PNNL-28828

Pacific Northwest NATIONAL LABORATORY

Ultra-Sensitive Measurements of Large-Volume Radioxenon Samples Using an Ultra-Low-Background Proportional Counter (ULBPC): Final Report

July 2019

CE Aalseth
BG Fulsom
KS Thommasson
ER Edwards
EK Mace
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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

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Pacific Northwest National Laboratory
Richland, Washington 99352

Contents

Figures

Tables

1.0 Introduction

This project investigated the feasibility of analyzing radioxenon samples in much larger quantities than currently used by the International Monitoring System (IMS). There is interest within the PTS and the international community in the ability to obtain xenon samples using the output of industrial oxygen plants, which could provide samples that are larger by three orders of magnitude, or more, than those currently provided by IMS stations. Such samples would best be analyzed using internal-source gas proportional counters, though the details of that approach and its sensitivity and limits were previously not examined. This report details the outcomes of a task designed to 1) analyze xenon radioisotope data collected previously via internal-source gas proportional counting and 2) collect additional gas proportional counter measurements to determine feasible gas blends for large volume xenon measurements.

1.1 Motivation

The baseline sensitivity goal for a large volume radioxenon (LVXe) measurement is the ability to routinely quantify the background radioxenon concentrations around the world. Figure 1 shows how the average radioxenon backgrounds fluctuate due to various anthropogenic sources (e.g. medical isotope production facilities), but the baseline natural background from the crustal abundance contributions is consistently in the range of 0.01 mBq/m^3 to 0.05 mBq/m^3.

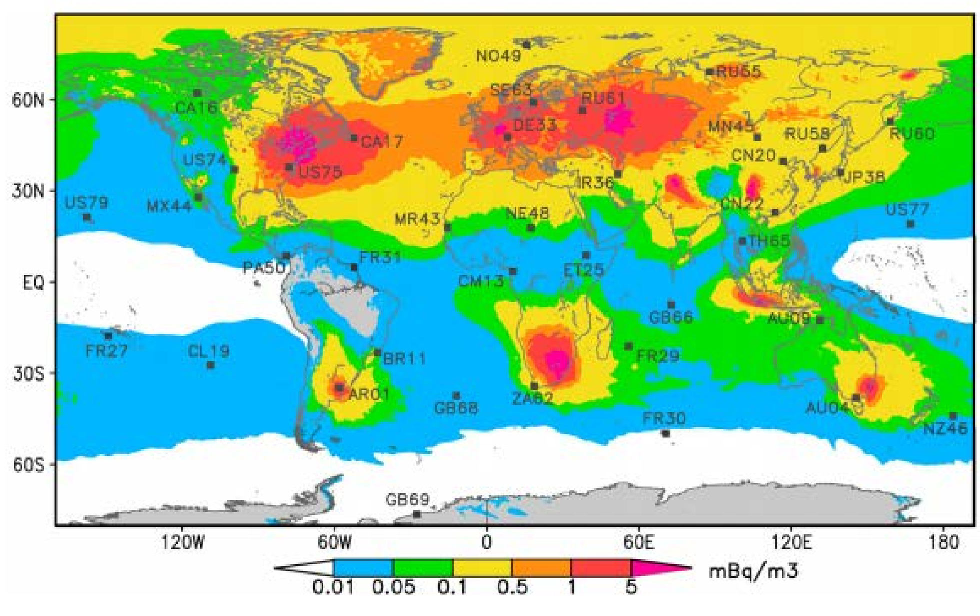

Figure 1. Annual average activity concentrations of ^{133}Xe calculated from two years of simulated data, at ground level. Note that the radioxenon spikes observed from anthropogenic sources result in an average elevation above the natrual background levels of 0.01 to 0.05 mBq/m^3, but there are days when the local concentration is consistent with natural levels. [1]

Considering a background sensitivity goal of 0.01 mBq/m^3, the required detector performance can be calculated. As will be seen in the following work, a viable operating pressure for a PNNL-developed proportional counter [2] is 3 atm with an operating gas composition of 98% Xe and 2% CH_4 (see Section 2.1.2). Using these operating parameters, the performance for this 100-cc ultra-low-background proportional counter (ULBPC) design can be calculated. The nominal internal volume of an ULBPC is 100 cm^3 and, based on previous modeling and measurements, the detection efficiency is expected to be approximately 88% for ^{131m}Xe and ^{133}Xe [3]. For an operating pressure of 3 atm and a detection efficiency of 88%, the active xenon volume is 259 cm^3. In whole air, xenon is present at the concentration of 87 ppb (0.087 cm^3 per m^3 of air), giving an equivalent air volume within the detector of 2,977 m^3 of air. In order to measure background levels of radioxenon (0.01 mBq/m^3), the detector needs to be capable of measuring 30 mBq of activity, which is much higher than the demonstrated sensitivity of an ULBPC of 2 mBq for a 12-hour measurement. For an activity of 2 mBq measured with a 12-hour count (see Section 2.3), a LVXe sample counted in a ULBPC detector can expect to be sensitive to 0.00067 mBq/m^3. In order to obtain this detection sensitivity, the chemistry process will require a large radon rejection factor, but that impact is not studied in this report.

