

**Mo-99 2014 TOPICAL MEETING ON
MOLYBDENUM-99 TECHNOLOGICAL DEVELOPMENT**

June 24-27, 2014
Hamilton Crowne Plaza
Washington D. C.

**Measuring Radiolytic- and Fission-Gas Generation in an Aqueous
Uranium-Sulfate Target Solution in Accelerator-Based Mo-99
Production**

M. Kalensky, T. A. Heltemes, J. F. Schneider, D. L. Bowers, S. D. Chemerisov, A. J. Youker,
P. Tkac, K. J. Quigley, J. F. Krebs, D. Rotsch, and G. F. Vandegrift
Chemical Sciences and Engineering
Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439-4854 – USA

ABSTRACT

Irradiation of aqueous uranyl-sulfate solutions and fissioning of U-235 evolve a variety of gases that need to be characterized to ensure safe and efficient operation of these highly dynamic systems. The particular gases of interest are water vapor, hydrogen, oxygen, iodine, and noble gases. The micro- and mini-SHINE experiments being performed in the LINAC Accelerator Facility at Argonne have been used to study the production of these gases in water and acidic sodium-bisulfate and uranyl-sulfate solutions. The real-time quantities of radiolytic gas produced from neutrons, high-energy x-rays, and fission products have been sampled using an in-line analysis loop. Samples to measure fission-gas release are captured throughout the run for later gamma analysis. Three experimental setups have been tested: a closed solution capsule, a once-through system, and a closed-loop system. The results from these experiments provide key insights to designing a production-scale system.

1. Introduction

Argonne National Laboratory (ANL) is performing experiments in support of a potential domestic producer of molybdenum-99 (Mo-99), SHINE Medical Technologies (SHINE), as part of the National Nuclear Security Administration (NNSA) Global Threat Reduction Initiative's (GTRI) program in the development of a domestic Mo-99 production pathway. SHINE is developing a Mo-99 production method which creates the radioisotope product by neutron-induced fission of LEU in a sub-critical aqueous solution of uranyl sulfate.

Critical to the development of this production method is an understanding of the fission and radiolytic gasses produced during the process. Experiments were performed at the Van de Graaff accelerator facility to analyze the radiolytic gases evolved as a result of low Linear Energy Transfer (LET) bombardment of sodium bisulfate and uranium sulfate solutions. These experiments were designed to simulate the conditions inside the sub-critical solutions of the SHINE Mo-99 production system. During irradiation, radiolytic gases are generated from solution through decomposition of water to form gaseous hydrogen and oxygen.

Experiments performed at the LINAC accelerator facility are also used to support SHINE. In these experiments uranyl-sulfate solutions will be subjected to a neutron flux causing fissions at rates up to a density similar to that of the production facility. These experiments will be conducted using 2 mL solution samples (micro-SHINE Phase I & II), a 5 L uranyl-sulfate solution vessel (mini-SHINE Phase I) and 20 L uranyl-sulfate solution vessel (mini-SHINE Phase II).

2. Van de Graaff Experiment

The setup shown in Figure 1 was designed with two interconnected systems, the process loop and the sampling manifold. The process loop is a closed loop of stainless steel tubing that consists of the target sample, the electron beam and a peristaltic pump. The target sample is inserted into a holder directly in the accelerator beam path. The holder is attached to a recirculating pump and water bath to provide continuous cooling to the sample. The Van de Graaff accelerator has a 3 MeV pulsed-electron beam that impinges on the cooling water and quartz tube in the setup. Electrons and X-rays interact with the test solution, generating radiolytic gases in the sample tube. The sample tube has an inlet and outlet through which headspace gases can be continuously recirculated throughout the process loop. Recirculation of gas is achieved using a peristaltic pump.

