INL/MIS-21-63667-Revision-0

Novel Methods to Produce an Argon-37 Standard

August 2021

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Project Tracking Number: 18A12-076
Project Title: Novel Methods to Produce an Argon-37 Standard
Principal Investigator: Edna Cárdenas Directorate: D Division: 210
Co-Investigators: Troy Robinson, Mathew Snow, Jessica Ward, Jacob Brookhart, Brian Bucher, Ari Foley
Directorate: D Division: 210
NUC/CAES/Other-Co-Investigator(s): J. Stoner Institution: IAC ORCID: 0000-0002-2107-5699
Initiative: CIP Investigative Technologies for Nonproliferation and Nuclear Forensics 3.1.3.1

Budget Summary (only if different from original proposal)**:**

Year	Fiscal Year	Funding Source	Budget (dollars)
Year-1		**LDRD**	**$174,000**
		NUC	
		CAES	
		Other (Industry/university)	
Year-2		**LDRD**	**$206,000**
		NUC	
		CAES	
		Other (Industry/university)	
Year-3		**LDRD**	**$189,250**
		NUC	
		CAES	
		Other (Industry/university)	
Year-4		**LDRD**	**$16,900**
Total Budget Request			**$586,150**

General Project Description for Public Release:
The purpose of this research was to produce a measurable quantity of radioactive argon-37 (^{37}Ar) through photonuclear production methods. The detection of ^{37}Ar, above background levels, uniquely and clearly indicates the underground detonation of a nuclear device. Fission neutrons generated from a nuclear blast interact with calcium, present in rocks and soil in the underground environment. [1] [2] [3] The interaction of these fission neutrons with calcium-40 (^{40}Ca) produces ^{37}Ar, through a ^{40}Ca(neutron, alpha)^{37}Ar reaction. The gas then seeps through the underground environment to the surface for detection by on-site inspectors. Inspections are performed to aid in the regulation of nuclear non-proliferation treaties such as the Comprehensive Nuclear-Test-Ban treaty. Due to a half-life of approximately 35 days, detection is possible long after the detonation, making its identification valuable during on-site inspections. Successful production of ^{37}Ar on a small scale would provide proof of principle leading to opportunities for yet-to-be realized large scale sample production. An ^{37}Ar standard would give on-site inspectors the ability to calibrate their detectors and measure detector efficiency thus providing higher accuracy in quantifying detected ^{37}Ar. An ^{37}Ar standard would also provide authentic samples to test novel detectors and improve models predicting the diffusion of ^{37}Ar in an underground environment.

Current research into the production of ^{37}Ar utilizes neutrons generated from nuclear reactors on samples containing ^{40}Ca. This research proposes photonuclear production of ^{37}Ar through photon bombardment on potassium-39 (^{39}K), ^{40}Ca, and ^{38}Ar using electron linear accelerators (LINACs). LINACs are more readily available than nuclear reactors utilized for experiments and have a wide range of power output, allowing for the optimization of ^{37}Ar production and potentially providing an alternative production pathway. Figure 1 displays the probability of reaction i.e., the reaction cross sections for the proposed photonuclear pathways. Figure 1b shows the reaction cross sections weighted by the isotopic abundance providing a clearer picture of the production probability in unenriched samples. If all parameters are constant and unenriched irradiation samples are used, the largest production outcome would come from irradiating ^{39}K as shown in Figure 1b (for an electron beam with energies beyond the energy thresholds of the reactions). However, the reaction cross sections for ^{39}K have not been evaluated experimentally, thus not included in the Evaluated Nuclear Data File (ENDF), therefore, determining the most effective production pathway must be explored experimentally. [4] [5]

