

## **In-Process Monitoring of Molten Salt Composition by Voltammetry and Automated Sampling-Based Techniques**

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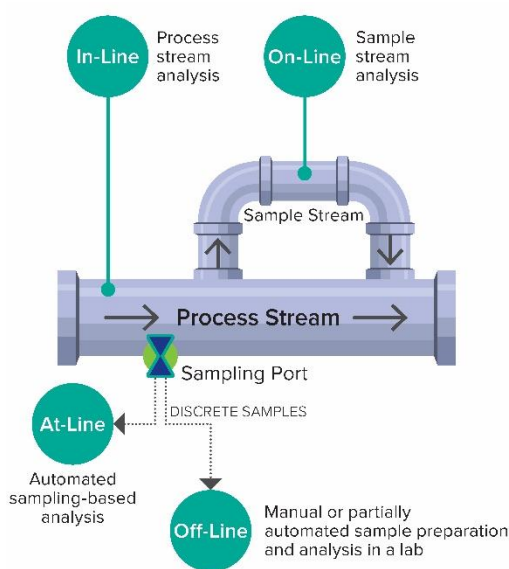
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### **Abstract**

Currently, material accountancy for in-process nuclear materials requires a significant amount of sampling and destructive analysis in a laboratory. However, there is a growing interest in reducing the reliance on laboratory analysis by using near real-time process monitoring data to draw safeguards conclusions. This safeguards paradigm will be particularly valuable for molten salt reprocessing facilities, which have highly complex material flows and cannot implement an accountancy tank as is used at aqueous reprocessing plants. Argonne National Laboratory, with support from the Materials Protection, Accounting, and Control Technologies (MPACT) program within the U.S. Department of Energy Office of Nuclear Energy, is developing a suite of tools to enable process monitoring, material tracking, and pattern recognition for molten salt safeguards. The new tools include a sampling loop platform for sample extraction and on-line optical analysis and electrochemical tools for in-situ salt characterization. The sampling loop platform has undergone preliminary testing, and the electrochemical tools have been demonstrated to provide stable, accurate measurements over long durations in engineering-scale process equipment. Development and testing efforts for these new capabilities are reported herein along with a discussion of remaining technology gaps.

### **Introduction**

Material accountancy in electrochemical fuel reprocessing is challenging due to complex flows of material, which include continuous phase change processes, batch transfers of material of unknown composition, and multiple salt recycle streams. Additionally, elevated temperatures and corrosive fluids preclude the use of standard process monitoring technology. To address these challenges several new process monitoring tools are under development to provide high-fidelity material tracking measurements at key points in molten salt facilities.<sup>1</sup> However, several gaps still exist with regards to the long-term stability of new techniques, the physical integration of new techniques into industrial processes, and the integration of techniques into a systems-wide integrated safeguards approach. This report covers technology that is under development at Argonne National Laboratory to fill some of these technology gaps. This includes electrochemical sensors for in-situ monitoring and salt handling platforms to support automated on-line, at-line, and off-line monitoring. On-line process monitoring involves direct sample stream analysis, at-line process monitoring involves sample analysis near the process, and off-line monitoring involves manual or partially automated sample preparation and analysis in a laboratory. A schematic outlining the process monitoring terminology used in this report is presented in Figure 1.



**Figure 1.** Process monitoring terminology categorized by process location. No standard process monitoring terminology exists in the nuclear field, so this terminology (which is based on common terminology used by vendors of chemical process monitoring equipment<sup>2</sup>) is recommended by the authors for characterizing molten salt nuclear process monitoring approaches. At-line process monitoring is generally automated for deployment in harsh process conditions but may be partially automated if accessibility allows.

Simple electrochemical sensors are inherently robust due to the absence of moving parts, solid-state electronics, or optical components. Due to their ability to measure a variety of parameters and to perform reliably in high-radiation, high-temperature, and high-corrosivity environments<sup>3, 4</sup>, electrochemical sensors will likely be deployed in situ for the monitoring of electrochemical fuel processing equipment. Electrochemical sensors are capable of continuous near real-time in-process measurements of the salt potential, the salt level, and the concentrations and oxidation states of actinides, lanthanides, and corrosion products. These measurements can be used to detect off-normal behavior in electrochemical reprocessing equipment and to maintain optimal process control.

