Studying the Removal of Krypton from Xenon in Saturation

Dan Baxter, Dan Akerib, Tom Shutt

Department of Physics
Case Western Reserve University
Cleveland, OH 44106

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1. Abstract

Liquid xenon experiments are becoming more prominent as a viable way to search for dark matter. In these experiments, it is important to use liquid xenon free of any radioactive impurities, specifically krypton. Since xenon of necessary purity is not available commercially, the krypton must be removed in laboratories, in our case by a process using chromatography. Chromatography is the study of separating gases by passing them through an absorbing material, in our case charcoal, with a carrier gas. Xenon and krypton will pass through at different speeds due to different absorption constants. While this process is relatively well studied, the removal system is generally saturated with large amounts of the mixture to expedite the process. Under saturation, nearly all of the binding sites in the charcoal become used, so some gas that otherwise would have been absorbed passes through much more quickly. Under this scenario, the process no longer follows the well-studied model and is the focus of this experiment. As part of this project, a setup has been constructed capable of running controlled amounts of helium carrier gas and xenon through charcoal at controlled flow rates in order to study the chromatography within the saturated regime. Variables which are to be adjusted in the process include the helium flow rate and pressure, as well as the xenon mass fraction. Ultimately, the goal is to produce a model for the removal process that can be utilized during the production phase of future liquid xenon dark matter experiments.
2. Background

Over the past century, enormous strides have been made in determining the energy makeup of the universe, yet scientists have only been able to directly detect a tiny fraction of the energy composition that exists. In fact, baryonic matter only makes up around 4% of the total energy density of the universe.\(^1\) However, other measurements determine the lower limit of all matter to be at least 20%.\(^1\) The difference between these two values is explained by what is referred to as dark matter. Whether it is simply a flaw in our understanding of gravity or some form of physical matter which cannot be observed by our telescopes has not been determined.

One of the leading candidates for dark matter is the WIMP, or weakly-interacting massive particle. As dark matter, these particles would not interact with photons via the electromagnetic force, and as such are undetectable by telescopes. They may be far more massive than other weakly-interacting particles, for example neutrinos, to account for the large amount of dark matter in the universe. Lastly, as the name implies, they would occasionally interact with normal matter via a weak force.

3. Motivation

A primary method of detecting WIMPs involves xenon detectors. These detectors use large amounts of xenon in the liquid and gaseous phases. Xenon makes an ideal target because of its stability and its large nuclear radius. A WIMP will occasionally interact with the nucleus of one of the xenon molecules via a weak force in a scattering event. This interaction will expel
some number of electrons and emit light. The light can then be detected by photomultiplier tubes while the electrons can be drifted in an electric field to precisely record the location of the event. Such detections can be seen as direct evidence for the existence of WIMPs, and by extension, dark matter. The frequency of events can be used to determine more precisely the mass and cross section of WIMPs.

One of the main difficulties in such an experiment is that these interactions do not occur often and are not the only interactions that can produce free electrons or photons. It is extremely important to reduce background by minimizing all other sources of such interactions that could otherwise be mistakenly interpreted as a WIMP event. One of the leading collaborations in the detection of WIMPs is the LUX experiment in South Dakota with which I am working. To reduce background, the detector has been moved far underground to eliminate cosmic rays that would otherwise obscure the desired signals. Once underground, the detector is placed in a large vat of water which will shield the xenon from most of the radiation from the rock in the cave.

One significant source of background which cannot be easily removed through clever choice of location is krypton-85. This isotope of krypton is radioactive with a half-life of greater than ten years and is contained in all commercially available xenon. Unfortunately, the levels at which the krypton is present in commercially available xenon are four to five orders of magnitude greater than desired for the LUX experiment. In order to successfully measure the WIMP interactions in a detector the size of LUX, krypton levels in the xenon must be reduced to less than 5ppt. A method was developed that is capable of removing krypton far beyond commercially available levels by the LUX collaboration using principles of chromatography.
Chromatography is the process of separation of two fluids by flowing them through an absorbent that will alter their flow rates independently.

![Diagram of chromatography system](image)

Figure 1: A simplification of the system’s design and function.