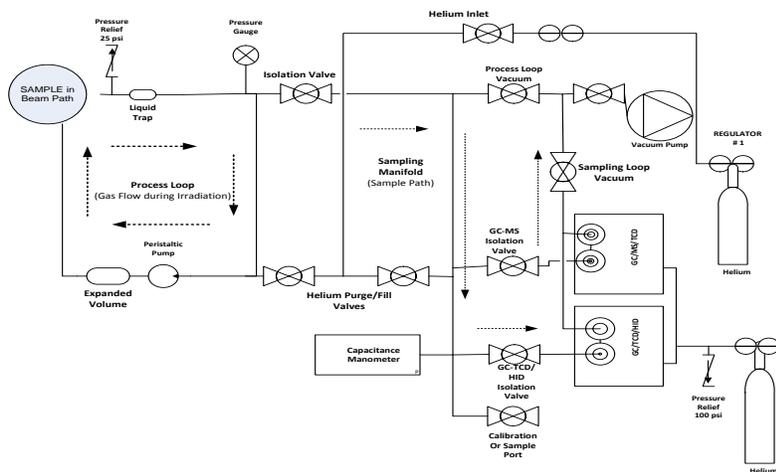


Figure 1. Experimental setup at the Van de Graaff Accelerator Facility.

The sampling manifold is connected to the process loop by a bellows valve. The sampling manifold consists of a capacitance monometer, vacuum pump, and two analytical instruments connected by stainless steel tubing and a series of valves used to either evacuate, measure pressure, or analyze the gaseous constituents in the manifold. The gases are analyzed using two gas chromatographs (GC). One GC (a SRI-8610C) has a Thermal Conductivity Detector (TCD) and a Helium Ionization Detector (HID). Separation is achieved with a 13X molecular sieve and Haysep-d columns. The other (a Shimadzu QP2010) has a TCD and a quadrupole mass selective detector (MS) with two molecular sieve 5A columns.

2.1 Sodium Bisulfate Solutions Summary

Table 1, Figure 2, and Figure 3 provide experimental data for the irradiation of sodium bisulfate solutions. Figure 2 and Figure 3 show total μmoles of analyte (either hydrogen or oxygen) versus accumulated dose in Gy during the five hour experiment. Each data point is at the sampling time for the analyte. Each figure is displayed for the analyte at the various sodium bisulfate concentrations at a particular pH. These data follow with the tabular data such that the final point on the graph is the value listed in Table 1.

Table 1. Results from the irradiation of sodium-bisulfate solutions. For the hydrogen and oxygen production data, line 1 is the total production value in μmoles and line 2 is the G-value in molecules per 100 eV.

Na_2SO_4 (M)	Energy Deposited (Gy)	Initial pH	Final pH	Hydrogen Production	Oxygen Production	H_2 to O_2 Ratio
0.46	2.38×10^8	1.01	0.95	652	291	2.24
				1.37×10^{-2}	6.11×10^{-3}	
0.59	2.36×10^8	1.00	1.15	646	281	2.29
				1.32×10^{-2}	5.76×10^{-3}	
1.26	2.30×10^8	1.01	1.01	1092	508	2.15
				2.29×10^{-2}	1.07×10^{-2}	
0.38	2.24×10^8	1.31	1.25	804	380	2.12
				1.74×10^{-2}	8.20×10^{-3}	
0.63	2.32×10^8	1.31	1.15	610	267	2.28
				1.27×10^{-2}	5.56×10^{-3}	
RODI Water	2.35×10^8	6.30	8.52	131	55	2.37
				2.65×10^{-3}	1.12×10^{-3}	
0.1 M H_2SO_4	2.23×10^8	0.99	0.93	815	351	2.32
				1.76×10^{-2}	7.59×10^{-3}	

2.2 Hydrogen and Oxygen Evolution

The total production of hydrogen and oxygen was fairly consistent among the various low sodium-bisulfate concentrations. Even at a different pH, total production of hydrogen and oxygen was similar. It was also consistent with 0.1 M H_2SO_4 . There may not have been enough variability in these tests to observe significant differences. Variability may be due to beam positioning. The highest salt concentration (1.26 M Na_2SO_4), showed the greatest increase in gas production. Further investigation is necessary, but preliminary results indicate that increasing the sodium-bisulfate concentration will cause an increase in H_2 and O_2 production.

The hydrogen-to-oxygen ratio was consistent over the range of sodium bisulfate concentrations. The ratio stays slightly above a ratio of 2 to 1. The greater solubility of oxygen (7.6 mg/L at 20°C) as opposed to hydrogen (1.6 mg/L at 20°C) in water will tend to make the headspace gases richer in hydrogen; generation of peroxide rather than oxygen gas will also cause this effect. Deviations from a ratio of 2.2 to 1 across the range of concentrations were slight.

