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PNNL-28564

In-Situ Electrochemical Testing of Uranium Oxide Alteration under Anoxic Conditions

EBS Activities

March 2019

Edgar C. Buck
Xiao-Ying Yu
Jenn Yao
Sayan D. Chatterjee

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
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Abstract

Prediction of the corrosion behavior of spent uranium oxide (UO_2) fuel is needed for developing predictive performance assessment models for a geologic repository. Currently, the Fuel Matrix Dissolution Model (FMDM) is being used for modeling UO_2 chemistry in the Engineered Barrier System (EBS) and includes the effects of oxidants, oxygen and hydrogen peroxide generated from radiolysis of the fuel in contact with water, as well as the role of hydrogen on limiting corrosion. In this report, efforts to validate the FMDM model using *in situ* liquid cells in the scanning electron microscopy (SEM) are described. The System for Analysis at the Liquid Vacuum Interface (SALVI), was invented at the Pacific Northwest National Laboratory (PNNL) and is a device that enables the investigation of solid-solution systems within the electron microscope. Initial efforts have concentrated on building the testing system for radioactive materials and exploring the use of the SALVI cell on UO_2 particles.

Summary

Work this period has involved establishing the capabilities to perform *in-situ* electrochemical corrosion testing of uranium oxide in the electron microscopy. Equipment for performing this type of work was purchased and built. An *in-situ* Linkham (McCrone Associates, Westmount, IL) THMS 600 liquid stage for conducting corrosion experiments was purchased as well as a CHI 660 E (CH Instruments, Inc., Austin, TX) electrochemical workstation. Equipment for building electron microscope capable testing cells including a PIE Scientific (Union City, CA) Tergo™ Plasma Cleaner and low temperature oven were also obtained. Furthermore, we purchased a vacuum capable feedthrough port from ThermoFisher, Inc. (Hilsboro, OR) that replaced an existing port on the FEI Quanta 250FEG Scanning Electron Microscope (SEM) and would allow the electrical lines from the Echem workstation into the *in-situ* cell once inside the electron microscope. Additional staff that were experts on electrochemistry and the operation of the *in-situ* cells were brought onto the project.

Characterization of nuclear materials in solid particles or particles in liquid slurry, particularly in high level waste, can establish the elemental, organic, and isotopic compositions that effect the properties of the materials during nuclear fuel cycle activities and processes. Techniques to evaluate such detailed information, even at small concentrations, can support nuclear materials and science programs by increasing our ability to manage and control nuclear materials. However, radioactive materials analysis in liquids and slurries can be challenging using bulk approaches. We have developed a vacuum compatible microfluidic interface, system for analysis at the liquid vacuum interface (SALVI), to enable surface analysis of liquids and liquid-solid interactions using scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). In this work, we illustrate the initial results from the analysis of liquid samples of importance in the geologic disposal of uranium dioxide (UO_2) spent nuclear fuel in a repository environment using in situ liquid SEM and SIMS. Our results demonstrate that multimodal analysis of UO_2 materials is possible using SALVI and in situ chemical imaging. Both in situ liquid SEM and SIMS can be used as new approaches to analyze radioactive materials in liquid and slurry forms of high-level nuclear wastes.

Acknowledgments

ECB thanks RPL Management for access to the Radiological Microscopy Suite (RMS) at PNNL and for the modification of existing instruments for conducting these experiments. XYY and JY thank the support of the Pacific Northwest National Laboratory TOP program for the support to obtain the initial *in situ* liquid SIMS results of uranium samples. The programmatic support of this work is from the DOE Nuclear Energy Spent Fuel Waste Science Technology (SFWST) program. Pacific Northwest National Laboratory is operated by Battelle under the contract DE-AC05-76RL01830.

Acronyms and Abbreviations

2D	two-dimensional
3D	three-dimensional
BSE	Backscattered Electron Imaging
EBS	Engineered Barrier System
EDS	X-ray energy dispersive spectroscopy
FMDM	Fuel Matrix Dissolution Model
MPM	Mixed Potential Model
PDMS	polydimethylsiloxane
RM	Radiolysis Model
SALVI	System for Analysis at the Liquid Vacuum Interface
SE	Secondary Electron Imaging
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
SNF	spent nuclear fuel
ToF-SIMS	time-of-flight secondary ion mass spectrometry

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1.0 Introduction

In a reducing or anoxic environment, the oxidation of uranium dioxide (UO_2) spent nuclear fuel can only occur from the production of oxidants from radiolysis of contacting water in the Engineered Barrier System (EBS) of the geologic repository. Within the SFWST program, a model that captures the role of oxidant production is term the Radiolysis Model (RM). The EBS environment, however, is expected to limit oxidation through the production of H_2 gas from anoxic corrosion of iron. These processes have been described in a Mixed Potential Model (MPM) or Fuel Matrix Dissolution Model (FMDM) from modeling the corrosion rate of spent fuel that combines the RM sub-model with an electrochemical corrosion model.(Buck and Wittman 2014, Jerden Jr, Frey et al. 2015)[1, 2] The EBS that contains other components may result in more complex processes also occurring.(Caporuscio, Palaich et al. 2017)[3] Previous, experimental validation of the corrosion model under oxidizing conditions has used flow through experiments but these would be inadequate to describe the processes that might occur under anoxic conditions. To validate the FMDM, it is necessary to obtain measurements of the values predicted by the model, namely, the electrochemical corrosion potential. Besides using macroscale approaches to study the multiphase chemistry, it is important to probe the interfacial phenomena at the solid-liquid interface directly using novel chemical imaging approaches. Of particular relevance to the new approach presented in this report, a commercial *in situ* liquid cell was recently used to study the electron beam induced radiolysis of UO_2 particles in solution (Buck, Wittman et al. 2018) and the dissolution of boehmite(Conroy, Soltis et al. 2017). A vacuum-compatible and transferrable microfluidic reactor, namely System for Analysis at the Liquid Vacuum Interface (SALVI), was invented at the Pacific Northwest National Laboratory (PNNL) and it has enabled *in situ* liquid scanning electron microscopy (SEM) (Yang, Yu et al. 2011, Yang, Zhu et al. 2014) and *in situ* liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) (Yang, Yu et al. 2011, Yu, Yu et al. 2017). Compared to the existing wet cell SEM approaches, (Thiberge, Zik et al. 2004, Nishiyama, Suga et al. 2010), the liquid surface is probed directly by the primary electron beam, because the microfluidic cell is partially open to vacuum with micrometer-sized apertures. In addition, the beam effect and memory effect can be minimized by flowing the liquid (Yang, Yu et al. 2011, Yang, Zhu et al. 2014). This technique has provided an unique *in situ* chemical mapping approach for investigating challenging solid-liquid, air-liquid, and liquid-liquid interfaces, as illustrated by Ding et al., Sui et al., and Yu et al. (Ding, Zhou et al. 2016, Sui, Zhou et al. 2017, Yu, Yao et al. 2018). This multi-modal imaging tool could also be used to study materials relevant to geological disposal where we are interested in several complex interfacial processes. We started studies with two model systems, UO_2 and iron oxide (Fe_3O_4) in

water, to demonstrate feasibility and to develop the capabilities to perform research for spent fuel. These two systems also represent the major chemical components described in the FMDM for the EBS.

