 3 atm. The plot in Figure 3 compares these data to the sum of the tritium and radiocarbon EGS4 response functions where each function is normalized by the appropriate specific activity from the analysis shown in Figure 2. The error bars correspond to one-sigma uncertainties.

Insert Figure 3 here.

Next, some useful notation is introduced. e_{AB}^H denotes the fraction of ^3H decays expected (determined from EGS4) to appear in an energy window from A to B, and similarly for fractions of ^{14}C decays, e.g., e_{AB}^C . As for measured count rates, S_{AB}^{tot} denotes the total rate observed in a window from A to B, and a particular source for the counts is indicated by the superscript. Lastly, V denotes the methane sample volume (STP) and $\text{eff}_{vol} = 0.90$ is the empirically-determined “effective volume” of the PNNL proportional counters, i.e., decays in 90% of the gas volume give rise to electron avalanches and thus detection by the system.

Given the above notation, the tritium specific activity, s , can be expressed as:

$$s = \frac{1}{V e_{AB}^H \text{eff}_{vol}} (S_{AB}^{tot} - S_{AB}^C - S_{AB}^{det}) = \frac{1}{V e_{AB}^H \text{eff}_{vol}} \left(S_{AB}^{tot} - \frac{e_{AB}^C}{e_{BC}^C} S_{BC}^C - S_{AB}^{det} \right) \quad (1)$$

where AB defines the tritium window and BC the radiocarbon window. The sum of terms in parentheses corresponds to the estimate for tritium counts in the tritium window, and equals total counts minus backgrounds from radiocarbon and the detector (and its environment). In the second equality, the radiocarbon background (in AB) is re-expressed in terms of the radiocarbon counts in BC as this quantity can be measured directly without significant tritium interference. Specifically, for the assumed radioisotope concentrations and final optimized choice of $B=10.3$ keV (discussed in Section 3), the number of tritium counts in BC is less than 1% of the number of radiocarbon counts in BC.

To derive a useful equation for the uncertainty in s , one uses the property of a Poisson process that the uncertainty in a number of counts is equal to the square root of the count number. For example, the uncertainty in S_{AB}^{tot} satisfies:

$$\left(\sigma_{S_{AB}^{tot}} \right)^2 = \left(\frac{\sigma_{N_{AB}}}{T} \right)^2 = \frac{N_{AB}}{T^2} = \frac{S_{AB}^{tot}}{T} \quad (2)$$

where N_{AB} denotes the number of counts detected in AB during a time interval T . Applying standard error propagation to (1) along with relationships of the sort exemplified above, leads to the following equation for the uncertainty in s :

$$\sigma_s = \frac{1}{V e_{AB}^H \text{eff}_{vol}} \sqrt{\frac{1}{T} \left(S_{AB}^{tot} + \left(\frac{e_{AB}^C}{e_{BC}^C} \right)^2 S_{BC}^C + S_{AB}^{det} \right)}. \quad (3)$$

Finally, since the total count rate in AB is equal to the tritium, radiocarbon, and detector rates, equation (3) becomes:

$$\sigma_s = \frac{1}{V e_{AB}^H \text{eff}_{vol}} \sqrt{\frac{1}{T} \left(S_{AB}^H + S_{AB}^C + \left(\frac{e_{AB}^C}{e_{BC}^C} \right)^2 S_{BC}^C + 2S_{AB}^{det} \right)}. \quad (4)$$

For the candidate gas fills with the assumed radioisotope levels, the S_{AB}^C term in (4) is greater than the others by at least an order-of-magnitude. Focusing for now on only this term highlights the main factors to be considered in the optimization. Dropping the secondary terms and solving for the time T gives:

$$T = \frac{S_{AB}^C}{(V e_{AB}^H \text{eff}_{vol} \sigma_s)^2} = \frac{12.6 V e_{AB}^C}{(V e_{AB}^H \text{eff}_{vol} \sigma_s)^2} \text{ cm}^{-3} \text{ day}^{-1} \quad (5)$$

where the factor of 12.6/cm³ day converts between radiocarbon concentration and activity. In what follows, the times quoted are those required for a 10% relative uncertainty in s . Substituting this condition along with the numerical factors results in:

$$T = 156000 \frac{e_{AB}^C}{V (e_{AB}^H)^2} \text{ cm}^3 \text{ days} \quad (6)$$

