



## Study of a zirconium getter for purification of xenon gas

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### ABSTRACT

Oxygen, nitrogen and methane purification efficiencies for a common zirconium getter are measured in 1050 Torr of xenon gas. Starting with impurity concentrations near  $10^{-6}$  g/g, the outlet impurity level is found to be less than  $120 \times 10^{-12}$  g/g for O<sub>2</sub> and less than  $950 \times 10^{-12}$  g/g for N<sub>2</sub>. For methane we find residual contamination of the purified gas at concentrations varying over three orders of magnitude, depending on the purifier temperature and the gas flow rate. A slight reduction in the purifier's methane efficiency is observed after 13 mg of this impurity has been absorbed, which we attribute to partial exhaustion of the purifier's capacity for this species. We also find that the purifier's ability to absorb N<sub>2</sub> and methane can be extinguished long before any decrease in O<sub>2</sub> performance is observed, and slower flow rates should be employed for xenon purification due to the cooling effect that the heavy gas has on the getter.

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### 1. Introduction

Liquefied noble gases have been widely adopted as a particle detection medium in recent years. These materials are attractive candidates for detectors due to their low ionization potential, high scintillation efficiency, and, in the case of xenon, high density and stopping power [1]. The successful operation of these detectors requires that the noble liquid should be almost entirely free of non-inert impurities such as O<sub>2</sub> and H<sub>2</sub>O because these species impair the transport of both scintillation light and ionization charge.

Achieving extremely low levels of electronegative impurities is of particular concern for ionization detectors. For example, the presence of O<sub>2</sub> at only the part-per-billion level will give rise to a free electron lifetime of several hundred microseconds which is comparable to the drift time of many present-day detectors [2]. Next generation experiments will require drift distances an order of magnitude larger than those currently existing, and therefore a proportional increase in the purity must be obtained. Reliably achieving such purities is a significant technical barrier that these experiments must overcome.

While a variety of noble gas purification technologies have been shown to give good results [3–10], the most common technology in use today is the heated zirconium getter. Zirconium is an effective absorbent because its surface bonds with virtually any non-noble gas species [11], including O<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, CO<sub>2</sub>, and

CH<sub>4</sub>. These getters are operated at a temperature of several hundred degrees Celsius which encourages impurities that are bonded to surface sites to diffuse into the bulk, leaving the surface available for additional gettering. The efficiency improves significantly as the temperature increases due to the decrease in the diffusion time [12–14].

Zirconium getters designed for noble gas purification are commercially available, and the SAES Monotorr series in particular has been widely adopted for particle detection applications. SAES specifies and guarantees the performance of the Monotorr for helium and argon service, but they have not performed any measurements in xenon due to the high cost of this rare gas. We are not aware of any previous measurements of the performance of the Monotorr in gaseous xenon with sensitivity at the part-per-billion level.

It is reasonable to expect that the getter performance in xenon will be similar to that of argon and helium, and xenon detectors have seen good results while using these purifiers. Nevertheless, it is conceivable that the getter temperature may be negatively affected by the high mass of this noble gas, and this could reduce the purifier's efficiency.

Here we report measurements of the xenon purification efficiency of the SAES Monotorr PS4-MT3 [15]. We have studied the performance of this zirconium getter for removal of O<sub>2</sub> and N<sub>2</sub>, two common electronegative impurity species found in small quantities in virtually all sources of xenon. We have also studied the removal of methane, a less common contaminant which is present in the atmosphere at only the part-per-million level. Methane is not electronegative, so it does not present a problem for charge transport. In fact, a few percent of methane is

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sometimes added to xenon in order to increase the charge drift speed [16]. Methane can also have negative consequences, however, because it quenches the dimer molecules responsible for the fluorescence emission [17].

