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High Pressure Marinelli for counting Low Activity Compressed Gas Samples

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Abstract

Quantification of low-activity noble gases in air is typically accomplished through separation of the noble gas from air followed by radiometric assay. This work is aimed at quantification of radioactive noble gas in air without extraction. A high pressure aluminum Marinelli counting vessel was designed and fabricated that can be placed on a coaxial high purity germanium detector for gamma counting. Characterization of the performance of this Marinelli using MCNP modeling, large excesses of activity, and low-activity noble gas in air is discussed. Minimum detectable concentrations achieved during a 24 hour count are: 5, 50, and 1 Bq/m^3 for ^{133}Xe, ^{131m}Xe, and ^{135}Xe, respectively.

Keywords

High Pressure, Marinelli, Noble Gas, Gamma Counting, Radioactive Xenon

Introduction

The Comprehensive Test Ban Treaty (CTBT) prohibits nuclear tests above and below ground, under water and in space [1]. This is to retard and discourage the development of increasingly effective nuclear arms and to protect people and the environment from the harmful effects of radioactive fallout [2]. Although the CTBT has not been ratified by all members and is not yet in force, the Comprehensive Test Ban Treaty Organization (CTBTO) is in the process of building and commissioning the International Monitoring System (IMS). This monitoring system utilizes a variety of methods to look for illicit nuclear detonations that include: seismic sensors [3], hydroacoustic microphones [3], infrasound detectors [4], and radionuclide collection and analysis stations. By a combination of these detection methods developing nuclear weapons through detonation is difficult, if not impossible to do without being discovered.

The radionuclide collection and analysis stations screen samples for radionuclide particulates [5] and radioactive xenon isotopes [6] that are characteristic of nuclear detonations. Radiometric quantification of xenon radioisotopes in air is done routinely by automated collection and separation systems [6–9]. These instruments must be calibrated regularly in order to validate correct operation and ensure that results provide reliable quantification. Inter-laboratory comparisons can verify that the stations are providing equivalent results across the IMS.

The Idaho National Laboratory (INL) provides calibration standards specifically tailored to testing the analytical capabilities of xenon detection equipment. Standards for testing equipment that separates xenon from air are made by diluting quantitative amounts of radioactive xenon into compressed whole air. During instrument development, xenon radioisotope standards that do not require separation from air are desirable to test the radioactive counting hardware without the complication of separation. Such standards are made by diluting radioactive xenon into stable xenon[10].

During standards production it is desirable to non-destructively quantify the radioactive xenon without the introduction of uncertainty caused by the separation from air. An alternative to extraction of xenon is to analyze the whole air sample. Marinelli beakers are typically used for counting large-volume, low-activity samples such as soils or water

[11]. Marinelli beakers or "inverted well beakers" [12] consist of a large cylinder that has an inverted well in the bottom that fits over the detector head of gamma detectors, often a high purity germanium (HPGe) detector [11]. This shape minimizes the distance between a detector head and a large volume sample under analysis. The current commercial option for gas analysis by gamma counting is a Marinelli beaker with 1.4L capacity and a maximum pressure of 10 psig.

Current radioactive xenon in air standards produced by INL are certified by calculating the final concentrations in air based on the activity of xenon radioisotopes and the total mass of air added. Error propagation provides the uncertainty for the certified values. The current process, however, does not provide a means of independently verifying the final mixed standard, or the ability to detect problems that may occur during the transfer of activity or mixing operation.

This work was undertaken to build a high pressure Marinelli that provides direct, non-destructive quantification of a mixture of radioactive xenon in air standard. A secondary goal of this work is to provide same-day qualitative confirmation that radioactive xenon isotopes were successfully added to the standard before the packaged standard is shipped. The aluminum Marinelli, whose design and testing is described in this article, provides a direct, non-destructive analysis technique for the quantification of small concentrations of xenon radioisotopes in air as a part of gas standard certification in the INL production process.

Experimental

Monte-Carlo Modeling

Both the flat and round Marinelli geometries (see Fig. 1) were tested using the MCNP6 computer code. Each model calculation performed $5x10^7$ particle histories and determined the counting efficiency using the pulse-height tally. The source was modeled as isotropic, monoenergetic (81, 163, and 249 keV for ^{133}Xe, ^{131m}Xe, and ^{135}Xe, each modeled separately) photons that were emitted from random positions within the air sample cavity of the high pressure Marinelli. Calculations were performed on a desktop PC and required approximately 6 minutes each.