2.0 Large-Sample Detector Performance

This section describes the assessment and demonstration of the internal-source gas proportional counter performance (beta spectroscopy) for two different PNNL proportional counter designs for LVXe samples.

2.1 Detector Performance Characterization

2.1.1 Large-Volume Prototype detector (~0.64 L)

An early prototype large-volume gas proportional counter with a 0.64-liter internal volume was tested in parallel with the 100-cc ULBPC detector experiments (Section 2.1.2). Initial tests to validate the gas seals of the large-volume prototype detector (which had not been operated in some time) were successfully completed before testing for high pressure capability. The challenge of using the large-volume prototype was the thickness of the outer walls of the detector (made from commercial-grade copper) which made energy calibration difficult. The wall thickness varied from 1.2" (maximum) to 0.42" (minimum) which greatly attenuated any sealed calibration source used from outside the detector. In order to calibrate the large-volume prototype, a radioxenon spike was introduced inside the detector. The large-volume prototype detector is shown in Figure 2.

Figure 2. Large-Volume Prototype Proportional Counter (~0.64 L volume)

A small spike of ^{131m}Xe (~1 cc) was loaded in the large-volume proportional counter along with standard P10 gas (90% Argon, 10% methane) for a total pressure of 7 atm. The two ^{131m}Xe peaks at 129-keV and 159-keV were clearly seen and are shown in Figure 3 with gaussian fits to extract the detector resolution and provide an energy calibration. Previous loads in this detector at low pressures (1 and 3 atm) were unsuccessful (not able to calibrate given the absence of peaks/features); the higher-pressure load at 7 atm provided better stopping power and the ^{131m}Xe peaks were sufficient for calibration purposes.

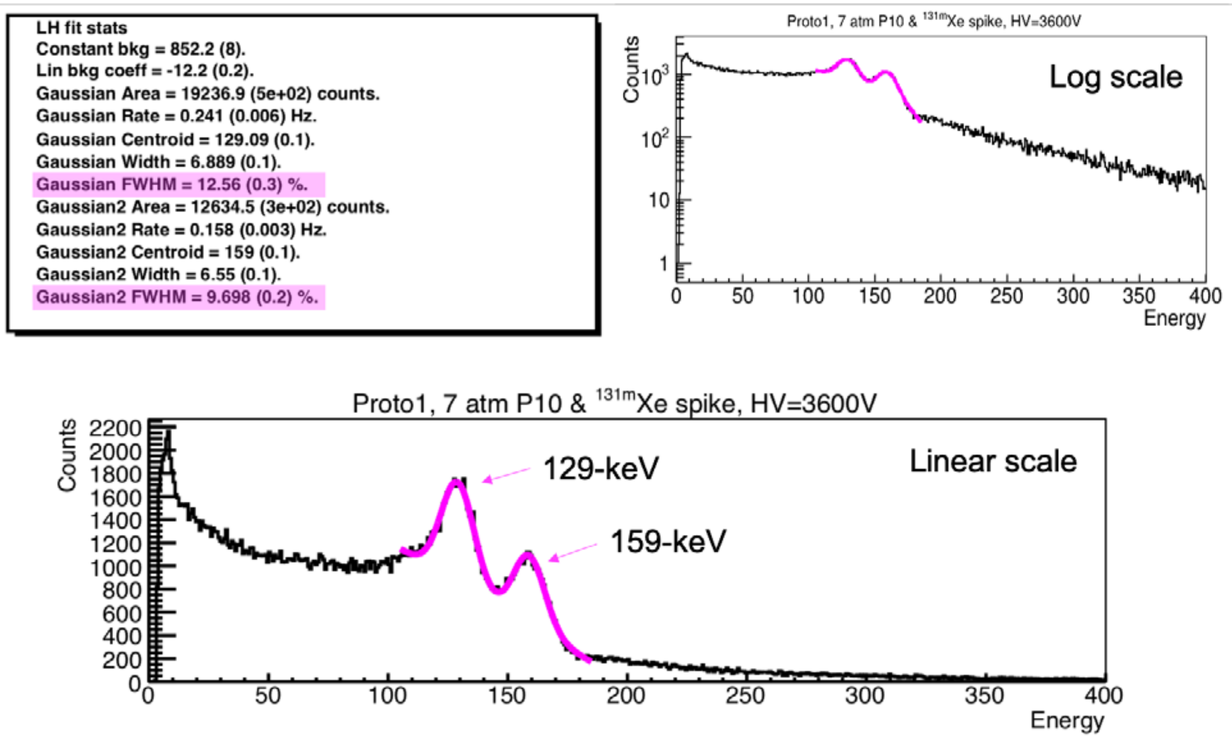

Figure 3. Large-Volume Prototype energy calibration with ^{131m}Xe spike at 7 atm

As described earlier in the Motivation Section 1.1, this large-volume detector is not strictly necessary in order to be sensitive to atmospheric background levels of radioxenon. However, this detector was considered as an alternative to the 100-cc ultra-low-background proportional counters. The initial tests of the large-volume prototype detector demonstrated viability for high-pressure measurements and successful calibration using a prepared ^{131m}Xe spike as shown in Figure 3. This large-volume detector could be used for LVXe measurements at high pressures, though a sample this large is ultimately not needed to probe expected environmental background levels of radioxenon.

