

**OPERATIONS OF THE
AUTOMATED RADIOXENON SAMPLER/ ANALYZER - ARSA**

James C. Hayes, Keith H. Abel, Theodore W. Bowyer, Tom R. Heimbigner,
Mark E. Panisko, Paul L. Reeder,
Justin I. McIntyre, Robert C. Thompson, Lindsay C. Todd, Ray A. Warner
Pacific Northwest National Laboratory

Sponsored by U.S. Department of Energy
Office of Nonproliferation and National Security
Office of Research and Development
Contract No. DE-AC-76RL0-1830

ABSTRACT

The Automated Radioxenon Sampler/ Analyzer (ARSA), designed and built by Pacific Northwest National Laboratory (PNNL), for the Department of Energy, has exceeded measurement requirements for noble gas measurement systems established by the Comprehensive Nuclear-Test-Ban Treaty. Two units, one at PNNL and a second, sent to DME Corp. of Florida, were built and extensively tested. Both systems have successfully demonstrated stable xenon yields greater than 1.5 cm³ for an eight-hour collection period, corresponding to minimum detectable concentrations for ¹³³Xe on the order of 0.1 mBq/m³ three times per day. High stable xenon yields are critical in obtaining these low minimum detectable concentrations.

A history of testing and results that led to the high xenon yields of the ARSA system is presented. A compilation of field tests, laboratory tests and baseline tests that led to cost reduction, power savings and size reduction of the ARSA are also discussed. Lastly, the type of data generated from the ARSA of interest to data center personnel are discussed.

Key Words: noble gas, xenon, radionuclides, collection, ARSA, CTBT.

OBJECTIVES

The Automated Xenon Sampler/ Analyzer (ARSA) was designed and built by the Pacific Northwest National Laboratory with support and guidance from the Department of Energy's Comprehensive Nuclear-Test-Ban-Treaty (CTBT) Research and Development Office and called out by the CTBT for detecting and quantifying radioactive xenon, a key signature of a nuclear detonation. The function of the ARSA is to aid other international monitoring systems, hydroacoustic, infrasound and seismic, in determining if an explosion originated from a nuclear or a conventional detonation. As authorized by the CTBT for radionuclide monitoring systems, the ARSA detects ^{131m}Xe , ^{133}Xe , ^{133m}Xe as well as ^{135}Xe ¹. The minimum required detectable concentration (MDC) for ^{133}Xe was outlined by the CTBTO to be $< 1 \text{ mBq/m}^3$ for 24-hour samples. The ARSA has established the minimum detectable activity for ^{133}Xe near the level of 0.1 mBq/m^3 using a NaI(Tl)-based beta-gamma coincidence spectrometer for 8-hour samples, and hence meets the specifications called out by the CTBT by more than an order-of-magnitude. The spectrometer was designed at PNNL and subsequently the concept adopted and a spectrometer built at the FOA in Sweden to measure the energy-energy correlation distributions of low energy x-rays and gamma-rays emitted in coincidence with betas and conversion electrons for all the Xe isotopes listed above. The low MDC is achievable not only because of the low background counting but also in part due to the large quantity of stable Xe collected during the 8-hour sampling cycle. Two units built by PNNL have consistently collected and isolated 1.5 cc of stable Xe from an 8-hour cycle resulting in the impressive Xe collection figure of merit 0.1875 cc/hr.

ARSA Operations

The ARSA operates on three basic principles, (1) Xe collection (2) Xe purification and (3) Xe quantification (see figure 1). The Xe collection and purification processes are based on adsorption of Xe onto an adsorbent (charcoal) held at cryogenic temperatures. During the 8-hour Xe collection phase, 48 m^3 of compressed atmospheric gas is driven through a set of pressure swing dryers that entrap and eliminate CO_2 and water vapor from the process stream. The dry air is then driven through an air chiller that cools the air to less than -110°C . The cold air is in turn used to self-cool a radon trap (PreRT) to less than -95°C , and is then used to self-cool a larger main charcoal trap (MCT) to less than -90°C . The gas that passes through the PreRT, including the Xe, is stripped of radon, exits the trap and directed through the MCT. Xenon is then collected on the cold charcoal within the MCT. During collection of Xe, other atmospheric gases also adsorb on the charcoal. At -90°C , however, only small amounts of O_2 , N_2 , Ar, CH_4 , Kr, and CO and even less He, H_2 and Ne remain on the charcoal of the MCT after collection. To eliminate the residual atmospheric gases that do collect on the MCT, vacuum is applied to the cold MCT for approximately 1-hour. Additional cooling occurs in the MCT when vacuum is applied due to the reduction of pressure in the trap and from the heat of evaporation of the condensed gases as they evaporate from the charcoal. The temperature drops from -90°C to less than -110°C and subsequently begins to warm. At the end of the vacuum step the temperature of the charcoal in the MCT is less than -80°C . This vacuum technique is effective in removing most of the aforementioned atmospheric gases while leaving the Xe on the trap. Removal of atmospheric gases prior to chemical and cryogenic manipulation is critical not only for optimization of chemical separation but also for quantification of Xe since these gases interfere with transport and composition gas measurements.

