Krypton Removal via Gas Chromatography for the LZ Experiment

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Abstract. Trace radioactive noble elements are a source of electron recoil backgrounds in liquid xenon-based detectors. Commercially available research-grade xenon contains krypton at a concentration of up to 100 ppb g/g as a byproduct of its extraction from the atmosphere. About 1 ppt of this residual krypton is ^{85}Kr, a beta emitter with an endpoint energy of 687 keV and a half-life of 10.8 years. The science goals of the LZ dark matter experiment require that the ten tonnes of detector xenon contain a total krypton concentration of no more than 300 ppq g/g. To achieve this, a gas charcoal chromatography system was built and operated at SLAC National Accelerator Laboratory to remove krypton from the xenon prior to deployment in the detector. Using two charcoal columns in parallel to continuously process xenon, the system was automated to operate largely without human intervention, and achieved a final purity of 123 ± 10 ppq krypton in the full ten tonnes of xenon. We present an overview of the design and operation of the LZ krypton removal system at SLAC, and discuss some of the unique challenges encountered and lessons learned during the purification campaign.

INTRODUCTION

The LUX-ZEPLIN (LZ) detector is a xenon-based dark matter direct detection experiment located 4,850 feet (1,478 m) underground at the Sanford Underground Research Facility (SURF) in Lead, South Dakota [1]. The core of LZ is a dual-phase xenon time projection chamber (TPC) containing 10 tonnes of xenon with a 7-tonne active volume. External backgrounds in LZ are mitigated in a variety of ways, including various forms of shielding and a sophisticated outer detector veto system. Internal backgrounds due to radioactivity are more challenging to mitigate, and are largest contributor to electron recoil backgrounds in LZ [2]. While radon emanation from detector components contributes the majority of these backgrounds, trace radioactive contaminants within the xenon itself also play a significant role.

Xenon is isolated from the atmosphere via distillation, and contains traces of other noble elements as impurities, including the radioactive isotopes ^{85}Kr and ^{39}Ar. Being nearly inert, they are not removed during *in situ* purification by the hot zirconium getter, and their decays are not rejected by a fiducial volume cut due to their uniform distribution throughout the liquid xenon. ^{85}Kr is a beta emitter with a half-life of 10.8 years and an endpoint energy of 687 keV. It is an anthropogenic isotope, generated primarily by nuclear fuel reprocessing, and makes up roughly 10 parts-per-trillion (ppt, 10^{-12}) of atmospheric $^{\text{nat}}$Kr. The research grade xenon obtained for LZ contained an average of 5 parts-per-billion (ppb, 10^{-9}) $^{\text{nat}}$Kr by mass, with individual bottles ranging from 10 ppt to 100 ppb. To reduce the rate of electron recoil backgrounds from ^{85}Kr to a rate comparable to that of pp solar neutrinos, the mass-averaged $^{\text{nat}}$Kr concentration of the LZ xenon must be no more than 300 parts-per-quadrillion (ppq, 10^{-15}).

^{39}Ar, also a beta emitter, is produced by cosmic rays in the atmosphere primarily by the $^{40}\text{Ar} + \text{n} \rightarrow {}^{39}\text{Ar} + 2\text{n}$ process. It has an endpoint energy of 565 keV, a half-life of 269 years, and an isotopic abundance of about 1 ppq. The original research-grade xenon contained about 20 ppb $^{\text{nat}}$Ar on average, and we require the background contribution from ^{39}Ar to be no more than 10% of the ^{85}Kr rate. For a $^{\text{nat}}$Kr concentration of 300 ppq, this implies a limit of 9 ppb $^{\text{nat}}$Ar, much less stringent than the $^{\text{nat}}$Kr requirement due to the low isotopic abundance of ^{39}Ar. As explained below, this level of argon reduction is readily achieved in the process of krypton removal.

