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NGSI FY15 Final Report

Innovative Sample Preparation for in-Field Uranium Isotopic Determinations

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1. Introduction & Background

1.1. Our FY14 Final Report¹ included an introduction to the project, background, literature search of uranium dissolution methods², assessment of commercial off the shelf (COTS) automated sample preparation systems³, as well as data and results for dissolution of bulk quantities of uranium oxides, and dissolution of uranium oxides from swipe filter materials using ammonium bifluoride (ABF). Also, discussed were reaction studies of solid ABF with uranium oxide that provided a basis for determining the ABF/uranium oxide dissolution mechanism. This report details the final experiments for optimizing dissolution of U_3O_8 and UO_2 using ABF and steps leading to development of a Standard Operating Procedure (SOP) for dissolution of uranium oxides on swipe filters.

2. Temperature Control

2.1. We have previously demonstrated that the temperature during the sample dissolution process plays a significant role in recovery of uranium from the swipe¹. Because this was such an important parameter we studied the time-dependent heating profile of our samples in conventional versus convection ovens. Gravity convection ovens employ a fan to rapidly distribute heat throughout the oven cavity providing a more uniform heat distribution and faster temperature equilibrium. It has been previously found, for beryllium analysis, that convection ovens provide faster and more efficient dissolution of beryllium oxide from industrial hygiene swipes⁴. To study the oven and sample temperature profiles, we inserted a calibrated thermocouple into the oven chamber and a second thermocouple was immersed in one tube of a sample digestion batch. Both ovens were preheated and equilibrated to the temperature set point prior to analysis and the oven doors were opened for the shortest possible time to load the sample tray. For both types of ovens the chamber temperature did not vary greatly when the door was opened and equilibrated to the set point relatively quickly, with the convection oven performing a little better in this respect relative to the conventional oven, as would be expected (Figure 1). Our data showed the sample liquids took a surprising long time to equilibrate with oven chamber temperature. For the conventional oven, 10 mL of sample took 55-60 minutes to equilibrate. For the convection oven, the equilibrium time was reduced to 35-

40 minutes. With these experiments we confirmed the convection oven was superior to the conventional oven for quick sample heating. A convection oven was used for all subsequent experiments described here.

Figure 1

2.2. To test sample digestion with the convection oven we measured the recovery of U_3O_8 as a function of time and temperature to optimize the dissolution process. For 25 μg of U_3O_8 loaded onto Whatman 41 ashless filters, full recovery of the uranium occurred after 40 minutes of heating with the sample temperature reaching 80°C (Figure 2). Under these conditions we have consistently obtained recoveries of >90% for U_3O_8 from swipes.

Figure 2

3. Optimization of ABF extraction of U_3O_8

3.1. Based on the oven temperature studies we repeated several experiments involving dissolution of U_3O_8 on swipes in order to optimize the procedure. We varied the temperature from 25°C (room temperature) to 80°C. Higher temperatures were not explored due to the possibility of boiling the sample and eliminating the need for special heat-resistant sample tubes. The digestion time was set at 50 minutes for this set of experiments. From Figure 3a, it can be seen that recoveries of >90% were achieved at 60°C and complete recoveries occurred at 80°C for all three concentrations of uranium oxide (2 μg -low, 10 μg -medium, and 20 μg -high per swipe). We also varied the digestion time from 10 minutes to 60 minutes at a fixed temperature of 80°C. Although the recoveries were somewhat inconsistent, we obtained the adequate recoveries at an incubation time of >40 minutes, with the most consistent recoveries occurring at 60 minutes. Based on both temperature and time studies, shown in Figures 3a and 3b, we

have determined the optimal conditions for U_3O_8 dissolution is 80°C for 40-60 min in 1% ABF using a 10 mL sample volume. It should be noted that the dissolution time corresponds to the total time the sample spent in the oven and not the actual time at sample temperature. As previously reported the dissolution solution takes up to 40 minutes to reach equilibrium temperature using a pre-heated convection oven. Under these optimized conditions we are consistently getting greater than 90% recovery of uranium with uranium concentration ranging from 2 μ g (low), 10 μ g (medium), and 20 μ g (high) per swipe.