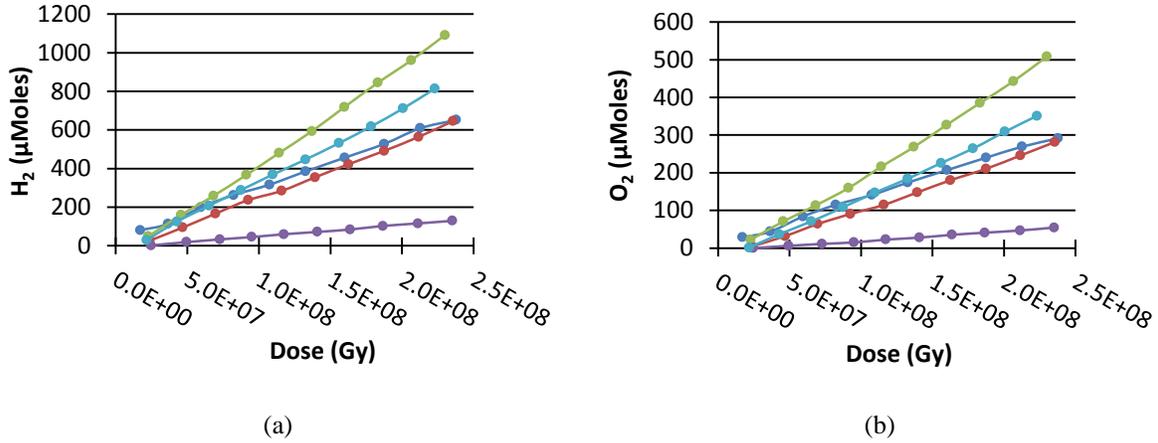


Figure 2. Hydrogen (a) and oxygen (b) evolution versus dose for various Na_2SO_4 concentrations at pH 1. In these figures deionized water is (—●—), 0.1 M sodium bisulfate is (—●—), 0.46 M sodium bisulfate is (—●—), 0.59 M sodium bisulfate is (—●—), and 1.26 M sodium bisulfate is (—●—).

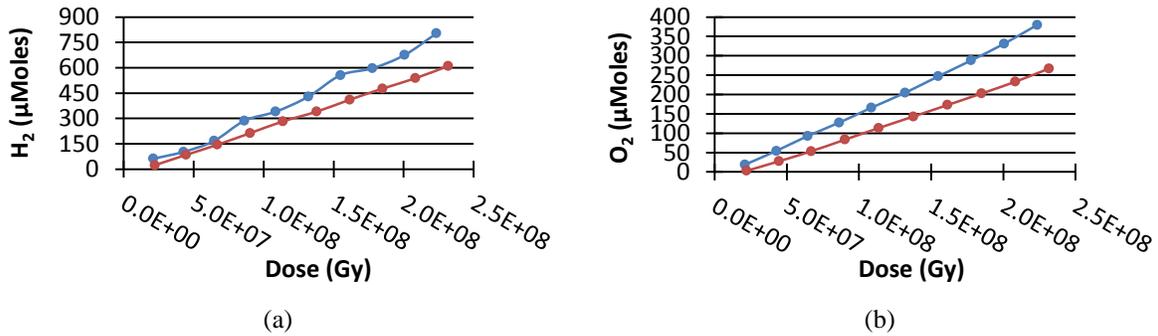


Figure 3. Hydrogen (a) and oxygen (b) evolution versus dose for various Na_2SO_4 concentrations at pH 1.3. In these figures 0.38 M sodium bisulfate is (—●—) and 0.63 M sodium bisulfate is (—●—).

2.3 Uranyl Sulfate Solutions Summary

Table 2 and Figure 4 provide experimental data for the irradiation of uranyl sulfate solutions. Figure 4 shows total μmoles of analyte (either hydrogen or oxygen) versus accumulated dose in Gy during the five hour experiment. Each data point is at the sampling time for the analyte. Each graph is displayed for the analyte at the various uranyl-sulfate concentrations at a particular pH. These data follow with the tabular data such that the final point on the graph is the value listed in Table 2.