Gas charcoal chromatography

In the LZ krypton removal system, gas-phase chromatography is used to separate noble elements from one another based on their differing adsorption strengths onto activated charcoal. As noble gases flow through a charcoal column, they adsorb onto the charcoal due to van der Waals forces, which arise from small variations in the polarization of the

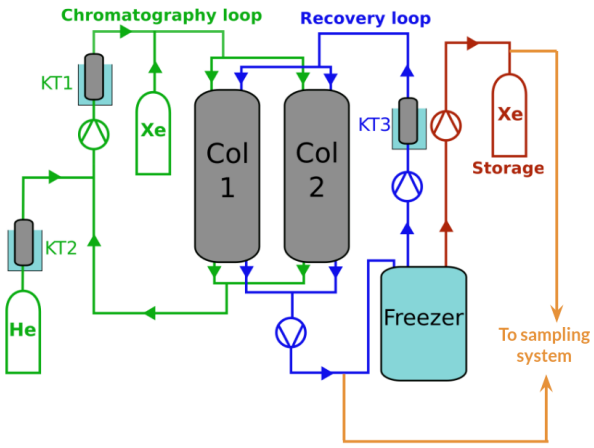

FIGURE 1: A block diagram of the krypton removal system, illustrating the three main subsystems and connection points to the sampling system.

atoms. These fluctuations induce image dipoles on the conductive surface of the charcoal, attracting the temporarily polarized atoms and causing them to adsorb onto the surface [3].

Because the polarization strength is directly related to the spatial extent of the electron cloud of the atom, the heavier noble gases are more strongly adsorbed. They spend a higher fraction of their time in the stationary (adsorbed) phase and thus will transit the charcoal column more slowly than lighter nobles, leading to separation of the different species. In the krypton removal process, the krypton traverses the charcoal column more quickly than the xenon and is discarded as it exits, leaving the purified xenon behind. In addition to krypton, other lighter noble gases such as argon are removed in this process. Helium, which interacts minimally with the charcoal, is used as a carrier gas, with a flow rate tuned to produce good separation between the krypton and xenon.

SYSTEM OVERVIEW

A block diagram of the LZ krypton removal system at SLAC is shown in Fig. 1. The system can be divided into three main subsystems: the chromatography loop, the recovery loop, and the storage system, each of which is described in more detail below.

Chromatography cycle

The chromatography process takes place within two cylindrical columns which are 4.3 m tall and 1 m in diameter, and contain roughly 400 kg of activated charcoal. The use of two columns enables parallel processing, in the sense that chromatography can take place in one column while purified xenon is being recovered from the other. Helium circulation in the chromatography loop is driven by a RIX piston compressor and controlled by a proportional control valve in a partial bypass loop. The column pressure is maintained at 1.35 bara, and typical helium flow rates are 600–1200 SLPM. The system is located in a semi-outdoor space, and the average velocities of krypton and xenon through the column depend strongly on ambient temperature. The flow rate is adjusted to compensate for this effect and maintain the duration of the chromatography cycle at about 3 hours for good separation with maximal processing efficiency.

To begin the chromatography cycle, a steady flow of circulating helium is established in the loop. 16 kg of unprocessed xenon is then fed into the top of the column at a rate of 145 SLPM from one of two feed stations, each of which connects to nine vendor-supplied cylinders. Because the feed is driven by cylinder pressure, xenon flow cannot be maintained once the pressure drops below about 2 bara. A cryopump consisting of seven 4 L bottles within a liquid nitrogen dewar is used to extract the remaining few kilograms of xenon from the vendor cylinders, which can then be

