Measurement of PTFE Outgassing for the XENON Experiment

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Abstract

The XENON experiment relies heavily on well-controlled measurements to detect the predictedly low levels of WIMP nucleus-scattering. Any quantities of contaminant oxygen, in particular, can be detrimental to the experiment since they may absorb ionization electrons produced in nuclear recoils. Thus, outgassing from all materials in contact with the xenon must be closely monitored and understood. The aim of this project has been to find the time and temperature dependent outgassing rates of oxygen in PTFE, the main contributor to outgassing in the XENON experiment.

1 Introduction: XENON and the importance of outgassing

1.1 The Case for WIMPs

There are many different pieces of evidence, which point towards the existence of dark matter. To delineate but a few, we have galactic rotation curves, gravitational lensing, and the large scale structure of the Universe, all of which indicate that there is more mass in the Universe than meets the eye.

Galactic rotation curves plot the velocities of objects (such as stars or giant molecular clouds) against their radii from the center of the galaxy. The visible matter in our galaxy is mostly concentrated at the center, thus leading us to believe that the rotation curve should be a "Keplerian decline" (i.e. \( v \propto r^{1/2} \)). However, instead of this shape, we have repeatedly measured rotation curves that have a steep increase in velocity towards the center of the galaxy and then remain flat at greater radii. At the very center, the galaxy’s mass distribution most closely fits the model of a uniform sphere and, at larger radii, a halo, linearly increasing in mass. This halo is unaccounted for in visible matter, and is thus believed to be dark matter.

Another indication of the existence of dark matter is gravitational lensing. According to Einstein’s theory of general relativity, massive objects distort spacetime. Light will always travel in the most direct path in spacetime, and, therefore, if spacetime is bent, light will bend, too. This is what we see happen around very massive objects such as galactic clusters, and leads to distorted images of objects behind the cluster. From the level of distortion in the images, we can evaluate the mass of the cluster. However, the masses we calculate for these clusters much exceed the masses we would expect given the visible matter detected. Thus, there must be an extra source of matter unaccounted for.

Another piece of evidence for dark matter is the large scale structure of the Universe. Quantum fluctuations in the energy of the Universe before and during inflation led to small anisotropies in the cosmic microwave background, and it is these anisotropies that led to the large scale structure of the universe, including galaxies, clusters and...
superclusters. Dark matter, however, is required to explain the rate of the development of these structures. Furthermore, the properties of dark matter can be better understood through simulations comparing the simulated development of a universe with dark matter of different properties to the observed Universe. Cold dark matter—i.e. non-relativistic—best explains the development of the Universe.

One of the most popular candidates for cold dark matter is the Weakly Interacting Massive Particle (WIMP), a product of supersymmetry. WIMPs are theorized to be a new elementary particle—not part of the standard model— which only interact with standard matter through the gravitational and weak forces (and potentially any other equally weak forces not included in the standard model). WIMPs would be much heavier than the standard model particles, and also would fulfill the cold DM requirement.

There are other candidates, however, such as self-interacting massive particles and axions, which may be closer to the true form of dark matter. It is unclear at this time which—if any—of these candidates will be successful.

1.2 XENON Experiment

The XENON collaboration aims to detect WIMPs directly. Their most recent detector, called XENON1T, is located in Gran Sasso, Italy at the Laboratori Nazionali del Gran Sasso. It comprises a time projection chamber (TPC) filled with approximately 2000kg of xenon, in both liquid and gaseous states. A uniform electric field is present in both the liquid and gaseous phases—though the field through the gaseous phase is stronger—and at the bottom and top of the chamber are photomultiplier tubes (PMTs).

Fig 1. XENON experiment (Gaudiman)

XENON is designed to detect nuclear recoils from WIMP-nucleus scattering. When, theoretically, the WIMP first collides with an LXe nucleus, the xenon scintillates and releases photons detected by the PMTs as S1. The collision also produces ionization electrons, which drift upwards in the chamber (due to the electric field) and enter the gaseous section of the TPC. Here, the field is much stronger, and accelerates the electrons until they interact with the GXe and produce a second round of scintillation, detected by the PMTs as S2.
It is the spacing and ratio of the amplitudes of S1 and S2 that allows us to differentiate between electronic recoils ($\gamma$ and $\beta$ background) and nuclear recoils (from WIMPs and neutrons). Thus, the presence of any impurities such as H$_2$O or O$_2$ is extremely detrimental for the accuracy of the instrument. Not only can these gases interact with the ionization electrons (thus reducing their concentration and lifetimes), but the absorption spectra are similar to the wavelengths of the scintillation photons produced during nuclear recoils. Hence, it is crucial to limit the presence of any such impurities in the system.