We have chosen to study methane removal from xenon for several reasons. First, methane is largely inert, so it represents one of the most challenging cases for a xenon purifier [14,18–20]. Second, our measurement technique is sensitive to methane at concentrations as low as  $60 \times 10^{-12}$  g/g, and therefore we can measure the purifier performance very accurately for this gas. Finally, methane isomers such as  $^{14}\text{CH}_4$  or  $\text{CH}_3\text{T}$  are candidates for internal beta calibration sources for large liquid xenon experiments. Since these sources would need to be removed from the xenon at the conclusion of the calibration run, it is important to understand quantitatively the performance and limitations of the zirconium getter for this impurity.

## 2. Measurement technique

The xenon handling system for our experiments is shown in Fig. 1. Xenon gas is stored in one of two 15.73 l aluminum storage cylinders and supplied to the system through a regulator. The gas is cryopumped into the second cylinder by immersing it in liquid nitrogen. The plumbing is designed to allow the gas to flow either through the purifier (purify mode) or around the purifier (bypass mode). Flow rates were measured using a mass flow meter from MKS. The absolute scale of the flow meter is calibrated by transferring a known mass of xenon gas at a constant rate through the meter.

To measure the purity of the xenon gas before and after purification, we use an RGA/coldtrap technique described in Ref. [21]. We use a leak valve to sample the gas composition at the output of the purifier. The chemical composition of the sampled

gas is measured by a residual gas analyzer (RGA, model: SRS RGA200), a mass spectroscopy device which operates at low pressures ( $10^{-5}$  Torr or less). To improve the sensitivity of the method, we remove most of the xenon from the low pressure gas sample with a liquid nitrogen coldtrap before it reaches the RGA. The impurities which we study in this paper ( $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{CH}_4$ ) have relatively high vapor pressures compared to xenon at 77 K, and they survive the cold trap in large enough quantities to be measured. The selective rejection of the xenon gas allows the sampling rate of the leak valve to be vastly increased without saturating the RGA with a high partial pressure of the bulk xenon gas. The measurement is calibrated by preparing xenon gas samples which are spiked with known amounts of the various impurities under study. Using this method the RGA's impurity sensitivity is boosted from  $\sim 10^{-5}$  to  $60 \times 10^{-12}$  g/g for methane. For  $\text{N}_2$  the limit of detection is less than  $10^{-9}$  g/g and for  $\text{O}_2$  it is about  $120 \times 10^{-12}$  g/g. The limitations for the different species are due to their specific background levels. All signals used for data analysis were background subtracted to compensate for outgassing in the plumbing from the coldtrap to the RGA. We expect the boost in the RGA's performance to be an order of magnitude greater if the plumbing from the coldtrap to the RGA is baked. We note here that the concentration of impurities in the xenon gas is observed to be linear with the partial pressure measured by the RGA, so that a factor of 10 reduction in the partial pressure corresponds to a factor of 10 reduction in the concentration. See Ref. [21] for additional details.

We use 3.25 kg of xenon initially purified to the part-per-billion level using a Monotorr purifier. After this initial purification, the used zirconium cartridge was replaced with a new one. Helium with a purity level of 99.999% is added to the xenon with a concentration of  $8 \times 10^{-9}$  g/g to serve as a tracer gas during measurements. The tracer provides a useful calibration signal because it is unaffected by both the purifier and the cold trap.