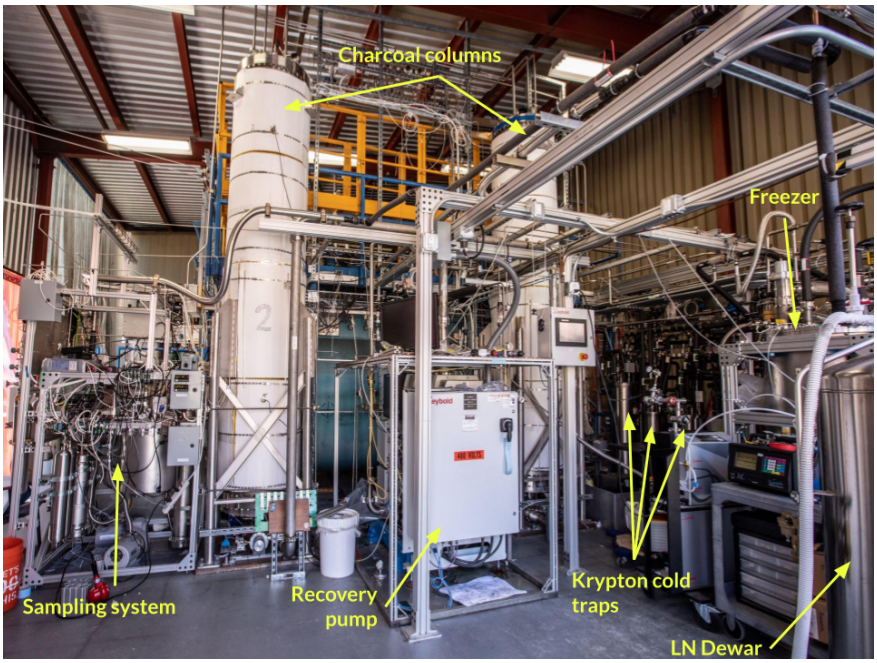

FIGURE 2: Physical layout of the krypton removal system at SLAC.

fed at high pressure in a subsequent run.

Throughout the chromatography cycle, krypton emerges from the column and is captured in a charcoal "krypton trap," called KT1. KT1 is a small column, 16.4 L in volume, containing 9.7 L charcoal topped with 6.7 L zeolite molecular sieve. The trap is cooled with liquid nitrogen to maximize retention of the captured krypton. Circulating helium enters KT1 from the top and first passes through the zeolite, where any trace air gas contamination is captured, and then passes into the charcoal layer where krypton carried from the chromatography column is adsorbed. The helium itself passes easily through the trap and continues to circulate. Two smaller krypton traps, containing 11.2 L of charcoal, are used elsewhere in the krypton removal system: KT2 removes potential contaminants from helium entering the system, and KT3 helps to maintain purity in the recovery loop.

During the chromatography cycle, the output of the column is monitored by a binary gas analyzer (BGA) manufactured by Stanford Research Systems (SRS) [4]. The BGA uses measurements of the temperature and sound speed in a mixture of two gases (in this case helium and xenon) to calculate the relative concentrations of each species. Fig. 3 shows the BGA measurement throughout one chromatography cycle. When the xenon concentration at the column outlet exceeds a set threshold (typically 2.5% xenon by mass), circulation in the chromatography loop is stopped and valves at the top and bottom of the column are closed. Properly timing the end of chromatography is important to prevent xenon from entering KT1, where it can form an ice plug or displace krypton from the charcoal and back into circulation. The detection method of the BGA makes it particularly well-suited for this application because of the large difference in mass, and thus sound speed, between helium and xenon. A residual gas analyzer (RGA) [5] is used as a backup method of xenon detection, using a CuSum change detection algorithm to combat noise in the RGA signal [6]. Fig. 4 shows a comparison between the two detection methods.

Recovery of purified xenon

When the chromatography cycle is complete, the purified xenon is recovered from the column by flushing with helium gas at a high volumetric flow rate [7]. The column pressure is maintained at 10–15 mbar, which gives a recovery time of 2.5–3 hours, depending on the ambient temperature. In parallel processing, the overall production rate is minimized when the recovery cycle is shorter than chromatography.

Circulation in the recovery loop is driven by a three-stage version of the Leybold DryVac DVR 5000 vacuum pump, consisting of a RUVAC WH 2500 roots blower [8] backed by two DV 650 screw pumps [9] in series. A KNF

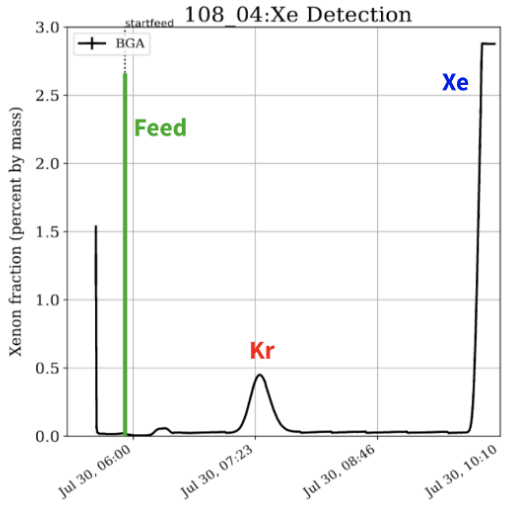

FIGURE 3: Data taken by the BGA throughout one chromatography cycle. This data was taken with high krypton content xenon (roughly 600 parts-per-million); the krypton peak is not normally visible in the BGA output. Because the BGA is calibrated to measure xenon fraction in helium, the krypton peak is not to scale.

