Development of solid materials for UF_6 sampling

Final Report on the development of the HORUS system

Nuclear Engineering Division

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EXECUTIVE SUMMARY

This project demonstrated that a device using majority Commercial Off the Shelf (COTS) components could be used to collect uranium hexafluoride samples safely from gaseous or solid sources. The device was based on the successful Cristallini method developed by ABACC over the past 10 years. The system was designed to capture and store the UF_6 as an inert fluoride salt to ease transportation regulations. In addition, the method was considerably faster than traditional cryogenic methods, collected enough material to perform analyses without undue waste, and could be used either inside a facility or in the storage yard.

In its final iteration, the Handheld Operation for Rapid Uranium Sampling (HORUS) was slightly over 1 ft³ and weighed less than 15 pounds. The unit was capable of running for at least 1 hour without replacing battery packs and utilized Li-ion and NiCad commercial-production level batteries to avoid shipping issues with prototype level batteries. The alumina traps that capture the UF_6 could safely store up to 120 mgs of material with a 5x safety factor under a total operation time of ~10 minutes from setup to strike. The actual collection time was <20 seconds. The system had onboard power, vacuum and gas flushing systems to ensure operator safety. Multiple test campaigns were performed to show that the system could be safely flushed of material prior to removing the sample. These tests also characterized the cross contamination potential and the source pressure/collection relationship.

A version of HORUS participated in a field test at Pacific Northwest National Laboratory in late FY17 along with two other technologies. The unit was able to collect material from a mock sample tap successfully despite the failure of two solenoid valves. A redesigned unit, HORUS-4, was made to solve the issues identified during this test and is ready for additional testing.

CONTENTS

Executive Summary	i
Contents	ii
Figures.....	iv
Tables.....	iv
Acknowledgments.....	v
Acronyms and Initialisms	vi
1 Introduction.....	1
1.1 Traditional Collections.....	1
1.2 Difficulties with sampling.....	1
1.3 Opportunities to improve	1
1.4 Collection Chemistry	2
1.5 Conceptual design for a portable unit	2
2 Material Studies	4
2.1 Setup.....	4
2.2 Tungsten Exposures	4
2.3 Uranium Exposures.....	5
3 Engineering	7
3.1 HORUS-1	7
3.1.1 Vacuum System.....	7
3.1.2 Control system.....	11
3.2 HORUS-2.....	11
3.2.1 Vacuum System.....	11
3.2.2 Control system.....	13
3.3 HORUS-3.....	13
3.3.1 Vacuum System.....	15
3.3.2 Control system.....	15
3.4 HORUS-4.....	15
3.4.1 Vacuum System.....	15
3.4.2 Control system.....	17
4 Collection Efforts.....	19
4.1 Uranium collection characteristics	19
4.2 Passivation layer tests	19
4.2.1 Water mitigation.....	19
4.2.2 Flushed with N ₂	20
4.2.3 Exposed to UF ₆ for set amount of time	21
4.3 Loading/breakthrough tests.....	21
4.4 Flushing/holdover tests	23
4.5 Nitric Acid Flush.....	24
4.6 Source pressure tests	25
4.7 Cross contamination tests.....	28
4.8 Operational Lessons and Instrument Disassembly	29
4.8.1 Unwanted uranium deposition	29

4.8.2 Water Trap.....	30
5 Field Testing	31
5.1 Test setup and commissioning	31
5.2 Field Test Notes	33
5.3 Further testing	33
6 Project Summary.....	34
7 References.....	35

FIGURES

Figure 1. Concept diagram of hand held device.....	3
Figure 2. Testing Rig (tungsten):.....	4
Figure 3. Analysis of Tungsten hexafluoride deposition on alumina grit.....	5
Figure 4. A photo of the source system	6
Figure 5. Uranium deposit on alumina	6
Figure 6. Block diagram for the original HORUS-1.....	7
Figure 7. Chromatography columns filled with alumina for use in the previous year's tungsten hexafluoride experiments.	9
Figure 8. The final implementation of the laboratory set-up, also known as HORUS-1	10
Figure 9. Photos of the original steel trap design and its successor, both with quick disconnects	10
Figure 10. A photo of the water bath and vacuum pump set-up during decommissioning.	11
Figure 11. A block diagram and photograph of HORUS-2.	12
Figure 12. Sled and plumbing design for HORUS-3, showing the original inception with quick connects.	14
Figure 13. Photos depicting the electrical housing grooves and modular construction along with the completely assembled unit.....	14
Figure 14. A block diagram of the HORUS-4 design	16
Figure 15. Clear PVC trap filled with approximately 2 grams of alumina	16
Figure 16. The control panel of the HORUS-4 unit.....	17
Figure 17. Connections and rear panels of the HORUS-4 unit	18
Figure 18. Chart relating the mass fraction of uranium recovered (actual/expected) as a function of the exposure number for a particular sample in a successive run of exposures	20
Figure 19. Close-up photo of a partially exposed chromatography column	22
Figure 20. Uranium mass present in successive effluent samples from exposed alumina columns	25
Figure 21. Plot demonstrating the lack of a relationship between the uranium hexafluoride source pressure and the amount of material recovered	27
Figure 22. A chart demonstrating the relationship between the change in source pressure and the recovered mass of uranium	28
Figure 23. The HORUS UF ₆ DA Sampler Installation for the Phase I Rodeo	31

TABLES

Table 1. Multiple breakthrough tests using alumina-packed chromatography columns	23
Table 2. Holdover experiments using pair of columns	24
Table 3. Collected masses and measured mass ratios for the cross contamination tests	29
Table 4. Sample results from PNNL Field Test	32
Table 5. Total uranium results by kinetic phosphorescence analysis (KPA)	33

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ACRONYMS AND INITIALISMS

ABACC.....	Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials
ANL	Argonne National Laboratory
CA	Contamination Area
COTS	Commercial Off the Shelf
DA.....	Destructive Analysis
HORUS	Handheld Operation for Rapid Uranium Sampling
IAEA	International Atomic Energy Agency
ICP-MS	Inductively Coupled Plasma – Mass Spectrometer
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
IR.....	Infrared (spectroscopy)
IS	Ion Source
HORUS	Handheld Operation for Rapid Uranium Sampling
KPA.....	Kinetic Phosphorescence Analysis
LOD	Limit of Detection
ORNL.....	Oak Ridge National Laboratory
OSHA.....	Occupational Safety and Health Administration
PNNL	Pacific Northwest National Laboratory
RWP	Radiological Work Permit
UF ₆	Uranium Hexafluoride
VDC	Voltage Direct Current
XRF.....	X-Ray Fluorescence

1 INTRODUCTION

As part of the comprehensive safeguards package at gaseous enrichment facilities, uranium hexafluoride (UF_6) samples must be taken for enrichment verification. Gaseous samples can be obtained either from cylinders or directly from process lines. These samples have associated transport and handling risks and require vacuum rated samplings cylinders. By capturing and storing these samples as an inert salt, these hazards can be mitigated. This is the basis behind the Argentine Agency for Accounting and Control of Nuclear Materials Cristallini technique (ABACC-Cristallini) currently under development. However, this method requires facility modifications and has not yet been widely adopted.

This project aimed to develop a field-portable, hand-carried system to utilize the ABACC-Cristallini method for sampling uranium hexafluoride; the method stores the sampled material as uranyl fluoride. The system reduced the weight of sampling materials carried by an inspector and reduced the necessary sampling time. Additionally, the developed device could be used to collect measurements at existing facilities using inspector-controlled technology. The device utilized a modular and commercially available construction philosophy to reduce costs.

1.1 TRADITIONAL COLLECTIONS

Currently, samples are collected from a Gas Centrifuge Enrichment Plant for a number of reasons including for analysis to meet customer specification and verification of the plant's operation under a safeguards agreement. Concerning the later application, samples can be taken directly from the sample tap or from the feed/product cylinders on site. These samples are then transported back to the safeguards laboratory (IAEA or Regional Safeguards Authority) for isotopic determinations.

1.2 DIFFICULTIES WITH SAMPLING

While this activity seems straightforward, the logistics of sampling can be quite involved. For samples taken at the GCEP tap, care must be taken not to introduce any impurities into the multimillion-dollar enrichment plant during sampling. If sampling at the cylinder, there is a long process to retrieve the target cylinder, which may be residing in an exterior storage yard, and return it to the facility where it will be weighed and possibly homogenized in an autoclave.