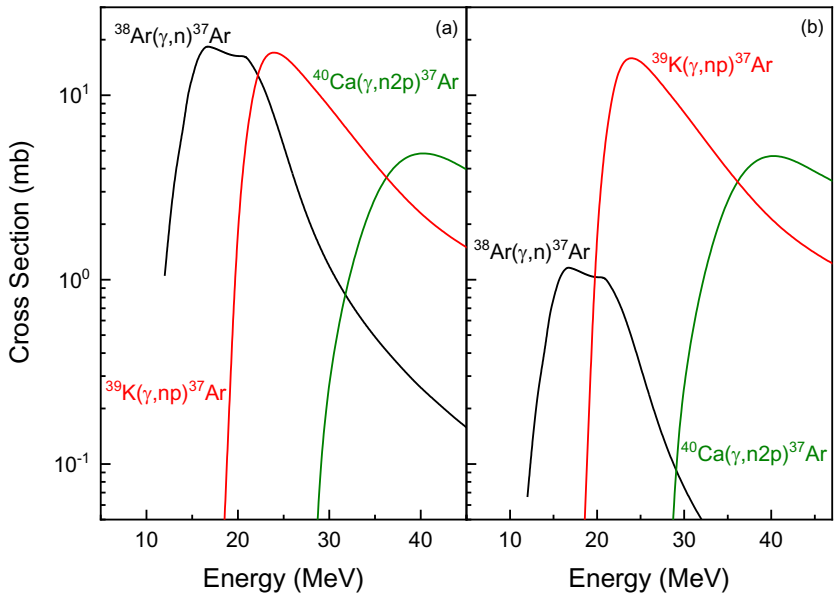

Figure 1 Reaction cross sections for the three ^{37}Ar photonuclear pathways. [4] [5] The absolute cross sections in (a) are compared with the cross sections weighted by the natural isotopic abundance in (b) to show the reaction probability from irradiating unenriched samples.

The research team, in collaboration with staff at the Idaho Accelerator Center (IAC), completed a wide variety of tasks that have led to the success of this project. The team fabricated a custom-built detection chamber designed to fit commercial Amptek SDD X123 silicon drift detectors and hold our radioactive gas samples. Samples irradiated on the 25 MeV LINAC at the IAC, required design of a sample holder that would not only hold the sample, but also ensure the produced gas would not escape containment. It was also necessary that the holder be fabricated so that the gas could be transferred into our custom-built gas manifold for processing. We successfully fabricated flame-sealed quartz holders that allowed for gas transfer into our vacuum sealed manifold. In addition to these requirements, it was necessary that targets irradiated on the high-power LINAC at the IAC were designed to withstand high temperatures imparted by high-energy electrons. These custom-built holders allowed us to successfully irradiate KCl samples on the lower power accelerator and ultra-pure argon (UPA) and calcium chloride ($CaCl_2$) samples on the high-power LINAC. The UPA sample required an aluminum gas irradiation vessel that was fitted to a custom-built gas transfer manifold that was attached to our detection chamber. The $CaCl_2$ samples required fabrication of a leak proof quartz vessel contained in an aluminum thermal conductor. Furthermore, the team successfully developed a gas extraction method that was demonstrated on an irradiated KCl sample. In addition, the team developed a method to estimate detector efficiency and determine sample self-attenuation. These experiments, conducted at building IF-611 at Idaho National Laboratory (INL), allowed us to quantify production of ^{37}Ar from UPA and KCl samples.

Scientific/Technical Accomplishments form the project:

This year we were able to verify ^{37}Ar production by irradiating both KCl and UPA samples. Isotope production is typically verified by comparing the half-life and measured peak energies of the produced isotope to the theoretical values of the known isotope. To calculate the half-life, the decay rate of the irradiated sample is plotted against the elapsed time from the end of irradiation. The half-life is then determined by an exponential fit of the data, as detailed in Figure 2. The data plotted in Figure 2 were measured in 12-hour time increments from a 30.6 ± 2.0 g KCl sample irradiated on 6/1/2020 for approximately 7.7 hours with 22 MeV end-point energy bremsstrahlung photons pulsed at 200 Hz. The electron beam generated an average charge per pulse of 234.41 nC. The fitted data gives a half-life of 34.91 ± 0.20 days. A comparison of the measured half-life to the theoretical half-life for ^{37}Ar, 35.04 ± 0.04 days, indicates that the theoretical half-life is within the uncertainty of the measured half-life. [6] In addition, the energy spectrum presented in Figure 3 displays measured peaks at energies of 2.6 and 2.8 keV that are consistent with theoretical decay energies from ^{37}Ar. Altogether, similarities in the measured half-life and decay peaks to the theoretical values indicate the production of ^{37}Ar from an irradiated KCl sample.