Figures 3a,b

4. Dissolution of UO_2

4.1. As previously discussed¹ UO_2 is less reactive in ABF solutions than U_3O_8 and is therefore more difficult to dissolve in bulk (mg quantities), but it appears that for smaller (μg quantities), ABF is effective in dissolving UO_2 deposited on swipes. Figure 4 shows the dissolution of 5, 10, and 30 μg of UO_2 per filter. The ABF concentration was 1% and the samples were heated for 45 minutes at 80°C. For each UO_2 concentration a sample was maintained at room temperature to serve as a control. We obtained >90% recovery for all uranium concentrations. A somewhat high recovery for the 30 μg control sample was observed. Subsequent follow-up experiments show this result was anomalous with subsequent control sample being closer to 50-60% recovery.

Figure 4

4.2. Figure 5 shows a time study where dissolution times varied from 1-24 hours at 80°C using a 1% solution of ABF. Dissolution is 100% complete after 24 hours and >80%

complete after 4 hours using uranium concentrations from 2 μ g (low), 7 μ g (medium), and 15 μ g (high) per swipe.

Figure 5

4.3. We also studied the effect of ABF concentration on UO₂ dissolution in order to decrease the long dissolution times shown in the data presented in Figure 5. Figure 6 shows dissolution of UO₂ using ABF concentration ranging from 1-10% (w/v), heating at 80°C for 1 hr. Interestingly, the greatest recovery occurred at the lowest ABF concentration, although it should be noted that this particular batch of swipes showed considerable amount of variation in uranium concentration as witnessed by the large error bars.

Figure 6

The optimum ABF concentration for UO_2 dissolution was found to be 1% (shown in **Figure 6**). The higher ABF concentrations didn't have an increased effect on uranium dissolution. The optimum time it takes to dissolve UO_2 was found to be 4 to 6 hours, but after 1 hour, we still get at least 80% uranium dissolved (shown in **Figure 7**).

Figure 7

4.4. A long term reproducibility study was completed for UO_2 using the optimized conditions (1% ABF and heated at 80 °C for 1 hour). Over 5 consecutive days triplicate samples of three different concentrations (2 μg -low, 7 μg -medium, and 15 μg -high per swipe) were run. Results are shown in **Figure 8**. We consistently achieved recoveries >85% on average. These same optimized conditions for UO_2 dissolution also work for U_3O_8 dissolution.

Figure 8

5. Conclusions

5.1. The goal of this project was to develop a simple and effective method for dissolution of uranium oxides from environmental swipe samples. Ideally the method would be useful in the field for quantitation of uranium and determination of uranium isotopics. The method had to be relatively fast, safe for the operator, simple to implement by a non-technical expert, uses minimal equipment, and supplies, easily transported, compatible with existing down-stream sample preparation and analysis techniques, and cost effective. Our approach was to substitute traditional acid-based digestion methods with a uranium extraction technique based on dilute solutions of ABF. We have demonstrated our method is effective in dissolving U_3O_8 and UO_2 deposited on cotton swipe materials. A summary of this method's performance based on our desired performance criteria is as follows:

- **Effectiveness:** We have demonstrated our ABF technique routinely achieves >85% recovery of U_3O_8 and UO_2 from swipes. This method can be considered quantitative. Although we have not performed isotopic analysis on the digestates, we do not anticipate isotopic fractionation to be an issue with such large recovery found with this method.
- **Speed:** This method takes approximately 90 minutes to complete as compared to >8 hours for traditional methods based on total digestion of the sample and filter

material using mineral acids. The method is suitable for parallel sample processing and is inherently automatable.

- **Compatibility:** We have demonstrated the product of this method is suitable for further analysis using techniques such as ICP-OES, ICP-MS, and other atomic spectroscopy techniques. In addition there is no reason, with minimal matrix modifications, the ABF solution can be further processed using standard chromatographic technique, such as those used for radiochemistry.
- **Complexity:** This method is very simple. The method requires the operator to place the swipe in a test tube, add ABF, and incubate the solution in an oven at a set temperature and time. Optionally, the solution may need to be filtered with a syringe filter to remove particulates that were associated with the original sample. A skilled or technically-trained operator is not required to successfully implement the method.
- **Equipment and Supplies:** The only equipment and supplies required could be found in any standard analytical laboratory. These include: a convection oven, pipettes, test tubes, test tube rack, and syringe filters (optional).
- **Fieldability:** This method can easily be adapted for field operations. Besides equipment, supplies, and reagents, the only requirements are standard electricity to power the oven. Given the relatively low incubation temperatures required, it is conceivable a solar-powered oven would suffice.
- **Transportation:** All equipment and supplies can easily be transported. All components are rugged and can be packaged into a travel case. In addition, ABF is much less hazardous to transport than mineral acids. If necessary the ABF can be transported as a solid and made into the solution form on-site.
- **Cost:** The equipment, supplies, and reagents are very inexpensive and all can be found commercial off the shelf. All items are also readily available from laboratory or medical supply stores.
- **Safety:** Although our studies were not specifically designed or tasked to provide a comprehensive safety analysis of the method, our experience and background research concluded dilute solutions of ABF are safe to handle using common protective equipment such as safety glasses, nitrile gloves, and adequate ventilation. This method is certainly less hazardous than traditional methods that used hot, concentrated mineral acids. Specific applications of this method must be independently evaluated for safety concerns and hazard mitigation in accordance with the user's specific safety program.