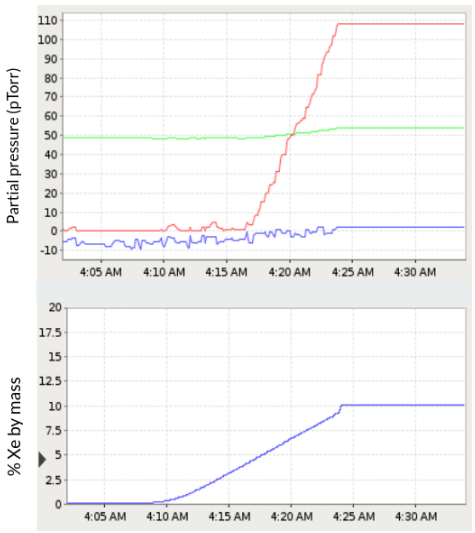

FIGURE 4: Comparison of the outputs of the RGA (top) and the BGA (bottom) at the end of chromatography. The RGA data shows the detected xenon level (blue), the calculated CuSum (red), and the threshold for ending chromatography (green). The BGA signal exhibits much lower noise and does not require a change detection algorithm.

diaphragm pump brings the column down to recovery pressure from 1.35 bara by transferring most of the helium to the other column, where it will be used in the next chromatography cycle. When circulation begins in the recovery loop, the KNF pump is bypassed, and a mass flow controller at the column inlet maintains a steady column pressure.

The circulating helium carries the purified xenon out of the column and into the freezer where it is collected. Inside the freezer, the helium-xenon stream travels through a series of finned aluminum plates with high surface area. Pressurized liquid nitrogen flowing through a thermally coupled copper line cools the plates to −185 °C (88 K). Xenon gas freezes out of the stream onto the cold plates, while helium exits through the bottom of the vessel. A photo of the freezer interior is shown in Fig. 5. About 250 kg of xenon ice can be collected in the freezer before ice deposited on the inlet or outlet tubes begins to restrict the flow.

A port at the outlet of the DVR connects to a 4 L bottle in the sampling system for purity analysis of the recovered xenon. Sampling the recovered xenon at different times throughout the cycle can be used to assess different potential sources of contamination. Samples taken at the very beginning of the recovery cycle capture the first xenon out of the column, providing insight into the effectiveness of the chromatography process. Krypton contamination in these early samples indicates incomplete separation from the xenon during chromatography. After a few minutes of recovery, all residual krypton from chromatography will be removed from the column, so samples taken later in the cycle are sensitive to contamination sources within the recovery loop, including the DVR itself.

One of the most significant challenges to preserving purity in the recovery loop is maintaining the cleanliness of the DVR. The pump has a specified maximum leak rate of 10^{-5} mbar·L/s, due to rubber seals on the pump body, but our purity requirements dictate no more than 10^{-8} mbar·L/s air ingress. The pump is housed in an acrylic box purged with nitrogen to reduce the potential for krypton contamination from air. Another potential source of contamination is the set of gearbox spaces of the pump, which contain oil for lubrication and are not fully isolated from the process space. Contaminants in the process space, such as krypton from an incomplete chromatography, can dissolve into the oil and then be released during subsequent recovery cycles. To combat this effect, we developed a technique for removing dissolved gases from the oil *in situ*, similar to sparging. By pumping on these spaces while the DVR is circulating, helium from the process space is drawn through the oil spaces at a high volumetric flow rate. Because the pump is running during this process, the gears churn the oil, exposing a large surface area to the flowing helium and drawing out dissolved gases. Typically only 10 minutes of pumping per gear space is needed to reestablish purity in the DVR after a contamination event.

The progress of recovery is monitored with an RGA via a capillary connection at the DVR outlet. Circulation in the