1.1 The SALVI Cell

The vacuum compatible microfluidic device, termed SALVI was developed at PNNL by Yu and co-workers (Yang, X.-Y. et al. 2011, Yu, Yang et al. 2011, Yu, Liu et al. 2013). The design details have been provided in many other papers and a version of SALVI is now available commercially as Wet Cell II Liquid Probe System marketed by Structure Probe, Inc. (West Chester, PA). A polydimethylsiloxane (PDMS) block with a 500 μm wide by 300 μm deep channel was bonded with a 50 nm thick SiN membrane after oxygen plasma treatment, although other channel configurations are possible depending on the application. Approximately 10 μL of the analyte liquid mixture was injected into SALVI via its polytetrafluoroethylene tubing and sealed by polyether ether ketone union afterwards. A photo of a SALVI device is shown in Figure 1A.

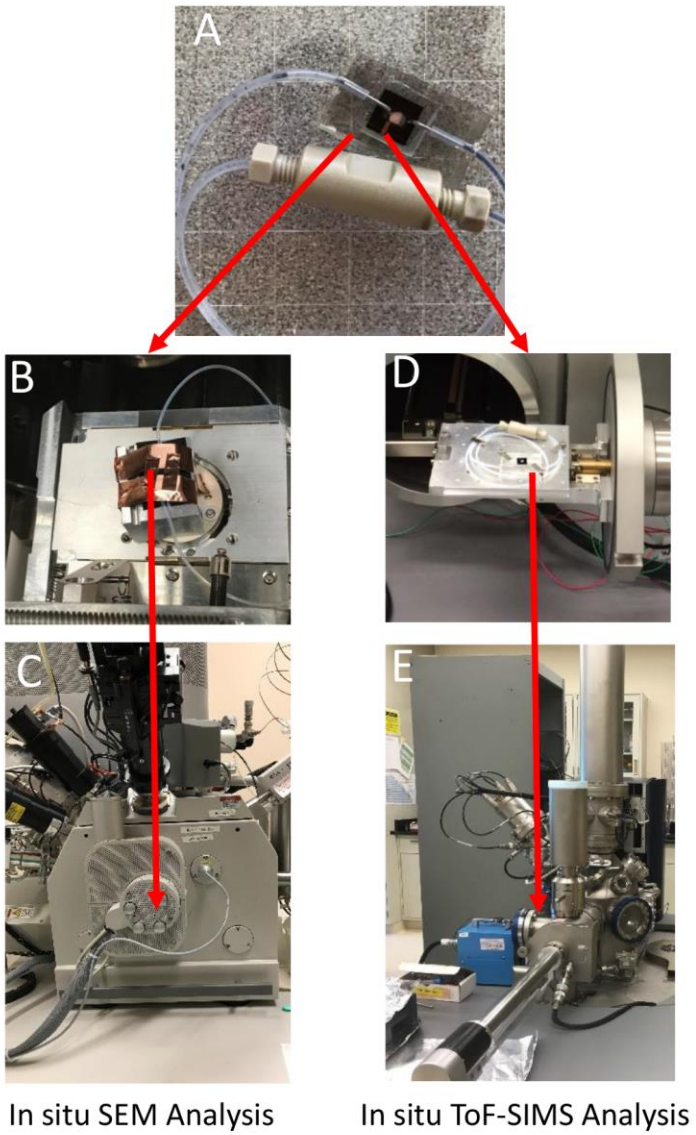

Figure 1 A) The vacuum compatible SAVLI device; B) SALVI installed on the SEM stage in the Quanta SEM (C); D) SALVI installed on the ToF-SIMS stage before loading to the loadlock in the IONTOF ToF-SIMS V instrument (E).

2.0 Experimental Procedure

2.1 *In Situ* Liquid SEM and *In Situ* Liquid ToF-SIMS

Figure 1 illustrates the workflow of *in situ* SEM and *in situ* ToF-SIMS analysis enabled by SALVI. The liquid sample is injected into a SALVI device (Figure 1A) and enclosed before mounting on the SEM stage (Fig. 1B). The liquid sample can be imaged in either low vacuum (~10^{-1} Torr) or high vacuum mode (< 10^{-5} Torr) using SEM (Figure 1C). Similarly, after securing the SALVI device loaded with liquid on the ToF-SIMS sample stage (Figure 1D), the liquid sample can be directly measured using ToF-SIMS under high vacuum condition (i.e., ~ 10^{-7} Torr), providing SIMS mass spectra and two-dimensional (2D) and three-dimensional (3D) images.

2.2 In Situ Liquid SEM

Two FEI Quanta 3D FIB-SEM instruments were used for liquid analysis. Both low and high vacuum modes were used. The uranium oxide (UO_2) radiological material was analyzed in the Radiological Processing Laboratory (RPL) on a ThermoFischer Quanta 250 FEG SEM. The Fe_3O_4 in deionized water (DI) mixture was analyzed using another Quanta SEM. Standard operation procedure of *in situ* liquid SEM was used to conduct SEM analysis.(Yao, Arey et al. 2017) The accelerating voltage was 20 keV and current 110 pA in the low vacuum mode. The accelerating voltage was 25 keV and current 130 pA in the high vacuum mode.