The collection efficiency of the adsorbent depends on the vapor pressure of Xe at the collection temperature in relation to the partial pressure of Xe in the gas stream². The resulting collection efficiency is improved by either lowering the temperature of the collection adsorbent or by increasing the partial pressure of the gas to be collected, in this case Xe. The collection traps temperatures are based on the output temperature of the chiller. An output temperature of -110°C results in the charcoal trap temperatures of nominally -90°C . Since the temperature of the traps are as low as the cooling system can maintain, the partial pressure of Xe must be increased to effect the collection efficiency of Xe on the adsorbent. An equally important function of the vacuum step is the removal of oxygen from the MCT as heat is applied to the MCT during the purification phase of operation.

In order to increase the vapor pressure of Xe in the gas stream and reduce competition for adsorption sites on the charcoal, the ARSA was designed to remove the interfering atmospheric gases during the Xe collection phase of operation. Some small amount of radon, however, can pass through the PreRT and collect on the MCT. Also, CO₂ can be present on the charcoal from the collection phase or can be introduced into the gas process stream during the Xe purification phase from a gas leak in the system. Cautionary steps have been taken for assurance that neither gas makes its way through the purification phase. After vacuum has been applied to the MCT, it is externally heated to 175° C. To elute Xe from the charcoal, nitrogen (240 cc/ min, >99 % purity) is passed through the heated charcoal for 180 min. After exiting the MCT, the nitrogen stream is passed through a trap filled with decarbite (a NaOH based chemical), the only expendable chemical in the system, to remove any remaining CO₂. The process stream is then routed through a post radon trap (PRT). The PRT is a second radon trap filled with 1/8", 5Å molecular sieve and is thermostatically cooled to a temperature in the range of -50° C by opening and closing a valve from the cold waste gas stream that exits the collecting MCT into a cooling loop inside the PRT. At this point in the process, the gas stream is primarily nitrogen and Xe. The gas is then passed through a final charcoal trap (FCT) that contains approximately 0.5 g of charcoal. The FCT is cooled externally to less than -95° C from the process gas stream as it exits the chiller. Elution of Xe from the MCT has been timed to insure all of the Xe has been removed from the MCT. After 180 min of Xe concentration onto the FCT, vacuum is applied to the trap to remove most of the nitrogen. The MCT could not be cooled while vacuum is applied since the trap is cooled by the gas process stream as it flows through the trap. Cooling of the FCT, however, is maintained during the entire vacuum step.

Sample transfer from the FCT to the counting cell is accomplished by heating the FCT to 275° C then volumetrically expanding the gas into a detector cell. Recently we have experimented with the use of a syringe transfer pump to recover the sample that remains in the FCT after the expansion step, see below. Once in the cell, the gas is counted for 24 hours. After a 24-hour count in the nuclear detector system, the gas is volumetrically expanded into a calibrated volume where the quantity of Xe is determined with a thermal conductivity detector (TCD).

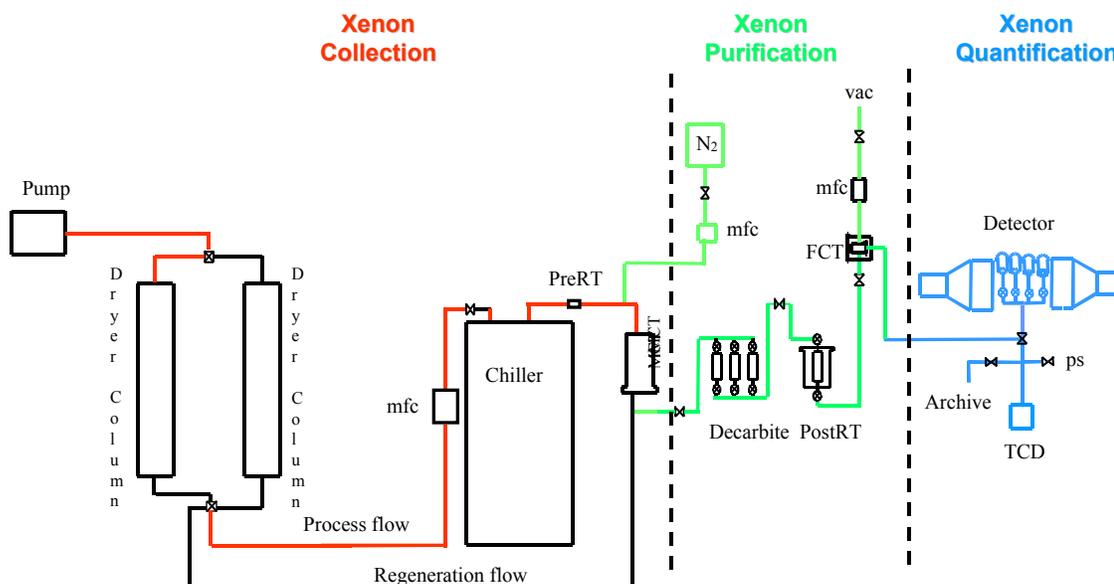


Figure 1. Simplified flow schematic depicting Xe collection, Xe Purification and Xe Quantification.