2.1.2 Ultra-Low-Background Proportional Counter (ULBPC) detectors (100-cc)

PNNL has developed an ultra-low-background measurement capability utilizing 100-cc ultra-low-background proportional counters (ULBPC) as seen in Figure 4 and the PNNL Shallow Underground Laboratory (SUL) [2, 4]. These detectors are used for measurements of multiple isotopes and primarily uses a blend of argon and methane for the sample blend. Previous measurements of radioxenon in these detectors used a small spike of radioxenon activity (<1cc) on top of a carrier blend of P10 (90% Ar, 10% CH_4) at pressures ranging from 3 to 10 atm. As was established earlier in this document, a greater volume of xenon is needed to reach crustal abundance background levels of xenon. The ULBPC detectors are pressure limited to 10 atm for safety reasons, so the maximum potential amount of xenon in a ULBPC would be 100% Xe at10 atm. Data was collected over a range of operating voltages (proportionality data) on a series of P10:Xe loads in order of increasing xenon to determine if there was a limit to the amount of xenon before detector resolution/performance was compromised (Table 1).

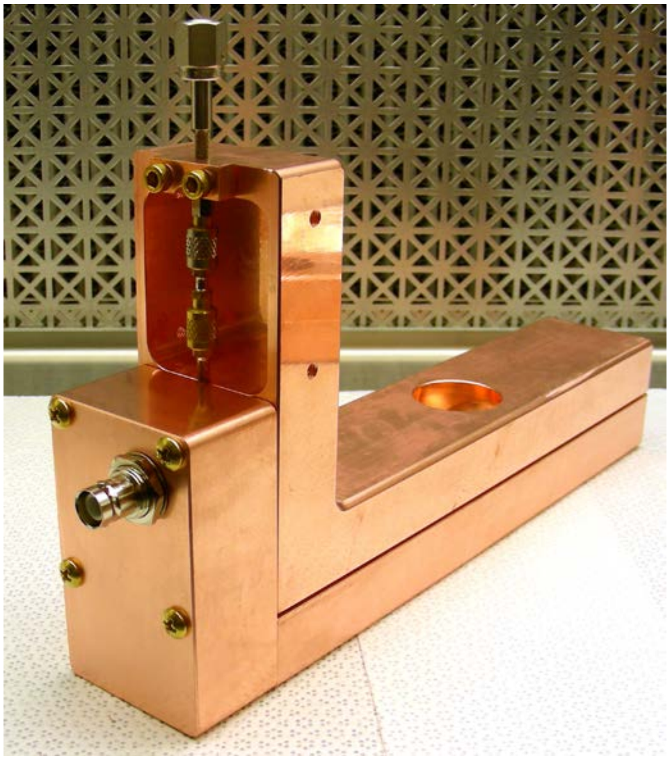

Figure 4. Ultra-low-background proportional counter (ULBPC)

Table 1. ULBPC P10:Xe loads with increasing xenon volume

Load ID	*P10:Xe Ratio*	*Pressure* (atm)	*Resolution of 59.5 keV peak at 4 gain*
LB412	100:0	3	7.60%
LB433	90:10	3	9.76%
LB443	80:20	3	11.38%
LB435	70:30	3	11.63%
LB436	60:40	3	10.79%
LB437	50:50	3	12.63%
LB438	40:60	3	13.34%
LB439	30:70	3	12.80%
LB440	20:80	3	12.38%
LB441	10:90	3	8.93%
LB442	0:100	3	7.55%
LB445	0:100	5	9.31%
LB448	0:100	7	12.33%
LB449	0:100	10	11.93%

Data was successfully collected over a range of P10:Xe loads from 100% P10 (0% Xe) through 100% xenon (0% P10) loads. Poor resolution, high dead time, and pile-up in the data increased in higher pressure loads, indicating the need for further adjustments. A study reported in Knoll [5] used xenon with (some small percentage) of methane. Additional tests in the ULBPCs using a blend of xenon with a small fraction of CH_4 (2%) were successful at lower pressures (3 atm) and provided lower dead times and better detector resolution for spectral analysis. This blend of 98% Xe and 2% CH_4 successfully demonstrates that a 100-cc ULBPC can measure the volume of xenon required to reach atmospheric crustal abundance background levels. Measurements were collected in the PNNL SUL using this gas blend to understand the detector performance in the low-background counting system [6]. A background and radioxenon measurement were collected in a ULBPC at the final gas blend and are described in the following sections.

2.2 Background Measurement in ULBCS0

A blend of 98% Xe and 2% CH_4 was loaded into two 100-cc ULBPC detectors (reference numbers 2S01 and 263) and counted in PNNL's Shallow Underground Laboratory in the Ultra-Low-Background Counting System (ULBCS) [2, 4, 6]. These two measurements demonstrated the spectral response of the detector with this new gas blend and provided a detector background spectrum to use with radioxenon demonstration measurements at the same gas blend and pressure.

The background spectral response of the 100-cc ULBPC at 3 atm with 98% Xe and 2% CH_4 is shown in Figure 5. The background count rate from 3-400 keV is 158.0 ± 2.04 cpd for a 3 atm 98% Xe and 2% CH_4 blend.