2.3 In Situ Liquid ToF-SIMS

A TOF-SIMS V spectrometer (IONTOF GmbH, Münster, Germany) was used in this work. The pressure in the main vacuum chamber was maintained below 4×10^{-7} Torr.(Yang, X.-Y. et al. 2011) The SiN window was cleaned by a 1 keV O_2^+ beam to remove impurities with a scanning area of 500×500 μm^2 prior to analysis. An electron flood gun was used to compensate surface charging during analysis. A pulsed 25 keV Bi_3^+ primary ion beam was used with a current ~0.36 pA. The focus spot was about 0.45 µm in diameter and the scan area was 2 µm in diameter. A pulse width of 150 ns was used to punch through the SiN membrane.(Yu, Zhou et al. 2016) The pulse width was changed to 50 ns to obtain a relatively higher mass resolution in the latter portion of the depth profile. More experimental details have been reported elsewhere (Zhou, Yao et al. 2016, Yu, Yu et al. 2017).

2.4 Liquid Sample Preparation

Iron oxide (ACS grade) was purchased from Sigma Aldrich and was used as is. The DI water was from a Barnstead Nanopure system. The UO_2 particles used in the *in-situ* SEM analysis were crushed from a parent UO_2 solid and size fractionated. Material sieved to <45 μm in diameter was used for the experiments. The UO_2 in DI liquid mixture was prepared by diluting a stock solution multiple times. The concentration of UO_2 was estimated to be ~10 ppm.

The liquid samples containing UO_2 particles used in liquid SIMS analysis were prepared from the CRM U030-A uranium isotopic standard.(Laboratory 2013) The CRM U030-A was dissolved in 3.5% nitric acid (HNO_3) solution to dilute the concentrated sample to 10 ppm. The 3.5% HNO_3 was analyzed as the solvent control.

3.0 RESULTS AND DISCUSSIONS

In this milestone report, we describe the initial steps in developing *in-situ* liquid SEM and *in-situ* liquid SIMS of materials relevant to the EBS environment. Because SALVI is transferrable among different analytical platforms, it is possible to conduct more than one type of chemical imaging of the same sample using the microreactor to introduce liquid samples in an instrument that requires vacuum. The vacuum compatible microfluidic interface, SALVI, was developed to study liquids using vacuum surface tools including SEM. To study the oxidation and reduction of UO_2, an electrochemical version or the E-cell is being adapted. The feasibility of using SALVI for *in-situ* characterization of particles in liquid has been demonstrated in several other studies (Yu, Liu et al. 2013, Yu, Yu et al. 2017). This report shows the initial results of *in-operando* study of spent fuel relevant systems using the SALVI E-cell. Two FEI Quanta 3D FIB-SEM instruments were used to analyze the iron oxide (Fe_3O_4) in deionized water (DI). Both low and high vacuum modes SEM were used. The radiological material was analyzed in the Quanta 250 FEG SEM housed in the Radiological Processing Laboratory (RPL) at PNNL. Non-radiological materials were analyzed to optimize imaging conditions elsewhere.

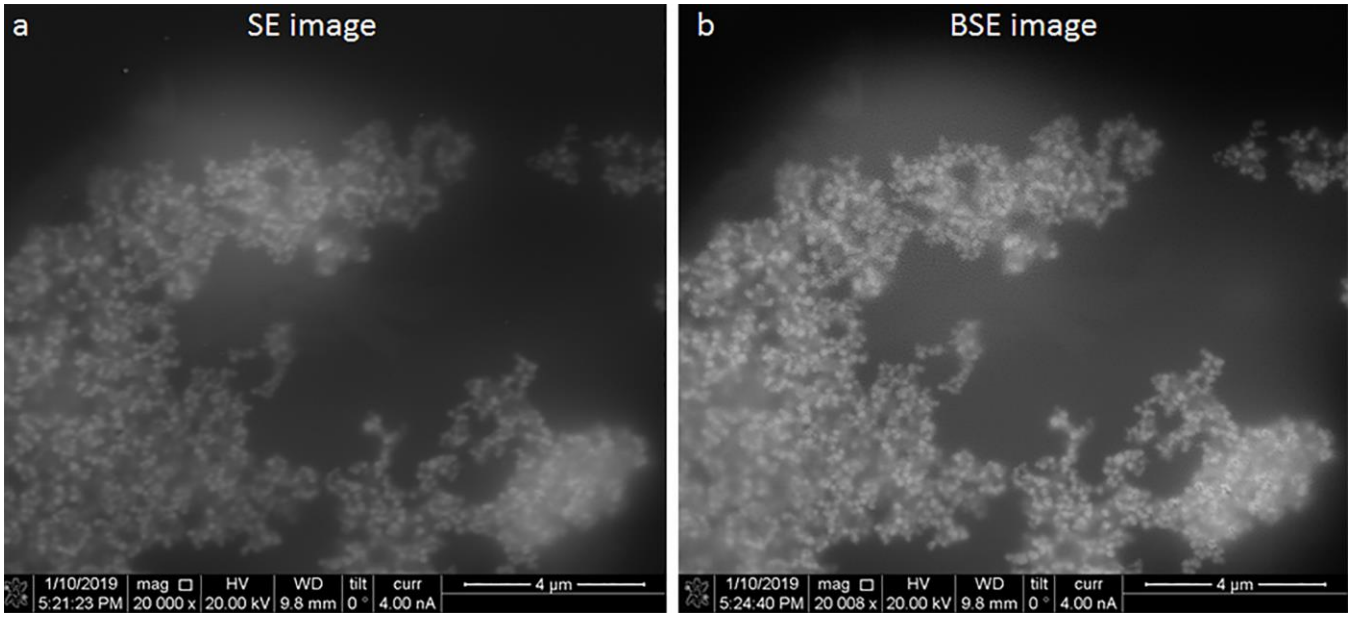

Figure 2 *In-situ* liquid SEM imaging of Fe_3O_4 particles in high vacuum (a) SE imaging and (b) BSE imaging using SALVI and a FEI Quanta 3D FIB-SEM.

Figure 2 depicts SEM secondary electron (SE) and backscattered electron (BSE) imaging results of Fe_3O_4 particles in the high vacuum mode in a microchannel. The SE and BSE images were collected at the same

location. The SE and BSE images show the particle size and morphology in liquid. *In-situ* energy-dispersive x-ray spectroscopy (EDS) spectrum (results not shown) collected at the same location verifies elemental composition. This result supports the follow-up study of spent fuel materials using the novel *in-situ* liquid SEM to study particle evolution of relevance in EBS. The goal of this work is to conduct *in-operando* SEM of UO_2 simulating the spent fuel conditions. Figure 3A depicts the experimental setup including an electrochemical station connected with a SALVI E-cell (see insert). Figure 3B shows a series of cyclic voltammograms obtained with this setup using a standard solution consisting of 2 mM $K_3Fe(CN)_6$ and 1 M KNO_3 in DI water. Reagents were acquired from Sigma-Aldrich. This initial result demonstrates the performance of the approach prior to using radiological materials. *In-operando* results and the application of *in-situ* SEM imaging in studying nuclear materials will be performed in later studies.