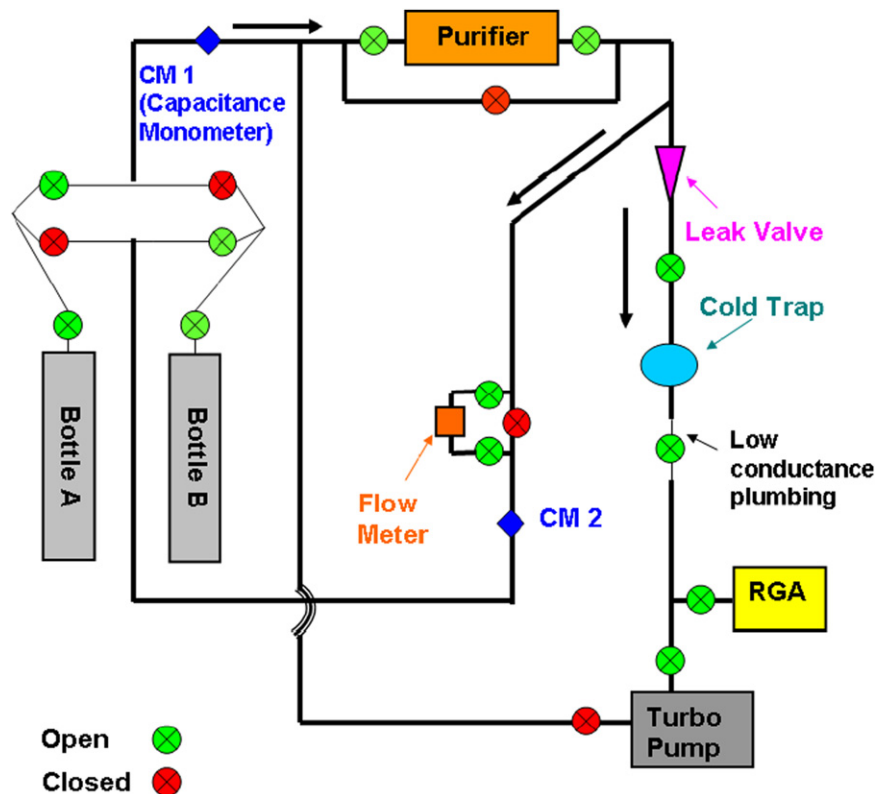


Fig. 1. The xenon handling system for the experiment. The impurity concentration of the gas is analyzed downstream of the purifier using the coldtrap and RGA.

The purification efficiencies were calculated from the initial and final values of the impurity-to-helium ratio. We normalize our measurements to the helium signal in order to make small corrections for changes in gas pressure and flow rate. Note that these corrections are typically at the level of only a few percent. To prepare spiked samples impurities of interest are injected into a known volume connected to a pressure gauge. Using purified xenon the impurity is flushed out of the injection volume and is cryopumped into a storage bottle to allow for full mixing. Uncertainties in the prepared mixtures are within 5% and are determined from the uncertainty in the injection volume and the error in the pressure gauge.

For each test the xenon handling system is first filled with roughly 1050 Torr of static xenon gas spiked with  $10^{-6}$  g/g of the specific impurity under study. For this initial fill, the purifier is operated in bypass mode, so that the leak valve samples the unpurified gas. The leak valve to the coldtrap is opened and the RGA partial-pressure measurements are allowed to stabilize. This calibrates the partial-pressure measurements in terms of the known concentration of the impurity in the spiked gas sample. Then the plumbing is switched to purify mode and xenon is made to flow from its supply bottle to a collection bottle passing through the purifier at a fixed flow rate. The output pressure of the purifier is maintained at 1050 Torr  $\pm$  3% during data acquisition to maintain a constant leak rate into the coldtrap and RGA. The partial pressure of the impurity is allowed several minutes to stabilize, and then its value is recorded. At the conclusion of the measurement, the input to the cold-trap is closed to get a background measurement. In some tests, using lower leak rates, the leak-valve is opened further at the end of the measurement to increase its sensitivity before closing the input.

For highest sensitivity measurements, it is crucial to minimize the backgrounds in the coldtrap. This can be accomplished by making the unpurified gas measurement after the purified gas measurement, because the unpurified gas can contaminate the coldtrap and RGA plumbing with residual background levels for some period of time. For these tests the background level is measured first while the coldtrap remains closed and the xenon handling system is filled with purified gas. Then the purified xenon is allowed to flow through the purifier for 20 min at a fixed rate before the leak valve to the cold trap is opened. If no change in the impurity level is seen, we place a limit on the purified signal by assuming that the residual impurity concentration in the purified gas is less than 20% of the observed background level. Finally we normalize the measurement (or limit) to the known impurity concentration in the spiked xenon gas by bypassing the purifier and recording the resulting impurity level with the RGA.