### 1.3 Outgassing

Unfortunately, however, these gases may be released into the TPC through the process of outgassing. Outgassing is the term used to describe the process whereby gases are released from a material. There are many mechanisms by which outgassing can occur, including desorption, diffusion, permeation and leaks— as is demonstrated in Fig 3. Any materials in contact with the xenon may be culpable: stainless steel wires, PMTS, and the PTFE container the xenon is housed in.

The type of outgassing most relevant to the experiment is highly dependent on the time scale. At short times, desorption, which is the release of gases and vapors that have been adsorbed onto the material’s surface, is the primary form of outgassing. Desorption occurs at a rate of $\frac{dC(t)}{dt} = C_0 K_1 e^{-K_1 t}$, where $C$ is the concentration of molecules on the surface of the material. This results in very rapid exponential decay of the desorption rate.
Once the desorption phase has ended, diffusion takes over as the primary form of outgassing. Diffusion is the transport of one material through another. At short times, the outgassing rate is given by: 

\[ q = C_0 \left( \frac{D}{\pi t} \right)^{1/2} \]

where \( D \) is the diffusion constant, and \( C_0 \) is the internal pressure of the gas dissolved in the material.

At longer times, when the bulk starts to become depleted, the diffusion equation becomes

\[ q = 2DC_0 \exp \left( -\frac{\pi^2 D t}{4d^2} \right) \]

where \( d \) is the thickness of the material. Thus, we can see that the depletion of the bulk is highly dependent on the thickness of the material.

The diffusion constant, \( D \), is not constant for all temperatures, however. In fact there is an exponential dependence on temperature: 

\[ D = D_0 e^{-E_D/kT} \]

1.4 Importance of Outgassing for XENON

Hence, since XENON is extremely sensitive to oxygen impurities, it is incredibly important to understand and monitor oxygen outgassing in the system. We correct for the electrons lost to impurities in the XENON data analysis, and thus it is important to understand how this correction will evolve over time. Out of all the materials in contact with the xenon, PTFE is the most substantial contributor to outgassing. Thus, it is crucial to know the diffusion constant of oxygen through PTFE at temperatures as low as liquid xenon. This is especially important as PTFE prepares for its newest upgrade, XENONnT, an eight tonne detector, which will have a much larger surface area in contact with the PTFE container. Surprisingly, the temperature-dependent diffusion rate of oxygen through PTFE is not known. Thus, the aim of this project has been to uncover the temperature-dependent diffusion constant of oxygen through PTFE.

2 The Outgassing System

2.1 Throughput method

In order to measure the diffusion constant of oxygen, we must measure the outgassing rates of the PTFE at different temperatures. Once we have the outgassing rates, we can convert them to diffusion constants using the formula: 

\[ q = \frac{2DC_0}{d^2} \exp \left( -\frac{\pi^2 D t}{4d^2} \right) \]

To calculate the outgassing rates, we used the throughput method. This method involves placing the sample in a high vacuum chamber with an orifice of known conductance. The outgassing rate can be calculated by the formula: 

\[ Q = C(P_u - P_d) \]

where \( Q \) is the outgassing rate, \( C \) is the conductance, \( P_u \) is the pressure in the sample chamber and \( P_d \) is the pressure outside of the orifice. However, the downstream pressure is so small compared to the upstream pressure that it can be ignored for our purposes. Hence, we only need to know the pressure of the sample chamber to know the outgassing rates.
2.2 The Apparatus

Fig 4. Outgassing apparatus

The outgassing system is comprised of a main chamber, access port, bypass pumping port with angle valve, orifice, HiPace 300 turbo, MVP 070-3 diaphragm pump, PKR 251 full-range pressure gauge, and Extorr 200M RGA (Uppal). The samples are introduced to the main chamber through a gate valve, and the chamber is evacuated through the bypass valve and, to a lesser extent, the orifice. The orifice is of a known conductance.

Fig 5. Outgassing system schematic (from XENON Columbia wiki)

The cooling system works by a relay valve controlling the flow of liquid nitrogen from the tank into chamber. The valve is open for a larger fraction of time depending on by how much the chamber needs to cool. A copper tube transports this liquid nitrogen through the aluminum plate and then releases the gaseous nitrogen to the air outside the chamber, cooling the plate in the process.

We monitor the system with 3 temperature sensors and one pressure sensor. The temperature sensors include: one to measure the temperature of the cooling plate (T-Plate), another which is clamped to the sample to measure the temperature of the sample (T-Sample), and a last one to measure the temperature of the room (T-Ambient).