3. Optimization

Since the tritium measurement dominates sensitivity considerations under the assumed tritium and radiocarbon concentrations, equation (4) for the uncertainty in the tritium specific activity is the appropriate quantity to be minimized by choice of experimental method and analysis. Keeping only the dominant term in (4) due to the radiocarbon background in the tritium analysis window, leads to expression (6) for the approximate counting time required to achieve a tritium concentration precision of 10%. All terms are included in the final counting times presented near the end of this section, but first the discussion focuses on three elements that can be varied to minimize count times in expression (6):

1. The upper energy bound of the tritium window (B)
2. Methane percentage of the fill gas (PXX)
3. Methane sample volume (V)

These latter two elements determine the response functions, e^H and e^C . Note that methane percentage, sample volume, and fill pressure are not independent quantities, and for clarity's sake, different pairs from these three variables are sometimes used to identify gas fills.

To investigate the impact of changing the tritium window, a particular gas fill must be assumed, and in anticipation of the optimized choice, results are presented for a 9-atm P35 fill. However, what follows is similar for any of the candidate gas loads. The tritium window's lower bound, A, is set equal to 1.5 keV to be sufficiently separated from the system's electronic-noise floor. The window's upper bound, B, is determined by finding the value that minimizes the factor in expression (6) that depends on B, namely $e_{AB}^C / (e_{AB}^H)^2$.

Figure 4 graphs the counting time expression (6) versus the upper bound and demonstrates the existence of a minimum at 10.3 keV. The plot's general shape can be understood by looking at the 9-atm P35 response functions shown in Figure 1. One might naively choose an upper energy bound equal to the tritium endpoint of 18.6 keV (thinking it best to maximize tritium counts), though as the upper bound is decreased, the small percentage loss of tritium counts near the endpoint energy is more than balanced from a sensitivity perspective by the loss of radiocarbon counts which act as background. The effect is significant as the counting time for a choice of $B=10.3$ keV is 69% of the time if the tritium endpoint is used instead. Previous work using pure methane count gas chose a similar endpoint (9.7 keV) by optimizing the signal to background ratio in their detector (Krajcar-Bronić *et al.* 1986).

Insert Figure 4 here.

Next, consider the effect on the counting time from varying the gas fill methane percentage while fixing the sample volume. This focuses attention again on the expression $e_{AB}^C/(e_{AB}^H)^2$ from (6), though in the previous paragraph $e_{AB}^C/(e_{AB}^H)^2$ is considered a function of B , whereas in the present context it is a function of the gas fill (B is set equal to 10.3 keV).

A methane volume $V=200$ cm³ (STP) is chosen and $e_{AB}^C/(e_{AB}^H)^2$ calculated from the EGS4 results for a series of different gas fills. The resulting counting times from (6) are plotted as a function of fill methane percentage in Figure 5. The points represent integral gas pressures from 3 to 8 atm, or equivalently, methane percentages (rounded to two significant digits) of P67, P50, P40, P33, P29, and P25, while the curve is a quadratic fit to these six points. Figure 5 demonstrates how for a given methane sample, the counting time is minimized by adding as much argon, i.e., moving as far along the curve to the left, as the detector allows. Typical constraints include maximum operating pressure and/or electronic components (Canberra 2014) that limit the achievable gas gain as pressure increases (Mace *et al.* 2013).

Insert Figure 5 here.

Figure 5 can be explained by considering the stopping power of the gas. As the pressure of these fills increases (decreasing methane percentage), stopping power also increases, and therefore radiocarbon decays with incomplete energy deposition shift to higher energies in the response function. For these pressures, tritium decays already deposit their full energy and thus the tritium response doesn't change. The net effect is larger signal-to-background ratios for smaller methane percentages as radiocarbon background counts move out of the tritium analysis window. Figure 6 shows this shift explicitly in the form of EGS4 results for the relevant radiocarbon response functions.

Insert Figure 6 here.

Now consider what happens when the methane sample volume (V) is also allowed to change. In Figure 7, curves corresponding to $V=200, 250$, and 300 cm³ (STP) are shown, similar to the one in Figure 5. Note the interplay between sample volume and methane

percentage – for example, the P10 fill with 200-cm³ sample and P20 fill with 250-cm³ sample have nearly the same counting time. For clarity, the EGS4 generated points used to fit for the three curves are not shown. Instead, plotted on each curve is the point that represents a pressure of 10 atm. This is the assumed maximum fill pressure for the PNNL proportional counters and therefore the segments to the left of these points are operationally inaccessible. The arrow in Figure 7 indicates the general direction for optimization of the gas fill.