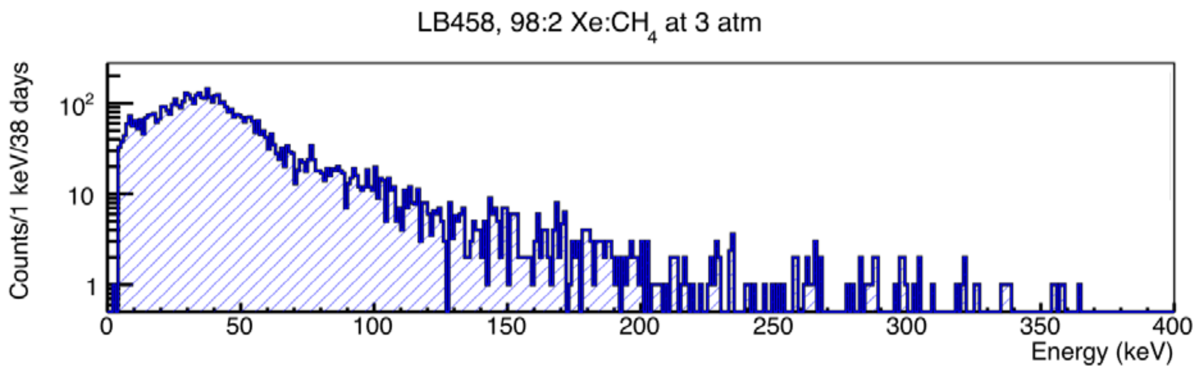

Figure 5. Background spectrum from 100-cc ULBPC with 3 atm of 98% Xe and 2% CH_4

2.3 Radioxenon measurement in ULBCS0

Using the same blend as the background measurement in Section 2.2, a radioxenon sample with ^{131m}Xe and ^{133}Xe was loaded into a 100-cc ULBPC detector at 3 atm (with 2% CH_4) and counted in the ULBCS in PNNL's Shallow Underground Laboratory. While the spectrum is not isotopically pure, it allows for the calculation of the minimum detectable activity based on the spectral response, detection efficiency, and the desired isotope [7]. Using the half-life for ^{133}Xe and the measured background rate of 158 cpd in the ROI, the minimum detectable activity is calculated to be 2 mBq for a 12-hour measurement. As was noted in Section 1.1, for an activity of 2 mBq measured with a 12-hour count a LVXe sample counted in a ULBPC detector can expect to be sensitive to 0.00067 mBq/m^3. This is well below expected environmental levels at 0.01 mBq/m^3.

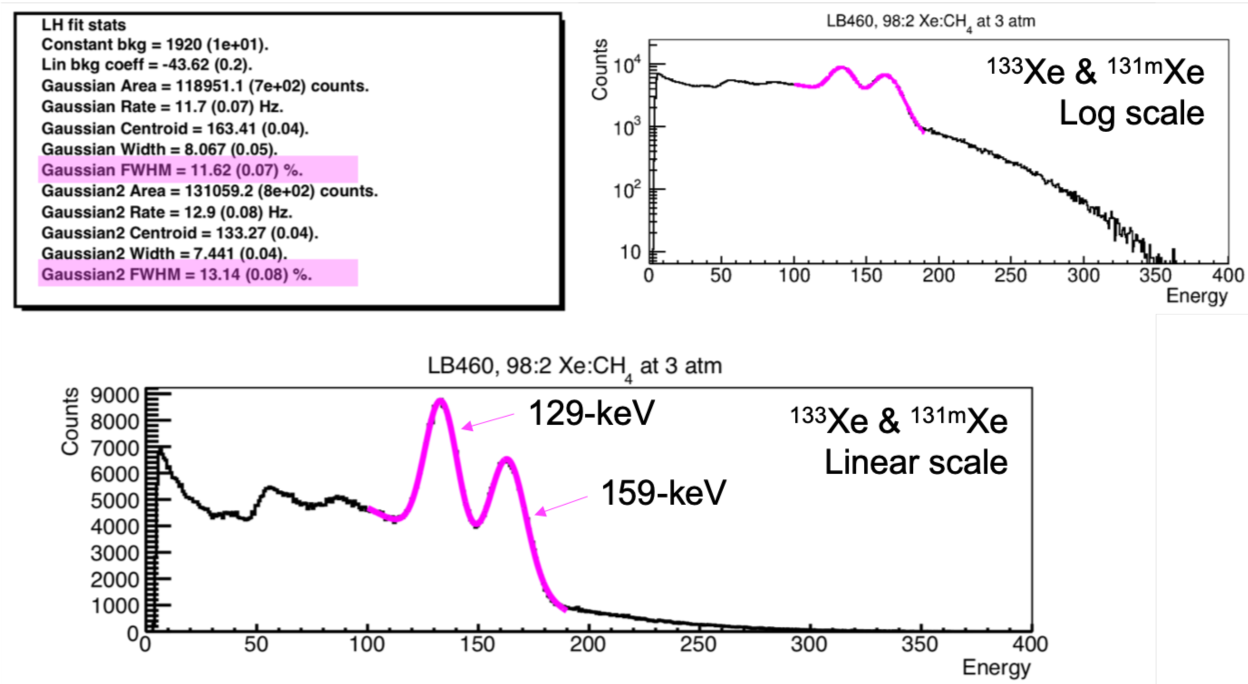

Figure 6. Spectrum of ^{133}Xe and ^{131m}Xe in a 98:2 Xe:CH_4 gas mixture. The improved stopping power of the xenon compared to argon results in better separation of peaks from ^{131m}Xe at 129 and 159 keV.