The objectives of the experimentation described herein were to optimize the operating efficiency of a functional ARSA unit for the end purpose of increasing the stable Xe yield. Although the ARSA is heralded for the low MDC, a measure of the nuclear detector, the yield of stable Xe not only indicates how well the system operates, but also assists in lowering the MDC of the system. The MDC of the nuclear detector is proportional to the volume of Xe and inversely proportional to the square-root of the background, and therefore, an increase in the Xe yield has a large impact towards lowering the MDC of the ARSA system. In order to optimize the Xe yield, we recently concentrated on two areas. First was removal of CO₂ from the gas stream in order to eliminate flow obstructions (due to CO₂ freezing in the lines), reduce the amount of decarbite used in the system and to reduce interference during quantification of stable Xe. Second was to increase the transfer efficiency of the gas from the FCT to the detector cell using a transfer pump. We also report on the quantification of stable Xe using a TCD.

RESEARCH ACCOMPLISHED

Pressure Swing Dryers

Since water vapor and carbon dioxide are the major adsorption interference of Xe on activated charcoal, they are the most important to remove from the gas stream prior to cryogenic collection. The atmospheric abundance of CO₂ is nominally 300 to 500 ppmv. With a relatively high sublimation temperature of -79° C, up to 2.4 m³ of CO₂ can adsorb on the -90° C main charcoal trap during an 8-hour collection cycle. Although charcoal has a large surface area, the adsorption capacity of Xe on charcoal is diminished from atmospheric levels of CO₂ competitively adsorbing on the charcoal. It is postulated that CO₂ and water vapor bond to the charcoal by Van der Waals forces³. In addition, water bonds to an available oxygen atom

on the surface of the charcoal via hydrogen bonding. Additional water molecules then bond to the bonded water molecule, again by hydrogen bonding, causing microscopic liquefaction to occur at the surface of the charcoal. When enough water and CO₂ bond to the surface of the charcoal through repeat of these mechanisms, the micro-capillaries within the charcoal become blocked. Blockage of the capillaries results in reduction of the vast surface area within the matrices of capillaries and pores in the charcoal such that Xe adsorption becomes greatly reduced. Additionally, the ARSA operates at temperatures low enough to freeze CO₂ in the chiller lines and the transfer lines between traps. If CO₂ freezes in the process lines, flow to the traps will be reduced and eventually will stop, resulting in automatic shutdown of the system⁴. Additionally, if high enough concentrations of CO₂ reach the TCD, the calculated Xe yield will be impacted. The effect of CO₂ in the TCD will be discussed below.

While several variations of dryers that both remove water and CO₂ have been constructed and tested, the most successful to date have been pressure swing regenerative dryers. Pressure swing dryers consist of two drying columns operating in tandem. A high-pressure stream of gas flowing through the column removes water vapor and CO₂ while a low-pressure stream of waste-dry air that exits the MCT flowing through the second column, regenerates the adsorbent.

Two different adsorbents were tested within the drying columns. In the first test system, mixed columns of 13X molecular sieve and activated aluminum oxide (alumina) were used. Generally, low CO₂ levels and low dew points were obtained from operating conditions of 100 slpm and 100-psig (700 kPa) as observed by dew point sensor and gas chromatography/ TCD (GC/ TCD) analyses. The CO₂ level was determined from the dryer outputs to exceed 2 ppmv, however, a total of 96 cc of CO₂ was collected on the MCT during 8-hour runs. To eliminate all of the CO₂ in the gas stream after the MCT, the stream was passed through a decarbite trap prior to collection on the final charcoal trap. The regeneration of the dryer columns required heating the columns to nominally 400° C for several hours with a flow of CO₂-free air. The heat given off to the room and the power consumption (a few hundred Watts) from the dryers made regenerative heating prohibitive. The molecular sieve columns were field tested at the Environmental Measurements Laboratory (EML) on the ARSA system⁵. During these tests, dryer reliability was problematic, as was high CO₂ levels in the counting cell. Xenon yields at EML were on the order of 1.0 to 1.2 cc for an 8-hour run.

An improved version of the pressure swing regenerative dryers using pure alumina as the adsorbent was then tested. This configuration provided superior CO₂ removal and eliminated the need for heating to regenerate the adsorbent. The operation, however, was the same as described above for a pressure swing dryer. The CO₂ levels from the exit of the dryers were below 1 ppmv, and in fact could not be observed in the TCD response of a calibrated GC/TCD used independently for analyzing the air stream composition (see below). Figure 2 shows the CO₂ concentration in the final gas product from Xe samples collected from automated running of the ARSA at PNNL during the latter part of June, 1999. The low concentrations of the CO₂ levels observed were indicative of the dryer performance.