Table 2. Results from the irradiation of uranyl sulfate solutions. For the hydrogen and oxygen production data, line 1 is the total production value in μmoles and line 2 is the G-value in molecules per 100 eV.

Initial $\text{UO}_2(\text{SO}_4)$ (g-U/L)	Energy Deposited (Gy)	Final $\text{UO}_2(\text{SO}_4)$ (g-U/L)	Initial pH	Final pH	Hydrogen Production	Oxygen Production	H_2 to O_2 Ratio
88 g-U/L	1.71×10^8	63.5	1.0	0.64	2972 8.20×10^{-2}	1446 3.99×10^{-2}	2.05
138 g-U/L	2.29×10^8	116	1.0	0.63	1320 2.78×10^{-2}	634 1.34×10^{-2}	2.08
298 g-U/L	2.03×10^8	262	1.0	0.58	1092 2.59×10^{-2}	459 1.09×10^{-2}	2.38

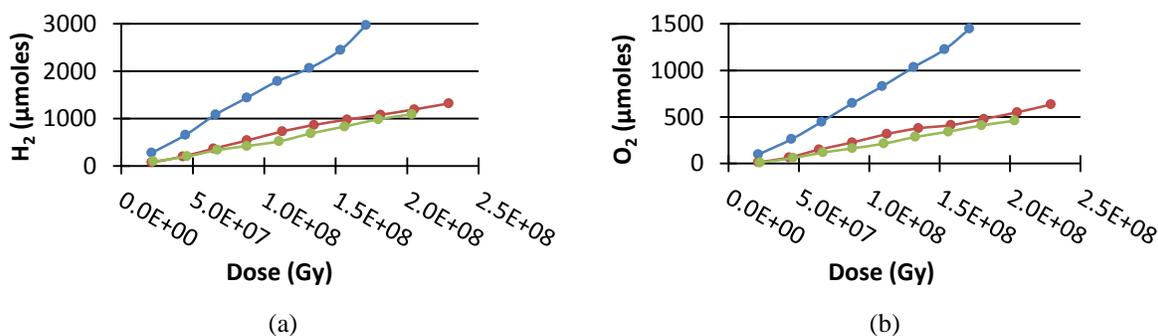


Figure 4. Evolution of hydrogen (a) and oxygen (b) for various uranyl sulfate solution concentrations during irradiation at the 3 MeV Van de Graaff accelerator. In these figures, uranyl sulfate concentrations are 88 g-U/L (—●—), 138 g-U/L (—●—), and 298 g-U/L (—●—).

2.4 Precipitation of Uranyl Peroxide

Uranyl peroxide was precipitated from solution for each of the uranyl sulfate experiments. It was assumed to be the peroxide because of previous experiments on uranyl sulfate solutions. The peroxide was also indicated by the fact that the solid re-dissolved (due to peroxide autodestruction) when the slurry was placed in a hot water bath. Density measurements were performed on the post-irradiated solutions after the precipitate was filtered to determine the final resulting uranyl-sulfate concentration. Those data are listed in Table 2. The percentage of uranium to precipitate decreased as the concentration of uranium increased. At 88 g-U/L, 28% or 24.5 g-U/L precipitated to a final concentration of 63.5 g-U/L. At 138 g-U/L, 16% or 22 g-U/L precipitated to a final concentration of 116 g-U/L. Finally at 298 g-U/L, 12% or 36 g-U/L precipitated to a final concentration of 262 g-U/L. Hydrogen peroxide formation during irradiation is assumed to be causing the precipitation. Experiments performed and listed in the next section show that this can be avoided by using a catalyst for peroxide destruction.

Consistently, the pH of all solutions decreased with dose. This was likely due to the formation of uranyl peroxide, which follows the equation



The production of hydrogen and oxygen was quite high for all experiments. There was a definite trend showing that as the uranyl-sulfate concentration increased, the production of H₂ and O₂ decreased. This is probably due to the consumption of H₂O₂ in solution by uranium. The ratio of H₂/O₂ was at or slightly above 2/1, favoring the production of hydrogen as the uranium concentration was increased.