Following the high-activity measurement of the radioxenon sample shown in Figure 6, a new background measurement was collected to look for xenon carryover. The ULBPC detector was loaded with 3 atm of 98:2 Xe:CH_4 blend using the current standard process of three P10 fills and purges to flush the detector volume before the final 3 atm background load. Radioxenon carryover was detected in the ULBPC in excess of the background (Figure 7). The carryover percentage was estimated to be 0.006% of the activity of the original radioxenon spike. For the expected activity of IMS samples, this carryover is essentially zero.

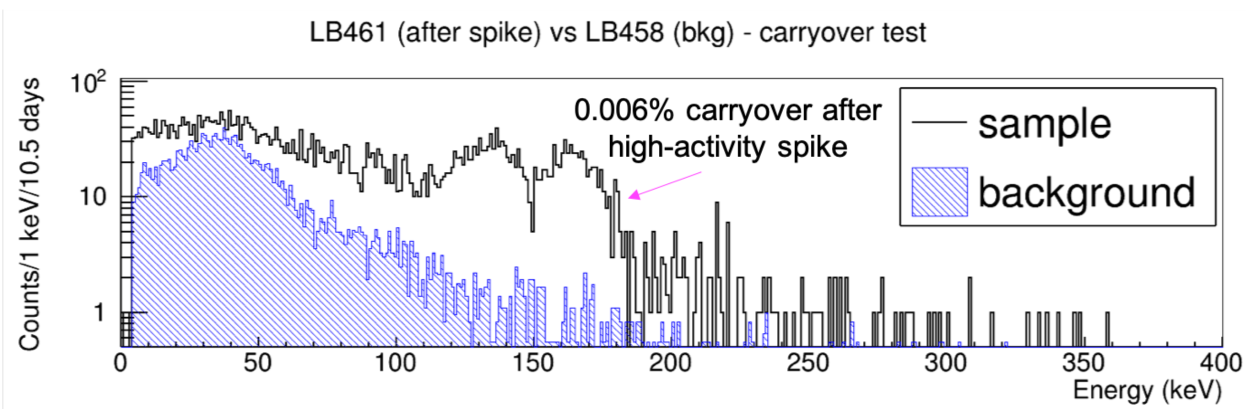

Figure 7. Carryover measurement following high-activity radioxenon spike shown in Figure 6. The calculated carryover was estimated to be 0.006%, essentially zero for normal IMS sample measurements.

3.0 Software Improvements for Radioxenon Discrimination

The potential sensitivity to the relevant xenon isotopes (^{131m}Xe, ^{133}Xe, ^{133m}Xe, ^{135}Xe) was estimated by using simulations based on scaling results from previously-collected ULBPC counter data. Data were analyzed using the ROOT data analysis framework [8] with the RooFit toolkit [9]. To extract the number of signal events of each type, a fit to reference spectra was performed, including four components: ^{131m}Xe, ^{133}Xe, ^{135}Xe, and detector background. Reference spectral shapes were based on spectra drawn from data collected with a 100cc-volume ultra-low background gas-proportional counter detector [2]. Calculations were based on an estimated detector efficiency of 88%. For the radioxenon samples, the detector was filled with P10 (90% Ar, 10% CH_4) gas to a pressure of 7 atm with a small volume (~1cc) of radioxenon gas added (Table 2). No xenon was added to the detector when collecting the background measurement. A ^{133m}Xe sample was also provided but due to the initial activity and the complicated nature of the direct feed-down decays to ^{133}Xe, it was found to be insufficiently pure for use in this analysis. The spectral distributions for each component are shown in Figure 8, with an example implementation of the fits shown in Figure 9.

Table 2. Data samples used for spectrum templates.

Sample	*Activity* (Bq)	*Collection Time* (s)
Xe-131m	0.95	241776
Xe-133	2.38	161742
Xe-133m	3.49	150606
Xe-135	131.68	27741
Background	N/A	4085600