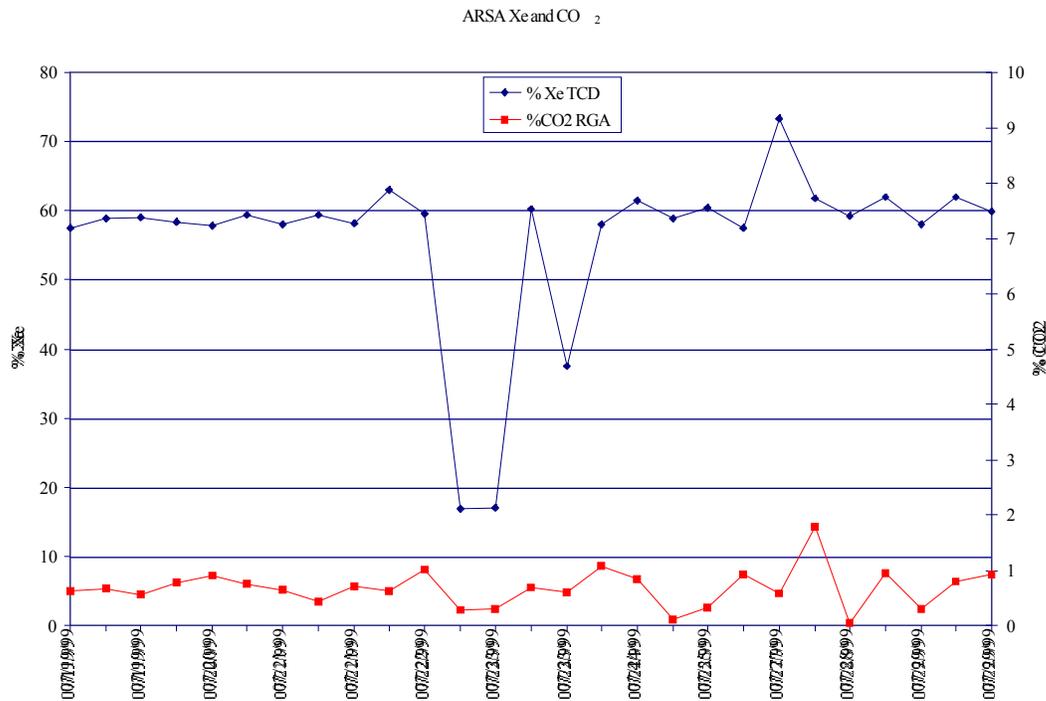


Figure 2. Xenon and CO₂ levels for ARSA final gas samples obtained from operating condition for the dates between 7/19/99 and 7/29/99. Carbon dioxide below the 1% levels are typical.

The method for analyzing the CO₂ was created in the Vapor Analytical Laboratory at PNNL⁶. Passivated SUMMATM canisters (850 cc) were utilized for sample collection. Aliquots of the collected vapor were analyzed using a GC/TCD. The analytes were identified by matching the sample peak retention time with that of a traceable gas standard mixture. The instrument was calibrated at five different concentrations for CO₂ over a range of 17 to 2100 ppmv. An average response factor from the calibration was used for quantification. Quality control objectives were achieved using both initial and continuing calibration verifications. Blank samples were run to detect the presence of any contamination and carryover. Samples were collected at the beginning and end of each pressure swing cycle and cycle times were varied from 5 to 10 min.

The dryer testing was conducted using the dryer columns that were attached to an operating ARSA. Gas was collected from the gas stream that originated after the process air had been dried and scrubbed of CO₂, and was collected into the SUMMA canisters. After the sample was collected, the SUMMA canister was connected to a gas manifold that contained a sample port, a pressure sensor, an inert gas line and a vacuum port. The sample valve was opened to the evacuated gas manifold and a pressure reading of the sample was obtained. The pressure in the SUMMA canister was adjusted to approximately 1400 torr, using vacuum for high-pressure samples, or by dilution with ultra-high purity nitrogen for samples that were less than atmospheric pressure. A 5-cc aliquot was drawn out of the pressure-adjusted SUMMA canister using a valved gas-tight syringe. The sample was then injected into a 1-cc sample loop on a HP 5980 GC/TCD. The 1-cc sample loop is open on both ends to allow for excess sample from the 5-cc syringe to flush the loop. The sample was then directed from the 1 cc sample loop to a fused silica precolumn, via a 6-port valve, where heavy components (organics) are removed from the gas stream. The remaining gas was passed onto a GS-Q column where CO₂ is retained. Using a two-valve system on the GC, the samples are eluted and measured with an on-board TCD.