Only one data set is taken per day, and the purifier is left at its operational temperature overnight. This is done as a precaution to make sure that the absorbed impurities have time to diffuse into the bulk of the getter, an issue that we discovered while using an older, mostly exhausted purifier. See Section 4 for more details.

### 3. Purifier efficiency results

We define the purifier efficiency to be the fraction of a given impurity which is removed by the purifier in a single pass under specified flow and temperature conditions. The inefficiency is the fraction of the impurity which remains after a single pass.

#### 3.1. Methane purification efficiency

Among the impurities that we measure, the purifier has the smallest total absorption capacity for methane, so we tested methane purification first. During the course of these

experiments, the purifier was exposed to roughly 16 mg of methane, which is less than the 10% of the cartridge's estimated capacity. To create the xenon-methane mixture we use a methane supply bottle which has a stated purity level of 99.999%. In the following, we report results for two purifier temperatures, 400 and 450 °C. Unfortunately, we do not have physical access to the zirconium in the getter, so we cannot measure these temperatures directly. Instead, we quote these temperatures based upon the manufacturer's specifications [22]. Please contact SAES technical support before modifying the getter temperature.

A typical dataset is shown in Fig. 2. For this data the xenon was spiked with  $1 \times 10^{-6}$  g/g of methane, and the purifier temperature is 450 °C.

This particular experiment proceeded as follows. Prior to the data shown in the plot, the coldtrap was cooled to liquid nitrogen temperature, and the leak valve was opened. The xenon plumbing system is initially filled in bypass mode with the unpurified xenon gas, and the RGA detects a partial pressure of about  $3 \times 10^{-7}$  Torr of methane. At time  $t=0$ , the plumbing is switched to purify mode, and the xenon gas is made to flow at 7.1 SLPM. The helium is unaffected by the purifier, so its partial pressure remains constant, but the methane partial pressure is seen to drop by about a factor of 300 over the next few minutes. The xenon partial pressure remains constant due to the action of the coldtrap. At 22 min, the leak valve is closed, and the helium and methane levels drop to their background values, while the xenon pressure again remains constant.

Fig. 3 shows a similar dataset, taken at 7.1 SLPM and 400 °C. In the 400 °C dataset, we see the methane drop sharply as expected when switched to purify mode, and then rise slowly by a factor of  $\sim 2.5$  over the next 20 min. In the 450 °C dataset (shown in Fig. 2) the slow rise is not present. We infer from these results that the getter efficiency is reduced at 400 °C by the cooling effect of the flowing xenon gas, while at 450 °C the getter is able to maintain its full efficiency.

Fig. 4 shows how the purification inefficiency for methane depends on gas flow rate and purifier temperature. These results are also listed in Table 1. As expected, the purifier performed best for methane at the higher getter temperature and at lower flow-rates. At 450 °C and 2.5 SLPM the methane purification efficiency is better than 99.99% and consistent with background, while at 400 °C and 10 SLPM the efficiency drops to 92.5%.