Most of this apparatus had previously been designed and assembled. However, before carrying out the data collection, we did do upgrades to the temperature sensor system (including replacing the ADC, rewiring the temperature sensors and creating a new chip to deliver 5V to the ambient temperature sensor), and also created a new
aluminum piece to hold the sample temperature sensor within the sample chamber.

2.3 Procedure

In order to begin a round of measurements, we must first close the sample chamber, and evacuate the chamber. First, we pump using the roughing pump and then open the access valve slowly in order to start the turbo pump. Once the pressure equilibrates, you may begin to take time-dependent measurements at room-temperature. However, in order to take temperature-dependent measurements, you must wait until the change in outgassing rate over time is much smaller than the changes due to temperature (approximately one week). More explicitly, if outgassing is the function $O(t, T)$ of time and temperature, for the first week we would first take measurements of $O(t, 237K)$. Then, once the changes in outgassing due to time changes were negligible, we would investigate $O(1\text{week}, T)$.

To take an individual measurement, we must first close the bypass valve. This is important due to the throughput method, since we do not know the conductance of the bypass valve. By closing the bypass valve and allowing gas to flow only through the orifice (of known conductance), we can use the equation $Q = CP$ to calculate outgassing. However, when we close this valve, the pressure increases. Thus, we must wait for this to equilibrate. As will be discussed later, this became a more complex issue than we anticipated, but we concluded that waiting 40 minutes was sufficient, and by using an asymptote fitter we could even better estimate the final pressure.

![Fig. 6 Pressure asymptote fit](image)

After the pressure has equilibrated, we can take the residual gas analyzer (RGA) scan, to be able to separate the pressure of oxygen from the pressures of other gases. The RGA works as a mass spectrometer, ionizing different gases and then using a radio frequency quadrupole to separate them. More specifically, a filament above a cathode is heated, which releases electrons to be accelerated towards the anode. This electron beam ionizes the gas surrounding it, creating positive ions. The ions hit the ion collector wire, which produces a current proportional to the pressure of the gas. The gases are separated using four metal rods with a time-varying electrical voltage, which allows only ions of a particular mass to enter. The RGA takes a scan with AMU ranging from 0 to 200 and with spacing of 0.1 AMU.
In order to do this, we must first turn off the pressure gauge since the RGA and pressure gauge cannot work simultaneously. Then, we can control the RGA through the Windows software Extorr. We let the RGA run for 15 minutes before saving the file and turning back on the pressure gauge and closing the bypass valve again.

![Fig. 7 Extorr Residual Gas Analyzer (Extorr)](image)

3 Measurements

3.1 Cooling Tests

Before removing the sample in order to take the background tests, we performed cooling tests on the (already very much degassed) sample to ensure that the improvements we made to temperature sensors were working. While these tests do not provide much information on outgassing rates of PTFE (since the sample had been pumped for about a year), they provided some valuable insights on taking the actual data.

On July 6, 2018, we closed the bypass valve and then took RGA scans at room temperature, -20°C, -60°C, and -100°C, waiting two hours in between measurements. The first measurement took longer (as is pictured below) since there were a few issues starting up the RGA. Otherwise, the RGA measurements took 15 minutes each.

![Fig. 8 Extorr Software taking RGA scan](image)
One of the main things we noticed in doing these tests was that the pressure becomes very unstable during cooling. This is due to the valve opening and closing to let in the liquid nitrogen, and, as can be seen below, this instability only increases as the temperatures drop (since the valve needs to be open for longer). As a solution to this problem in future rounds, we decide to turn off the relay power before taking the RGA scan.

Another observation from the test run was that the sample temperature does not get as low as the set-point (or plate temperature). I found that the difference between set point and sample temperature could be described by this function: Setpoint = 1.279 * (T_sample) − 10.501 where the $R^2$ value was greater than 0.99.
3.2 Background measurements

We first performed baseline background tests to be able to eventually subtract these baseline measurements from the actual data. On July 9, 2018, after opening the sample chamber in order to remove the PTFE, we closed the gate valve. We began pumping with the roughing pump, and then switched to the turbo pump, which we used to pump the chamber for another 16 hours. Then, we took RGA scans every 8 hours in order to monitor the background outgassing rates over time. We took 7 measurements between July 10 and July 14.