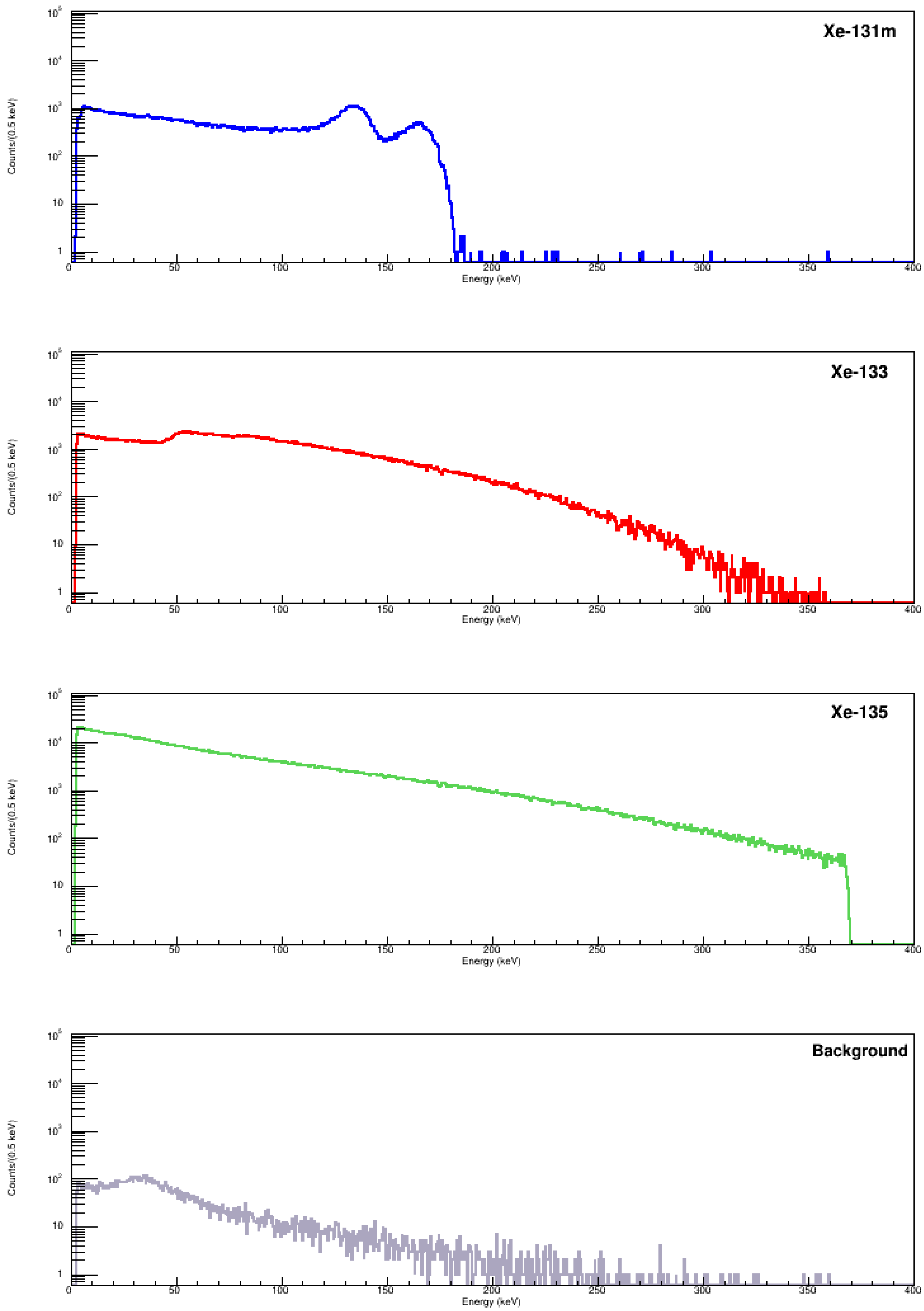

Figure 8. Decay spectra for radioxenon isotopes and detector background used as simulation input.

Simulated datasets were generated by randomly sampling from the spectral template distributions, with numbers of input events chosen according to simulated measurement time, detector efficiency, and expected isotopic activity ratios. The number of initial events of each type and their uncertainty were then extracted by fitting the data. These results were examined over scans of the input parameter spaces of interest to determine expected detection sensitivities.

To estimate the minimum detectable activities and measurement time, simulated data sets were produced with input activities from 0.005 to 0.1 mBq/m^3 in 0.005 mBq/m^3 steps, and measurement times were varied from 5 minutes to 2 hours in 5-minute increments. The activity concentration of one radioisotope at a time was varied while the other two were held fixed to average values taken from the global measurements summarized in Figure 6 of M.B.Kalinowski et al. [1]: ^{133}Xe/^{131m}Xe = 16.7 and ^{135}Xe/^{133}Xe = 0.05. At each activity and time step, 30 data sets were generated and fitted using the spectral templates previously described. An example of one trial is shown in Figure 9. To determine the minimum measurement time for a given activity (and vice versa), the relationship between the signal significance, defined as the average yield divided by the standard deviation for the 30 trials, versus the variable in question was fitted with a power law function (e.g., see Figure 10). The point where the significance reaches a value of 1.65 was used to estimate the 95% confidence level for a detection. The resulting distributions of these points for each isotope are shown in Figure 11 for the minimum expected detectable activity as a function of measurement time. The simulations indicate that a detection apparatus of this specification could detect radioxenon activity concentrations approaching 0.01 mBq/m^3 in less than 2 hours for ^{131m}Xe and ^{135}Xe, and on a much shorter order of minutes for ^{133}Xe for levels similar to expected background.