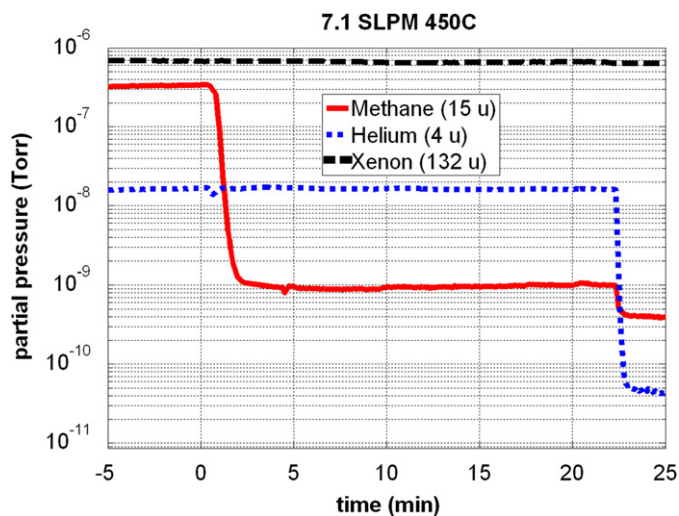
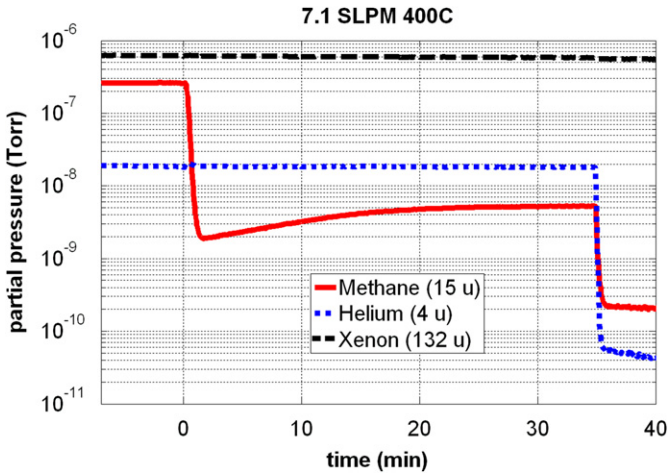
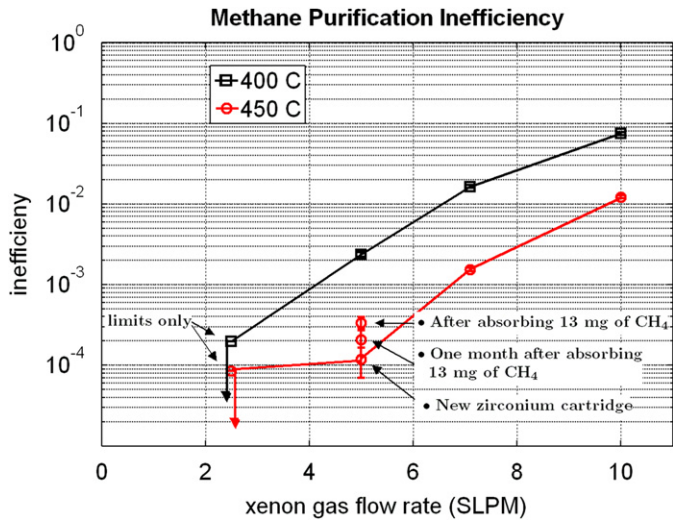


Fig. 2. A plot of methane purification data at 450 °C and 7.1 SLPM. The leak valve rate is set to 43 Torr L/min. See text for further details.



**Fig. 3.** Methane purification data at 400 °C and a flow rate of 7.1 SLPM. The leak valve rate is 43 Torr · L/min. We attribute the slow rise in the methane signal in this data to the cooling effect of the xenon on the getter. Compare to the 450 °C data shown in Fig. 2, where no rise is evident. Note that 400 °C is the default getter temperature.



**Fig. 4.** Methane purification inefficiency as a function of flow rate, for two purifier temperatures. The inefficiency is defined as the fraction of the incoming methane which remains at the purifier output.

**Table 1**

Purification results for O<sub>2</sub>, N<sub>2</sub>, and methane. Initial concentrations are accurate to within 5%. The error in inefficiency is calculated from the final and initial background-subtracted signals, each normalized to helium. Each data point was determined by averaging a stabilized signal over a period of 1 min. The typical standard deviation in the signal was found to be 2%.