6. References

1. Yoshida, TM, Leibman, CP, Meyers, L, and Xu, N "Innovative Sample Preparation for in-Field Uranium Isotopic Determinations. LA-UR-14-29701, 2014.
2. Meyers, L, Leibman, CP, Drake, R, Chamberlin, B, Castro, A, Yoshida, T, Xu, N. "Uranium Oxide Dissolution Review" LA-UR-14-23647, 2014.
3. Meyers, L, Castro, A, Xu, N. "Assessment of COTS Automated Sample Preparation Systems for Uranium Swipe Dissolution" LA-UR-14-25693, 2014.
4. Goldcamp, MJ, Goldcamp, DM, Ashley, K, Fernback, JE, Agrawal, A, Millson, A, Marlow, D, and Harrison, K. J of Occ and Env Hygiene, 6:735-744, 2009.

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Dissolution of Uranium Oxides on Swipes and Filters using Ammonium Bifluoride

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2. INTRODUCTION

This procedure details the quantitative dissolution of triuranium octoxide (U_3O_8) and uranium dioxide (UO_2) collected on filter or swipe material. Dissolution of uranium oxide is accomplished by means of a dilute aqueous solution of ammonium bifluoride (ABF) assisted by incubation at elevated temperature.

3. PURPOSE

This standard procedure provides written guidance detailing the analytical processes followed by laboratory personnel when determining the concentration of uranium oxide material on filter media via digestion by ammonium bifluoride. A general analyst will be able to consistently generate data by following the procedure outlined below.

4. SCOPE AND APPLICATION

This procedure identifies the necessary equipment and materials and describes the steps involved in uranium dissolution on swipes and filters using ABF.

Swipe samples are digested in a convection oven for uranium dissolution in a dilute ABF solution. The filtered solution sample is then analyzed by Inductive coupled plasma optical emission spectroscopy (ICP-OES) or other suitable techniques. Uranium solutions derived from this procedure may be suitable for other analytical techniques or processes, but have not been tested, as such.

This procedure has been demonstrated to be effective on upto 50 μg (as U) of U_3O_8 or UO_2 on Whatman 41 filters and Texwipe TX304 cotton wipes. Higher concentrations of uranium or different swipe materials may not yield the same results.

5. SUMMARY OF METHOD

Environmental swipes containing uranium oxide are digested in a convectional oven for a desired time period at a maximum temperature of 80°C in dilute 1% (w/v) ABF solution. After heating for the specified time, the samples are cooled and filtered. Samples are then analyzed using ICP-OES for analysis. Analyte concentration is typically reported in units of ug/filter for swipe samples.

6. DEFINITIONS

- 6.1. ABF: Ammonium bifluoride
- 6.2. ICP-OES: Inductive coupled plasma optical emission spectroscopy
- 6.3. U_3O_8 : Triuranium octoxide
- 6.4. UO_2 : Uranium dioxide
- 6.5. U: Uranium
- 6.6. (w/v) weight per volume

7. RESPONSIBILITIES

- 7.1 Line Management
 - Authorizes work and workers in accordance with the IWM process
 - Ensures individuals assigned to perform work under this procedure are trained and qualified.
- 7.2 Trained and Qualified Individuals
 - Perform this procedure as written, except as noted.
 - Contact supervision for non-compliant conditions.
 - Adhere to the safety and security requirements required to perform operation.