These samples are generally collected through one of two methods. For tap and cylinder headspace samples, a receiving vessel is attached to the source and immersed in liquid nitrogen. This causes the gaseous UF_6 to solidify in the tube thus producing a sample that can be isolated via valve and separated. For cylinder samples post homogenization, the hot cylinder may be tapped to allow liquid UF_6 to flow into a sample bottle. The cylinder would then be re-weighed after cooling and returned to the storage yard.

1.3 OPPORTUNITIES TO IMPROVE

There are a number of inefficiencies with this approach. The main issue is that both methods collect a large amount of sample, approximately ten to hundreds of grams. For the safeguards analysis, milligrams of material would be sufficient to complete multiple replicates. Due to the inaccuracy in cryogenic sampling, enough material (~10 grams) must be collected

in the receiving vessel to be accurately weighed, thus increasing the amount collected. Liquid samples are even larger with up to 1 kg being collected in a large bottle, which is subsequently split into several batches. Reducing the collected mass to less than a gram would likely allow the material to be collected without stringent weighing requirements. As for collections from cylinders, if the long process of retrieving and sampling the tank could be reduced or eliminated, then a significant time savings could be realized.

The other main opportunity (which ABACC seized on with their Cristallini method) lies in the transportation of UF₆, which is highly regulated. Bulky pressure-vessels must be used to ship the material as it is a toxic gas. By changing the form of the uranium to an inert salt, the shipping onus would be reduced dramatically to the point where some samples could be hand carried.

1.4 COLLECTION CHEMISTRY

The general chemical process being studied has been under development by ABACC and the greater nuclear industry for >40 years. When UF₆ is exposed to a hydrated material (in this case alumina), the hexafluoride reacts with the water to form a uranyl salt and hydrofluoric acid. Given a suitable substrate, the hydrofluoric acid will back-react to form additional water and fluoride salts.

The Cristallini method uses alumina pellets in a P10 tube to collect samples. The tube is placed under vacuum and the contents within are subsequently exposed to UF₆. As the water in the alumina is consumed, the reaction slows and eventually the tube is removed and sealed. In past tests, the method has been shown to collect 600 mg of uranium in approximately 80 minutes (which is on the same order of time as cryogenic collections).

1.5 CONCEPTUAL DESIGN FOR A PORTABLE UNIT

The Cristallini method works well and is currently undergoing certification as a standard method. However, the method is a fixed laboratory implementation; this makes it ideal for taking samples from the tap or from a cylinder in a special withdrawal station in the facility. It does not reduce the time required to retrieve and prepare the cylinder. Therefore, by making a version of this system that utilizes the same chemistry but can be taken to the cylinder, large time and effort savings can be realized. This system could also be used at sample taps if a full Cristallini station had not been installed or certified yet.

The design basis for the portable version required on-board power and vacuum systems, safety features to protect the operator, the ability to flush and clear the system as well as the flexibility to be mated to several potential uranium sources. The system was made from inexpensive, off-the-shelf components to reduce overall cost and decrease maintenance. The original conceptual design is given in Figure 1.

- *Pump* – A small battery operated pump was needed to provide a driving force for the system. The pump was also used to evacuate the system prior to use and to help evacuate the system after collection of the sample (with nitrogen assist). These pumps needed to be

COTS components and could be purchased in configurations that would be resistant to attack by UF_6 . The pump was purchased to operate on 12/18 VDC that could be easily supplied by COTS battery packs. The pump discharge needed to be sufficient to pull a significant amount of process gas into the sample chamber in a short amount of time.

- *Dry gas purge* – In order to completely flush the system after use, COTS nitrogen, nitrous or carbon dioxide cartridges (similar to those used in the food industry) needed to be used to provide a dry system flush. These cartridges are readily available and provide approximately 1 liter of dry gas. These cartridges would provide a convenient method to flush the system and remove as much process gas as possible prior to removing the sample cartridge, enhancing the safety of the system. Ultimately, these cartridges were passed over in favor of an in-house nitrogen supply bottle for ease of experimentation, but the benefits of a cartridge method on a commercial system are still valid and desired.
- *Sample and filter module* – Using a packed bed of substrate material, a sample cartridge was envisioned that would couple with both the pump and the cylinder connection hardware. It was also desired that the cartridge have features that facilitate stripping of the material off the bed by the analytical laboratory staff, such as ports for the introduction and removal of acids, gas purges, etc. The cartridge needed to resist attack by HF long enough to allow the neutralization agent to react completely. A high performance filter, such as a molecular sieve, was planned for the sample (or pump) outlet to prevent any UF_6 from exiting the apparatus. The filter module also needed to ensure that any residual HF was captured and neutralized.

Figure 1. Concept diagram of hand held device. *The components contained within the tan housing were under consideration during the conceptual design phase. The components outside the box were considered uncontrollable.*

2 MATERIAL STUDIES

2.1 SETUP

In order to test potential adsorbent materials prior to completely engineering a field deployable system, a testing rig was created that could deliver a reliable supply of tungsten hexafluoride at ~80 Torr. For complete details, please see this project's FY16 annual report [1] and report on material testing [2]. A summary of that work is provided here for completeness and context.

As shown in Figure 2, the testing rig was composed of a concentrated source of material that was directed via a valve into a nickel-lined 1-gallon expansion tank. This tank was filled with tungsten to the room temperature vapor pressure of UF_6 , ~80 Torr, for testing applications (note: the room temperature vapor proof tungsten hexafluoride is >760 Torr). The outlet of the tank was connected to a series of material cartridges packed with various substrates. The cartridges were then connected to a guard trap and a vacuum pump that was vented through a water trap. This allowed for safe testing under relevant conditions.

Figure 2. Testing Rig (tungsten): This setup was used to demonstrate the proof of concept of gas transport and collection of a reactive hexafluoride.

2.2 TUNGSTEN EXPOSURES

The testing rig was used to capture tungsten hexafluoride on multiple substrates. Generally, ~100-200 micron alumina powders performed well and captured test charges of 0.1 grams of tungsten hexafluoride. The total collection time was generally on the order of minutes (1-3), which is significantly faster than the original Cristallini method. The alumina samples showed no breakthrough of material to subsequent samples or to the system trap.

Samples were submitted to the Argonne Analytical Chemistry Laboratory to determine total tungsten content via total dissolution of the substrates followed by ICP-MS analysis. In general, the medium grain alumina samples retained the predicted amount of tungsten and downstream samples showed no discernable tungsten deposits. Figure 3 shows some of the qualitative measurements made of fresh tungsten deposits in a column packed with alumina.

Figure 3. Analysis of Tungsten hexafluoride deposition on alumina grit. *Left - XRF spectrum showing the tungsten content at the top of the sample column (blue) and the bottom (red); Right - IR image of the top of the column during deposition showing the high localization of the reaction in the upper 1 cm of substrate.*

2.3 URANIUM EXPOSURES

A second system was setup up analogous to the tungsten setup to test materials with uranium. While the research team was confident that the uranium would behave in a similar fashion, a set of samples was collected to test that hypothesis. The uranium gas was supplied to the system by a small imitation facility set-up (Figure 4). The unit consisted of an evacuated P10 tube filled with solid uranium connected to a charge tank. The charge tank was initially 125 mL in size (not pictured) but was replaced with a 3.8 L when the larger volume was needed. The UF_6 was allowed to sublime into the evacuated tank and the volume of the charge tank helped mitigate the effects that a drop in supply pressure might have on collection characteristics. There were also a pressure transducer and a nitrogen supply valve fashioned on the charge tank; the pressure transducer enabled the operator to control the supply pressure by only allowing the UF_6 to sublime to a desired pressure before closing the valve between the P10 tube and the charge tank. The nitrogen supply allowed the operator to flush the charge tank, ridding it of whatever gas it contained. This system would eventually become HORUS-1.

The uranium collection proceeded as expected with deposition occurring in the first of three consecutive alumina packed columns (Figure 5). At this point, the concept of the project was determined to be feasible and the work scope shifted to engineering and control. The collection parameters for UF_6 with respect to pressure, amount collected, time, etc. needed to be determined for the final concept. In addition, robust engineering controls needed to be implemented to ensure worker safety and facility acceptance.

Figure 4. A photo of the source system. *The pressure transducer is to the left, the charge tank is clearly visible and the nitrogen inlet is to the right. The solid UF₆ source is obscured by the pressure transducer.*

Figure 5. Uranium deposit on alumina. *This sample showed high specific uptake and proved that the concept developed for tungsten would also work for uranium. The color change as a result of deposited uranium is evident and the sharp division between exposed and not-yet exposed alumina can be clearly seen. The loose frit above the deposition area can also be seen to have reacted with the UF₆.*

3 ENGINEERING

This section details the mechanical and electrical engineering involved in the various implementations of HORUS. These iterations show the progression from a viable concept to a field test ready version.