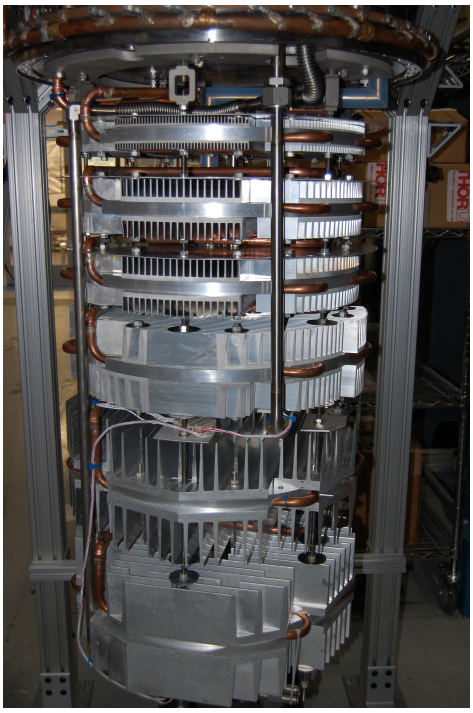

FIGURE 5: A photo of the freezer internals prior to installation, showing the finned aluminum plates for freezing xenon and the copper liquid nitrogen lines that provide cooling power.

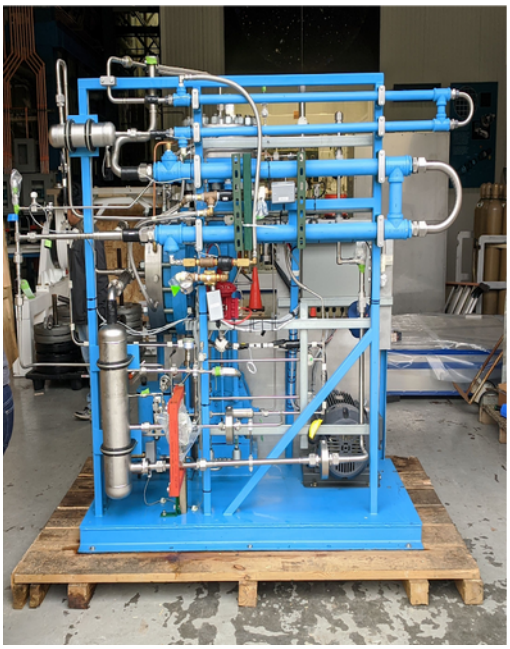

FIGURE 6: The Fluitron diaphragm compressor for xenon storage, shown prior to installation.

recovery loop is stopped either when 99% of the xenon has been recovered, or when the chromatography cycle in the other column ends, whichever comes later. Any residual xenon in the column is captured in KT1 in the subsequent chromatography cycle and later recovered when the trap is cleaned, making the overall process virtually loss free.

Storage

Once the freezer has been filled to near capacity ($\sim$250 kg) with xenon ice, preparation begins for the storing the xenon into cylinders. Before the xenon is warmed up to gas phase, the remaining helium in the freezer must be removed. As xenon freezes onto the freezer plates during recovery, small amounts of helium become entrained in the xenon ice. If this helium remains in the xenon when it is condensed into the LZ TPC, it can diffuse through the quartz windows of the PMTs and cause afterpulsing [10]. Based on an estimate of this diffusion rate, a safe limit for the helium concentration was set at no more than 200 ppb.

A helium concentration of about 1 part-per-million (ppm, 10^{-6}) can be achieved by pumping on the xenon ice with a turbopump for many hours. To further reduce the concentration to less than 200 ppb, the helium reduction process includes an intermediate step of liquefying the xenon. After about 90 minutes of pumping on the xenon ice, the freezer is warmed up just enough to induce a phase change. With the xenon liquefied, much of the embedded helium is released into the gas phase. The xenon is refrozen and then reopened to the turbopump for another 90 minutes of pumping. This method reduces the helium concentration to roughly 10 ppb.

After the helium removal, the xenon is warmed up again by cartridge heaters embedded in the aluminum plates. Additional heating power is provided by warm nitrogen gas flowing through the copper liquid nitrogen line. A Fluitron D1-20/120 two-stage metal diaphragm compressor, shown in Fig. 6, compresses the xenon gas into one of the storage packs, each of which contains twelve 49.1-L DOT-3AA-2400 cylinders. Twelve storage packs are required to contain the full 10-tonne xenon payload, with about 69 kg xenon per cylinder at a pressure of 65 bara. The storage packs are instrumented and equipped with a purge system to limit the inbound leak rate while empty, and additionally pumped to