Transfer Pump

Transfer of Xe from the FCT to the nuclear detector cell in the ARSA system was accomplished by simple volumetric expansion of the gas that collected on the charcoal to an evacuated cell that is part of the nuclear counting system (see elsewhere in these proceedings⁷). The final charcoal trap is heated to 275° C for several minutes until the trap is completely heated then three valves are opened to allow the hot gas to expand into the transfer tubing and into the cell. The cell volume is 6.4 cc, the volume of the transfer tubing is 1.8 cc, and the FCT filled with charcoal has an estimated 1.5 cc volume. It was determined through liquid nitrogen collection of the gas from the FCT that 35% of the sample was left in the lines and the FCT. Addition of a syringe transfer pump to aid in the transfer of the Xe from the FCT into the cells has increased the Xe yield over 25 %. As shown in figure 3, after addition of the syringe transfer pump, the Xe yield in the cell increased from nominally 1.4 to 1.5 cc to near 2.0 cc resulting in an improved figure of merit 0.25.

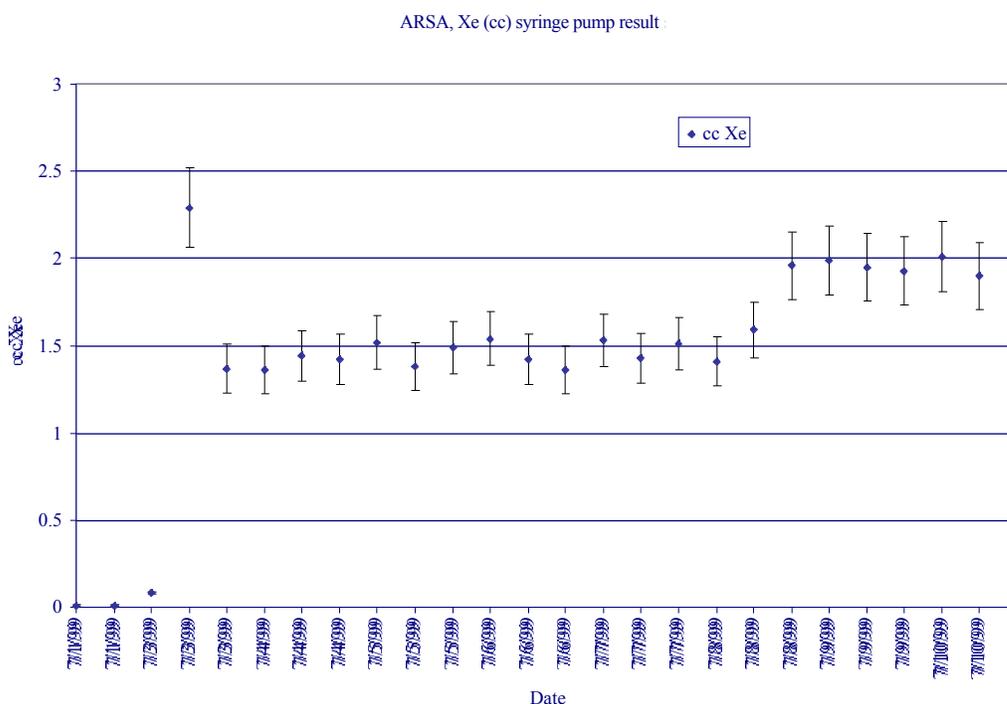


Figure 3. Stable Xe yields for the month of July. The increase in yield on the 9th was due to addition of a syringe transfer pump.

The transfer pump was operational on July 8, 1999, however, the stable Xe results in an operating ARSA are not determined until 24 hours after the transfer. Therefore, the results for the transfer on the 8th are determined on the 9th. The Xe yields that are low, less than 1 cc, and high, up to 5 cc, can be typical for a startup of the ARSA. The yields during the startup state depend on the system state just prior to the system shutting down and the time when the system is started. In order to achieve 100% duty cycle, the ARSA was designed with duplicate collection moieties and a partial duplicate purification train. This arrangement allows the system to collect gas on a MCT for a chosen time on one moiety while the other moiety (a duplicate MCT) proceeds with purification and quantification. The low yields that result from the startup are due to the ARSA software control program starting the purification process on one side and the collection process on the other. The MCT from the initial purification process does not have any collected gas on the trap resulting in a low, or no Xe yield (figure 3). Conversely, during the initial collection, the software that controls the gas processing is designed to wait for a time synchronization to allow the three daily samples to be processed and recorded at the same time each day. The control program enters a wait

state until 2:00, 10:00 or 18:00 GMT (or other programmable time) depending on when the system finishes the first cycle of the control program. The wait state often will create a situation where the collecting MCT may collect gas for up to 16 hours. The extended collection times are evident in a high Xe yield on the first cycle after a system restart (see Xe > 2.3 cc in figure 3.)