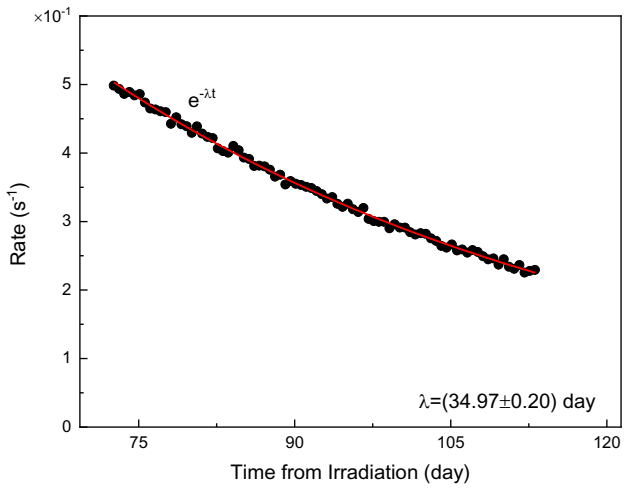

Figure 2 Rate of decay curve (●) of data measured from a 30.6 g KCl sample irradiated on 6/1/2020. An exponential fit (—) of the data is also presented.

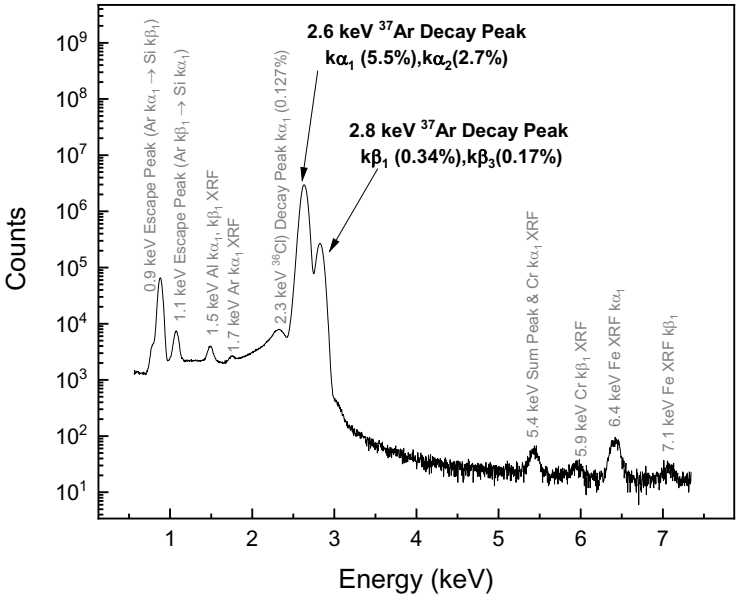

Figure 3 Energy spectrum measured of chemically separated argon produced from a 30.6 g KCl sample irradiated on 6/1/2020. Counts are a sum of 12-hour measurements taken from 6/4/2020 to 9/23/2020.

A 0.071 g UPA sample was irradiated on the high-power accelerator at the IAC using a 39.5 MeV end-point energy bremsstrahlung photon beam. The beam was pulsed for 9 hours at a repetition rate of 300 Hz and generated an average charge per pulse of 778 nC. Calculation of the half-life, using the decay rate from the 2.8 keV peak, yields a half-life of approximately 15.05 ± 0.66 days which in not statistically equal to the theoretical half-life for ^{37}Ar, however, measured peaks do align with peaks that were observed in the KCl sample. Figure 4 displays the energy spectrum of the KCl sample, described in Figure 3, with the UPA spectrum overlaid for comparison. Although the spectra are minorly shifted by 0.04 keV, due to calibration differences, the similarities in peak energies indicate that the same isotopes were measured in both samples and include ^{37}Ar. We speculate the discrepancy in the measured half-life in the UPA sample was likely due to leaking in the detection system.