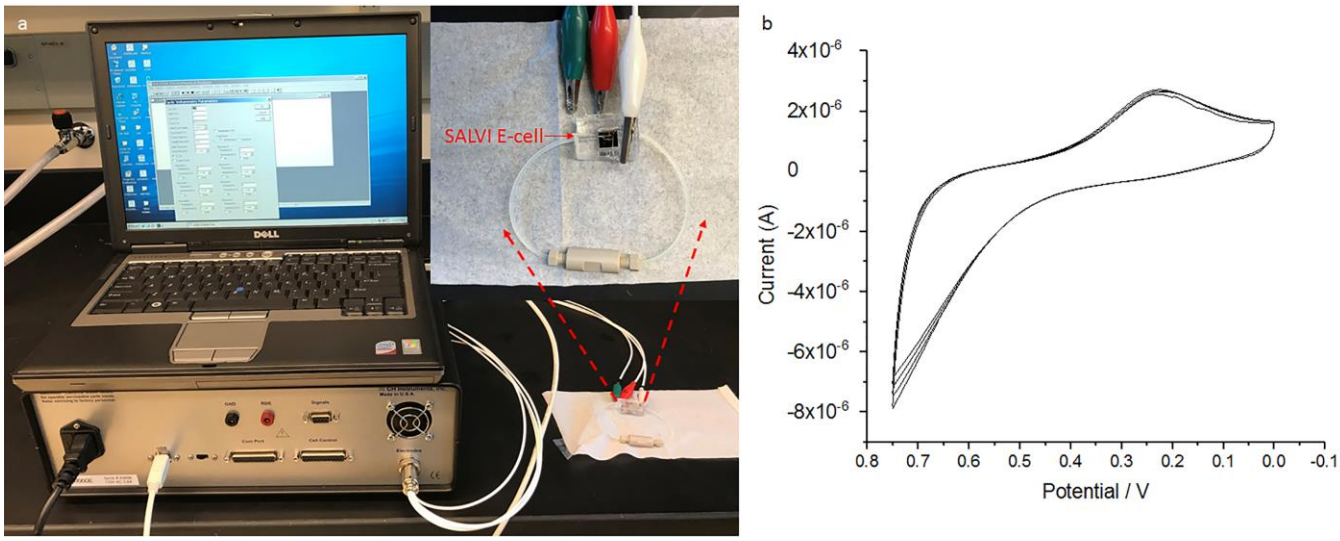

Figure 3 (a) *In-operando* SEM setup showing the SALVI E-cell (insert) connected with an electrochemical station; and (b) cyclic voltammograms acquired using this setup.

3.1 *In-Situ* Liquid SEM Analysis of UO_2 Particles

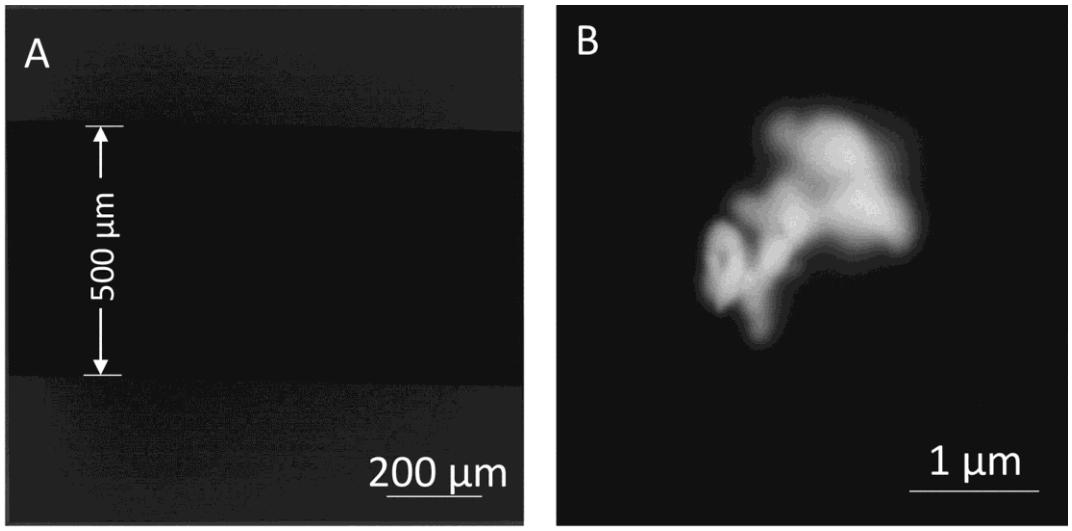

Figure 4 A) The BSE image of the SAVLI microchannel imaged under low magnification and B) a BSE image of a UO_2 particle in the channel in the low vacuum mode.

Figure 4 presents the backscattered electron (BSE) images of UO_2 particles in DI water acquired by applying *in-situ* SEM and SALVI under the low vacuum mode. This result demonstrates the feasibility of directly monitoring the radioactive particles in liquid without any separation or desiccation prior to SEM analysis. Compared to the well-known environmental SEM (ESEM) mode, this approach keeps liquid intact within a microchannel (Figure 4A) and offers in situ images of particles in liquid (Figure 4B). Figure 5 shows *in-situ* liquid SEM imaging results in the high vacuum mode. The secondary electron (SE) and BSE images clearly show iron oxide particles in DI water. This finding is confirmed by the *in-situ* energy-dispersive x-ray spectroscopy (EDS) spectrum collected at the same location where SE and BSE images were taken. Our results demonstrate the flexibility of *in-situ* liquid SEM in analyzing particles of relevance in EBS liquids using SALVI. It is worth noting that the images obtained in the high vacuum mode offer better image resolution compared to those acquired in the low vacuum mode.