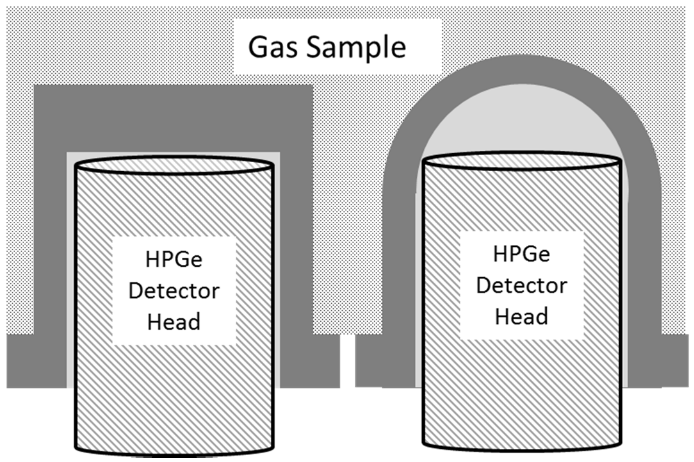

Fig. 1 Two alternative bottom Marinelli shapes: flat and round

Marinelli geometries were established from the fabrication design blue-prints. The MCNP Marinelli design was simplified by eliminating the stainless steel outer shell leaving an essentially bare sample air volume.

The HPGe detector geometry used in the model was approximated from the manufacturer provided Quality Assurance Data sheet. From the data provided in the HPGe documentation, it appears that the germanium crystal's physical dimensions were measured in the factory, but the other dimensions involving the germanium's dead layer, detector housing thickness and dimensions, and internal spacing were given as nominal values. Verification of the dimensions on the detector's internal configuration could be obtained by x-raying the detector head. This is not feasible due to the need to keep this detector in service for the production of gas standards.

Radioactive Xenon Counting Experiments

The production and isolation of the ^{131m}Xe, ^{133}Xe and ^{135}Xe are described in a previous publication[10].

Air used in this study was obtained (Norco Gas, Inc.) as bottled whole compressed air. The air was allowed to age for more than 90 days to ensure that any radioactive xenon that may have been present in the gas at the time of bottling had decayed away. Un-spiked samples of the air were loaded in the aluminum Marinellis and counted for more than 80,000 seconds to obtain background spectra and to verify that no radioactive xenon was present (MDC by isotope in Bq/m^3: ^{131m}Xe = 52; ^{133}Xe = 5; ^{133m}Xe = 10; ^{135}Xe = 1).

Xenon is typically moved via cryogenic transfer involving cooling either glass or metal surfaces with liquid nitrogen and waiting for the xenon to freeze solid before sealing the container holding the xenon. Because of the high pressures involved with the Marinelli, it was not advisable to directly freeze the xenon in the Marinelli for fear of damaging the vessel's structural integrity. An alternative method was developed where a stainless steel length of tube bent in the shape of a U (U-tube) was attached to the Marinelli prior to loading with xenon. The xenon was then cryogenically transferred to the U-tube. After the U-tube was sealed, it was connected to the Marinelli on one end, and a compressed gas source on the other. Compressed air was then allowed to flush the xenon from the U-tube into the aluminum Marinelli. Compressed air was added until the system until the pressure reached 500 psig. Although the system is rated to 1000 psig, the operating pressure of 500 psig was used to prevent the samples from being vented through the pressure relief valve that was set to vent at 1000 psig. When the correct pressure was reached, all of the valves were closed and the U-tube and Marinelli were disconnected from the compressed air source and from each other.

Scoping experiments on the mass balance of introducing xenon samples into and removing them out of the U-tube showed that approximately 3 μL of xenon becomes stuck in the U-tube. To decrease the total loss of activity, approximately 10 cc of carrier xenon was added to the radioactive xenon spike. This sample volume loss was used to estimate the xenon residue independently of counting the U-tube. The estimated activity loss was verified by direct radiometric assay of the U-tube to quantify the residual radioactive xenon that remained in the U-tube during the transfer. Estimated and observed radioactive xenon U-tube residues are shown in Table 1. Because the lost radioactive xenon activities were more than two orders of magnitude below the uncertainty of the original spike material, the experimental activities were not corrected to reflect the activity losses. The counting efficiency using the aluminum Marinelli with an HPGe detector was determined by the ratio of the decay corrected counts obtained from the aluminum Marinelli count to the initial activity of the radioactive xenon aliquot.