The functionality of electrochemical sensors is based on the application of current or potential waveforms to electrodes immersed in salt. Quantification of the salt composition is achieved via analysis of the corresponding response to the applied electroanalytical signals.<sup>5-10</sup> The application of electroanalytical techniques for determination of actinide concentrations in molten salts has a long history dating back to the 1950's.<sup>11</sup> Typical techniques that are used include cyclic voltammetry<sup>3, 11, 12</sup> chronopotentiometry<sup>13</sup>, and pulse techniques such as normal pulse voltammetry<sup>4</sup> and differential pulse voltammetry<sup>14</sup>. Recent work has further developed use of these types of techniques<sup>15-17</sup>. The radiation encountered in radiological environments has a minimal effect on the electrochemical response for these types of sensors.<sup>18, 19</sup> Although numerous electrode configurations have been utilized in molten salt systems over the past several decades<sup>12, 17, 20, 21</sup>, Argonne has developed a unique electrochemical sensor design that involves the use of an array of electrodes to which a coordinated sequence of signals is applied. The multielectrode array enables accelerated measurement rates while also permitting information about the salt depth to be readily extracted.<sup>22</sup> Accurate determination of the salt depth is crucial in order to generate quantitative values as voltammetric approaches based on the magnitudes of oxidation and reduction currents rely on knowledge of the electrode's immersion area.<sup>12</sup>

Current solutions for validating and cross-checking these electrochemical measurements require manual sampling and off-line analyses. However, these slow and costly protocols will eventually be replaced with on-line and at-line techniques once sampling loop technology and automated sample handling capabilities become available. One key challenge for sampling-based material accountancy in electrorefiners and other molten salt unit operations is inhomogeneity. While the salt is expected to be well mixed due to thermal convection, entrained fines and surface dross must be considered for any sampling approach. A potential solution to this issue is to use a sampling line to draw salt from below the dross line and to circulate significantly more salt through a sampling loop than is extracted as samples. A pneumatically actuated salt extractor design is presented here which is under development for producing on-demand samples from a sample stream of flowing salt. The design is capable of high-throughput sample generation, which is a method that can support representative sampling through the averaging-out of random sampling errors. This platform was designed to support high-throughput sampling-based measurements to not only improve the timeliness of sampling-based analysis, but also to reduce statistical uncertainties of measurements.