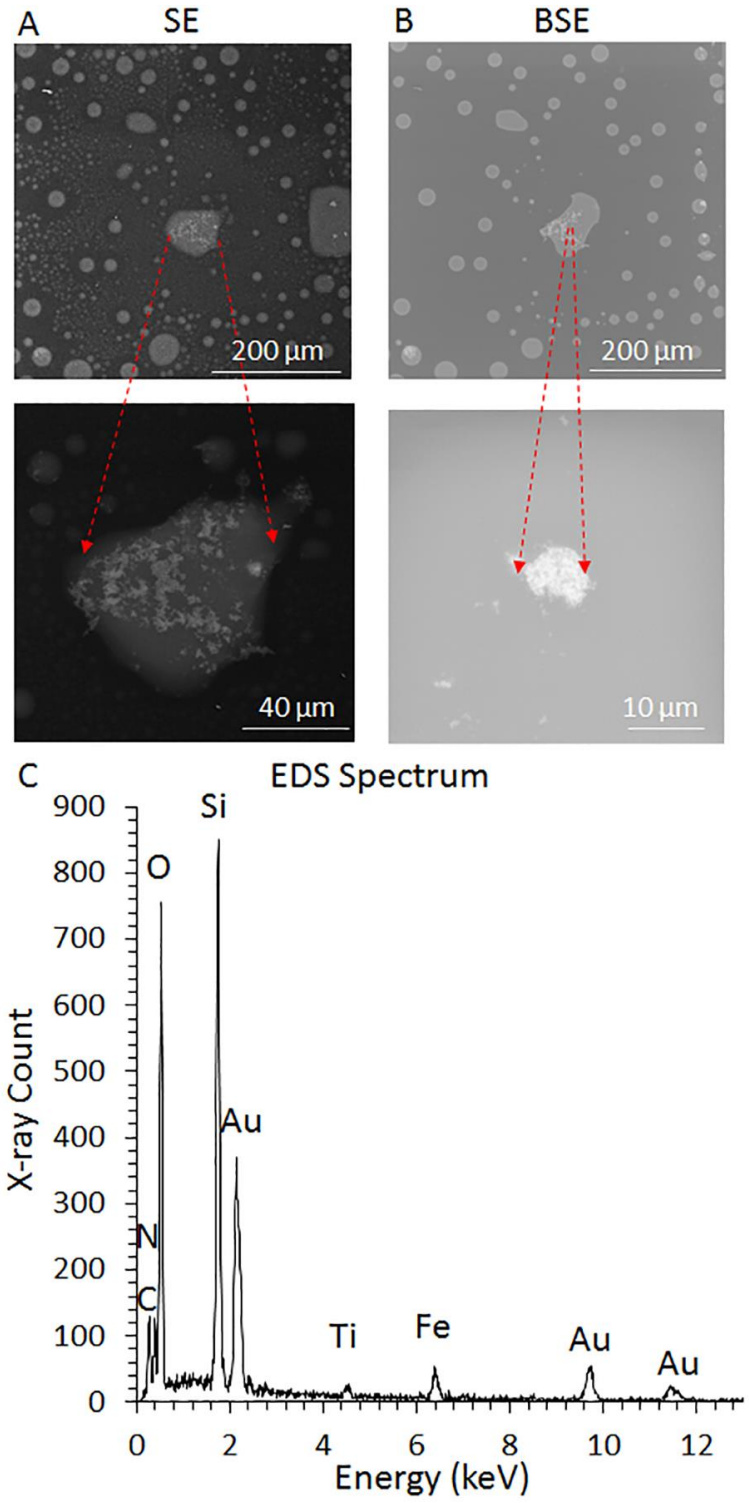

Figure 5 *In-situ* SEM imaging of Fe_3O_4 in DI water. A) SE images, B) BSE images, and C) an EDS spectrum in the high vacuum mode.

Compared to previous *in-situ* liquid SEM works using SALVI cells, we have made some development in this work. First, thinner SiN membrane was used. The images collected in Figure 4 and Figure 5 were obtained using 50 nm thick SiN membrane instead of 100 nm. Second, apertures were not used in the SEM imaging. Because we used thinner SiN windows, it is possible to acquire reasonable BSE images in the low vacuum mode. In the high vacuum mode, we also tried to do away with milling holes on the SiN membrane. The imaging results are also reasonable. This change makes our SALVI *in-situ* liquid SEM more flexible in handling diverse samples.

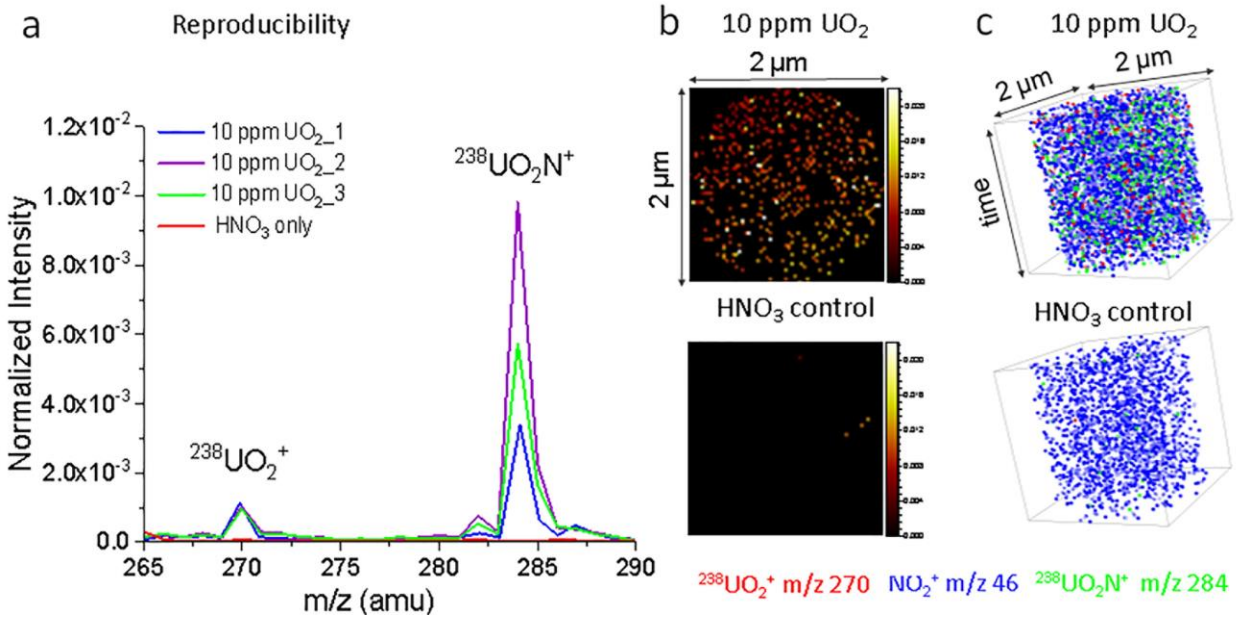

Figure 6 In-situ ToF-SIMS results: A) normalized SIMS spectra of 10 ppm UO_2 and HNO_3 control; B) normalized 2D images of $^{238}UO_2^+$ (m/z 270); and C) normalized 3D images of key observed uranium species in the 10 ppm UO_2 sample and HNO_3 control sample. Peaks are normalized to the total ion intensity.