3.1 HORUS-1

The HORUS-1 system was originally designed as a functional copy of the tungsten hexafluoride (WF_6) exposure system described here and in the FY16 year-end report [1]. The purpose of the system was to take the lessons learned in the FY16 analogous tests and implement them in a similar system to prove the chemistry and kinetics of UF_6 collection behaved similarly to WF_6 , as expected. It was also intended as a test system that would be characterized and modified to test new designs, parts, and procedures. As such, the final design of HORUS-1 is significantly different from its initial design. Changes in design for all versions of HORUS will be mentioned in this section, though the motivation behind such changes will not. The next section, which details the tests and experiments performed with HORUS-1, will describe the consequences of the results in relation to instrument design.

3.1.1 VACUUM SYSTEM

While HORUS-1 was initially designed to mimic the WF_6 instrument closely (see FY16 year-end report), there were some changes in material and hardware choices with the understanding that HORUS-1 was a more permanent installation than the WF_6 collector was. A depiction of the original HORUS-1 design is given in Figure 6.

Figure 6. Block diagram for the original HORUS-1. *The attached mock facility is also shown. The valves labeled with letters are manual ball valves while those labeled with numbers are diaphragm solenoid valves. To the left of the red line is the depicted mock facility set-up that did not change throughout the experiments. To the right of the red line is HORUS-1 as designed with quick disconnects, the first change made to the column-style HORUS unit. The vacuum pump exhausted through a water bath.*

A ball valve (Swagelok: SS-43GS4) separated the uranium source from HORUS-1 and allowed the operator to control the introduction of uranium into the forward section of the instrument. Because the solenoid valves eventually showed themselves to be leak-prone, (see section 4.8.1 for details) a second ball valve was introduced, between valves *D* and *I*, to allow the user to separate HORUS-1 and the supply unit without breaking containment on either system.

After the ball valve, uranium would pass into a section of instrument containing a pressure transducer (MKS 722B13TGA2FJ) and a nitrogen supply valve; this section of instrument was terminated by a solenoid valve (Peter Paul 52X05700GP). Originally, the nitrogen supply valve was a single solenoid valve with a supply pressure of ~5 PSI; however, the single valve was replaced by double-valve system to allow controlled introduction of discreet amounts of nitrogen at a time.

The terminal solenoid valve separated the transducer section of the instrument from the trap section of the instrument. The trap and associated hardware changed significantly over the lifetime of HORUS-1. Initially the solenoid valve led to a plastic Luer-lock stopcock that controlled flow to a series of vertically oriented chromatography columns filled with alumina and sodium fluoride. A similar set-up to the column design is shown in Figure 7 while the final set-up is shown in Figure 8.

The columns were terminated by another stopcock that eventually lead to the vacuum pump portion of the instrument. This set up was replaced by a pair of ball valves and a stainless-steel trap, which was connected to the system by a pair of quick disconnects (Swagelok: SS-QC4-D-400 and SS-QC4-B-400) as shown in Figure 9. The pump-side ball valve was eventually removed and the trap quick disconnects were replaced by ultra-Torr fittings depicted later (Swagelok: SS-4-UT-6-400).

Any gas that did not react with the alumina, namely nitrogen or air, passed through the trap and was removed by the vacuum pump. Initially the pump was a single, four-stage diaphragm pump (Thomas 7011ZVR/12VDC), but it was quickly replaced with four single-stage pumps (Thomas 1410VD/12VDC) connected in series. The pump exhaust was directed through a pair of water baths (Figure 10). The first was filled with 18 M Ω water to allow for pH and fluoride content testing as a way to test for HF breakthrough. The second was filled with a saturated calcium carbonate solution. A ball valve was added between the pump exhaust and the water bath, which was eventually replaced with a check valve to prevent back-flow after the pumps were turned off.

Figure 7. Chromatography columns filled with alumina for use in the previous year's tungsten hexafluoride experiments. *This arrangement was copied over to the first instance of HORUS to prove that the chemistry of uranium hexafluoride behaved sufficiently similarly to move forward with experiments. The HORUS set-up was book-ended by stopcocks rather than having one in between each trap, as shown here. The uranium rig also only utilized the smallest columns. Gas passed from top to bottom in order to keep the powder compressed during evacuation, exposure, and nitrogen flushing.*

The columns were terminated by another stopcock that eventually lead to the vacuum pump portion of the instrument. This set up was replaced by a pair of ball valves and a stainless-steel trap, which was connected to the system by a pair of quick connects (Swagelok: SS-QC4-D-400 and SS-QC4-B-400) as shown in Figure 9. Columns were switched to quick connect traps so that the system would better match a field-deployable unit and section 4.2.3 gives the appropriate justification for the change to Ultra-Torr fittings.

Figure 8. The final implementation of the laboratory set-up, also known as HORUS-1. *The pressure transducer is to the left, the nitrogen inlet is at the bottom, the uranium source is at the top and the trap is to the right. The photo was taken during decommissioning and so the hose connecting the trap to the vacuum pumps has already been cut.*

Figure 9. Photos of the original steel trap design and its successor, both with quick disconnects. *The curved shape proved difficult to pack properly with alumina and was quickly changed to a straight tube with ninety-degree elbows. The male/female orientation was preserved though, as it kept the user from inserting a trap backwards. Frits were inserted in both elbows on the tub side, one acted as one side of the packing wall for alumina while the other acted as a back-up filter in case gas flowed backwards through the system. A third frit inside the tube was used to keep the alumina compacted regardless of orientation. Alumina was packed towards the side with the vacuum pump so to use the flow of gas to keep the trap compacted.*

Any gas that did not react with the alumina, namely nitrogen or air, passed through the trap and was removed by the vacuum pump. Initially the pump was a single, four-stage diaphragm pump (Thomas 7011ZVR/ 12VDC), but it was quickly replaced with four single-stage pumps (Thomas 1410VD/ 12VDC) connected in series.

Figure 10. A photo of the water bath and vacuum pump set-up during decommissioning. *Gasses flowed from the vacuum pump exhaust (upper left), through a water bath filled with 18 M Ω water, and finally through a water bath filled with a saturated calcium carbonate solution.*

3.1.2 CONTROL SYSTEM

The instrument was initially operated in a purely manual style, requiring the user to physically turn ball valves or flip switches to activate solenoid valves. Eventually the solenoid valve used to expose the trap to uranium was wired with an additional timer circuit allowing the user to control the total exposure time more precisely. Both the solenoid valves and the pump system were powered via the same power supply (BK Precision 1550 DC Power Supply). While initially 24 V valves and pumps were used, the system was eventually switched to 12 V pumps and valves as 12 V batteries are more easily sourced. The two pressure transducers were powered and monitored using their proprietary power supplies.

3.2 HORUS-2

HORUS-2 was designed with the intent to prove that the instrument could be miniaturized into a portable unit. The unit was completely self-contained with the exception of inert gas supply, which was supplied via a small bottle of pressurized nitrogen. The housing for HORUS-2 was made of custom-built extruded aluminum frame and aluminum sheeting. The electrical components were separated from the vacuum plumbing by an aluminum sheet with power running to the valves and pumps through a hole in the sheet.

3.2.1 VACUUM SYSTEM

The plumbing diagram for the unit is given in Figure 11 and is representative of the initial design. Small changes were introduced because of lessons learned from HORUS-1 after HORUS-2 had already been built, but those changes are carried through to HORUS-4 and so will be better represented later in this report.

Figure 11. A block diagram and photograph of HORUS-2. *The nitrogen supply was not contained within the unit but instead attached via compression fitting and braided hose, as visible in the photograph. The quick connects photographed here were replaced with ultra-Torr fittings before testing the unit in the laboratory. The control unit was permanently attached on top and the backup trap was plumbed into the system with compression fittings.*

Again working from the uranium source, the first component of the instrument was a facility-specific connection attached to a female quick-connect. That quick connect mated with its complement on the instrument, which then immediately passed through the aluminum housing to a solenoid valve. That valve lead to the same transducer/nitrogen section of the instrument as described before, with a double solenoid valve system for the nitrogen inlet and a single solenoid valve leading to the trap. Beyond the single solenoid valve was a ball valve to protect the uranium source should a leak occur or a valve fail.