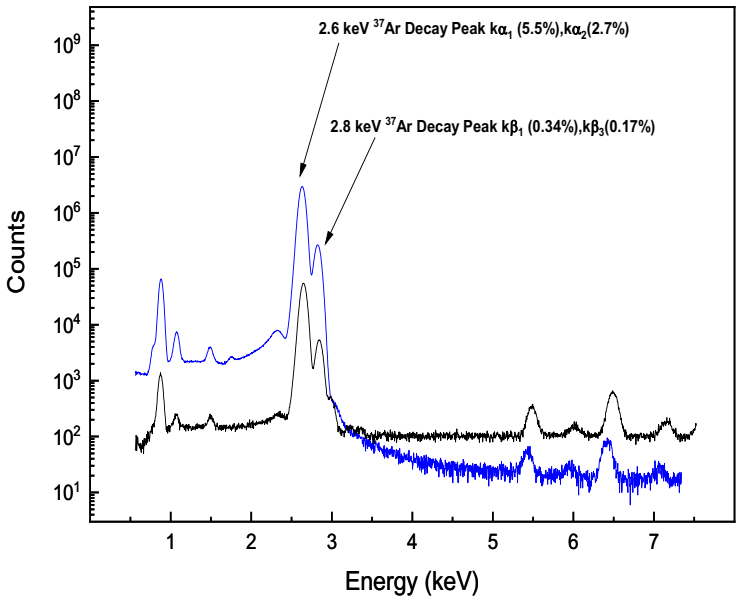

Figure 4 Energy spectrum measured from argon extracted from the KCl sample (——) discussed in Figure 3 and overlaid with an energy spectrum measured from a 0.071 g UPA sample (——). The UPA spectrum includes a sum of 12-hour measurements that begin on 4/13/2020, three days following irradiation, and continuing to 6/11/2020.

As with half-life the measurement, the rate of decay is required to quantify production. However, production calculations also require an estimation of the detector efficiency and the self-attenuation of the radioactive sample. Detector efficiency is generally determined by measuring decay rates from sources that have decay energies close to the observed energy of the isotope of interest. More accurate efficiency comes by using sources in the same phase and geometry to the geometry and phase of the sample being measured. Therefore, the most accurate efficiency calculations for ^{37}Ar would require a gas source with decay emissions as close as possible to 2.6 and 2.8 keV. To determine the production, an efficiency experiment was performed at the National Security Laboratory building IF-611. The team was able to acquire metastable xenon-131 (^{131m}Xe) gas which decays with x-rays at energies at approximately 4.1, 4.4, 4.5, and 4.7 keV. [7] For these experiments, a radioactive metastable ^{131m}Xe sample of known activity was transferred into a detection chamber that was fabricated to the same specifications used to design the chamber for the ^{37}Ar measurements. To determine the efficiency a measurement of the xenon self-attenuation was also required because the attenuation is expected to be high for x-rays at low kiloelectron volt energies. The self-attenuation was determined by adding a known quantity of stable xenon to the radioactive ^{131m}Xe and measuring the decay rate. The decay rate was measured again following the addition of more stable xenon. This process of adding stable xenon and assaying the sample again was repeated until the pressure in the x-ray detector chamber was approximately equal to the atmospheric pressure. Although the decay energy of x-rays emitted from ^{131m}Xe are larger than the decay energies from x-rays emitted from ^{37}Ar, our best estimation of production utilized the measurements determined from the xenon experiments. To characterize ^{37}Ar production, the team used a calculated efficiency of $3.13 \times 10^{-3} \pm 4.14 \times 10^{-4}$ determined from these xenon experiments.

The self-attenuation experiment described using a xenon sample was replicated using ^{37}Ar, extracted from a KCl sample, and natural argon to increase the sample density. A graph of the self-attenuation as a function of density is presented in Figure 5. The data trend allows us to estimate the self-attenuation of additional ^{37}Ar samples thus allowing us to calculate production. Utilizing the trend, the self-attenuation was calculated for the UPA sample described in Figure 4 resulting in an estimated ^{37}Ar yield in the detection chamber, of 1.5 ± 0.3 μCi · g^{-1} · kW^{-1} and an estimated specific activity of 14.2 ± 2.5 μCi · g^{-1} both calculated from the initial UPA mass. The same trends for the self-attenuation were utilized to calculate the production of the KCl sample also described in Figure 4. Using the initial mass of the KCl sample and an accelerator power of approximately 1 kW, the estimated ^{37}Ar yield and the specific activity in the detection chamber is 0.17 ± 0.03 μCi · g^{-1} · kW^{-1} and 0.17 ± 0.03 μCi · g^{-1}, respectively.