Figure 6 shows replicate measurements of an ICP-MS standard liquid with trace-level of uranium in comparison with the solvent HNO_3 control. Figure 6A gives three replicate ToF-SIMS mass spectra of 10 ppm UO_2 in HNO_3 and a spectrum of HNO_3, demonstrating the observation of UO_2^+ (m/z 238) and the data reproducibility of uranium peaks in the positive ion mode. 2D images (Figure 6B) and 3D overlay images (Figure 6C) provide chemical spatial distributions of the uranium molecular species (i.e., m/z 270 $^{238}UO_2^+$, m/z 284 $^{238}UO_2N^+$) in ppm level. Our *in-situ* liquid SIMS results thus verify the reproducibility of *in situ* ToF-SIMS approach to study U containing liquid samples. Moreover, our results show that this is a promising approach to characterize radioactive materials at trace level and in the micrometer scale.

4.0 Electrochemical Experiments on the UO_2 system

Initial electrochemical experiments were conducted to calibrate instruments and procedures in preparation for the samples of UO_2 for the *in-situ* work.

4.1 Electrochemistry in KNO_3(pH = 3)

The electrochemistry of U(VI) was run using a three-component electrochemical cell, with Pt-disc working electrode, Pt wire auxiliary electrode and Ag/AgCl as reference electrode. The substrate exhibits a strong dependence on the nature of the electrolyte media. The voltammogram of U(VI) nitrate dissolved in 0.1 M KNO_3 showed two irreversible processes that were not present in the blank. The higher potential process at 0.23 V is assigned to a $UO_2^{2+} \rightarrow U^{4+}$ reduction while the process at -0.4V is assigned to a $U^{4+} \rightarrow U^{3+}$ reduction (Figure 7).

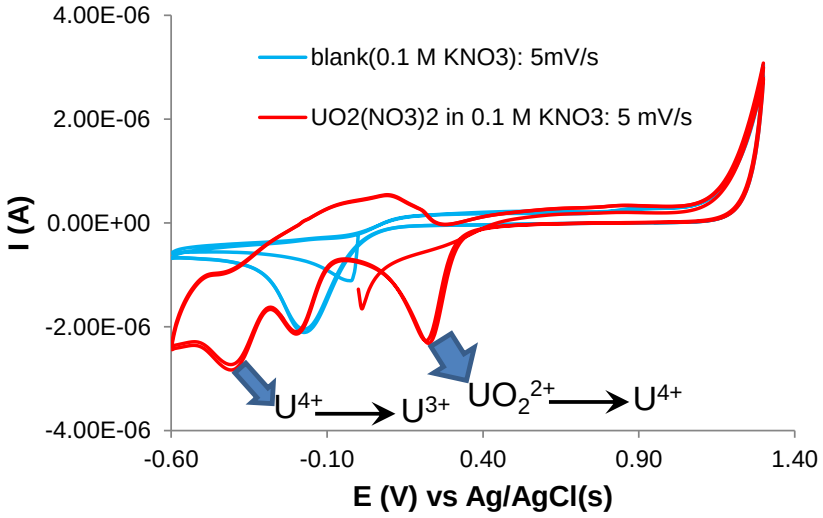

Figure 7 Cyclic voltammogram of 10 mM Uranyl(VI) nitrate in 0.1 M KNO_3.

The voltammogram of U(VI) nitrate dissolved in 0.1 M HNO_3 using the same three-electrode electrochemical set-up showed a quasi-reversible process at -0.23 V that was not present in the blank. The process is assigned to a $UO_2^{2+} \rightarrow U^{4+}$ reduction (Figure 8).

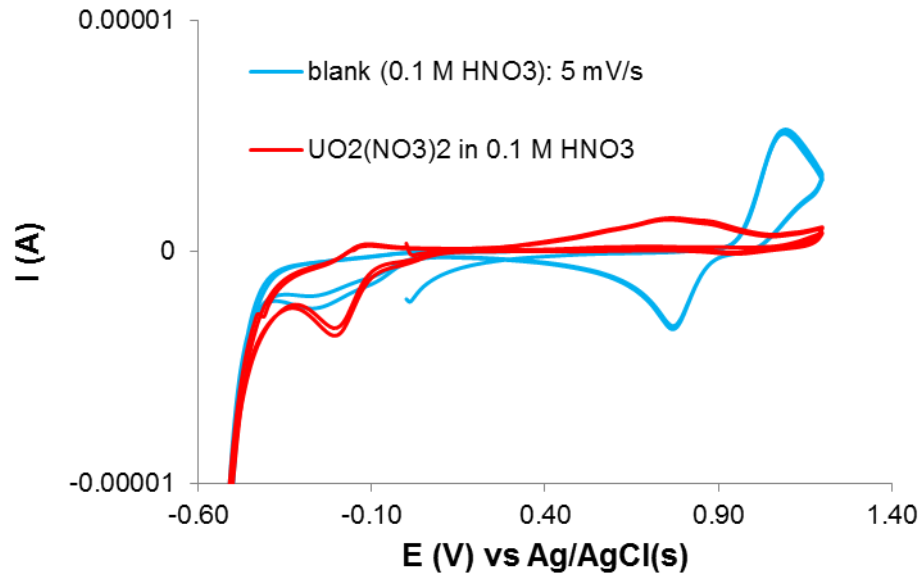

Figure 8 Cyclic voltammogram of 10 mM Uranyl(VI) nitrate in 0.1 M HNO_3.