Table 1 Experimental data for feed ampoule activity, U-tube residual activity (estimated and observed), and measured efficiency

Experiment Name		Feed Ampoule Activity (Bq)	Estimated Residual Activity (Bq)	Observed Residual Activity (Bq)	Counting Conditions MDA (Bq)
Flat	^{133}Xe	8,900 ± 200	2	4.1 ± 0.3	0.6
	^{133m}Xe	100 ± 10	0.03	< MDA	0.7
	^{131m}Xe	35,000 ± 2,000	9	11 ± 1	4
	^{135}Xe	1,720 ± 90	0.4	0.72 ± 0.04	0.09
Round	133Xe	8,900 ± 200	2	3.6 ± 0.3	0.9
	133mXe	100 ± 20	0.03	< MDA	1
	131mXe	35,000 ± 2,000	9	10 ± 3	7
	135Xe	1,720 ± 90	0.4	0.55 ± 0.05	0.1

Following the determination of counting efficiencies for both Marinelli types (round and flat bottomed) for all three isotopes tested ($^{131m,\ 133,\ 135}$Xe) actual gas standards were loaded into the Marinellis and counted. Pressure of the samples was 950 psig to maximize the sample available for assay. Using a different pressure than was used to determine counting efficiencies can introduce bias into the results. The magnitude of the bias was explored using MCNP calculations. Modeling results showed that less than a 1% performance loss between 500 psi and 1000 psi pressurized samples. Air sample size was determined by the mass difference between the empty and loaded aluminum Marinelli. Each determination consisted of 6 separate counts of the same aliquot of activity in the same Marinelli. The Marinellis were counted alternately and repositioned before each count. To protect the HPGe detector from damage, the Marinelli, that weighs approximately 22 kg, was designed with a slight excess of diameter in the inner void, and slightly more height than was necessary. After the Marinelli was placed over the detector, the head of the HPGe detector was gently moved up into the Marinelli void until contact occurred (the total distance was between 1–2 cm of vertical height adjustment). Each count was stopped after the total counts in each region of interest was greater than 40,000.

Theory

Aluminum Marinelli Design Considerations

The design of the Aluminum Marinelli was dictated by constraints set by: 1) the size of the HPGe detector head, 2) the space within the lead shielding enclosure, and 3) an arbitrarily selected 1000 psig sample pressure. A Marinelli was designed to fit within these constraints: large enough orifice to accept the detector head, outer shell small enough to provide clearance for the flange bolts that hold the upper and lower pieces together, walls thick enough to withstand 1000 psig. Two possible shapes were proposed for the inner Marinelli wall (wall separating the air sample and the detector head: round and flat (see Fig. 1). Based on structural strength, the round would provide a thinner wall, but the sample would be slightly further away from the detector head (see Fig. 2). Because the effect of the thinner wall and the larger distance from the detector, it was not clear which design would provide the best performance, and thus both were built and tested.

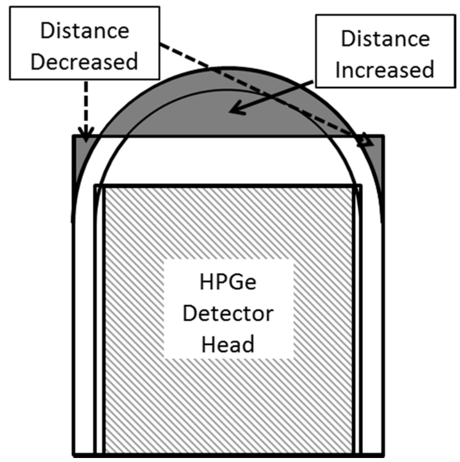

Fig. 2 An overlay of the round and flat bottom Marinellis showing the net distance increase and decrease caused by switching from the flat to the round bottom Marinelli

Aluminum was chosen as the material for the lower wall due to its strength, machinability, and lower attenuation than stainless steel. Beryllium has lower attenuation than aluminum, but machining is problematic due to health concerns with beryllium dust. Carbon also has a lower attenuation than aluminum, but manufacturing high pressure carbon composite Marinelli was an expensive and complex task to be attempted only after proof of concept was achieved.