Insert Figure 7 here.

In addition to the 10-atm pressure constraint, the PNNL proportional counters are limited to an operational voltage no greater than 5000 V because of elements in the preamplifier electronics. This impacts the choice of fill gas since the detector is always operated at around the same gas gain, independent of fill, to produce a dynamic energy range appropriate to the dual tritium-radiocarbon measurement. Thus, the voltage required to achieve this specific gas gain increases with either the methane percentage (additional quench gas) or with the total pressure of the gas load (the higher the total pressure of the gas, the higher the voltage required to reach the same gas gain) in the detector. As part of the optimization, one could allow the electronic gain of the analog-to-digital converter to vary, therefore providing a greater dynamic range for the operating voltage, though for now the electronic gain is kept the same as in previous studies that characterized the system’s electronic noise.

The above discussion means that detector operation for a gas fill represented by a point farther along the arrow in Figure 7 requires a higher voltage. For example, the P25 (10-atm) point requires a voltage of 4800 V compared to a voltage of greater than 5000 for the P30 (10-atm) point. Table 2 in Section 4 includes these and other experimentally determined voltages. Combining the pressure and voltage constraints determines an operationally accessible 2-dimensional region in Figure 7 (the upper part of the arrow coincides with this region’s boundary). The optimized gas fill is the one represented by a point in this accessible region with the smallest counting time.

Table 1 lists the theoretical counting times for various candidate gas fills based on the full expression (4) for the uncertainty in the specific tritium activity (values shown in Figure 7 are approximately 25% smaller as they include only the dominant term). Methane percentages in 5% increments were investigated and the lowest counting time for an accessible operating point is produced for a 9-atm P35 gas load. As a reminder, these are times needed for a 10%-precision measurement of a 6 TU tritium concentration where concomitant in the methane sample is a 120%-modern radiocarbon level. Because background data is unavailable for each specific fill, the same background is assumed throughout, namely $S_{AB}^{det} = 14$ cpd. This count rate is based on a month of background data from a detector filled with 9 atm of P35 and located in PNNL’s shallow underground laboratory (Seifert *et al.* 2013). This background spectrum is shown in Figure 8. Actual rates for other gas fills would modify count times at the 1% level since the detector

background term contributes roughly only 5% to the time and the term itself changes by at most 20% between fill types (based on additional background data).

Insert Table 1 here.

Insert Figure 8 here.

Figure 9 summarizes these results by plotting the counting times in Table 1 as a function of methane percentage and pressure. In addition, each point is labeled by operating voltage, which shows how the voltages increase for both increasing methane percentage and pressure. The final gas fill choice of P35 at 9 atm lies near the minimum counting time for operationally accessible fills, i.e., $P \leq 10$ atm and $V \leq 5000$ V.

Insert Figure 9 here.

4. Additional Performance Considerations

For the gas fills considered, the energy resolution curve tends to degrade with an increase in operational voltage (for each fill, the applied voltage produces the same gas gain). This trend can be seen in Table 2, which lists resolutions measured at 8.0 keV (Cu x-rays) and 59.5 keV (^{241}Am gamma-rays). Many proportional-counter applications require better energy resolution (Charles and Cooke 1968), a feature which helps determine fill type, e.g., a few atmospheres of P10 is typical. However, the tritium-radiocarbon method only depends on summing counts over broad energy windows and therefore degraded resolution is not much of a concern.

Insert Table 2 here.

In order to determine the energy resolution closer to the tritium window's lower bound and to obtain an additional energy calibration point, a 9-atm P35 fill was spiked with a trace sample of ^{37}Ar . These data, obtained during two-and-a-half days in the PNNL shallow underground laboratory, are shown in Figure 10. The ground-to-ground state electron capture of ^{37}Ar to ^{37}Cl produces an energy peak at 2.82 keV due to the resulting atomic shell cascade (Firestone *et al.* 1997, Aalseth *et al.* 2011). The counts shown in the figure are after veto and pulse-shape-discrimination cuts (Aalseth *et al.* 2012b) and the ^{37}Ar peak is seen to be well separated from the detector threshold at 1.5 keV. The full-width-half-maximum (FWHM) of this peak is 22.6 ± 0.9 %.

Insert Figure 10 here.