The LUX detector requires roughly 400kg of purified xenon before it can become operational. This is problematic because a model for removal by chromatographic methods has only been established for small inputs relative to the amount of absorbent.\(^2\) As is shown in Figure 1, a gas can be flowed through a column of absorbent, in this case charcoal. As it moves through the column, the gas molecules become polarized and are attracted to the charcoal by Van der Waals forces in what is known as physical absorption.\(^3\) This slows the progression of the gas throughout the column and causes dispersion. When large amounts of xenon are input, the binding sites of the absorbent become saturated by these interactions and more of the gas is able to pass through unhindered.\(^3\) In such a situation, the model of chromatographic
separation is found to not accurately represent the system. A more complete model is essential for understanding the mechanism for xenon purification.

4. Previous Work

Great strides were made in the field of chromatography in 1956 by J.J. Van Deemter.\textsuperscript{4} He took the work of previous scientists and consolidated it to develop what is now known as the Van Deemter Equation. Using this equation, most of modern chromatographic theory has been developed.

The absorption of a gas passing through the column can be accurately modeled using the equation:

\[ s = ky \]  

(1)

where \( s \) represents the number of gas molecules in the absorbed state per mass of absorbent in the column, and \( y \) is the number of gas molecules in the mobile state per volume.\textsuperscript{3} The remaining parameter, \( k \), which depends on the type of gas, has units of volume per mass and is referred to as the absorption constant. Calling \( k \) a constant is, however, misleading because it is only a constant in normal chromatographic theory. Under saturation, there is a limit to the amount of gas in the absorbed state which is directly related to the surface area of absorbent available. Even though charcoal has a high surface area, there is a limit to how much gas can be attracted to it. As such, there is a maximum value that \( s \) can reach, but theoretically no maximum value to how much gas can be input into the system. As such, it is apparent that, as \( y \)
becomes very large, k must become very small. The mathematical representation of saturation is when k begins to significantly decrease from its constant value.

In the unsaturated regime, when k can accurately be considered constant, the transit time of a gas through a column is represented by the equation:

$$\tau = \frac{kM}{\Phi}$$  \hspace{1cm} (2)

where \(\tau\) represents the transit time through the column, \(M\) is the mass of absorbent, and \(\Phi\) is the carrier gas flow rate.\(^2\) In order to discuss the origin of this equation (which will be derived in Section 7), it is important to introduce the concept of plate theory. It is possible to model the flow of gas through the column using a series of height equivalent theoretical plates of width H.\(^4\) A column of length L will therefore have N of these plates by the relationship:

$$N = \frac{L}{H}$$  \hspace{1cm} (3)

While the theory historically considers plates, it is possibly more intuitive to think of the column as being broken down into N discrete stages. The physical significance of N is diffusion. Specifically, as N decreases, diffusion decreases and conversely, as N increases, diffusion increases. An example of what may cause this would be increasing the flow rate of the carrier gas such that even the gasses that would otherwise be absorbed by charcoal begin to pass through the column far more quickly. This would result in a far reduced value of N and correspondingly reduced diffusion.

Inside of each theoretical stage, the amount of gas can be modeled as equivalent throughout the stage, and the probability of the gas within the stage being in the absorbed
versus mobile states is represented by \( k \). The mobile gas molecules are able to move through the column, while the absorbed gas is not. As such, starting with the first theoretical stage, a fraction \( k \) of the gas will become absorbed by the charcoal while the rest will be free to move to the next stage. In the next stage, the same will occur, and so on through all \( N \) stages. As the free gas flows into a stage, the free binding sites of that stage equilibrate to \( k \) and so on throughout the column. Gradually, the absorbed gas of each phase is released and travels through the column in the same way. In this way, the gas diffuses through the column. A visual representation of this discrete representation can be seen in Figure 3.

![Charcoal Column](image)

Figure 3: A visual representation of the \( N \) theoretical stages inside of the column as predicted with plate theory.

The ratio between absorbed and free gas in each plate is represented by \( k \).