2.5 Catalytic Destruction of Peroxide in Uranyl Sulfate Solutions

Table 3 and Figure 5 provide experimental data for the irradiation of uranyl sulfate solutions containing ferrous sulfate. The figures show total µmoles of analyte (either hydrogen or oxygen) versus accumulated dose (Gy) during the five hour experiment. Each data point is at the sampling time for the analyte. Each graph is displayed for the

analyte at the various ferrous sulfate catalyst concentrations for uranyl sulfate solutions. These data follow with the tabular data such that the final point on the graph is the value listed in Table 3.

Table 3. Results from the irradiation of 126 g-U/L uranyl sulfate solutions with the addition of ferrous sulfate catalyst.

Peroxide Catalyst	Energy Deposited (Gy)	Initial UO ₂ (SO ₄) (g-U/L)	Initial pH	Final pH	Hydrogen Production (μmoles H ₂)	Oxygen Production (μmoles O ₂)	H ₂ to O ₂ Ratio
0.99 mg/L FeSO ₄	2.31×10 ⁸	123.5	1.42	N.A.	239	163	1.47
9.9 mg/L FeSO ₄	2.31×10 ⁸	123.5	1.42	1.44	540	343	1.57
99 mg/L FeSO ₄	2.20×10 ⁸	123.5	1.42	1.37	462	302	1.53

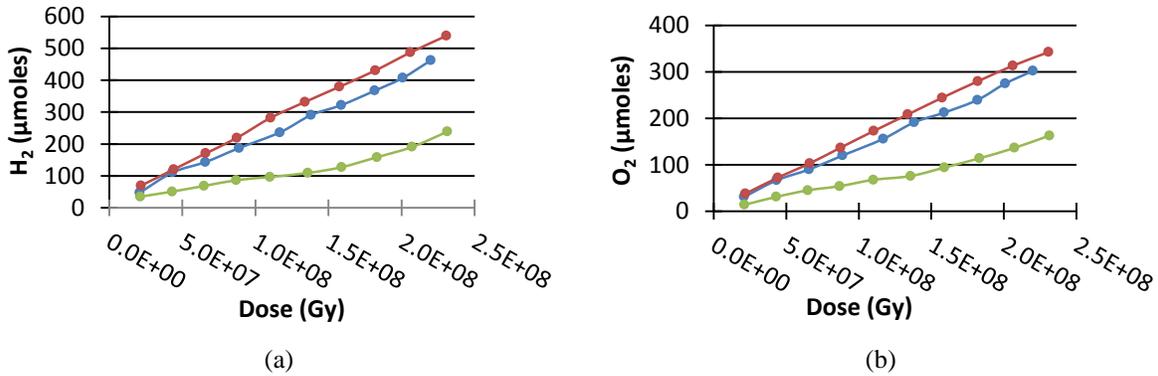
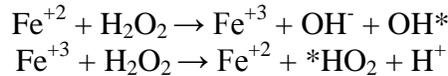


Figure 5. Evolution of hydrogen (a) and oxygen (b) from uranyl sulfate at 126 g-U/L for various concentrations of Fe(II) added to prevent precipitation. Iron sulfate concentrations are 0.994 mg/L (—●—), 9.94 mg/L (—●—), and 99.4 mg/L (—●—).

From the result of the irradiation of uranyl sulfate solution, a method for destroying hydrogen peroxide (H₂O₂) as it forms in solution is needed. Initially, we tested zirconium metal pieces in solution with the thought that the reactor vessel itself could catalyze peroxide. This test failed to show a decrease in uranyl-peroxide precipitation, so we pursued the route of having an ion in solution so as to make intimate contact with molecules of H₂O₂ as they are produced during irradiation. Ferrous ion (Fe⁺²) was chosen because it is known to react with H₂O₂ through the following reaction sequence[3]:



Because it also acts as a catalyst, ferric ion is reduced back to ferrous. The results are discussed below.

- **Precipitation of Uranyl Peroxide.** The uranyl sulfate solutions were examined post irradiation and none of those solutions formed the uranyl-peroxide precipitate.
- **pH Changes.** The solutions with ferrous sulfate added showed no change in pH.