Species	Gas flow rate (SLPM)	Temp. (C)	Init. conc. 10 <sup>-6</sup> (g/g)	Final conc. 10 <sup>-9</sup> (g/g)	1-pass eff. (%)	1-pass ineff. (%)
CH <sub>4</sub>	2.5 ± 0.05	400	1.2	< 0.24	> 99.98	< 0.02
CH <sub>4</sub>	5.0 ± 0.05	400	1.8	4.3 ± 0.36	99.76 ± 0.02	0.24 ± 0.02
CH <sub>4</sub>	7.1 ± 0.05	400	1.0	17 ± 0.07	98.35 ± 0.07	1.65 ± 0.07
CH <sub>4</sub>	10 ± 0.05	400	1.2	89.5 ± 3.6	92.53 ± 0.30	7.47 ± 0.30
CH <sub>4</sub>	2.5 ± 0.05	450	1.0	< 0.085	> 99.991	< 0.009
CH <sub>4</sub>	5.0 ± 0.05	450	1.8	0.162 ± 0.09	99.988 ± 0.005	0.012 ± 0.005
CH <sub>4</sub>	7.1 ± 0.05	450	1.0	0.190 ± 0.08	99.846 ± 0.008	0.15 ± 0.008
CH <sub>4</sub>	10 ± 0.05	450	1.8	22.1 ± 1.1	98.77 ± 0.06	1.23 ± 0.06
O <sub>2</sub>	12.6 ± 0.05	400	1.0	< 0.120	> 99.988	< 0.012
N <sub>2</sub>	12.6 ± 0.05	400	1.0	< 0.954	> 99.905	< 0.095

### 3.2. N<sub>2</sub> and O<sub>2</sub> purification efficiency

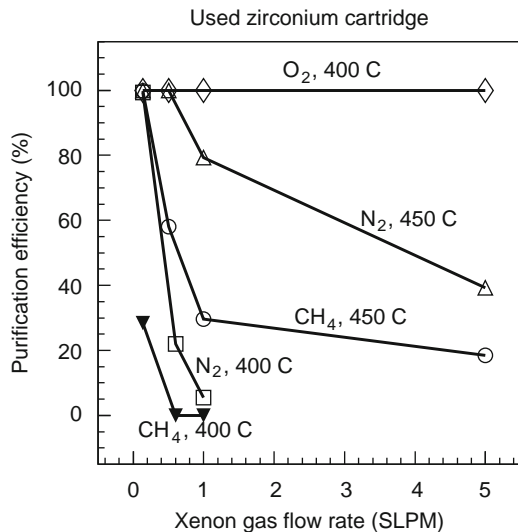
The getter cartridge was also tested with 10<sup>-6</sup> g/g of O<sub>2</sub> and 10<sup>-6</sup> g/g of N<sub>2</sub> at 400 °C and at a flow rate of 12.6 SLPM (the maximum achievable flow rate in our system). In purify mode, both O<sub>2</sub> and N<sub>2</sub> dropped to levels consistent with background, leading to upper limits for the one-pass purification efficiency of > 99.988% for O<sub>2</sub> and > 99.905% for N<sub>2</sub>. These efficiencies correspond to output purity levels of less than 120 × 10<sup>-12</sup> g/g for O<sub>2</sub> and less than 950 × 10<sup>-12</sup> for N<sub>2</sub>. We infer from the methane purification data that lower flow rates and higher temperatures will achieve even better purification efficiencies. For N<sub>2</sub> and O<sub>2</sub> the purification results in xenon gas are consistent with those quoted by the manufacturer for argon and helium.

### 4. Purifier lifetime and saturation

Other studies have observed eventual decrease in purification efficiencies due to capacity depletion [13]. To track the performance of the SAES PS4-MT3 as its capacity begins to be depleted, we collected the first and last methane datasets under identical conditions at a flow rate of 5.0 SLPM and a getter temperature of 450 °C. We find that after the zirconium has absorbed 13 mg of methane, the getter inefficiency increases from 0.01% to 0.03% (see Fig. 4). Furthermore, the measurement at 5.0 SLPM was repeated a third time after leaving the purifier with 1000 Torr of xenon at its operational temperature for one month without use. The purifier's performance appears to improve somewhat after this interim period. However, the final methane signal for this dataset was only a few percent above the background, and it is difficult to rule out a systematic effect of this magnitude over such a long time period.