After 7 days of pumping, on July 17, we began cooling tests. We used set-points of room temperature, -20°C, -60°C, -100°C and -140°C. We attached liquid nitrogen to the system and turned on the relay power in order to cool the chamber. We waited two hours after the original change in set-point before unplugging the relay (in order to limit the amount of pressure fluctuations due to the valve opening and closing). Then, we took RGA measurements as described above, changed the set-point again and turned back on the relay power.

3.3 PTFE measurements

On July 19, 2018, after the chamber had warmed to 20°C, we placed the PTFE sample in the sample chamber. Before inserting any components, we washed them with soap and water and scrubbed with acetone. We inserted the temperature sensor into the new aluminum piece and clamped it tightly to the sample. Then, we closed the gate valve. Next, we pumped the chamber, first using the roughing pump until the pressure was under 1 Torr, and then the turbo pump. Similar to the background rounds, we took RGA scans every eight hours, opening the bypass valve for 40 minutes before taking the scan.

By July 24, 2018, the outgassing rate was changing by less than 5% per day. This was adequately low to begin temperature dependent testing (since the preliminary tests showed that the outgassing rates changed by 50% due to temperature changes).

On July 26, 2018, we began the cooling tests. We took scans at room temperature, -20°C, -60°C, -80°C and -100°C. We waited until the temperature of the sample was changing less than 0.5°C per fifteen minutes (the length of the RGA scan). We also took care to unplug the relay in order to limit the pressure fluctuations.
4 Results and Analysis

4.1 Background measurements

During the course of the background measurements, we came to see the how critical the timing of opening the bypass valve is. While the first two measurements were taken with just having closed the bypass for 15 minutes, we decided to subsequently open it for 45 minutes, and realized that the asymptotic fits we were doing to find the estimated final pressures were not at their maxima. For the last two measurements we took, we left the bypass valve closed overnight and saw just how high the pressures could get. This accounts for the extraordinarily high last two outgassing rates. The other rates have been adjusted by only using the first 15 minutes of data and fitting the asymptote from those data. You can see below the final pressures that would have been used without this adjustment.

![Graph showing background time dependence: pressures](image)

Fig 12. Background time dependence: pressures

Compared to the previous plot, you can see that the "avg pressure" point is much higher and also more variable.

Given these adjustments, however, and disregarding the final two values, we see that the outgassing rates decrease substantially within the first 24 hours and thereafter do not change significantly, and average 1.5e-14 Torr*l/s.
Fig 13. Background time dependence: outgassings

For the temperature-dependent outgassing rates, we did not open and close the bypass valve for each measurement, but kept it closed throughout the day. This meant that instead of using an asymptote fitter to find the final pressures, we needed to find an average over a given time period before the RGA scan. To do this, we selected a range in which the pressure had equilibrated and then found the median pressure. Below is pictured the full pressure plot and the zoomed in pressure fluctuations before performing a specific RGA. The blue point represents the beginning of the averaging range, the red point the last of the averaging range and the green point the median pressure used in the outgassing analysis.

Fig 14. Background temperature dependence: pressures
Fig 15. Example pressure averaging

In order to limit the fluctuations due to the relay valve opening and closing with the liquid nitrogen (as you can see below, there were great fluctuations, especially at the lower temperatures), we decided to turn off the relay power before a measurement. This was fine to do since the slope of warming was less than one degree in the first half hour after unplugging the relay power.

Fig 16. Background temperature dependence: pressures and temperatures
Our results showed no substantial changes in outgassing for the first four measurements (the changes were on the same scale as for the room temperature measurements). It was unclear at the time why the lowest temperature measurement had such a low outgassing rate. As will be discussed later, there was an unforeseen complication with the relay, which led to this very low pressure.

4.2 Time-dependent measurements

While the background measurements were flat within 24 hours of pumping, we saw a slower decline in the outgassing rates of the PTFE sample. It took over 100 hours before the outgassing rates were changing less than 10% in a day. At this point the outgassing rates were approximately 3e-13 Torr*l/s, and background outgassing (at 1.5e-14 Torr*l/s) constituted only 5% of the outgassing. The best fit model, using the formula $a + b \times e^{-x/\tau}$, indicated that the outgassing would flatten completely at approximately 2e-13 Torr*l/s. At this point, background would constitute 7.5% of the outgassing.
4.3 Temperature-dependent measurements: first method

Once the outgassing rates were not changing significantly in a day, we were able to take the temperature-dependent measurements. As can be seen below, we saw similar patterns as in the preliminary tests, with both significant decreases in the pressure and increasing amounts of pressure fluctuations with cooling. However, once we began unplugging the relay to reduce these pressure fluctuations, we saw huge and sudden increases in pressure. For the third measurement (at -80°C) the pressure quickly increased and then settled down at a much higher pressure (close to the -20°C pressure). When we unplugged the relay after the -100°C measurement, the rise in pressure was even more dramatic.