U(VI) nitrate is only sparingly soluble in NaOH. The redox behavior using the same three electrode set-up showed a single weak low-current process that was not observed in the blank. This was tentatively assigned to a UO_2^{2+} → UO_2 reduction. (Figure 9)

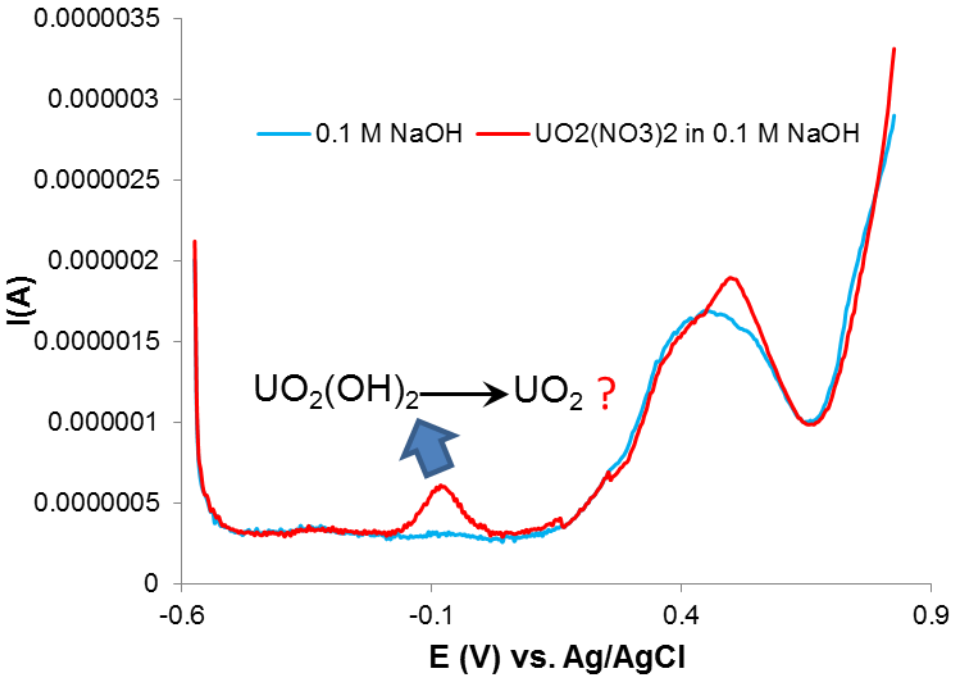

Figure 9 Differential pulse voltammogram of 1 mM Uranyl(VI) nitrate in 0.1 M NaOH

In the next reporting period, we will work with these systems inside the SALVI cell to obtain similar results so that we can establish how the smaller sized cell behaves.

In summary, the aim of this work is to investigate the corrosion of UO_2 corrosion *in-situ* in the Scanning Electron Microscope (SEM). The plan will be to measure the corrosion potential (E_{corr}) using an electrochemical workstation and a unique microfluidic reactor containing three-electrodes and compare this value to values developed by the FMDM for specific conditions. The SALVI cell (see Figure 10) can provide a methodology for obtaining these corrosion values for UO_2 under different conditions. This approach will aim to provide real-time and *in-operando* monitoring of UO_2 electrode stability and morphological changes at the microscale. The results will be utilized to validate models used for the corrosion rate of spent nuclear fuel in a geologic repository, using only small amounts of materials, and enabling a larger set of experiments to be conducted. Work in the next performance period will concentrate on building the UO_2 electrodes and running the experiments with different solutions and dissolved gas concentrations.

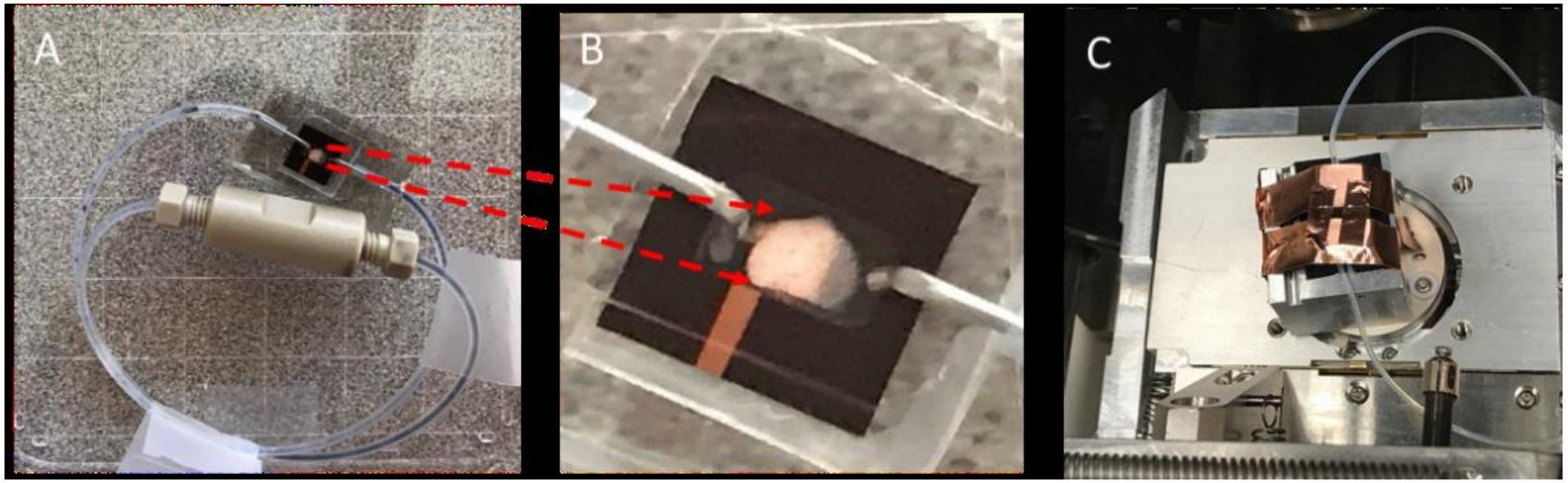

Figure 10. A) SALVI loaded with particles in DI water, B) an enlarged view of the detection area, and C) a SALVI device installed on the SEM sample stage prior to an *in-situ* SEM experiment.

5.0 CONCLUSIONS

We are developing the tools that will enable us to conduct *in-situ* liquid SEM analyses of UO_2 to validate the electrochemical model for long-term disposal of nuclear fuel. Furthermore, *in-situ* ToF-SIMS analysis could complement the *in-situ* SEM imaging and provide information on the U species forming in solution during the corrosion processes.