Mathematically, this process can be described by the Van Deemter Equation:

\[
H = E + \frac{B}{u} + Cu
\]  

(4)

where \( u \) is the velocity of the gas through the column, \( E \) is a constant factor resulting from imperfect packing of the charcoal, and \( B \) depends on the diffusivity of the gas in the mobile phase and yields the term that represents longitudinal diffusion.\(^4\) \( C \) depends on \( k \) and in normal chromatographic theory is considered constant. The third term can be thought of as the
resistance of the gas moving through the column. In fact, given a constant k, the diffusion is
governed by direct dependence on velocity so the last becomes the only significant term, and
the terms containing E and B are negligible in comparison. Given this approximation for H and
using Equation 3:

\[ H = \frac{L}{N} \propto \frac{LA}{\Phi} \propto \frac{M}{\Phi} \]  \hspace{1cm} (5)

where A is the cross sectional area of the column and the other variables are defined as before.

For the last part of the derivation, the movement of gas through the column can be
modeled by a series of coupled differential equations:

\[ \dot{y}_i = \frac{N}{\tau} (y_{i-1} - y_i) \]  \hspace{1cm} (6)

where \( y_i \) represents the number of gas molecules flowing through the \( i \)th theoretical plate per
volume and \( \dot{y}_i \) is its time derivative. Solving Equation 6 and plugging in the result of Equation 5,
the conclusion is Equation 2.\(^3\)
Separation can occur because two different types of gasses, here xenon and krypton, will have two different values of $k$ due to the different polarizability of the two gasses. By Equation 2, they will also have different transit times through the column. Specifically, xenon is far more polarizable than krypton and will take much longer to fully travel through the column. By taking into account the transit times and diffusion of each gas, it is possible to model the separation.

Unfortunately, Equation 2 above only holds in the unsaturated regime while $k$ remains constant, which is the central motivation for this project. For the sake of high production rate, the system needs to always be run in the saturated regime, and an accurate model of the process would help to greatly optimize the separation for the sake of obtaining higher purities or higher throughput systems.
5. Objectives

It is the goal of this project to design and construct a system capable of studying the chromatography in a saturated charcoal column. By studying the diffusion through a saturated column, it should be possible to more accurately model the process by which this occurs. This model could then be used to optimize the separation process for use in future xenon experiments to obtain higher purities more efficiently. The existing theory of chromatography that encompasses the non-saturated regime needs to be studied to determine whether or not it can be modified to include saturation, or if not, where assumptions must be made that accurately include this phase space.

After initial measurements are taken at atmospheric pressure, the system must be easily modifiable such that a pump can be attached to measure the effects of pressure on the separation. Previous experiments have modeled the absorption constant’s dependence on pressure for the purpose of avoiding saturation. Another possible measurement to be taken would be the effects of column cross sectional area versus height and absorbent mass. In addition, the thermodynamic properties of absorption may have a significant effect on the chromatography and cannot be neglected in a complete model. The temperature dependence of k in the unsaturated regime has already been studied but not incorporated into separation models.
6. Methods

In order to test new models of separation, I constructed a system to input xenon containing trace amounts of krypton through a charcoal column using a helium carrier gas so that I can measure the output with a residual gas analyzer (RGA) as shown previously in Figure 1. The bubble gauge attached to the output is used to calibrate the mass flow controllers and obtain accurate measurements of flow rate. The measurements from the RGA are used to study the exact transit times and diffusion of the output gasses. The flow rates of the input gasses are controlled using two Brooks 5964 mass flow controllers. All of these devices are controlled by an ADAM 6024 module hooked up to a nearby computer. As such, a program could be written to run through different flow rates and mass ratios to determine the exact dependence of the output on such variables. The cost of recovering the output gas was greater than the cost of the xenon being used, so a decision was made to vent instead of investing in a recovery system.
Figure 4: A diagram of the setup for the purpose of measuring the separation within the column. The xenon and helium flows will be controlled by two mass flow controllers then flowed through a charcoal column to be measured by a residual gas analyzer capable of determining their partial pressures versus time.

7. Results

The system to study the diffusion of gasses through a charcoal column has successfully been built and integrated into the lab network. It is capable of studying xenon flow rates up to 11.0 cc/s and helium flow rates up to 54.3 cc/s as can be seen in more detail from the calibration data in Figures 5 and 6. The mass of charcoal contained in the column initially being studied is 250g. A digital pressure measurement is used to verify that the pressure remains
constant over the duration of any tests that are performed. A photo of the system is shown in Figure 7.