8. SAFETY AND INCIDENT RESPONSE

In general, this analytical procedure involves the use of hazardous chemicals, heat sources, electrical systems, and pressurized systems. When working within the laboratory, personnel must wear the following PPE at a minimum: gloves, safety glasses, a lab coat, full-length pants, and closed toe shoes. All sample digestion is performed in a chemical fume hood. Typical ICP spectrometers utilize a high voltage RF power supply, pressurized gas sources, and recirculated water to operate under normal conditions. ICPs are manufactured with effective interlocks and engineered controls, which allow it to be operated safely. A hazardous condition would result if these controls were defective or intentionally defeated. The plasma itself is a source of intense UV radiation, ozone, and potentially toxic air emissions. The ICP exhaust must be safely vented from the laboratory.

In the event of an injury requiring medical attention, the affected individual shall receive initial treatment from Occupational Medical Clinic personnel unless otherwise directed by emergency responders or a health professional.

9. SAMPLE PRESERVATION AND STORAGE

ABF solution is stored in a plastic or telfon container with secondary containment. Uranium swipe samples are stored in petridishes according to their concentration ranges, which are stable and do not require preservation.

10. INTERFERENCES

Spectral interference arising from molecular species or concomitants in the sample can contribute to inaccurate measurement of the analyte of interest. Spectral interference is minimized through proper wavelength selection, use of interelement correction factors, and background correction points. Physical differences such as solution viscosity, high dissolved solids, and the presence of suspended material will adversely affect uptake, transport, and nebulization of solutions. Interferences are identified and minimized by matrix matching of calibration standards and samples; filtration and dilution; use of daily performance check standards; and routine instrument maintenance.

11. APPARATUS AND MATERIALS

Apparatus and Materials
Swipe Material (Whatman 41 filters or Texwipe TX304 Cotton Wipes)
15 mL BD polystyrene conical tube
14 ml BD Falcon polypropylene round bottom tubes
BG (Becton, Dickinson and Company) 0.7 μm GF/F syringe filters
BG (Becton, Dickinson and Company) 10 mL syringes
Convection oven
Vortex mixer
Manual pipette
Test tube racks
Forceps, tweezers, tongs
Chemical fume hood
Inductively Coupled Plasma Emission Spectrometer (ICP)
Water purification system
Personal computer
Personal Protective Equipment- gloves, safety glasses, lab coat
Ammonium bifluoride (Ricca Chemical Co)

12. PROCEDURE

- 12.1. Sample preparation should be carried out in a fume hood
- 12.2. Set temperature of convection oven to 80°C
- 12.3. Insert one trifolded swipe in a 15 ml polystyrene conical tube and push it all the way to the bottom using tweezers. Repeat for each sample
- 12.4. Accurately pipette 10 ml of 1% (w/v) ABF into each tube
- 12.5. Cap tubes and vortex each for a few seconds
- 12.6. Loosen caps to prevent overpressure and place the tubes in the oven at 80°C for 1 hr

- 12.7. Take tubes out of the oven and immerse them in room temperature water for 10 minutes to cool
- 12.8. Tighten caps and shake tube to mix solution
- 12.9. Filter the content of each tube into 14 ml Falcon polypropylene round bottom tubes using 10 mL syringe and 0.7 µm GF/F syringe filters. Filter a sufficient amount of solution as required for analysis
- 12.10. Analyze samples using ICP-OES or compatible technique

13. QUALITY ASSURANCE/QUALITY CONTROL

This procedure has been thoroughly tested to achieve maximum dissolution (>85%) of uranium oxide on swipe material under the specified process and conditions. This procedure does not address specific QA/QC requirements as those are specific to individual projects and programs. The analyst should incorporate adequate QA/QC processes and check samples as required.

14. DOCUMENTATION

None

15. WASTE MANAGEMENT

The accumulation, storage, and disposal of chemical waste generated by this procedure is governed by LANL waste management procedures as well as applicable local, state, and federal permits and regulations. The area waste management coordinator shall be consulted for all waste management issues. At a minimum:

- Process wastes are segregated according to chemical compatibility and disposal pathway.
- Waste profile forms are completed for each waste and a unique waste profile number (WPN) is assigned.
- A waste profile is required for each new waste stream.
- Waste profiles are reviewed and updated annually.
- Waste containers are labeled appropriately with the WPN, contents, location, and owner.
- Waste containers must be compatible with the waste being generated and shall be capped when not in use.
- Secondary containers shall be used for all waste accumulation areas and satellite storage areas.

16. TRAINING

Analysts performing work on customer samples shall be trained initially to this Standard Procedure. Before performing the activities described in this Standard Procedure, each employee must complete site-specific training and be authorized to perform work.

17. REFERENCES

None