The tubing passed outside the unit once again where a female quick-connect lead to the trap, pictured in Figure 11. The orientation of the quick-connects was such that the user could not accidentally actuate the valve on the instrument and introduce air into the uranium source. It also forced only one orientation when inserting the trap, preventing the user from inserting a trap backwards. The quick disconnects on the trap and the connection to the facility were eventually exchanged for ultra-Torr connections (see section 4.2.3 for justification).

After the trap, any residual gasses were fed back inside the aluminum housing and passed through a backup trap, designed similarly to the main trap, but smaller and in a straight line. Inert gasses then passed through four diaphragm pumps, connected together in a series, past a check valve, and finally out of the aluminum housing to be directed by the user as they see fit.

3.2.2 CONTROL SYSTEM

All the valves in the system were electrically actuated by switches mounted on the front of the unit. Each switch was fitted with an LED indicator light to notify the operator that power was passing through that portion of the control unit. The instrument was wired such that it could be run off of either batteries or external power supplies, both feeding through banana plug connections on the outside of the unit. The vacuum pumps were powered on a circuit separate from the rest of the components as they caused a shift in electrical ground making the pressure readout unreliable. The batteries used to run the system were 14.8 V Li-ion batteries (Dantona LION148A-8SG52-12) for both circuits. The valve and pressure readout circuit contained a voltage regulator that stepped the voltage down to 12 V. The pumps were simply run directly off the battery-supplied voltage.

The solenoid valve between the trap and the transducer portions of the instrument was wired such that it could be opened indefinitely or for a set period of time (0.3-20.0 sec). The collection time was controlled by a timing unit and a rheostat, the resistance of which was checked via two contact points on the outside of the instrument housing. A correlation between resistance and timer period was established and marked under the measurement points. The pair of solenoid valves for the nitrogen feed were wired such that only one of the two valves could be powered on at any time.

The unit also has two voltage readouts displaying the current voltage for each battery and third voltage readout displaying the voltage return from the pressure transducer. The readouts displayed in increments of 0.1 V, which translated to 10 Torr of pressure from the pressure transducer. The voltage output from the transducer was directly related to the pressure, in Torr, by a factor of 100. That is, 10 V corresponded with 1000 Torr, 1 V to 100 Torr, and so forth.

3.3 HORUS-3

This unit was designed and built for use in the sampling rodeo at Pacific Northwest National Laboratory. It incorporated lessons learned from HORUS-1 and 2 in sampling hardware, instrument control, and housing. The hardware housing was of a sled design (Figure 12) and was designed by an in-house designer. This allowed for small changes in overall length (due to varying tightness on the connections within the plumbing system) without having to re-machine the housing to fit.

Figure 12. Sled and plumbing design for HORUS-3, showing the original inception with quick connects. *The final iteration replaced the quick connects with ultra-Torr fittings and removed the handles. The electrical control box sat on top of the sled, attached to the two tabs on either wall. The device was totally enclosed with all the walls in place allowing access only the manual ball valve pictured here. Additionally, the double valve nitrogen system was positioned ninety degrees horizontally to the depiction here, for space considerations.*

Figure 13. Photos depicting the electrical housing grooves and modular construction along with the completely assembled unit. *The trap fittings on the unit pictured here are of the final, ultra-Torr style. The external nitrogen tank and regulator can be seen on the edge of the right-hand picture. The smaller printed box housed the batteries for the unit. Parts of the printed housing were strengthened with epoxy as needed.*

The electrical housing was printed via additive manufacturing in multiple pieces and assembled. All electrical components were mounted on 1/16 inch aluminum sheets that rested in grooves in the printed housing (Figure 13). The housing was mounted to the top of the sled with a feed-through hole to pass in power and communication to the vacuum system hardware. The housing was designed such that mounting would be adaptive to small changes in the sled

length. The batteries were contained within a separate compartment in the housing mounted on the lid of the electrical box.

3.3.1 VACUUM SYSTEM

The sampling system for HORUS-3 was nearly identical to HORUS-2 with the exception that the trap and connections were designed with ultra-Torr connections rather than quick disconnects. Due to time constraints, the ultra-Torr connections on the instrument were the same size, potentially allowing a user to insert the trap backwards.

3.3.2 CONTROL SYSTEM

Similarly, the electronics and control system for HORUS-3 were nearly identical to those of HORUS-2. Major changes to the electronics included the installation of an Ohmmeter so that the user could check the rheostat resistance with simply the flick of a switch and the conversion to pure battery power. An over-voltage and ring-down circuit was installed to protect the components from voltage spikes caused from cutting power to a valve. Finally, the voltmeter monitoring the pressure transducer output voltage was changed to a unit with ten times the precision of the previous component, increasing pressure granularity to one Torr.

3.4 HORUS-4

The final sampler design was built using the lessons learned from all the previous HORUS units and from the field test at PNNL. This unit involved major changes to the philosophy of design behind the unit; compactness, ruggedness, and simplicity were prioritized over the previous goal of minimizing the potential for catastrophic user-error. This resulted in a unit that was much smaller and significantly lighter than the previous designs. The unit was again built with only extruded aluminum framing and 1/16-inch aluminum sheets similar to HORUS-2.

3.4.1 VACUUM SYSTEM

The gas path through the system was functionally the same as the previous HORUS units, but key components were changed with the lessons learned from previous iterations and the new design philosophy in mind (Figure 14). The initial connection to the instrument, after the facility-specific fitting, was a KF-16 flange connected to a bulkhead that passed through the unit housing. Inside the unit the gas encountered a plug valve (Swagelok: SS-4P4T) which lead to the transducer/nitrogen section of the instrument. See section 4.8.1 for the justification to replace the solenoid valves with plug valves. KF-16 flanges replaced the old ultra-Torr connections for facility connections because of ease of use.

Figure 14. A block diagram of the HORUS-4 design. Valve 1 and 2 are plug valves while valve 2 is a three-way ball valve. The common route on valve 2 is plugged at the valve to create a miniature expansion chamber for nitrogen. Uranium hexafluoride flows from valve 1 to valve 3 and into the first alumina trap. The second trap is inside the case, not hand removable, and is for emergency backup only.

The double valve system of before was replaced with a single three-way ball valve where the common path was stopped with a plug nut. This mimicked the functionality of the double valve system with a single manual valve, allowing only one side of the connection to be open to a common area at a time.

The transducer/nitrogen section exited through another plug valve, which was connected to a bulkhead. On the outside of the housing, the gas passed through an ultra-Torr connection and into the trap, shown in Figure 15. Any inert gas passed through the trap and back past a second ultra-Torr fitting of different size, which prevented the trap from being inserted backwards. For this iteration of the instrument, the trap was made with a clear PVC tubing to allow the user to verify, visually, uranium deposition during collection.

Figure 15. Clear PVC trap filled with approximately 2 grams of alumina. The trap was built from 3/8-inch outer diameter tubing attached to 3/8 elbows. Port connectors were used to allow for variable connection sizes when prototyping, though permanent sized adapters would be preferred moving forward. Polypropylene frits are fitted inside the swage connection of both elbows on the PVC terminal ends; one contains the power while the other is a backup in case the frit visible in the photo fails. The 1/4-inch port connector is shown with a cap, which would be attached after exposure to prevent accidental sample contamination. The 3/8 port connector has a similar cap.

The inert gas then passed through a bulkhead to the inside of the unit, through a backup trap, through four diaphragm pumps in series, then past a check valve, through a bulkhead and out a KF-16 flange to be directed by the user as they see fit.

3.4.2 CONTROL SYSTEM

The electronics and controls were simplified to place more responsibility on the user, something that was considered acceptable given the relatively simple method of operation and the presence of a pressure readout to assess system configuration immediately. The plug and ball valves were manually operated by the user, which meant that the user must use an external timer to expose the trap to gas for the desired amount of time. The valve heads were passed through the front panel (Figure 16) to give the user control access without breaching the interior of the unit.

The batteries were switched to Dewalt commercial batteries (14.4 V: DC9091, 18 V: DC9182) mounted on the rear of the instrument (Figure 17). The battery change was due to a clarification in shipping regulations regarding lithium-ion batteries; mass-produced commercial batteries were considered a safe choice for legal purposes. The battery receptacles themselves were taken from the appropriate power tools and modified to fit through the wall of the instrument. Each battery had a voltage monitor displaying the voltage on the front and the pump circuit was switched to regulated 12 V power while the pressure transducer was unregulated. The pump circuit also contained a ring-down board to protect the voltmeter during voltage pikes caused by shutting off power to the pumps. Because there were no valves to power off, there was no dead-man's switch between the pump and transducer circuits should the pumps lose power. Each circuit was controlled by a switch in the back of the instrument.