Results and discussion

MCNP Modeling Results

The dimensions and material make-up of the Marinelli are rather simple to build into the MCNP model. Detailed and precise blue-prints were converted into a three dimensional replica of the Marinelli. The most challenging aspect of creating a virtual model that acts the same as the aluminum Marinelli is obtaining an accurate description of the HPGe detector head and housing. Ortec supplies a description of the layers, and thicknesses of housing materials, germanium crystal dimensions, and dead-layer thickness, but these are impossible to verify without irreversibly damaging the detector itself.

The MCNP results show a general bias over the counting experiment results (see Table 2) that range from 0.2 to 0.5% absolute efficiency (7 to 31% relative bias). We have attempted various exercises to explain this difference in the results. One theory was that the MCNP results are accurate, but the counting results suffered from losses due to sample retention in the u-tube during the transfer to the Marinelli. U-tube residues were counted using a calibrated counting geometry for the U-tube. The activity residues observed account for less than 0.05% of the total activity necessary to account for the total difference in the MCNP and counting experiment results.

Table 2 Comparison between MCNP modeling and Counting Experiment results

		MCNP Modeled Efficiency (% ± 1σ)		Counting Experiment Observed Efficiency (% ± 1σ)	
Isotope	E_γ(keV)	Flat Marinelli	Round Marinelli	Flat Marinelli	Round Marinelli
^{133}Xe	81	1.9% ± 0.1%	2.24% ± 0.09%	1.47% ± 0.03%	1.74% ± 0.03%
^{131m}Xe	163	2.94% ± 0.08%	3.28% ± 0.08%	2.5% ± 0.1%	2.9% ± 0.1%
^{135}Xe	249	2.50% ± 0.09%	2.75% ± 0.08%	2.2% ± 0.1%	2.5% ± 0.1%

Another possibility was that the HPGe dead layer estimated or calculated by Ortec was inaccurate. This was a promising avenue of inquiry because early models for the aluminum Marinelli that did not account for the HPGe dead layer showed efficiencies that were 53% higher than those modeled with the Ortec supplied dead layer thickness. A set of calculations were undertaken to vary the thickness of the HPGe dead-layer to see how much of a change would bring the MCNP results in line with the experimental measurements. These calculations showed widely varying thicknesses depending on the photon energy in question. The dead layers required to bring the results into line for $^{133, 131m \text{ and } 135}$Xe for the round Marinelli were: 1070, 1245, and 1240 μm, and for the flat Marinelli were: 1123, 1438, and 1459, respectively. It would be plausible that the dead-layer issue would be the source of the bias in the MCNP results if the dead-layer thickness results all approached a single dead-layer value. The results however are significantly different by isotope, and Marinelli shape, and thus this possible source of MCNP results bias is rejected. It is possible to x-ray the detector head to verify the HPGe crystal dimensions and explore the possibility of undisclosed attenuating absorbers in the detector head, but because this detector is in near constant use for gas standards production, taking it out of service to x-ray the head is not feasible.

Another possibility for the bias in the MCNP results relative to the counting results is an incomplete elevation of the detector head. We reposition the detector head with each count, so as to incorporate some of this random variability into the final efficiency. We did undertake MCNP calculations to see how much of an effect forgetting to raise the detector head would have on the observed count rates. The Marinelli internal shapes are not equal, and thus one requires more lift than the other to put the detector into place. The flat Marinelli requires 18 mm and the round Marinelli requires 13 mm of detector elevation to be properly positioned. The MCNP results show that forgetting to raise the detector in the flat and round Marinelli would decrease the count rate by 9.8% and 8.8%, respectively. Three assays of the round Marinelli where the detector was not raised and we observed a negative bias in those counts of 12 ± 4%. This is the maximum effect that would be observed due to detector elevation error. It is not likely that this maximum bias exists in all the results, but there is probably a partial negative bias due to the random effect of different operators raising the detector. The results in this paper are not corrected for this bias due to the difficulty to measuring reliably the detector height, but it is good to understand that some bias from this effect is probably present in the final results.