- **Hydrogen and Oxygen Evolution.** With ferrous sulfate was added as a catalyst, the total production of hydrogen and oxygen was significantly lower. Likewise, the ratio of hydrogen to oxygen was <2:1

3. Micro-SHINE Experiment

3.1 Phase I — Closed Capsule with a Static Headspace

In Phase I of the Micro-SHINE experiment, a 2 mL solution of uranyl sulfate in a closed capsule was placed in a neutron flux causing fissions to produce Mo-99. During the experiment radiolysis and fission gasses were generated. To ensure hydrogen did not build to unsafe concentrations an experiment was performed at the Van de Graaff accelerator facility to test whether a Pt/Zeolite catalyst in the static headspace of the capsule could efficiently recombine hydrogen and oxygen produced during radiolysis and keep hydrogen levels at <1%. During long irradiations, hydrogen and oxygen should form an equilibrium between production of gas and recombination of gas to water.

2 mL of uranium sulfate (126 g-U/L) was placed into quartz tube, similar in design as the one described above. Three grams of 1% Platinum/alumina catalyst material was placed into the upper chamber of the tube. The sample was irradiated for a period of time in the 2.5 MeV electron beam. Five hours was the longest irradiation period. The five-hour test deposits a dose of 2.4×10^8 Gy, which simulates five days of irradiation at the LINAC.

The gas sampling manifold was evacuated up to the solenoid valve located next to the sample tube, as shown in Figure 6. When the solenoid valve was opened, headspace gas was introduced into the GC sample manifold for analysis. The GC was equipped with calibrated HID and TCD detectors to determine the hydrogen concentration. This test was performed at increasing time intervals with the final test being the five hour irradiation.

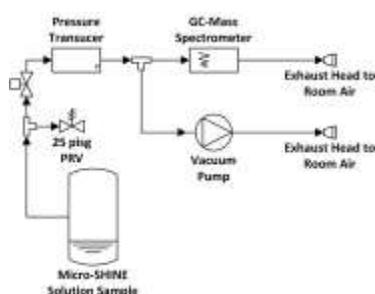


Figure 6. Diagram of the Phase I micro-SHINE experimental apparatus.

The sample tube design with catalyst in the upper chamber limits the hydrogen concentration to < 0.5%. Hydrogen built to a maximum concentration of 0.46% for the longest simulation. Total hydrogen in the headspace was limited to 15 μ moles. This compares favorably to previous experiments which show that as much as 200 μ moles of hydrogen could be produced during a five hour run. Figure 7 shows the concentration of hydrogen at the various doses. It shows that hydrogen rises to a point where it forms equilibrium between production and destruction at 0.46%.

It is important that the screen used to hold the catalyst allows for maximum diffusion between the sample headspace and the catalyst chamber. Five 1 mm slits in the glass acted as the screen to hold the catalyst pellets which are 3.2 mm in size.

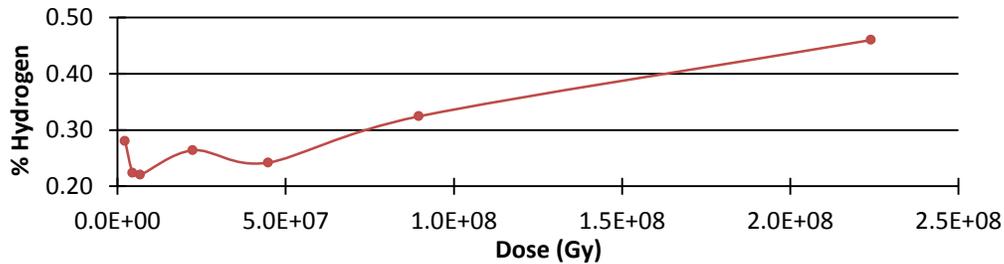


Figure 7. Hydrogen concentration in the Phase I micro-SHINE experiment.

3.2 Phase II — Capsule with a once-through helium sweep gas

Phase II of the micro-SHINE experiment will consist of a 2 mL sample of uranyl-sulfate solution with a headspace open for introduction and removal of a helium sweep gas. This experiment will yield real-time data for the production of radiolysis and fission gasses in the sample. Figure 8 shows a photograph of the stainless steel canister to be used in the experiment, and the internals are shown in diagram form in Figure 9. The capsule headspace will be cooled by a condenser coil prior to remove water vapor before analysis by the residual gas analyzer (RGA), as shown in Figure 10.