Looking at the outgassing rates, we also saw that the changes in outgassing due to cooling were extremely large—over an order of magnitude.
Both of these effects led us to the conclusion that the pressures we were measuring were not due to the outgassing alone. Instead, we believe that the tube which delivers the liquid nitrogen acts as a pump within the chamber since it is much colder than the chamber (at the temperature of liquid nitrogen). This causes the pressures to drop significantly in the chamber, especially as the temperatures get lower and the relay is powered for larger fractions of time. Then, after the relay is unplugged, the tube quickly warms to temperatures above the sample chamber (since part of the tube is exposed to room temperature). The gases which had been adsorbed on the tubes are quickly released, causing the rapid increase in pressures. Only once the equilibrium is reached again is the pressure actually measuring the outgassing rate.

Hence, while the data taken at room temperature is valid, these data are not. This also explains the sudden drop in pressure at the lowest temperatures during the background tests, and indicates that there may be no temperature dependence on the background outgassing at all. In order to test the true outgassing rates at low temperatures, we designed a new method.
5 Temperature-dependent measurements: a new method

In order to reduce the extra pumping from the copper tubing, we decided we would take the measurements in reverse: first cool the chamber to -150°C and then take RGA scans once the pressure has equilibrated, and as the chamber warms.

![Fig 23. PTFE temperature dependence: temperature and pressure as warming](image)

We began cooling at 8.30am on July 30 2018. At 10:45, we unplugged the relay and began the warming process. Unfortunately, however, the equilibration process took longer than expected, 7 hours. And hence we could only take one RGA scan before the end of the day (at -50°C), and two RGA scans the next day (at 7°C and 17°C). However, by interpolating between the RGA scan peak oxygen fractions, and taking pressure data from the log, we can reconstruct the trend. Below is pictured the exact ranges from which we took and averaged the pressure data.

![Fig 24. PTFE temperature dependence: pressure fluctuations during warming](image)
As can be seen, there are quite significant fluctuations in the pressure data, which can largely be attributed to the ambient temperature fluctuations. During the nighttime, the air-conditioning schedule changes, and thus the fluctuations become larger in both time and amplitude.

![Fig 25. PTFE temperature dependence (new method): outgassings](image)

The above plot’s outgassing error bars include a potential 50% error in the peak oxygen fraction—in addition to the usual pressure fluctuation error—and yet still the error bars remain small and show a clear positive trend. Using an exponential fitter, the trend is $\text{Outgassing} = 3.86e^{-14} \times \exp(0.023\times\text{Temperature})$, and has an $R^2$ value of 0.99.

Now, comparing these data to the background measurements—which, we concluded, were fairly constant at $1.5e^{-14}$ Torr *l/s—we see that the outgassing rates, especially at low temperatures, are very close to the background. Unfortunately, this is, to at least some part, due to the fact that we delayed taking these data, and so the sample had already been pumped for 10 days. However, while this may show that the above outgassing data has an offset, the trend should still be valid since the fluctuations in the background were minimal in the temperature-dependent tests we did.

### 6 Conclusions

To summarize, after upgrading the temperature-monitoring apparatus in the outgassing system, we successfully measured both the background and PTFE time-dependent outgassing rates. We discovered several flaws in the previously-used process of taking the temperature-dependent measurements, including, most significantly, that the liquid nitrogen tubing was acting as a pump, and artificially lowering the outgassing rates measured. We used a new method—first cooling and then taking the measurements during the warm-up—to measure the actual outgassing rates, and found an exponential dependence on temperature. Moreover, we discovered that at low temperatures under -20°C the outgassing rates become close to the background.

An important next step would be to repeat the method we developed for the temperature-dependent measurements immediately after monitoring the time-dependent outgassing rates, so to ensure we understand the full trend and background rates. In addition,
we would want to begin cooling in the afternoon so we could take more RGA scans at lower temperatures the next day and hence ensure that the the peak oxygen fractions we are using are correct.

Furthermore, as was evident in the pressure data during the warm-up of the chamber, the pressure fluctuations are highly correlated with the ambient temperature. Since the pressure changes due to changes in the sample temperature are much smaller than we had previously thought, these fluctuations become more significant and thus should be de-correlated using the ambient temperature data.

Finally, once sufficient data for the outgassing rates of PTFE have been collected, significant work must be done to establish the correct model and find the exact relationship between PTFE oxygen outgassing and temperature and time.

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8 References


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