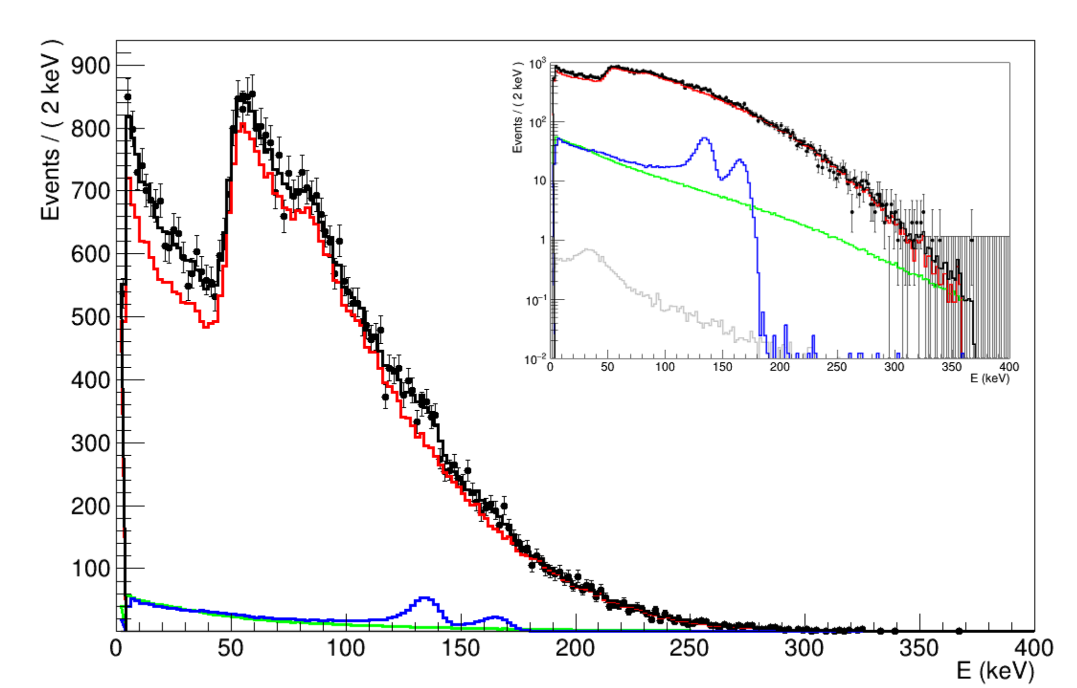

Figure 9. Example of a fit to a simulated data set. Main plot scale is linear in number of entries while the inset is in log scale. The data points and total fit are shown in black, with components Xe-131m (blue), Xe-133 (red), Xe-135 (green), and background (gray).

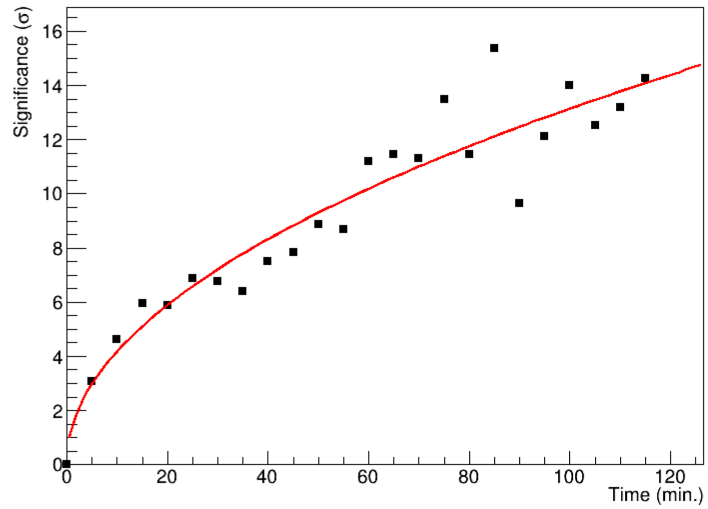

Figure 10. Example of relationship between signal significance and measurement time for a Xe-133 sample with atmospheric activity concentration of 0.03mBq/m^3.

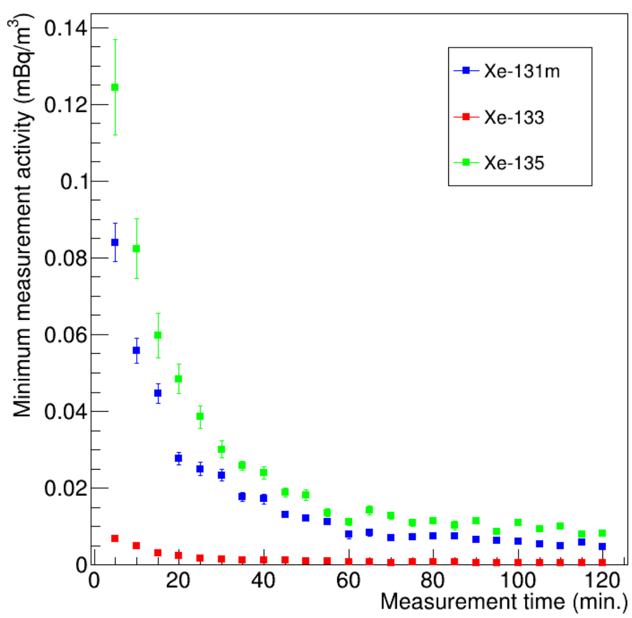

Figure 11. Estimated minimum detectable atmospheric activity concentration for a given radioisotope versus measurement time.