One potential concern of degraded resolution is its implications for the response functions, e^H or e^C . The EGS4-generated response functions assume perfect detector response, that is, no smearing of the deposited energy due to stochastic processes. To incorporate the actual response of the detector, the EGS4 results are convolved with (unit probability) Gaussian functions having widths equal to the detector energy resolution at the

energy of the Gaussian peak's location. For example, the modified value for the tritium response function at energy E is equal to:

$$\sum_{\varepsilon} e^H(\varepsilon) \text{Gaus}(E - \varepsilon; \sigma = \text{res}(\varepsilon)) \quad (7)$$

where the summation is over energies differing by 0.1 keV as this is the energy granularity chosen for EGS4. In practice, the sum is only over an energy band characteristic of the widths of the Gaussian functions.

As the counting times depend on response functions only through summing their values over the energy windows, the important modifications to the functions are those near the window edges. In physical terms, the impact on counting times is due to a net number of events being smeared into or out of the window across either energy bound. In addition, an examination of expression (7) determines that the value of a response function at energy E does not change if around E the original response function is linear and the energy resolution flat. That these conditions are strongly satisfied near the window boundaries explains why factors such as e_{AB}^H change by at most a few percent. Such changes do not significantly affect the optimization results.

5. Conclusions

Normal methods for measuring tritium and radiocarbon levels are incompatible with simultaneous measurement of both isotopes in the same sample. Proportional counting can enable concurrent measurement of these isotopes and this paper explores different loading conditions to optimize simultaneous measurement using methane as an analyte. Given current environmental tritium and radiocarbon levels, this dual radiometric measurement is challenged by the large concomitant radiocarbon background masking the tritium activity. The discussion provides guidance on minimizing the error associated with the resulting emission overlap.

Optimal gas-fill characteristics depend on the methane sample-size available and the details of the specific proportional counters being used, e.g., their gas volume, maximum operating pressure, operational voltage, etc. If one has a limited sample size then the fill choice is straightforward: load the counter with the full methane sample along with as much argon as allowed, e.g., by the maximum operating pressure. Of course, this assumes that the fill produced has adequate proportional-counting performance. The general validity of this procedure is demonstrated by Figure 5 whose curve corresponds to a fixed 200 cm³ sample. In short, a lower methane percentage produces counter response with fewer radiocarbon counts in the tritium window.

On the other hand, if there is enough methane relative to the maximum gas load of the counter, there are competing factors involved in the measurement sensitivity. That is the case in this study where we have assumed an unlimited methane sample and have been considering the specific counters developed recently at PNNL. For counters with different gas capacities (or other gas-fill types, rather than a mixture of methane and argon), one

could follow a similar procedure to determine the optimal gas-fill choices. Figure 7 along with Table 1 provide a good summary of the situation for the PNNL counters – the optimal fill being 9 atm of P35.

Even with this gas-fill choice (as well as optimization of the tritium window), the theoretical counting time for a 10%-precision tritium measurement assuming typical environmental tritium/radiocarbon levels is still somewhat long, around 11 weeks. However, there may be cases where a dual measurement provides relevant information that would be lost if the sample were to be separated and counted separately. For example, tritium and radiocarbon measurements can record different environmental events, e.g. radiocarbon can provide an assessment of carbon age in soil organic matter and the inclusion of tritium analysis can help assess the stability of these compounds. Similarly the use of two isotopes provides added resolution for assigning contributions from different source terms, e.g. regional atmospheric methane which is a compilation of natural (predominantly microbial) and anthropogenic sources (including fracking or landfill methane).

Further improvements in this area could be made by addressing a few key factors. First, the measurements in this paper were limited largely due to hardware constraints of commercial preamps and cables (<5000V); thus new, high-performance, low-noise electronics would allow for operating at an increased total pressure (which includes a greater sample size). Second, improvements may be made with larger detector sizes which would allow for greater sample sizes; however there is a trade off in increased detector volume since there is also an increase in backgrounds so further investigation would be needed to verify the enhancement is valuable.

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Figure

Figure 1. EGS4 Monte Carlo results for (a) tritium and (b) radiocarbon beta decays. Two gas fills are simulated: P10 at 3 atm and P35 at 9 atm.