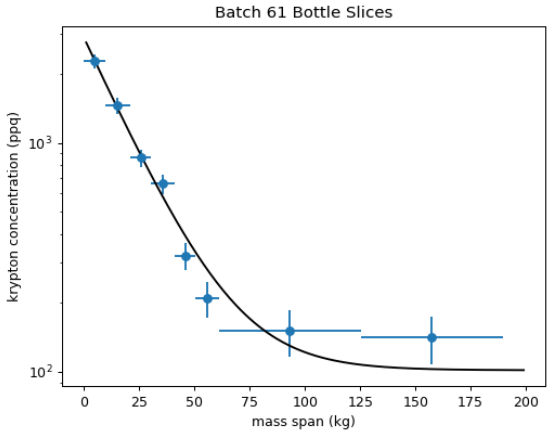

FIGURE 7: Krypton content of stored xenon versus cumulative mass stored, illustrating the effect of distillation during storage. Vertical error bars are errors on the measurement, and horizontal error bars denote the mass range from which the sample was drawn. The concentration exhibits an approximately exponential decay up to about 50 kg before leveling off at the limit of sensitivity of the sampling system.

high vacuum immediately prior to storage. More details about the design of the storage packs is available in [11]. The compressor is able to store xenon into the packs at a maximum rate of 200 SLPM, or about 1 kg/min. A connection from the storage packs to the sampling system allows each cylinder to later be individually assayed for krypton and helium content.

During the storage process, the xenon in the freezer exists in the liquid and gas phases. As the compressor removes xenon gas, the submerged plate heaters continuously warm the liquid to replenish the gas and maintain a pressure of 1.5 bara in the freezer. Because the krypton concentration is about 10 times greater in the gas phase than the liquid phase [12], the continuous removal and replenishment of the gas depletes the krypton content of the xenon remaining in the freezer, similar to a single stage of distillation. The krypton concentration versus cumulative mass stored follows a roughly exponential distribution, as shown in Fig. 7. This effect is used to separate the stored xenon into different cylinders based on purity. The xenon with the highest krypton content can later be reprocessed, if necessary, without reprocessing the entire batch.

Sampling system

Xenon samples taken during recovery and storage are assayed for krypton content and other impurities using a high-sensitivity sampling system [13]. The system utilizes a liquid nitrogen cold trap to separate impurities such as krypton from the bulk xenon before they are measured by an RGA. Xenon is slowly metered into the cold trap where it freezes onto the inner surface, leaving only a small amount of xenon vapor to emerge from the cold trap outlet. Impurities in the xenon largely remain in the gas phase, enriching the xenon vapor that exits the trap. While the RGA alone is sensitive to concentrations at roughly the ppm level, the cold trap sampler is sensitive to krypton concentrations down to 10 ppq. This technique is also used to determine the helium content of the xenon after storage.

AUTOMATION

Most aspects of the LZ krypton removal system are fully automated in order to maximize production rate and reduce operator burden. The chromatography and recovery cycles, xenon feed, transitions between column states, and preparation for storage are handled by a combination of a programmable logic controller (PLC) and Python software running on the slow control server. The system is capable of processing a full freezer batch, roughly 250 kg xenon, without human intervention for 2–3 days, swapping the columns between chromatography and recovery cycles every three hours and preparing for storage once the batch is complete. Xenon storage is the only process that requires a

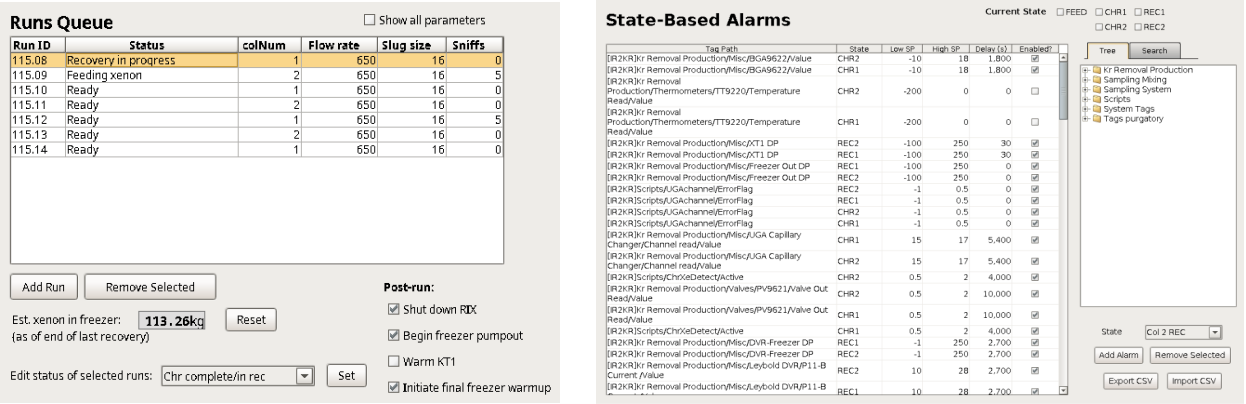

FIGURE 8: Screenshots of the Ignition user interfaces for run control (left) and state-based alarms (right).

human operator during normal operating conditions. Because it is the process with the highest potential for xenon loss, an operator is physically present whenever the storage compressor is in use.