Figure 16. The control panel of the HORUS-4 unit. The three valves in the system are controlled from the front where the pressure and battery voltage are also displayed. In this orientation, the uranium hexafluoride passes into the instrument from the top right, past the “pre transducer” valve, past the “post transducer” valve, then into the trap. Any inert gasses pass through the trap, through the pumps, past a check valve and out the KF flange partially obscured on the top right.

Figure 17. Connections and rear panels of the HORUS-4 unit. *Inlets and outlets were changed to KF-16 flanges in response to lessons learned at PNNL; primarily it was discovered that securing a hard-plumb connection to the facility may not always be feasible and that a braided hose on a KF-16 flange would be considered acceptable. The batteries were different sizes/voltages and could not be plugged into the wrong receptacle. The entire unit weighed 17 pounds.*

4 COLLECTION EFFORTS

4.1 URANIUM COLLECTION CHARACTERISTICS

Working primarily with HORUS-1, the uranium collection instrument was put through a wide variety of tests to characterize the instrument's properties as well as improve upon design flaws that only became apparent after laboratory experimentation. Principle questions included the following:

- What percentage of the uranium that entered the instrument is recoverable from the trap via nitric acid?
- Are there methods that can increase this recovery? Where does the “lost” uranium eventually end up?
- What is the loading efficiency of the aluminum powder used in the traps? What kind of loading profile does the powder exhibit?
- How much uranium is left in the instrument between sample exposures? Is there a way to minimize this holdover?
- How do the source pressure and the draw pressure affect the loading characteristics? Can knowledge of this effect be used to control the amount of uranium deposited in the trap?
- Do successive samples contaminate each other in any way, even following proper procedures to minimize the holdover in the instrument?
- Can the traps be cleaned and recycled for use later?

4.2 PASSIVATION LAYER TESTS

The inaugural tests of HORUS-1 were simply executed to prove that the instrument could collect uranium hexafluoride in a manner similar to the FY16 tungsten hexafluoride tests. For these initial tests, the instrument was drawing depleted uranium from a P10 tube attached to a 125 mL charge tank. It was also operated using only ball valves and plastic stopcocks; the traps used for these initial tests were adapted chromatography columns filled with approximately 2 grams of alumina. It was quickly discovered that water adhered to the internal surfaces of the instrument would react away some of the UF_6 as it entered the system.

4.2.1 WATER MITIGATION

It was decided to characterize and attempt to mitigate the effect that surface water had on the collection efficiency so that a predictable collection method could be implemented. For these initial tests, the instrument internals were exposed to air for a period of anywhere from a few minutes to a few weeks. The instrument was then evacuated to vacuum (~15 Torr), flushed with nitrogen, and successive samples were collected. For these tests, the samples were flushed with nitrogen twice after being exposed to the uranium hexafluoride.

The resultant data (Figure 18, “Evacuation Only” series) showed a “break-in” period where the initial recovery rate was significantly lower than the eventual, stable, recovery rate. It was theorized that sufficient exposures of the internals to UF_6 reacted away all of the surface water in the instrument resulting in a higher recovery rate.

Figure 18. Chart relating the mass fraction of uranium recovered (actual/expected) as a function of the exposure number for a particular sample in a successive run of exposures. The different series expressed in this chart are different methods attempted in order to reduce the number of samples required to reach a stable recovery fraction. The initial low recovery fraction seen in some of the series is a result of surface water on the inside of the system, which was deposited by ordinary exposure to air. The lower final recovery fraction for the last two series is likely due to the switch from chromatography columns to quick disconnects. Data of this type was not collected for ultra-Torr fittings.

A quick literature search was performed to understand the characteristics of adsorbed surface water and some plans were proposed to mitigate its effects. It was found that exposing a metal surface, such as the stainless steel and Monel nickel used in these experiments, to room air would result in a layer of adsorbed water on the surface which would be difficult to remove. [3]. Proposals for dealing with the water were as follows: heat the instrument to remove the surface water, flush the system with dry nitrogen to dissolve the water in the gas, or expose the internals to uranium hexafluoride for a set amount of time before taking the first sample. Heating the lines was considered impractical for the instrument and so the other two methods were tested.

4.2.2 FLUSHED WITH N_2

For the nitrogen flush attempts to mitigate the break-in period, the system was again exposed to air for approximately one minute. The system was then put under vacuum and flushed with nitrogen twice before collecting multiple samples. For another test, the system was simply purged with nitrogen at a constant rate, keeping the pressure at ~80 Torr for a

minute. As seen in Figure 18, neither test showed improvement towards shortening the break-in period, suggesting the entrained water is too strongly adhered to the metal's surface to be pulled off by only a few purges of dry nitrogen.

4.2.3 EXPOSED TO UF_6 FOR SET AMOUNT OF TIME

As a final attempt to reach collection stability sooner, the third method was tested. The internals of the instrument were exposed to air and evacuated again. It was flushed through with nitrogen once to rid the system of any atmospheric water and the system was exposed to uranium hexafluoride all the way up to the last valve before the alumina trap. The system was held in this state for one minute before immediately collecting multiple samples. The last two series in Figure 18 demonstrate a noticeable improvement on the break-in period, suggesting the prolonged exposure reacted off all of the internal water in the system so that it would not account for lost material in the subsequent samples. It should be noted that the absolute value of the recovered uranium was depressed, though the sample-to-sample collection was much more consistent. This decreased recovery coincides with the first uses of the quick connect fittings; the actual mechanism for the decreased recovery was never identified.

It should be noted that it is this tendency for uranium hexafluoride to react and deposit onto surfaces which have been exposed to air which lead to the switch from quick disconnects to ultra-Torr fittings. The quick disconnect fittings, with their long metal mating surfaces and internal valves, would foul within a number of exposures requiring them to be cleaned. They would also steadily lose the ability to hold a vacuum, both between connections and between a closed end and the atmosphere. Cleaning with a wet cotton swab would allow for additional exposures, but they would have to be cleaned in a nitric acid bath within approximately thirty exposures. Ultra-Torr connections, by contrast, had no internal moving parts and tolerances that were not as tight. This allowed them to be easily reused and re-exposed to UF_6 and air as the small buildup of salt on the connection's surface was not as detrimental to performance. The Ultra-Torr connections suffered no loss in their ability to hold vacuum during their service on this project.

4.3 LOADING/BREAKTHROUGH TESTS

Before switching over to a single trap system, which was more representative of a real-world apparatus, it was necessary to determine the loading capacity of the alumina. This was done by stacking multiple chromatography columns and intentionally breaking through to the second one. The reaction front was visually distinct, as should be obvious in Figure 19, and so controlling the penetration depth of the uranium was relatively easy. A few tests also stopped the reaction front short of breakthrough to test the sharpness of the leading edge in terms of uranium deposition.

Figure 19. Close-up photo of a partially exposed chromatography column. *The exposure front is easily visible and extremely sharp. The initial polypropylene frit was intentionally left above the level of alumina and it can be seen discolored in this photo. The second frit is also in the photo, but is the same bright white as the alumina and is indistinguishable from it. A change in the alumina-column wall optical interaction can also be seen, as the exposure color band extends into the visual space of the wall.*

The tests showed that the reaction front was extremely thin and that the loading capacity of the alumina was approximately 10% uranium by mass (Table 1). The loading capacity was relatively stable and independent as to whether the reaction front was exactly at the bottom of the column or ostensibly past it. This suggests that the initial reaction happens quickly and uses up all the water within easy access. It may be that a secondary reaction or diffusion into the alumina pores happens, allowing for greater loading capacity, but it was not observed in this experimental set-up.

Other experiments have demonstrated higher loading capacities for alumina, but they have also included significantly higher contact times with uranium hexafluoride and better characterization and optimization of the alumina. [4] [5] [6] A better capacity may be realized by merely selecting an alumina with better reaction characteristics such as a higher water content or larger pores, but FY16 experiments had already demonstrated this alumina as the best among those tested in terms of both reaction rate and characteristics under vacuum. Furthermore, this alumina had a water content of approximately 4%, which was ideal according to some literature experiments. [4] [5] However, those experiments relied on diffusion to load uranium onto the inside of 1 cm slugs and too high of water content caused the pores to plug up and block paths to the inside. It is not believed that internal diffusion is a significant part the loading capacity measured here and so plugging these pores in exchange for more surface reaction may be a valuable trade-off.