It was expected that larger production would result from the KCl sample than from the UPA sample. The lower yield and specific activity from the KCl sample may have resulted from either sample loss or partial gas extraction from the KCl salt. Additional experiments are required to verify the ratio of yield from KCl and UPA samples. Future experiments are also required to determine production from $CaCl_2$ samples. Although two irradiations of $CaCl_2$ were conducted, one

resulted in a sample breech and the other resulted in a failed gas extraction. Follow-on experiments would be required for large scale production, nevertheless this project was successful in photonuclear production and measurement of ^{37}Ar.

We would like to acknowledge our university collaboration with Idaho State University's Idaho Accelerator Center. Their support in the success of this project has been invaluable. In addition to aiding in the design and fabrication of sample holders, our detection chamber, and the transfer manifold, they supplied space and equipment for measurements counted over many months. Furthermore, Idaho Accelerator Center staff supported this research during the months when INL staff could not participate in the field due to the stay-at-home order issued during the COVID-19 pandemic.

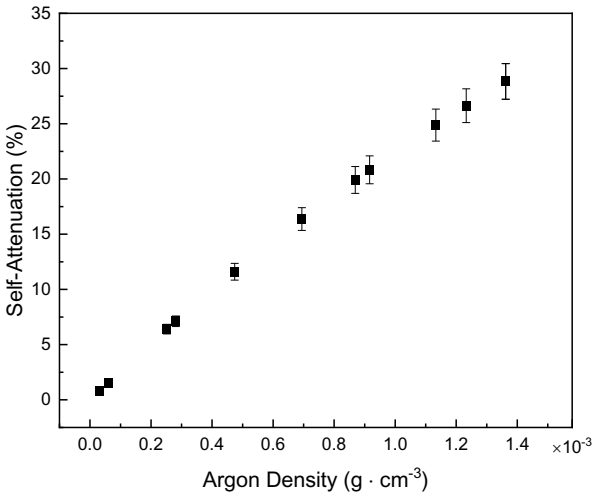

Figure 5 Self-attenuation as a function of argon density for the 2.6 keV x-ray emission.

Benefits to DOE:
Production of an ^{37}Ar standard would impact INL's National & Homeland Security core mission of advancing research in "security solutions that prevent, detect, and counter nuclear and radiological threats" specifically mission 1.1.1 to advance nuclear detection capabilities "particularly photo-nuclear processes" by improving the accuracy in quantifying detected ^{37}Ar. This research has laid the groundwork for large scale sample production as there is currently no commercially available consistent supply of ^{37}Ar. The LDRD research team has successfully produced and measured ^{37}Ar, an isotope that uniquely identifies the occurrence of an underground nuclear explosion and as such has played a role in researching "technology needs for detecting nuclear testing".

Follow-on Activities or Program Development Accomplishments: There is potential for funding from the Provisional Technical Secretariat of the CTBT Organization and other international agencies requiring Ar-37 for field exercises.

Research outputs: Publications, conference presentations, reports, IPs, awards, etc.:
INL/CON-19-55186 J. L. Ward, M. S. Snow, E. S. Cárdenas, "NOVEL METHODS IN PRODUCING ^{37}Ar STANDARDS", Radiobioassay & Radiochemical Measurements Conference, October 2019.

E. S. Cárdenas, A. A. Foley, B. M. Bucher, J. L. Brookhart, T. A. Robinson, M. S. Snow, J. L. Ward, "^{37}Ar Standard – Improves Radionuclide Monitoring Tools", Presented to NA-22 leadership in Washington D.C. October 2019.

INL/CON-20-60449 A. A. Foley, B. M. Bucher, J. L. Brookhart, T. A. Robinson, M. S. Snow, J. L. Ward, E. S. Cárdenas, "Novel Photonuclear Methods to Produce an Argon-37 Standard", American Nuclear Society Annual Winter Meeting 2020, November 2020.

Pipeline: Students/Interns, external Postdocs, professors, or other external consultants: While no longer interns both Jessica Ward and Ariana Foley were interns over a period while working on this LDRD. In addition, Edna Cárdenas was a postdoc at the onset of this LDRD.

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[5] A. J. Koning and D. Rochman, "Modern Nuclear Data Evaluation with the TALYS Code System," *Nuclear Data Sheets,* vol. 113, no. 12, pp. 2841-2934, December 2012.

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