Data has been taken to verify that the system is functional and is shown in Figure 8. This data set was taken primarily as a proof of concept which is why the full xenon curve is not included, so little information about the diffusion under saturation can be obtained from it. However, it is sufficient to declare that the system is fully functional. In addition, because of the shape of the output curves, it is clear that the krypton did not saturate in the column, while the xenon did. This is typical due to xenon’s dramatically higher polarizability. It takes a significant amount of time for the xenon to travel through the column and the tail is not of particular interest in this data run, so as mentioned, it was omitted.

The original theory has been explored in an attempt to modify it to include saturation. In the original derivation, Equation 6 comes from the fact that the total amount of gas in any stage of the column $n_i$ is represented by:

$$n_i = m_i + v y_i = \left(\frac{M}{N} k + v\right) y_i$$  \hspace{1cm} (7)

where $m$ is the mass in $i$th stage, $v$ is the empty volume of the $i$th stage, and the other variables are defined as before. Intuitively, the change of gas in the $i$th stage is represented by the amount entering the stage minus the amount leaving the stage:

$$\frac{dn_i}{dt} = \Phi \left(y_{i-1} - y_i\right)$$  \hspace{1cm} (8)

Plugging in Equation 7 and making the assumption that the volume contribution is negligible in comparison to the mass term, we obtain Equation 6. This is a reasonable assumption in the
unsaturated theory since most of the gas is absorbed as opposed to mobile. However, under
saturation both N and k change over the column itself in a way that is dependent on y_i and the
mobile contribution becomes significant. Therefore, taking this assumption and combining
Equations 3, 7, and 8:

\[
\frac{M}{L} \frac{d}{dt} (H_i k_i y_i) + v \dot{y}_i = \Phi (y_{i-1} - y_i) \tag{9}
\]

or

\[
\frac{M}{L} \frac{d}{dt} (H_i s_i) + v \dot{y}_i = \Phi (y_{i-1} - y_i) \tag{10}
\]

To simplify these equations further, it is essential to determine a relationship between H
and y which requires some assumptions be made. More data is required before any
simplification can be made from this point. Once the left side has been simplified down to its
dependence on y, the system of coupled differential equations can then be solved and the
transit time can likely be found. It is also essential understand H because it inherently implies
understanding the behavior of N, and as such the diffusion of a gas through the column.
Figure 5: Showing the calibration data for the Brooks 5964 mass flow controller being used for the helium flow. All calibration measurements were taken using a bubble gauge.

Figure 6: Showing the calibration data for the Brooks 5964 mass flow controller being used for the xenon flow. All calibration measurements were taken using a bubble gauge.
Figure 7: A photo showing the setup I have built. A diagram of its function can be seen in Figure 4. The gas panel is on the bottom with the electronics on the panel above.
Figure 8: The output of the constructed system as measured by an RGA showing the partial pressures of Xe134, Xe124, Kr86, and Kr in pTorr as a function of time since the Xe/Kr feed began. This data was taken given a 2.5 cc/s Xe feed containing trace amounts of Kr over 1000 seconds and a 25 cc/s He feed.
Figure 9: The same data run from Figure 8 plotted by taking the ratio of each partial pressure to the maximum value for that gas. The Kr86 data from above has not been included for the sake of clarity. It should be noted that near total separation was likely achieved during this run, although more precise measurements would be required to verify.

8. Discussion

The panel I have built has been proven to be functional and capable of taking the necessary data to study chromatography under saturation. With further measurements obtained from it, the theory of chromatography should be able to be modified to include the saturated regime. Specifically, intensive study must be done on transit times of xenon and krypton and of their diffusion through the column. By studying these effects, it should be possible to make assumptions that are able to simplify the calculation of the variables H and N
in such a way that can then be used to determine a relationship between transit time and diffusion and the variables of carrier gas flow rate, Xe/He mass ratio, charcoal mass, and pressure. It is expected that this relationship be far more complicated than in the simple unsaturated model.

9. Conclusion

The work to design and develop the system necessary to study this effect is complete. Advancement in the theory has proceeded to the point where it requires data to be simplified into a useable form. Further work with the theory is needed once the data is produced. Initial data has been taken using the constructed system, but not enough to come to any conclusions. Further study must be done over the full range of test variables. Given further data from the constructed system, a model should be able to be created that will optimize the process of krypton removal for future xenon dark matter experiments both in terms of purity from separation and total throughput.

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11. References