Table 1. Multiple breakthrough tests using alumina-packed chromatography columns. Each pair of columns was exposed until the reaction front was at the end of the first column, but not yet to the second column. The reaction front was determined by a color change in the powder from white to yellow. Loading fraction was found to be consistent across a range of exposed alumina masses from half a gram to over three grams. A doubling of exposed powder approximately doubled the contact time with the uranium hexafluoride gas.

	<i>Alumina Mass (g)</i>	<i>Uranium Mass (mg)</i>	<i>Loading Fraction (mg of U/g of Al₂O₃)</i>	<i>Notes</i>
Br1A1	0.9839	109.9 ± 3.6	110 ± 4	
Br1A2	2.9844	3.4 ± 0.1	1.1 ± 0.03	
Br2A1	0.531	61.5 ± 2	120 ± 4	Intentional Breakthrough
Br2A2	3.4606	15.9 ± 0.5	4.6 ± 0.14	
Br3A1	0.9295	51.5 ± 1.7	55 ± 1.8	Partial Exposure
Br3A2	2.1966	<LOD	--	
Br4A1	3.1165	375 ± 6	120 ± 2.1	
Br4A2	2.6383	<LOD	--	
Br5A1	2.2168	237 ± 4	110 ± 1.9	
Br5A2	2.409	<LOD	--	
Br6A1	2.4553	146 ± 2.5	60 ± 1.0	Partial Exposure
Br6A2	2.7226	<LOD	--	

4.4 FLUSHING/HOLDOVER TESTS

Before this set of experiments, the HORUS-1 system was changed to reflect the planned design for a field-deployable unit. The chromatography columns were replaced with a stainless steel trap attached via quick connects and the ball valves leading to and from the nitrogen/transducer section of the instrument were replaced with solenoid valves.

Up until this point, it was assumed that two flushes with nitrogen was necessary to clear out any residual uranium hexafluoride gas still inside the instrument after a trap was exposed but before it was removed. To test this assumption, samples were taken in successive pairs with two samples corresponding to one exposure. To start, a single column was attached to the system and exposed to approximately 40 mg of uranium, determined by the pressure drop in the charge tank. The system was allowed to pull vacuum as low as possible, which was approximately 12 Torr for these sets of experiments. After this, the terminal ball valve was closed and the exposed trap was replaced with a fresh one. The ball valve was opened and nitrogen was flushed through the system twice and the trap was removed. Table 2 shows the results of the experiment. Unfortunately, no experiment was performed to prove that flushing with nitrogen had any effect.

With the holdover data given in Table 2, and known values for the temperature and the pressure of the system for every experiment, the retained volume inside the instrument at the time of this experiment could be calculated. The final instrument, HORUS-4, had a significantly reduced pathway from introduction valve to trap bed and should have a similarly reduced holdover when left un-flushed.

Table 2. Holdover experiments using pair of columns. *The second trap in the pair collected the uranium hexafluoride left in the system after exposing the previous trap, but before pushing nitrogen through the system. Approximately two mg of uranium was left in the instrument, a number that should be smaller for the HORUS-4 unit, as it has less internal volume than the unit used to produce this data.*

<i>Sample ID</i>	<i>Recovered Mass (mg)</i>
H1A1	34.2 ± 1.0
H1A2	1.86 ± 0.11
H2A1	38.5 ± 1.1
H2A2	2.21 ± 0.12
H4A1	42.4 ± 1.2
H4A2	2.3 ± 0.12
H5A1	46 ± 1.3
H5A2	2.21 ± 0.12

Assuming the introduced nitrogen mixed perfectly with the gas in the instrument and that the gas pressure during one flush cycle ran from 20 Torr to 80 Torr and back down again, one flush would have resulted in a 75% reduction, approximately, in retained uranium within the system. Thus, carry over between samples with a double flush could have been around 0.125 mg of uranium, starting with 2 mg of residual uranium in the system. This was below the limit of detection for the ICP-OES and sample preparation methods used for data analysis. It is also below the detection limit in the cross contamination tests detailed in a later section.

4.5 NITRIC ACID FLUSH

In an effort to reduce material and labor costs, there was an incentive to re-use old hardware from sample cartridges after they were analyzed for uranium content. This required proving that there was no residual uranium in the system, or that any residual uranium was not removable via subsequent nitric acid washes.

Two separate experiments were devised to prove that all uranium had been removed from the hardware. The first experiment was to simply re-pack the returned hardware with alumina and re-submit the traps for analysis without exposure. When using the quick connects, approximately 0.2 mg of uranium was recovered from these samples. When using ultra-Torr connections there was no detectable amount of removable uranium on the re-packed samples. It is theorized that the residual uranium in the quick connect samples is due to poor solution contact with the internals of the quick connect hardware, not an inability of the nitric acid to remove uranium from those surfaces. In both cases, it was decided that the levels were sufficiently low to re-use hardware for laboratory tests. Fresh samples were used for all key experiments, including the exercise at PNNL.

The second experiment aimed to show that an overnight leach in 4 M nitric acid was sufficient to remove all the uranium from the alumina and hardware. It also aimed to show that a brief contact with nitric acid was sufficient for recovering the majority of the uranium for analysis. A pass-through rig was build such that nitric acid could be pumped through the trap and recovered on the other side. Nitric acid was pumped through in the reverse direction from exposure and collected in 5 mL fractions. After 10 fractions, the sample column was

exchanged for an empty column and the system was flushed with nitric acid to collect any uranium still in the system; in most cases, this flushing required more than 5 mL of solution. The hardware and alumina were then leached over-night according to the usual procedure and that solution accounted for the final fraction. Each fraction was analyzed separately for total uranium content and the data is presented in Figure 20. The data clearly shows that a quick-wash method would be sufficient to recover solutions suitable for isotopic analysis. The data also strongly suggests that an overnight soak in nitric acid is sufficient to extract all removable uranium from the alumina and hardware.

Figure 20. Uranium mass present in successive effluent samples from exposed alumina columns. The samples were flushed through with 4M nitric acid, with the exception of HN1, which was flushed with 1 M nitric acid. Aliquots were collected 5 mL at a time until the last two fractions represented here. The 11th fraction is the final flush to clear the lines and is larger than 5 mL while the 12th fraction represents the overnight alumina and hardware soak in 4 M nitric acid. The data clearly shows that the residual uranium left over from just contact with nitric acid is negligible, suggesting that an overnight contact with nitric acid would remove all possible uranium. HN5 was not exposed to uranium hexafluoride.

4.6 SOURCE PRESSURE TESTS

To measure the effect of source pressure on collection parameters, it was necessary to replace the 125 mL charge tank with a 4 L charge tank. The larger tank was purchased to approach real-world source characteristics; an enrichment facility or a tank from the yard has

an effectively infinite volume when compared to the milliliters collected by HORUS. The smaller tank would see a 20-40 Torr drop during sample collection whereas the larger tank would drop ~2 Torr. This small drop allowed for experiments where the source pressure was considered effectively constant during collection. The primary experiment of interest was whether the source pressure had any effect on the amount of uranium collection during a collection of a given duration.

The charge tank was evacuated and flushed with nitrogen several times and then filled with uranium hexafluoride from another P10 tube overnight. The source pressure in the tank rose to 100 Torr and successive collections were taken without recharging the large tank. The first four samples were taken with 9-second exposures, followed by a double flush of nitrogen for each exposure. The rest of the samples were taken with 18-second exposures and the traps were flushed twice with nitrogen after exposure. The entire range of pressures was sampled from 100 Torr to 40 Torr at which point the experiment was stopped due to time constraints.

The collected data analyzed a number of different ways, but few showed a strong correlation between the starting pressure and the amount of uranium deposited onto the trap. As a first approximation and assuming ideal behavior, the amount of uranium hexafluoride captured by the trap should be a two-part function, given in (1)

$$n = t(P_s - P_v)C + \frac{(P_s - P_v)V}{RT} \quad (1)$$

The first half of the equation represents the amount of hexafluoride pulled into the trap while the exposure valve was open. The second half of the equation represents the amount of hexafluoride that expanded into the HORUS unit as soon as the exposure valve opened. P_s is the source pressure, and P_v is the pressure at the highest vacuum attained before opening the valve. T is temperature and R is the ideal gas constant in appropriate units. Finally, t represents time and C is an empirical rate constant.