The PLC handles low level operations such as operation of valves and sensor readout. All controls related to xenon and equipment safety are handled by interlocks in the PLC logic. Most individual, discrete processes are also handled by PLC routines. These include starting and maintaining circulation in the chromatography and recovery loops, feeding xenon at the beginning of chromatography, and transitioning the columns between chromatography and recovery. It is programmed to handle a wide variety of failure modes and to transition the system into a safe state in case of emergency.

Ignition, a supervisory control and data acquisition (SCADA) software package by Inductive Automation, provides a variety of higher-level functions for instrument control and readout, including a graphical user interface designer, an alarm system, and a historian for sensor data. The run control software, which facilitates longer term production, is built within the Python scripting framework in Ignition.

Individual processes controlled by the PLC are coordinated by the run control system. It initiates the beginning of chromatography, feed, recovery, and storage preparation with appropriate timing based on system conditions. It is also responsible for monitoring the column outlets during chromatography and recovery and ending these processes as required. Each batch of xenon fed into the system is tracked until it reaches the freezer during recovery. A graphical user interface, shown in Fig. 8, allows operators to queue up a sequence of runs with different parameters and displays the progress of each. The queue also allows xenon samples to be scheduled, and interfaces with the sampling system's automation software to automatically collect and measure each sample.

The run control system also contains a facility for dynamic, "state-based" alarms, built on top of Ignition's native alarm functionality. These allow different alarm levels to be defined for different system states, as a complement to static alarms on each sensor. Each alarm state also includes user-defined delays, to prevent triggering by transient effects at the beginning of a process. This dynamic alarm infrastructure provides an early warning for operators when abnormal conditions occur during operation.

Automation of the sampling system enables samples to be taken from the recovery loop on request from the run control software and then automatically prepared and measured. At the beginning of chromatography prior to a scheduled sample, the sample bottle is prepared by pumping out and freezing with liquid nitrogen. The system idles until the next recovery begins and then initiates collection, pumpout, warmup and measurement of the sample. Small dewars are raised and lowered on pneumatic actuators for faster freezing and warming of the sample bottle and cold trap. Multiple samples can be queued for collection and measurement from various locations in the system, allowing the sampler to operate continuously without human intervention until all queued measurements have been performed.

RESULTS AND CONCLUSION

The krypton removal system began full time production in January 2021. Processing and delivery to SURF of the full 10.4-tonne xenon payload was completed in August 2021, and the xenon was condensed into the detector in September. All 144 cylinders were assayed at SLAC prior to delivery, for a final mass-averaged purity of $123 \pm$

10 ppq g/g ^{nat}Kr/Xe, comfortably below our requirement of 300 ppq g/g. The on-site sampling system at SURF measured an average concentration of 115 ± 17 ppq in the bottles after delivery, demonstrating that there was no detectable contamination during transport. After condensing the xenon into the detector, where it was combined with residual xenon from circulation tests, the overall krypton concentration was estimated at 144 ± 22 ppq. This value was corroborated by measurements of the delayed coincidence beta-gamma decays of ^{85}Kr in the detector, and is consistent with the fitted background model used in the first science results from LZ. The measured ^{nat}Ar concentration is 890 ± 134 ppt, which implies a negligible ^{39}Ar background contribution (<1 event) in the first science run [14, 15].

The LZ krypton removal system has demonstrated gas charcoal chromatography as an effective xenon purification technique at the 10-tonne scale. The automation infrastructure developed for this system enables complex operations to run safely and efficiently with minimal human intervention. By meeting the purity target of <300 ppq krypton, the campaign has successfully mitigated a potentially significant source of electron recoil backgrounds. The low background levels in LZ have enabled the experiment to establish the most sensitive limits to date on the spin independent WIMP-nucleon scattering cross section [15].

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