Considering the effect on the Xe yield of the extended collection time, we ran experiments collecting gas on one main charcoal trap for up to 4 days, continuously and intermittently. The results (figure 4) are even more pronounced than the startup collection shown in figure 3. The results of our extended collection studies show some yields near 5 cc of Xe. The yields at 4.2, 5.2 and 4.8 cc were from extended runs over a minimum of 4 days. Although these yields were not obtained in an 8-hour collection cycle, we are confident that the ARSA traps are sized large enough so an increase in flow rate will have similar effects on the Xe yield for an 8-hour cycle. We are also confident that the capacity of the final charcoal trap (FCT) is over-sized for 8-hour collections.

The results throughout the time frame shown in figure 4 represent an extended testing period. Often the ARSA was shut down for testing or upgrade of both software and hardware, or occasionally shutdown from hardware failures. The shutdowns are indicated, as described above, as a low yield (typically < 0.6 cc) followed by a high yield (typically > 2.5 cc). The low yields from 6/16/99 to 6/21/99 were due to a leak in the transferline caused during construction of the transfer pump. Time frames where the yields were stable for more than three or four days were results from typical stable ARSA operation. It should also be noted that up to 7/99 the ARSA ran on 60 Hz power. After 7/1/99 and until 7/18/99 the ARSA ran on 50 Hz power to test the system for world-wide power compatibility. As shown in figure 2, the Xe yields were averaging 1.6 to 1.7 cc until the system was converted to 50 Hz. After the conversion, the yields dropped to around 1.4 to 1.5 cc (operating without the transfer pump). After 7/18/99, the gas-processing portion of the ARSA was converted back to 60 Hz. The results are evident in the Xe yields as they surpassed the 2.3-cc mark. Several factors may aid to the increased yield when the system is run at 60 Hz. It was clearly evident that the output of the chiller had raised from -113°C to -110°C . The effect of the warmer chiller output air was also observed in the trap temperatures. The cooling of the PreRT, the MCT, and the FCT was increased at least 5°C . The effect of the temperature increase may not, however, explain the decreased in Xe yield when the system is run at 50 Hz. During the Xe collection phase we pull vacuum on the MCT as described earlier. Changing from 60 to 50 Hz may decrease the vacuum power enough to effect the removal of interfering gases.

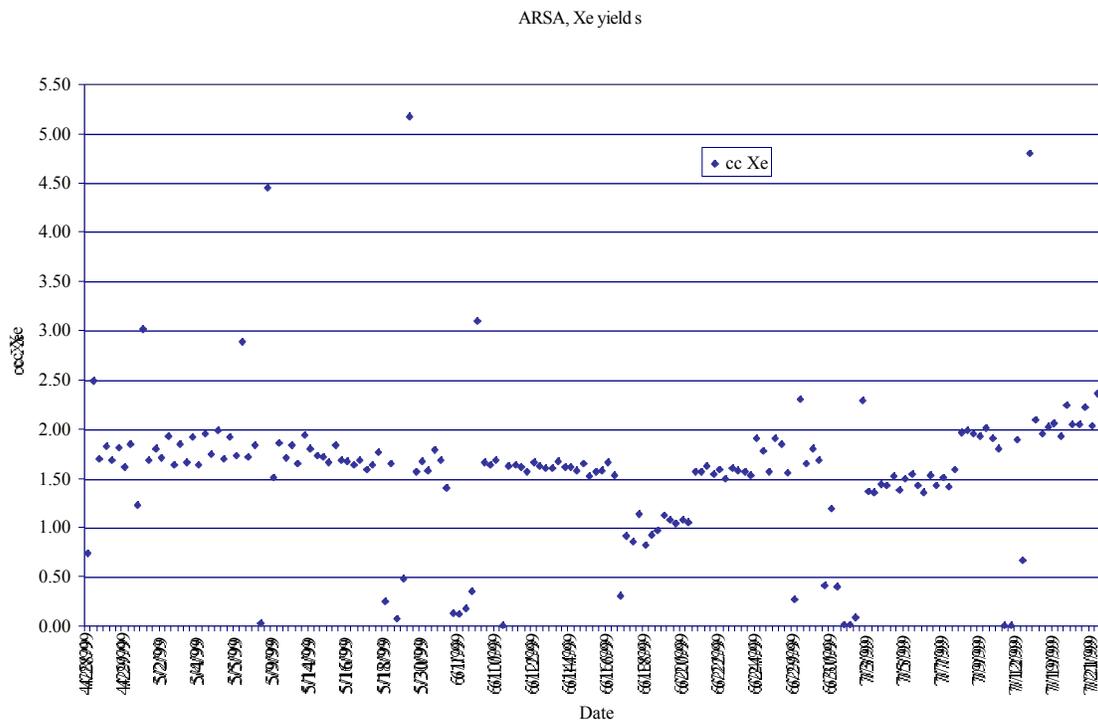


Figure 4. Xe yields (cc Xe) for the months of 4/99 through 7/99.