Figure 8. Micro-SHINE Phase II solution capsule.

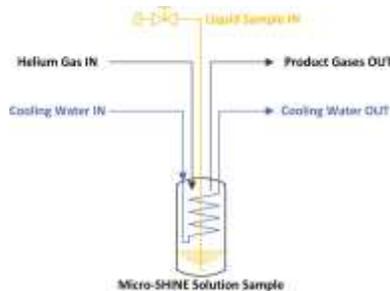


Figure 9. Diagram of the interior of the micro-SHINE Phase II solution capsule.

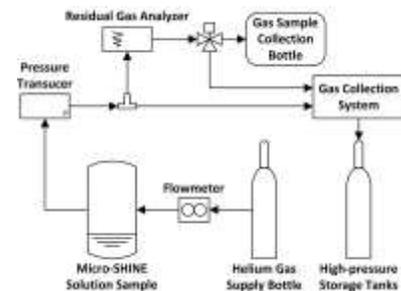


Figure 10. Block diagram of the micro-SHINE Phase II gas sampling system.

4. Mini-SHINE Experiment

These experiments are being performed at the LINAC facility. In Phase I of the mini-SHINE experiment, a 5 Liter solution of uranyl sulfate is irradiated with neutrons to cause fissions which produce the Mo-99 product. Phase II will consist of a 10 to 20 Liter uranyl sulfate solution. An experiment using a 5 liter salt solution (sodium bisulfate) will act as a surrogate solution to test the systems function and performance.

The objective of these experiments is to quantitate production rates and determine the composition of radiolytic gasses generated during operation of the system under varying conditions of power density, solution temperature, and startup conditions. Also, to examine

how fission rates in various fuel solutions effects gas generation. Gasses of particular concern are hydrogen and oxygen.

The experiment consists of three interconnected systems, Solution Vessel, Gas Analysis System, and the Gas Collection System, as shown in Figure 11. The solution Vessel will contain the 5 liter uranium solution. Neutrons are emitted from a tantalum target located in a dry well in the center of the solution. Headspace gasses are recirculated through a catalyst bed that recombines hydrogen and oxygen. The Gas Analysis System has a gas chromatograph (GC) with a mass selective detector (MS) and thermal conductivity detector (TCD) for periodic sampling and a residual gas analyzer (RGA) for continuous monitoring of the Solution Vessel. The Gas Collection System collects and stores waste gasses for safe disposal; it also keeps the entire system at sub-atmospheric pressure. Figure 12 and Figure 13 show the instrumentation and gas analysis apparatus, respectively.

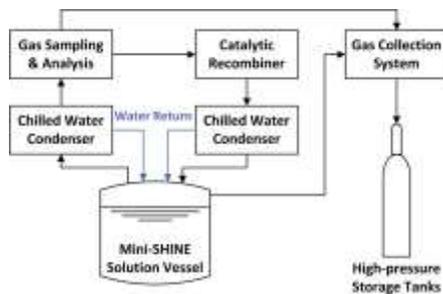


Figure 11. Block diagram of the mini-SHINE gas analysis and collection system.



Figure 12. Micro- and mini-SHINE gas analysis & collection instrumentation.



Figure 13. Micro- and mini-SHINE gas analysis enclosure.

4.1 Preliminary Sodium Bisulfate Results

A preliminary run with 5 L of 0.55 M sodium bisulfate (Na_2SO_4) and a 10 ppm ferrous sulfate (FeSO_4) peroxide destruction catalyst was conducted to test operation of the gas analysis system.

Figure 14 shows hydrogen, oxygen, and nitrogen from the start of the beam until three hours after the beam was turned off. Prior to the start of this experiment, an air leak occurred so there was a continuous inflow of atmospheric nitrogen and oxygen that interfered with a proper examination of data. There was also a problem with the cooling/condenser system which caused failure of critical components of the system, most importantly the catalytic recombiner. Figure 15 shows the rise in hydrogen and oxygen concentrations after the failure of the catalytic recombiner.