The equation can be rewritten as follows:

$$n = P_s \left(tC + \frac{V}{RT} \right) - \left(\frac{P_v V}{RT} + tP_v C \right) \quad (2)$$

The above is merely a re-organization of (1) to fit it to the form $y = mx + b$. In this case the source pressure, P_s , is considered the x variable. This linear relationship holds only if all variable aside from P_s are kept constant. This is not strictly the case for these sets of experiments, but a reasonable attempt was made at keeping all the variables in these equations as controlled and consistent as possible. Also missing from equation 2 is a measure of the amount of uranium lost to the trap hardware or changes in alumina hydration.

From this, the clear linear relationship in (2) should follow on a plot allowing for the extraction of the rate constant, C and a prediction method for the amount of material deposited in the trap for a given exposure. However, no clear linear relationship was found between the source pressure and the amount of material deposited on to the trap. Figure 21 is an attempt to fit the data to the above relationship given a constant collection time.

With only a weak correlation of collection mass to source pressure, the data does not sufficiently allow even an empirical model to predict the amount of uranium recovered from a

given sample from the source pressure alone. There are too many uncontrolled or poorly controlled variables in the current system—like vacuum pressure, which ranged from 20 to 14 Torr—to draw a clean relationship between any two particular variables. Recovered uranium as a function of source pressure was given as an intuitive example, but other relationships were also explored without success.

Figure 21. Plot demonstrating the lack of a relationship between the uranium hexafluoride source pressure and the amount of material recovered. *This plot suggests that there are too many uncontrolled variables in the experiment to demonstrate any real relationship between the recovered mass of uranium and the source pressure.*

The recovered uranium trended nicely with the expected recovery (Figure 22), which was calculated from the starting and ending pressures of the charge tank. However, in any real-world situation, the source volume will be so large that the source pressure will remain unchanged after sampling. The relationship does show, however, that the unit captures uranium in a repeatable way, given a known amount of gas. This means that it is the introduction of uranium into the system, and not the capture or recovery of that uranium, which is currently difficult to predict.

Figure 22. A chart demonstrating the relationship between the change in source pressure and the recovered mass of uranium. The linear and relatively predictable relationship shows that the unit captures uranium in a consistent manner and that it is the introduction of uranium into the system that is currently difficult to predict.

4.7 CROSS CONTAMINATION TESTS

Finally, the unit was tested with different levels of enriched and depleted uranium to determine what, if any, cross contamination occurs between samples. The theory being that if the source enrichment were switched, any cross contamination would show up as a deviation in enrichment from the source value. The updated HORUS-1 unit, terminated by ball valves on the source and trap connections, was modified to accept a KF-16 flange and the three enrichment source bottles were outfitted similarly. The first two samples were taken as depleted uranium, the third through six were taken from an enrichment around 3% by weight, the seventh through ninth were taken from an enrichment around 12% by weight, and the tenth and eleventh were taken from depleted uranium, again.

It should be noted that, with the exception of the depleted uranium samples, all the sources in this test consisted of standard sampling bottles (1S, Hoke tubes) with solid UF_6 and the container headspace. In all cases, the headspace volume was significantly less than previously tested; the large amounts of uranium recovered indicated that the system was directly sublimating material from the solid phase. This was a major achievement for the instrument and provided evidence that the unit could be used to sample directly off cylinders from the enrichment facility yard that may not have an accessible headspace (i.e., material frozen against valve).

Between each sample, the system was flushed twice with nitrogen, as per usual. To switch sources, the terminal ball valves were closed and the KF flange connection was broken.

There was always evidence of deposition on the inside of the KF flange, likely from reaction with the high vacuum grease used, which was not optimized for contact with uranium hexafluoride. The new source was attached and the ball valves were opened. The system was flushed twice with nitrogen to rid the system of air introduced from the KF flange connection. Normal sampling resumed after this.

Table 3. Collected masses and measured mass ratios for the cross contamination tests. *The last two columns describe the maximum amount of material in the given sample that could have actually originated from the same source as the previous sample and still be statistically consistent with the data given here. The discontinuous numbering is a result of traps discarded before exposure.*

<i>Sample No.</i>	<i>Collected Mass (mg)</i>	<i>U235/U238 Ratio</i>	<i>Maximum Held Over Fraction</i>	<i>Maximum Held Over Mass (mg)</i>
X01	21.1 ± 0.42	0.003 ± 0.001	N/A	N/A
X02	21.7 ± 0.43	0.003 ± 0.001	--	--
X03	79.7 ± 1.6	0.033 ± 0.001	0.033333	2.656667
X04	86.5 ± 1.7	0.033 ± 0.001	--	--
X05	92.8 ± 1.9	0.033 ± 0.001	--	--
X06	98.4 ± 2.0	0.033 ± 0.001	--	--
X07	72.4 ± 1.4	0.118 ± 0.001	0.011765	0.851765
X08	78.9 ± 1.6	0.118 ± 0.001	--	--
X09	98.5 ± 2.0	0.118 ± 0.001	--	--
X10	29.2 ± 0.58	0.003 ± 0.001	0.008696	0.253913
X13	25.0 ± 0.50	0.003 ± 0.001	--	--

Table 3 shows the results from ICP-MS analysis, which give no indication as to any cross contamination between samples. Given the uncertainty in the measurements, the maximum allowable cross contamination that would be consistent with the results given here is 0.25 mg. This value was obtained by finding the fraction of the current sample that would have to be represented by the previous sample to give a new ratio equal to the measured ratio plus the error. Obviously, for samples with the same measured ratio, this result becomes nonsensical; however, for samples with different ratios, reasonable values were obtained.

4.8 OPERATIONAL LESSONS AND INSTRUMENT DISASSEMBLY

4.8.1 UNWANTED URANIUM DEPOSITION

A number of operational lessons were uncovered throughout the course of this project; the lessons learned during testing were incorporated into later instrument design and even resulted in modification of the test set-up. For example, it was discovered that the vacuum pumps used could not hold a vacuum when turned off. Therefore, a check valve was necessary to keep gas from flowing backwards into the system.

It was also found that the solenoid valves would fail to seal when closed after a few exposures to uranium. It is suspected that uranium would react with material on the sealing face of the valve and leave a deposit based on conversations with process experts at ORNL. This deposit would hold the valve open causing it to leak, if only slightly. During normal use,

this was mitigated by adding a ball valve to seal the ends of the instrument and working quickly during exposure. The solenoid valves were eventually replaced with plug valves in an attempt to solve this problem.

Testing with the plug valves showed that they were able to hold vacuum down around 50 Torr after which they leaked slowly. It is suspected, however, that the leaking is not inherent to the plug valve design, but rather the grease reacting with the uranium hexafluoride upon exposure. This problem can be solved by using a grease rated for UF_6 exposure, such as Krytox AC fluoropolymer grease. Collaborators have also suggested AS 2022 Gems solenoid valves, which have been shown to work well with UF_6 , if an electrically actuated system is desired.

The uranium hexafluoride also reacted with vacuum grease used to seal the KF flange fittings, but the reaction did not seem to affect the seal appreciably, possibly due to the lack of moving parts. Whereas deposits on the plug valves had a visible thickness and were of a green/grey color, the deposits on KF flanges due to grease reactions were thin and usually colorless. Even thinner deposits directly on the metal were multi-colored but usually blue, suggesting the color arose from an interference effect caused by the layer thickness, much like water on oil. These deposits were found in multiple locations, but were local, suggesting that they were due to air leaking into the system. Some areas showed no signs of deposition whatsoever while others were covered in deposits with perceptible thickness.

4.8.2 WATER TRAP

Early in the experimental phase of the project, after each set of experiments the DI water trap was checked for any changes in pH as a method for checking for breakthrough. Any HF or UF_6 entering the trap would dissolve and lower the pH; there was no measured change in pH using color-changing strips and it was concluded that no material had escaped the instrument. Over time, the water was tested at more infrequent intervals, usually with no appreciable change in pH. However, as a final check, the trap water was analyzed for fluoride ions by in-house analytical lab services and a concentration of 9 ppm was found. As a confirmation, the pH was checked and found to be ~ 3 , which corresponded to an HF concentration of about 9 ppm. This contradicted the previous pH tests, using indicator paper, and meant that further investigation was necessary.

The analytical laboratory followed up the fluoride analysis with a uranium detection at approximately 1 ppb. Given a trap volume of only 250 mL, this represented about 250 ng of material, significantly less material than required to account for the previously mentioned fluoride concentration. It is likely that the uranium in solution, given such low concentrations, originated from the (briefly) open containers of frozen uranium hexafluoride when the source materials were being replaced.