Thermal Conductivity Detector (TCD)

The TCD is the tool chosen to analyze the composition of gas for the ARSA for several reasons. First, the TCD is relatively inexpensive compared to other methods such as a residual gas analyzer (RGA) - a mass spectrometer used in the first ARSA system field tested at EML⁵. Second, the TCD is small, and uses far less power compared to other measurement systems. The final reason is the long-term stability of the TCD unit. The thermal conductivity detector is calibrated for 0 to 100 % Xe in nitrogen and comes as a commercial-off-the-shelf instrument. The stable Xe yield is then calculated from the percent Xe, pressure and the analyze volume. The thermal conductivity detector has recently been modified to include a non-dispersive infrared detector (NDIR) to detect CO₂ in the Xe/ N₂ gas mixture and is currently being tested in the ARSA. Using the CO₂ monitor, we will be able to determine when the decarbide trap is spent or when the dryers are not functioning. Currently, the ARSA's operation is so stable that CO₂ is not expected to interfere appreciably with stable Xe measurements even without decarbide, unless there are severe problems with the operation of the dryers.

The calibration of the TCD was verified within the ARSA system at varying pressures as shown in figure 5. To verify the calibration, the TCD was connected to the gas analysis volume and a detector cell then evacuated to 20 mbar. Xenon (40% in N₂) was expanded into the evacuated cell and a calibrated analyze volume to the desired pressure. The pressure and TCD reading were recorded then the valve between the cell and the TCD was closed and the analyze volume was again evacuated. The contents of the cell were expanded into the analyze volume and the pressure and TCD values were recorded. This procedure was repeated until the pressure was below 90 torr. The data in figure 5 indicates accurate, short-term stable operation of the TCD for various pressures.

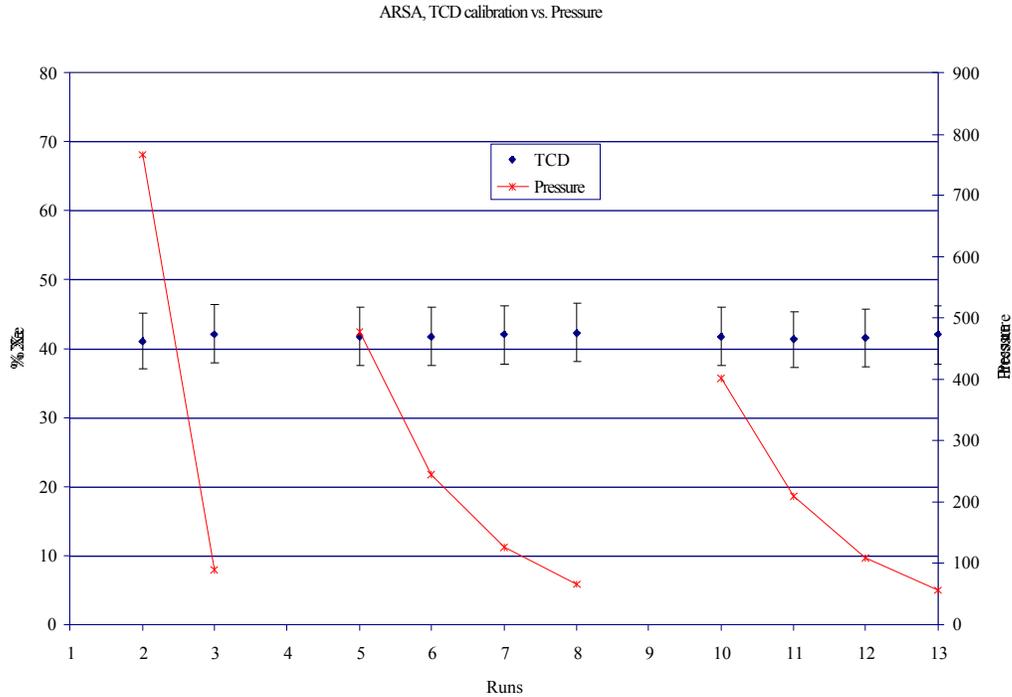


Figure 5. Thermal conductivity detector calibration verification with varying pressure. Readings were recorded from a TCD that was connected to an operating ARSA. Error bars are $\pm 10\%$ relative error.

The ARSA field model that was tested at EML used an RGA for determining Xe yield. The advantage of an RGA over the TCD is that the gas analyses included all of the atmospheric gases. As mentioned earlier, CO_2 breakthrough was problematic at EML. It was necessary to analyze the entire mixture of gas to determine how much of the mixture was Xe using an RGA. The technique used at EML for gas analysis with the RGA was well established and was used on the ARSA at PNNL to verify the TCD readings of actual gas samples. Figure 6 shows the TCD and RGA readings from 7/19/99 through 7/29/99. The RGA was calibrated using a gas standard that included Xe, Kr, CO_2 , CO and N_2 (all nominally 3%) in a balance of Ar. The calibration was verified using the same Xe (40%) in N_2 standard that was used to verify the TCD calibration. The RGA spectrum was run concurrently with the TCD during normal operating conditions.