6.0 References

Buck, E. C. and R. S. Wittman (2014). Radiolysis Model Formulation for Integration with the Mixed Potential Model, ; Pacific Northwest National Lab. (PNNL), Richland, WA (United States)**:** Medium: ED; Size: 32 p.

Buck, E. C., R. S. Wittman, C. Z. Soderquist and B. K. McNamara (2018). "Monitoring bromide effect on radiolytic yields using in situ observations of uranyl oxide precipitation in the electron microscope." RSC Advances **8**(33): 18227-18233.

Caporuscio, F. A., S. E. M. Palaich, M. C. Cheshire and C. F. Jové Colón (2017). "Corrosion of copper and authigenic sulfide mineral growth in hydrothermal bentonite experiments." Journal of Nuclear Materials **485**: 137-146.

Conroy, M., J. A. Soltis, R. S. Wittman, F. N. Smith, S. Chatterjee, X. Zhang, E. S. Ilton and E. C. Buck (2017). "Importance of interlayer H bonding structure to the stability of layered minerals." Scientific Reports **7**(1): 13274.

Ding, Y., Y. Zhou, J. Yao, C. Szymanski, J. Fredrickson, L. Shi, B. Cao, Z. Zhu and X.-Y. Yu (2016). "In Situ Molecular Imaging of the Biofilm and Its Matrix." Analytical Chemistry **88**(22): 11244-11252.

Jerden Jr, J. L., K. Frey and W. Ebert (2015). "A multiphase interfacial model for the dissolution of spent nuclear fuel." Journal of Nuclear Materials **462**: 135-146.

Laboratory, N. B. (2013). Certificate of Analysis CRM 125-A Uranium (UO_2) Pellet Assay, Isotopic, and Radiochronometric Standard. D. o. Energy. Argonne, IL**:** 3.

Nishiyama, H., M. Suga, T. Ogura, Y. Maruyama, M. Koizumi, K. Mio, S. Kitamura and C. Sato (2010). "Atmospheric scanning electron microscope observes cells and tissues in open medium through silicon nitride film." Journal of Structural Biology **169**(3): 438-449.

Sui, X., Y. Zhou, F. Zhang, J. Chen, Z. Zhu and X.-Y. Yu (2017). "Deciphering the aqueous chemistry of glyoxal oxidation with hydrogen peroxide using molecular imaging." Physical Chemistry Chemical Physics **19**(31): 20357-20366.

Thiberge, S., O. Zik and E. Moses (2004). "An apparatus for imaging liquids, cells, and other wet samples in the scanning electron microscopy." Review of Scientific Instruments **75**(7): 2280-2289.

Yang, L., Y. X.-Y., Z. H. Zhu, T. Thevuthasan and J. P. Cowin (2011). "Making a hybrid microfluidic platform compatible for in situ imaging by vacuum-based techniques." J. Vac. Sci. Technol. A **29**(6): article no. 061101.

Yang, L., X.-Y. Yu, Z. Zhu, M. J. Iedema and J. P. Cowin (2011). "Probing liquid surfaces under vacuum using SEM and ToF-SIMS." Lab on a Chip **11**(15): 2481-2484.

Yang, L., Z. Zhu, X.-Y. Yu, E. Rodek, L. Saraf, T. Thevuthasan and J. P. Cowin (2014). "In situ SEM and ToF-SIMS analysis of IgG conjugated gold nanoparticles at aqueous surfaces." **46**(4): 224-228.

Yao, J., B. W. Arey, L. Yang, F. Zhang, R. Komorek, J. Chun and X.-Y. Yu (2017). "In Situ Characterization of Boehmite Particles in Water Using Liquid SEM." Journal of Visualized Experiments **127**: e56058.

Yu, J., Y. Zhou, X. Hua, Z. Zhu and X.-Y. Yu (2016). "In Situ Characterization of Hydrated Proteins in Water by SALVI and ToF-SIMS." Journal of Visualized Experiments(108): e53708.

Yu, X.-Y., B. Liu and L. Yang (2013). "Imaging liquids using microfluidic cells." Microfluidics and Nanofluidics **15**(6): 725-744.

Yu, X.-Y., B. Liu, L. J. M. Yang and Nanofluidics (2013). "Imaging liquids using microfluidic cells." **15**(6): 725-744.

Yu, X.-Y., L. Yang, J. Cowin, M. Iedema and Z. Zhu (2011). Systems and methods for analyzing liquids under vacuum. uspto.gov. U. S. P. a. T. Office. USA, Battelle Memorial Institute**:** 16.

Yu, X.-Y., J. Yao, D. B. Lao, D. J. Heldebrant, Z. Zhu, D. Malhotra, M.-T. Nguyen, V.-A. Glezakou and R. Rousseau (2018). "Mesoscopic Structure Facilitates Rapid CO_2 Transport and Reactivity in CO_2 Capture Solvents." The Journal of Physical Chemistry Letters **9**(19): 5765-5771.

Yu, X., J. Yu, Y. Zhou, Y. Zhang, J. Wang, J. E. Evans, X.-Y. Yu, X.-L. Wang and Z. Zhu (2017). "An investigation of the beam damage effect on in situ liquid secondary ion mass spectrometry analysis." **31**(23): 2035-2042.

Yu, X., J. Yu, Y. Zhou, Y. Zhang, J. Wang, J. E. Evans, X.-Y. Yu, X.-L. Wang and Z. Zhu (2017). "An investigation of the beam damage effect on in situ liquid secondary ion mass spectrometry analysis." Rapid Communications in Mass Spectrometry **31**(23): 2035-2042.

Zhou, Y., J. Yao, Y. Ding, J. Yu, X. Hua, J. E. Evans, X. Yu, D. B. Lao, D. J. Heldebrant, S. K. Nune, B. Cao, M. E. Bowden, X. Y. Yu, X. L. Wang and Z. Zhu (2016). "Improving the Molecular Ion Signal Intensity for In Situ Liquid SIMS Analysis." J Am Soc Mass Spectrom **27**(12): 2006-2013.

Laboratory, N. B., Certificate of Analysis CRM 125-A Uranium (UO_2) Pellet Assay, Isotopic, and Radiochronometric Standard. In Energy, D. o., Ed. Argonne, IL, 2013; p 3.

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