#### 4.1. Purifier life-status light

The SAES PS4-MT3-R purifier is equipped with a life-status light which indicates when the absorption capacity of the getter has been exhausted. The control electronics for the purifier infers the status of the getter by measuring its resistance. As a practical matter, it is important to note that this measurement is sensitive primarily to O<sub>2</sub> and other oxygen containing impurities, since zirconium oxide has a higher resistance than pure zirconium. Other zirconium compounds, such as zirconium nitride, do not



**Fig. 5.** Purification results with an old zirconium cartridge. The purifier remains effective for O<sub>2</sub> removal, but N<sub>2</sub> and methane performance is seriously diminished. The purifier's life-status light still indicates 'good'.

cause a dramatic change in the resistance of the getter, and their presence will not be detected by the resistance measurement. Therefore the purifier's ability to remove N<sub>2</sub> and methane may be depleted long before the life-status light changes from 'good'.

In fact, when we initially tested our purifier with an older getter cartridge that had been in use in our lab for about two years, we observed that the purifier's performance with respect to N<sub>2</sub> and methane was dramatically diminished although the life-status was indicated as 'good'. At 0.5 SLPM the used getter cartridge was still effectively removing O<sub>2</sub> while allowing nearly 100% of N<sub>2</sub> and methane to pass through at 400 °C, as shown in Fig. 5. Note that this purifier model, when new, is rated for use up to a maximum flow rate of 20 SLPM for argon and helium. We also note that this model is designed to remove about 40 g of O<sub>2</sub>, 2–3 g of N<sub>2</sub> and about 200 mg of methane in its lifetime [22].

Before replacing the used getter cartridge, we performed a final test comparing its purification efficiencies at 400–450 °C, for N<sub>2</sub> and methane. The xenon used in the test had  $4 \times 10^{-6}$  g/g of methane and about  $30 \times 10^{-6}$  g/g of N<sub>2</sub>. The results are shown in Fig. 5. These tests confirmed that the used cartridge performs better at the higher getter temperature and at lower flow rates. We also observed that the performance of the used getter cartridge would improve somewhat after leaving the getter at its operational temperature for one or more days. This observation is consistent with the expected decrease in the impurity diffusion rate as the bulk zirconium becomes saturated near the end of its life.

In total, our results illustrate the utility of having a dedicated gas purity measurement device to monitor the performance of the getter.

## 5. Summary

O<sub>2</sub> and N<sub>2</sub> are removed from xenon very efficiently by the getter. Concentrations at the outlet are less than  $120 \times 10^{-12}$  g/g and  $955 \times 10^{-12}$  g/g, respectively, and are consistent with background. The corresponding single-pass purification efficiencies are greater than 99.99% and 99.9%, respectively. These values were measured at a flow rate of 12.6 SLPM, and at the default getter temperature of 400 °C. We expect that performance at

lower flow rates and higher temperatures is even better. These results are consistent with the manufacturer's specifications for the getter in argon and helium.

Methane removal from xenon is most effective at lower flow rates and higher getter temperatures. The removal efficiency is better than 99.99% at 450 °C and 2.5 SLPM and drops to 92.5% at 400 °C and 10 SLPM. We attribute the decrease in getter effectiveness at higher flow rates to the cooling effect xenon gas has on the getter.

For flow rates of five SLPM or higher, the residual methane concentration at the outlet of the getter can be decreased by about a factor of 10 by increasing the temperature from 400 to 450 °C.

After absorbing 13 mg of methane, we see residual methane in the purified gas increase by a factor of three. We attribute this effect to a partial saturation of the purifier's methane absorption sites.

The getter can become saturated with N<sub>2</sub> and methane while remaining effective for O<sub>2</sub> removal. For xenon use, the manufacturer's life-status light is not well suited for determining when N<sub>2</sub> or methane saturation has occurred. Therefore, additional techniques should be employed to determine the status of the getter with respect to these species. In many systems of interest for particle detection, we expect the N<sub>2</sub> capacity of the purifier to be exhausted before the O<sub>2</sub> capacity.

Since the getter performance in xenon improves at higher temperatures, it seems reasonable that higher temperatures should always be employed when purifying this heavy noble gas. Alternatively, a xenon gas pre-heater could be introduced immediately upstream of the purifier to reduce or eliminate the cooling effect. We have not attempted this strategy in our lab, but we would expect good results based on our experience with this purifier.

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