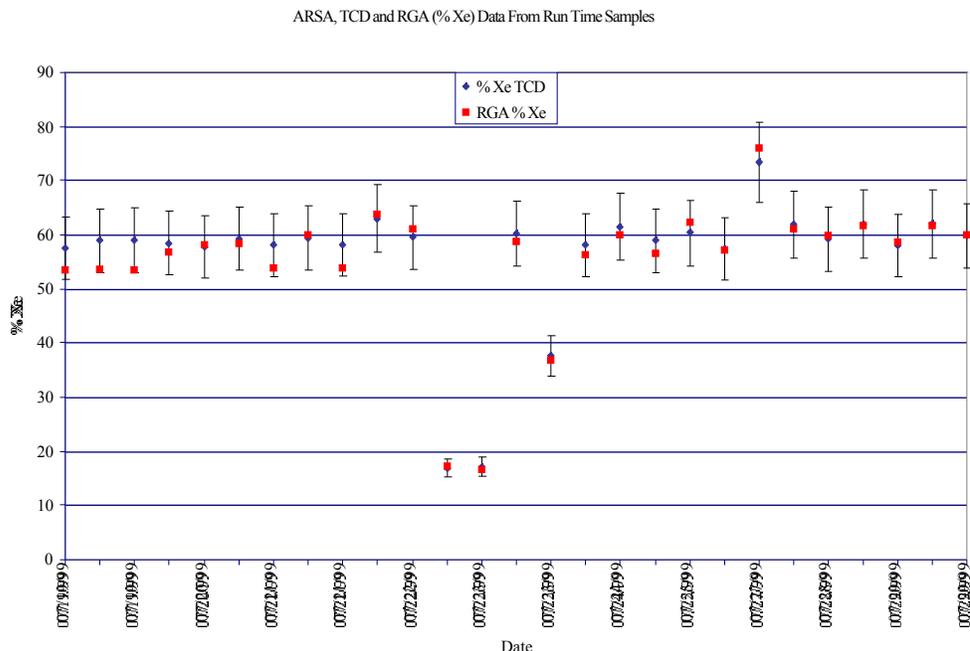


Figure 6. Thermal conductivity detector and residual gas analyzer readings for ARSA samples during typical operation. Error bars are $\pm 10\%$ relative error.

CONCLUSIONS AND RECOMMENDATIONS

Although the ARSA prototypes have been in functional for over a year, we are continuing to enhance the operation processes, add QA/QC checks and determine long term failure modes. We have achieved near complete removal of CO_2 and water from the gas process stream using pressure swing dryers. An added benefit to improving the dryer technology was power savings and increased reliability. Addition of the transfer pump has increased the transfer efficiency by 25% of the sample from the FCT to the detector cell. Additional testing to improve the pump efficiency is planned. The TCD analyzer has proven to be robust and reliable with the added benefit of a cost reduction of an ARSA unit by approximately \$20,000.

The significance of the data presented in this paper, however, reaches beyond simply testing components of the ARSA. We have not only presented tests that increase the operation efficiency of the ARSA through experimentation, we have also presented results that typify the quality of data that is obtained from a PNNL ARSA.

REFERENCES

- (1) Reeder, P., T. Bowyer, K. Abel, C. Hubbard, M. Panisko, R. Thompson, R. Warner, "Observation of ^{135}Xe with the PNNL ARSA System, PNNL-11654", August 1997.
- (2) Scarpitta Charles, S., Harley, Naomi H., "Adsorption and desorption of Noble Gases on Activated Charcoal: I. ^{133}Xe Studies in a Monolayer and Packed Bed", *Health Physics*, **Vol 59**, No. 4 (October 1990), pp.383-392.
- (3) Underhill, D.W., "The adsorption of Argon, Krypton and Xenon on Activated Charcoal", *Health Physics*, **Vol 71**, No. 2 (August 1996), pp. 160-166.

- (4) Abel, K.H., T.R. Heimbigner, T.W. Bowyer, M.E. Panisko, "ARSA Safety Systems", PNNL internal report PNNL-2142, February 1999.
- (5) Bowyer, T.W., K.H. Abel, C.W. Hubbard, M.E. Panisko, P.L. Reeder, R.C. Thompson, R.A. Warner, "Field Collection and Measurement of Radioxenon for the Comprehensive Test Ban Treaty", *Journal of Radioanalytical and Nuclear Chemistry* **Vol 240**, No 1 (1999).
- (6) PNNL. 1996. *Analysis Method for the Determination of Permanent Gases in Hanford Waste Tank Vapor Samples Collected in SUMMATM Passivated Stainless Steel Canisters*, PNL-TVP-05 Rev. 2, Pacific Northwest National Laboratory, Richland, Washington.
- (7) Ted W. Bowyer, Justin I. McIntyre, and Paul L. Reeder, "High Sensitivity Detection of Xe Isotopes via Beta-Gamma Coincidence Counting", 21st Seismic Research Symposium: Technologies for Monitoring The Comprehensive Nuclear-Test-Ban, In Print.