³ H Analysis Results ROI integral (3.0-19.0 keV): 9370 ± 100 - 1000 _{bkg} ± 20 - 135 _{14C} ± 10 = 8230 ± 100 Sample Decays: 13890 ± 170 Sample LT: 6.95 days Sample Volume: 9.12 STP cm ³ Specific Activity (cpd/cm ³): 220 ± 3 TU: 13230 ± 160	Full ROI Analysis Results ROI integral (3.0-400.0 keV): 10420 ± 100 - 1610 _{bkg} ± 20 = 8800 ± 100 Sample LT: 6.95 days Background LT: 21 days Gross rate: 1500 ± 15 (cpd) Net rate: 1270 ± 15 (cpd)	¹⁴ C Analysis Results ROI integral (19.0-157.0 keV): 1040 ± 30 - 600 _{bkg} ± 10 = 440 ± 30 Sample Decays: 730 ± 60 Sample LT: 6.95 days Sample Volume: 9.12 STP cm ³ Specific Activity (cpd/cm ³): 12 ± 1 Approximate pMC: 110% ± 9%
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Cedar Hills Landfill Sample in ULBPC 2-23

Figure 2. Data and analysis for measurement of tritium-radiocarbon concentrations in landfill methane sample. Spectra shown are counts for landfill sample and background data scaled to same live time (LT).

Figure 3. Comparison of landfill data with EGS4 simulations for response of 3-atm P10 gas fill. The background was collected using a 3-atm P10 gas fill with no sample, collected in the same detector, at the same gas gain as the 3-atm landfill sample.

Figure 4. Plot showing how counting time for the tritium measurement depends on the tritium window's upper energy bound, B (lower bound is fixed at 1.5 keV). The optimized method uses $B=10.3$ keV, corresponding to the location of the minimum.

Figure 5. Plot showing how counting time for the tritium measurement depends on gas fill methane percentage given a 200 cm³ (STP) methane sample. The points were calculated from EGS4 response functions and the curve is a quadratic fit to the points.

Figure 6. EGS4 generated radiocarbon response functions for the 6 gas fills represented by points in Figure 5. The change in shape of the distributions demonstrates how counts are shifted out of the tritium window (1.5 – 10.3 keV) as pressure increases.

Figure 7. Curves demonstrating how the tritium measurement counting time depends on gas methane percentage for methane samples (STP) of 200 cm^3 , 250 cm^3 , and 300 cm^3 . The points represent fills with pressures of 10 atm and the arrow shows the overall direction of fill optimization. The shaded region indicates the area of operational inaccessibility.

Figure 8. Background spectrum for 9-atm P35 gas fill acquired in PNNL shallow underground laboratory. Counts shown are after veto and pulse-shape-discrimination cuts. Background in tritium analysis window (1.5 – 10.3 keV) is determined to be 14 counts per day for a 32 day measurement.

Figure 9. Counting times from Table 1, plotted as a function of methane percentage and gas pressure. Points are labeled by the required operational voltage (in volts). P35 at 9 atm (shown as a star in the plot) is the final gas fill choice.

Figure 10. Spectrum of 9-atm P35 gas fill spiked with trace sample of ^{37}Ar . The peak is due to electron capture by ^{37}Ar .

Table 1. Counting times required for a 10%-precision tritium concentration measurement for various gas fills. The methane sample is assumed to have 6 TU tritium and 120%-modern radiocarbon concentrations.

Methane (%)	Pressure (atm)	Counting Time (days)
25	8	138
25	9	116
25	10	99
30	7	142
30	8	116
30	9	97
30	10	82
35	8	92
35	9	78
40	7	104
40	8	90

Table 2. Measured energy resolutions for candidate gas fills

Methane (%)	Pressure (atm)	Voltage (V)	8-keV FWHM (%)	59-keV FWHM (%)
25	8	4300	25.7 ± 0.2	27.9 ± 0.5
25	9	4500	39.4 ± 0.3	30.1 ± 0.3
25	10	4800	62 ± 1	51 ± 3
30	7	4150	24.2 ± 0.2	25.0 ± 0.5
30	8	4450	34.5 ± 0.3	30.9 ± 0.9
30	9	4700	39.0 ± 0.4	32.4 ± 0.8
30	10	5000 ^a	48.7 ± 0.6	58 ± 4
35	8	4600	41.0 ± 0.6	29.9 ± 0.5
35	9	4950	46.1 ± 0.6	35.5 ± 0.7
40	7	4425	38.3 ± 0.6	27.9 ± 0.8
40	8	4750	43.9 ± 0.6	27.5 ± 0.3

^a The operational maximum voltage of 5000 V produced slightly less gas gain than in the other fills.