The primary isotopic ratio of interest for nuclear explosion monitoring is the ratio of ^{133}Xe to ^{131m}Xe. As the ratio of ^{133}Xe to ^{131m}Xe deviates from 1:1, it is expected that the required activity measured by the detector to obtain an accurate ratio will increase. This was estimated with simulated samples of various Xe ratios, activities, and measurement times. For each ratio, the relationship between activity and the uncertainty of the fitted ratio was determined, and the minimum activity to achieve at least 10% uncertainty was determined. This is shown in Figure 12. As the ratio deviates from one, the required activity to perform the measurement with spectral response increases with an approximately power law relationship.

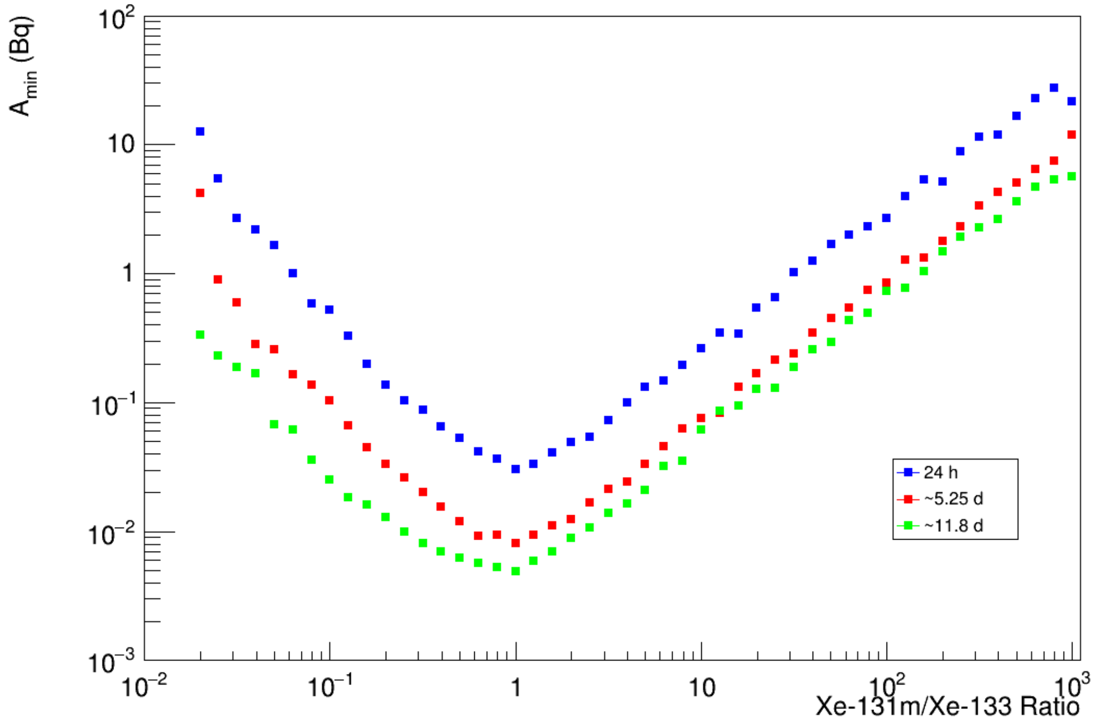

Figure 12. The required minimum activity of the dominant isotope for a 10% uncertainty measurement on the $^{131m}Xe/^{133}Xe$ ratio for a given ratio. Greater than 1 equates to more ^{131m}Xe and less than 1 represents more ^{133}Xe. Measurement times of 24 hours, one ^{133}Xe half-life, and three ^{131m}Xe half-lives are compared.

4.0 Conclusions and Future Work

After examining 0.67-liter and 100-cc PNNL-developed proportional counter designs, xenon spike and detector background measurements established that more than adequate sensitivity can be achieved with 3-atm xenon gas loads with a 2% CH_4 quench into the 100-cc PNNL ULBPCs.

Spectral resolution under these operating conditions is relatively good, suggesting that a combination of beta spectroscopy and decay-curve analysis can be used to quantify ^{133}Xe:^{131m}Xe ratios in environmental background samples. Due to transport times, measuring ^{135}Xe would be more challenging, and in this work resolving a ^{133m}Xe component in samples was not examined due to difficulties in collecting reference spectra.

This work demonstrates that the PNNL ULBPC has ample sensitivity to reach anticipated environmental background levels for ^{133}Xe and ^{131m}Xe, and next steps are seen as follows:

- Assess purification chemistry needs for preparing commercial air plant xenon for proportional counter use, e.g. removing any sample associated backgrounds, and develop chemical purification process to support initial demonstration measurements.

- Perform initial demonstration measurements with xenon procured from areas with frequent anthropogenic backgrounds, and ideally co-located IMS stations, to validate expected signals.

- Further refine radioxenon isotopic discrimination to allow better ratio determination, e.g. ^{133}Xe:^{131m}Xe.

- Extend demonstration measurements to “quiet” regions with low anthropogenic radioxenon backgrounds and perform a time-series study of background levels to assess consistency with predicted levels driven by crustal spontaneous fission rates.

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902 Battelle Boulevard
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