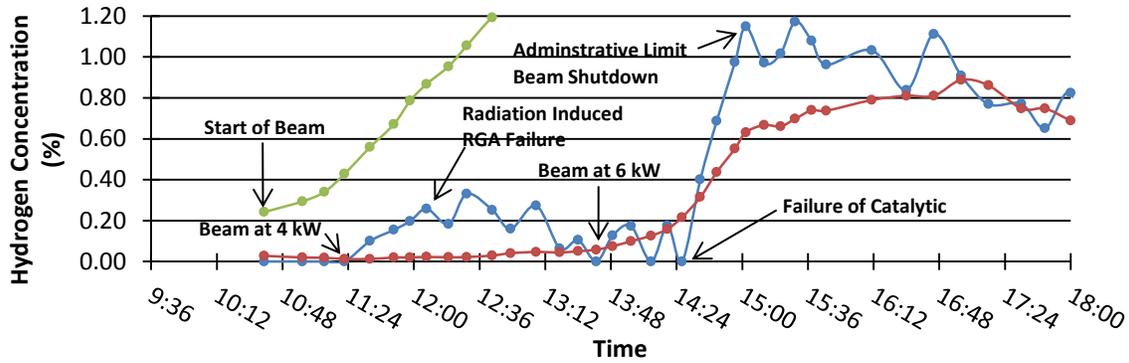


Figure 14. Gas concentrations for hydrogen (—●—), nitrogen (—●—), and oxygen (—●—) during the preliminary test of the Phase I mini-SHINE experiment using sodium bisulfate with a ferrous sulfate peroxide catalyst.

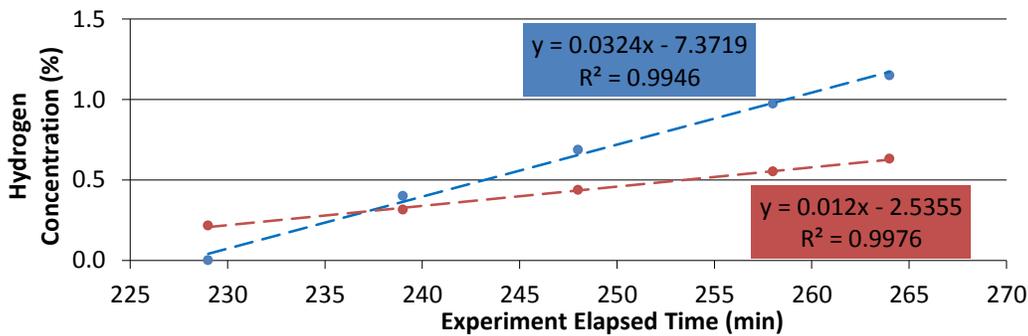


Figure 15. Linear fits to the hydrogen (—●—) and oxygen (—●—) concentrations after the failure of the catalytic recombiner and prior to LINAC beam shutdown.

5. Future Work

Future work for the gas analysis system will consist of completion of the Phase II micro-SHINE experiment using LEU, DU and HEU solution samples; Phase I mini-SHINE using uranyl sulfate; and Phase II mini-SHINE using sulfuric-acid and uranyl-sulfate solutions.

6. Acknowledgement

Work supported by the U.S. Department of Energy, National Nuclear Security Administration's (NNSA's) Office of Defense Nuclear Nonproliferation, under Contract DE-AC02-06CH11357. Argonne National Laboratory is operated for the U.S. Department of Energy by UChicago Argonne, LLC.

7. References

- [1] M. Kalensky et al, "Means to Eliminate Uranyl Peroxide Precipitation in SHINE Target Solution," Argonne National Laboratory, ANL/CSE-13/21 (APT76776), March 2013.
- [2] M. Kalensky et al, "Radiolysis of Nitrate and Sulfate Solutions," Argonne National Laboratory, ANL/CSE-13/21 (APT76911), November 2012.
- [3] J. De Laat and H. Gallard, "Catalytic Decomposition of Hydrogen Peroxide by Fe(III) in Homogeneous Aqueous Solution: Mechanism and Kinetic Modeling," *Environmental Science and Technology* **33**, November 1999.