It is not certain as to whether the fluoride originated from a singular event (i.e., a trap was coupled to the system backwards which allowed a free path through the trap), or whether the fluoride concentration in the trap slowly built over time. Therefore, the most liberal estimate of the fluoride breakthrough would be an even release per sample over the entire sampling campaign; in this case, each sample would exhaust 18 μg of fluoride and 2 ng of uranium.

5 FIELD TESTING

As part of a field test organized by the Office of International Nuclear Safeguards, HORUS was demonstrated in a sister facility at Pacific Northwest National Laboratory. This field test was conducted as a Rodeo with three labs demonstrating collections from a high fidelity laboratory system followed by high precision DA.

5.1 TEST SETUP AND COMMISSIONING

The Argonne HORUS sampler required inspection by PNNL electrical and pressure safety engineers prior to placing HORUS into service during the field test. The electrical safety inspection found that the sampler was powered using two lithium ion battery packs that each provided 14.8 VDC at 5.2 Ah capacity. No compliance issues or electrical hazards were identified by the inspection, because the sampler electronics power supply was below the OSHA hazard limit for energized conductor (i.e., ≤ 50 VDC). The pressure safety inspection determined that 150 ml DOT pressure vessel, used to flush HORUS with nitrogen during the sampling process, could not be filled at PNNL unless a pressure relief valve was installed to protect the vessel (500 psig design limit) from an over-pressure condition. To sidestep this issue, HORUS was simply supplied with 5 psig pressure-limited house argon. In this configuration, HORUS was classified as a minimal action system that did not require a PNNL pressure permit.

All new equipment that is installed and operated in PNNL laboratory spaces must undergo a hazardous assessment; a formal commissioning process was also required before HORUS could be used to collect samples from the UF₆ Sampling Tap Testbed. The system passed both of these checks. The UF₆ testbed Radiological Work Permit (RWP) did not need to be revised to facilitate HORUS UF₆ sampling, because the PNNL Radiological Engineer determined that a separate existing RWP adequately covered the scope of removing the HORUS sample cartridge after each DA sample collection.

Figure 23. The HORUS UF₆ DA Sampler Installation for the Phase I Rodeo

The HORUS sampler could not be placed within the testbed hood and directly connected to the sampling tap port, due to space constraints. Instead, HORUS was placed on a support table directly outside the hood, as shown in Figure 23. Stainless steel ¼” diameter tubing was installed to: 1) connect the HORUS inlet to a UF₆ sampling tap port; 2) to transfer the HORUS exhaust back into the hood, and 3) supply argon flushing gas to HORUS. A temporary posted Contamination Area (CA) was established around the HORUS sample cartridge as a boundary for possible uranium loss during cartridge removal.

Nine samples were collected from the PNNL sample tap for the DA rodeo and the upcoming Ion Source rodeo (both administrated out of NA-241). All of the samples collected or distributed, including engineering samples and blanks, are recorded in Table 4.

Table 4. Sample results from PNNL Field Test.

DA Sample ID	Purpose	Collection time (sec)	Pressure Drop (Torr)	Elapsed Time (minutes)	Vacuum Check pressure (Torr)
A01	<i>MS Lab Practice Sample</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>
A02	<i>Shipping Cover, No analysis</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>
A03	sacrificial trap	18	17.8	29	23
A04	Day2 MS/KPA DA Sample	18	19.14	12	24
A05	Day2 MS/KPA DA Sample	18	20.71	15	25
A06	Day2 MS/KPA DA Sample	18	21.6	8	23
A07	Day2 MS/KPA DA Sample	18	26.39	8	23
A08	Day2 MS/KPA DA Sample	18	20.71	7	24
A09	<i>Day2 MS/KPA DA Blank</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>
A10	<i>Day3 IS Rodeo Blank</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>
A11	<i>Day3 IS Rodeo Blank</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>
B01	Day3 IS Rodeo Sample	18	21.9	10	23
B02	Day3 IS Rodeo Sample	18	22.9	10	24
B03	Day3 IS Rodeo Sample	18	18.35	10	25
B04	Day3 IS Rodeo Sample	18	15.61	9	25

At the conclusion of the field test, the samples were analyzed against the other two methods from PNNL and LANL. Horus collected ~35 mg of material, per sample, on average for an 18 s collection (Table 5). The competitor methods collected significantly less material per sample (100’s of micrograms). In addition to total material, the samples were also analyzed for isotopic content; all three technologies fell within a 0.1% assay uncertainty band beating the accepted 0.7% standard; taken apart, the HORUS samples fell within a 0.05% band.

Table 5. Total uranium results by kinetic phosphorescence analysis (KPA)

<i>Sample</i>	<i>Mass by KPA (μg)</i>	<i>$\pm 1s$</i>
ANL-A03	38619	489
ANL-A04	46746	582
ANL-A05	31854	400
ANL-A06	36895	464
ANL-A07	32732	405
ANL-A08	28949	359
ANL-A09 Blank	2.70E-03	9.7E-05

5.2 FIELD TEST NOTES

The system required slightly longer pump down time than desired (a few minutes) but the operational time was within expected boundaries. In addition, the system was able to run for more than 2 hours on a single battery charge, far exceeding the design basis of 30 minutes. Conservative estimates prior to the test placed the battery life at ~1 hour but this benchmark was exceeded as well. Back up batteries were included with the system but were ultimately not needed. The sampling time for all samples was held constant at 18 seconds with the majority of the collection time required to pump down and flush the system. With the exception of the first sample, where a personnel issue delayed progress, the samples were processed in an average of 9.6 minutes each.

The pressure transducer and battery voltage (indicating remaining battery life) readouts were seen as especially useful during operation as the operator could verify that the system was working and had successfully pulled down to operational pressures. This was especially important during operation as two of the solenoid valves failed. It is hypothesized that the valves accumulated a deposit of reacted uranyl fluoride on the solenoid membrane due to the presence of grease or other contaminants that the manufacturer did not list. ORNL confirmed that this is a common occurrence as the operational requirements for hexafluoride service is typically above that of most manufacturers' definitions of hazardous service. The system could be operated with the single manual ball valve and a manual timer; this feature was included as a safety mechanism in the system to ensure that the system could be isolated.

The mass collection was slightly lower than expected from laboratory testing; this is likely due to the different internal volume of the PNNL charge tank. The Argonne system was a much larger volume ($>10\times$) than the PNNL system which may have restricted the amount that could be collected in the sampling time, though this is unconfirmed. Additionally, when two solenoid valves failed, the samples were collected manually and subject to additional error in operation of the valve. Regardless, the sample size was sufficient for analysis and consistent in mass.

5.3 FURTHER TESTING

After the setbacks that were observed during the field-test, a plan was made to iterate HORUS one last time (see section 3.4) to correct the shortcomings. This unit is ready for testing should the need arise. There has been some interest from the ABACC laboratory certifying Cristallini and efforts to collaborate are underway.

6 PROJECT SUMMARY

This project demonstrated that the concept of using an active vacuum system to collect uranium hexafluoride samples as inert salts is valid and can be further developed for routine collections. The HORUS device progressed from a theoretical concept to a field-tested device in less than 2 years. This represents a shift from TRL3 to TRL 6; this was aided by the use of commercial off the shelf technology for most components. As development cycles were not impeded by the need to wait on supporting technology, the system rapidly progressed to a working prototype.

As designed, HORUS-4 will be able to connect to a GCEP sampling tap, product or feed cylinders, hoke, P10, 1S or 2S cylinders for sampling or subsampling. The total time to setup, collect, and strike the system is <15 minutes total with additional time savings if multiple samples are drawn on the same source. This unique capability does not currently exist.

Several fundamental questions still need to be resolved to ensure the acceptable operation of the HORUS device in a real-world facility. The amount of uranium that is collected must be able to be predicted more accurately to ensure that shipping the final samples will be feasible under the reduced regulatory regime for solid samples. While we currently have no indication that there is a substantial cross contamination problem, a higher resolution isotopic measurement needs to be made on samples from multiple sources to confirm this assumption. Finally, control of system water needs to be addressed either in the form of reactive compounds to remove water from internal surfaces or an admission that some residual material in the system will be accepted as long as it doesn't affect system performance or cross contaminate any samples.

The system engineering must be refined and commercially compacted to reduce the form factor. Currently, the cost of the system is low enough that a unit could be built and deployed for <\$5,000 in materials; this cost may decrease if multiple units were built and distributed by a business entity.

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