Despite the bias in the MCNP results, they do show that the difference in performance between the round and flat Marinelli shapes are consistent with the counting results. The round Marinelli performs consistently better than the flat Marinelli at all gamma energies. The relative trends in MCNP and counting results are very well captured, with ^{131m}Xe showing the highest counting efficiency. As discussed above, no single source of bias can account for the differences between the two. Steps were taken to minimize the negative bias effects in the counting experiments. It is most likely that some dimension of attenuating materials in the detector head were not captured in the MCNP model, and resulted in higher efficiencies that are achieved in the actual detector operation. The counting results are, however, a real indication of the expected operation of the detector in the real world.

Marinelli Counting Performance

The Marinelli counting performance was carried out as described in the experimental section. When the Marinellis were loaded with a sample, they hold 0.11 ± 0.01 m^3 of air at 950 psig. The ^{133}Xe efficiency was lower than the ^{131m}Xe and ^{135}Xe (Fig. 2) which can be explained by the increased attenuation of gamma rays at lower gamma energies (^{133}Xe = 81 keV; ^{131m}Xe = 163.9 keV; ^{135}Xe = 249 keV). There was a bias in the round bottomed Marinelli over the flat bottomed Marinelli that was consistent across all gamma energies of approximately 0.3–0.4% absolute efficiency (Table 2). In all cases the improved performance of the round Marinelli was greater than the flat marinelli (approximately 15% better relative performance).

Low-level Counting Performance

Following the performance testing of the Marinellis, they were filled with air that had been spiked with radioactive xenon to see if the activity could be detected. The activity concentrations of radioactive xenon in these air standards were 25.2 Bq/m^3 ^{135}Xe and 0.27 Bq/m^3 ^{133}Xe (m^3 at 0°C and 1 atm). Within three hours of the beginning of the count, a weak but distinct peak was observed in the 249 keV energy region, confirming the presence of ^{135}Xe in the standard. The counting was continued until the sample activities had completely decayed. There were less than 1600 net total counts in the 249 keV peak and no counts above background were observed in the spectrum at 81 keV. Because the ^{135}Xe had died before the count was stopped, no quantitative results could be calculated. However, this experiment did show that a three hour count is sufficient length to verify ^{135}Xe is present in an air sample prior to releasing the standard for shipping. It may be possible to verify the presence of other isotopes if the air is spiked further in the future.

This performance is in line with the expected minimum detectable concentrations (MDCs) based on the detector background and measured efficiencies (see Table 3).

These MDC values do not meet the CTBT Preparatory Commission's requirement of 1 mBq/m3 ^{133}Xe [14], nor near what is achieved by ARSA (0.2 mBq/m^3 [14]), SPALAX (0.2 mBq/m^3 [15]), or SAUNA (0.6-0.9 mBq/m^3 [8]). These systems take advantage of the separation of the xenon fraction from bulk air (87 ppb Xe in air) to achieve much greater sensitivity. It is notable that these systems theoretically benefit from a 10^7 preconcentration of the xenon analyte, they only achieve a 10^5 improvement in sensitivity. The Aluminum Marinelli was not intended to maximize sensitivity, but to analyze an air standard without introducing uncertainty associated with xenon extraction.

Table 3 Minimum detectable concentrations achievable using the Aluminum Marinelli. MDCs were calculated from the counting experiments efficiencies

		Quick Screening Count (3 hour duration) MDC (Bq/m^3)		Long Count (24 hour duration) MDC (Bq/m^3)	
Isotope	E_γ(keV)	Flat Marinelli	Round Marinelli	Flat Marinelli	Round Marinelli
^{133}Xe	81	18	15	6.2	5.2
^{131m}Xe	163	160	140	56	48
^{135}Xe	249	4.1	3.6	1.4	1.3

Conclusions

The fabrication of a working high pressure Marinelli for counting low activity gases has been accomplished. Counting efficiencies and minimum detectable concentrations for $^{133,\ 131m\ \mathrm{and}\ 135}Xe$ were determined. These Marinellis do not meet the initial goal of direct, non-destructive quantification of the final mixed radioactive xenon in air standard. They have shown to partially meet the goal of same day qualitative verification of successful ioncorporation of the xenon radioisotope into the standard. Qualitative detection of ^{135}Xe was accomplished when starting with a concentration of 25.2 Bq/m^3 of air. No detection of ^{133}Xe at 0.27 Bq/m^3 of air was achieved in the same time frame. Improvements in performance may be achieved by using lower attenuating material, such as carbon composite materials.

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