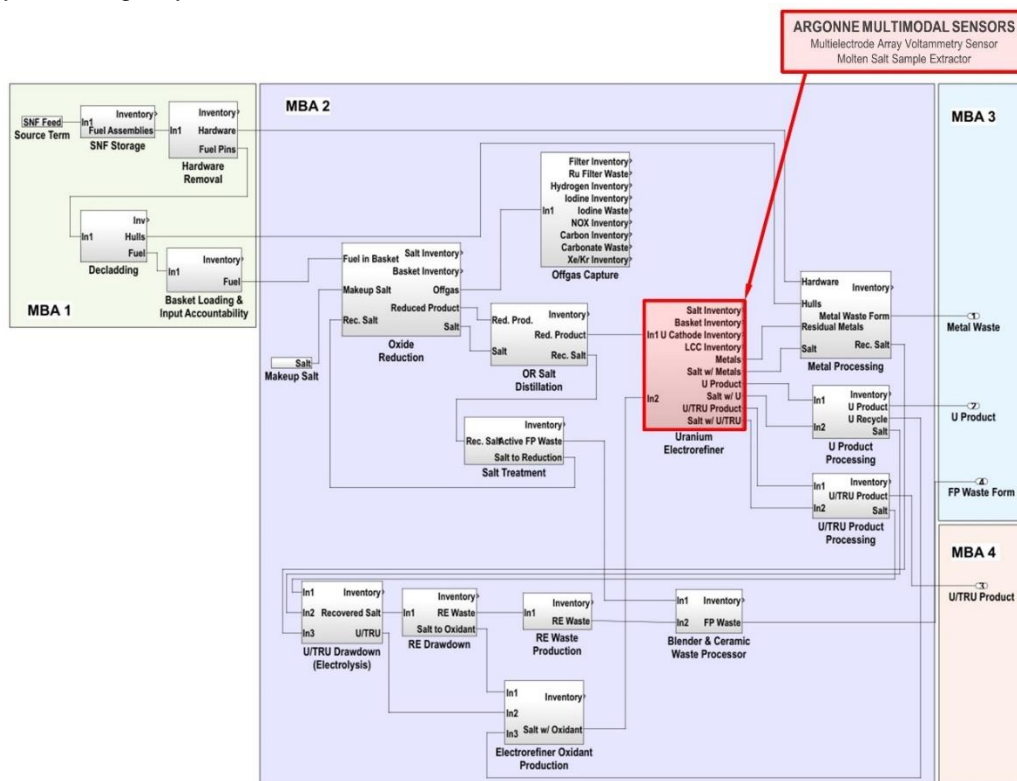
## Background

For any given process, process monitoring tools might be used to measure state variables (temperature, mass, volume, etc.), bulk properties (level, density, etc.), chemical and isotopic composition, speciation, and spectroscopic or radiation signatures. These measurements may be performed using in-situ, in-line, on-line, or at-line analysis. For nuclear safeguards in-process monitoring, the goal is to develop an integrated system of unattended measurements (both safeguards specific measurements and process monitoring measurements that are useful to the plant operator) that will supplement or replace traditional manual sampling and off-line analysis to achieve the rapid detection of material loss.<sup>23, 24</sup> To achieve a high level of advanced integration, safeguards must be considered from the very beginning of the nuclear facility design process. This safeguards-by-design approach will not only avoid expensive retrofits but will also support the iterative development of these integrated systems to optimize both facility and safeguards performance. Unfortunately, United States federal regulations currently lack sufficient guidance on advanced integrated in-process monitoring approaches. Regulators are working to resolve this issue<sup>25</sup>; however, the current lack of a sufficient regulatory framework to guide decision making is likely a deterrent to private sector investment to fill these technology gaps. For this reason, the on-going work on safeguards monitoring at universities and across the U.S. National Laboratory complex is essential to the safeguards-by-design effort.

As part of this safeguards-by-design effort, the U.S. Department of Energy (DOE) MPACT Program has a 2020 milestone to demonstrate advanced Safeguards and Security by Design for a virtual electrochemical reprocessing facility with advanced modeling tools and a distributed network of technology testbeds.<sup>23</sup> A major focus of this work has been the development and down-selection of process monitoring technologies to provide high-fidelity material tracking measurements at key points in a facility. A variety of optical, electrical, acoustic, and radiometric techniques are being developed to support in-process safeguards monitoring in molten salt facilities<sup>1, 26-28</sup>. The final selection of tools for deployment will be determined through an iterative development process supported by the modeling tools developed for the 2020 milestone<sup>23, 29</sup>, with consideration for operator preferences and evolving regulatory requirements.

As shown in Figure 2, DOE's MPACT program has categorized the electrorefiner as part of the second material balance area (MBA-2) within an electrochemical reprocessing facility.<sup>30</sup> MBA-2 consists of the region within the inert atmosphere hot cell facility. Input accountancy is a challenge for an electrochemical reprocessing facility because transuranics cannot be adequately measured before entering the electrorefiner due to the inhomogeneity of the feedstock. Furthermore, the electrorefiner has the largest inventory of transuranic species, so monitoring of the electrorefiner inventory is crucial for material

accountancy. Due to the slow build-up of the transuranic inventory within the electrorefiner over the course of reprocessing activities, the sensors that monitor the electrorefiner must have high accuracy, stability, and longevity.



**Figure 2.** MBA Structure for the Generic Electrochemical Facility<sup>30</sup> with indicated principal measuring locations of Argonne's multimodal sensor technology.

The main focus of Argonne's electrochemical reprocessing work under the MPACT program has been the development of technologies for monitoring electrorefiners. Electrorefiners are used to refine pure metallic species from a mixed alloy precursor material.<sup>31</sup> For reprocessing of spent light water reactor fuel, this step typically occurs after an oxide reduction step has generated metallic products from the metal oxide fuel constituents. During electrorefining, the mixed uranium and transuranic (U/TRU) metals are placed into a basket that acts as an anode, and purified materials are transported to cathodes where they are electrodeposited. Due to its relatively low electronegativity, pure uranium metal is first plated out of the system, and transuranic and lanthanide chlorides build up in salt. Removal of the transuranic species occurs periodically during a U/TRU recovery step that consists of co-deposition of uranium and plutonium into a molten cathode typically consisting of Cd.<sup>31</sup> Lanthanides and other electronegative metal ion species that build up in the salt are eventually removed during a drawdown step that typically consists of an electrolysis process.<sup>32</sup> Accurate concentration measurements are required to track materials throughout all these process steps.

Given the limitations of any individual technique, a multimodal combination of sensor technologies will likely be required to provide the necessary monitoring performance.<sup>1</sup> In-process molten salt composition monitoring in future facilities can be carried out by parallel, complementary techniques that will provide cross-validation of measurements in near real-time. Measurement tools could include more robust in-line/in-situ measurement techniques such as the voltammetry sensors reported here as well as higher-precision sampling-based techniques that rely on on-line, at-line, or off-line measurements.

A reliable method for the collection of representative salt samples to support these on-line, at-line, or off-line measurements has been identified as a key safeguards challenge.<sup>23</sup> Existing sampling methods generally rely on the insertion of a sample probe (a tube or a bucket) into the salt.<sup>33-36</sup> These techniques are susceptible to producing non-representative samples due to the small cross-section of salt that is sampled, the low-throughput nature of the techniques, and the risk of contamination from surface dross. Existing dip-probe samplers couple various mechanical and vacuum operations to retrieve samples, and mechanisms have been developed that appear to effectively mitigate the risk of dross contamination.<sup>33-36</sup> However, these mechanisms still need to be thoroughly validated for long-term use because non-representative samples resulting from dross contamination could have a significant impact on measurement accuracy for these low-throughput techniques. For complete material accountancy, characterization of the surface dross (by techniques such as sampling or stand-off optical analysis) may also be required, although this topic is outside the scope of this work.

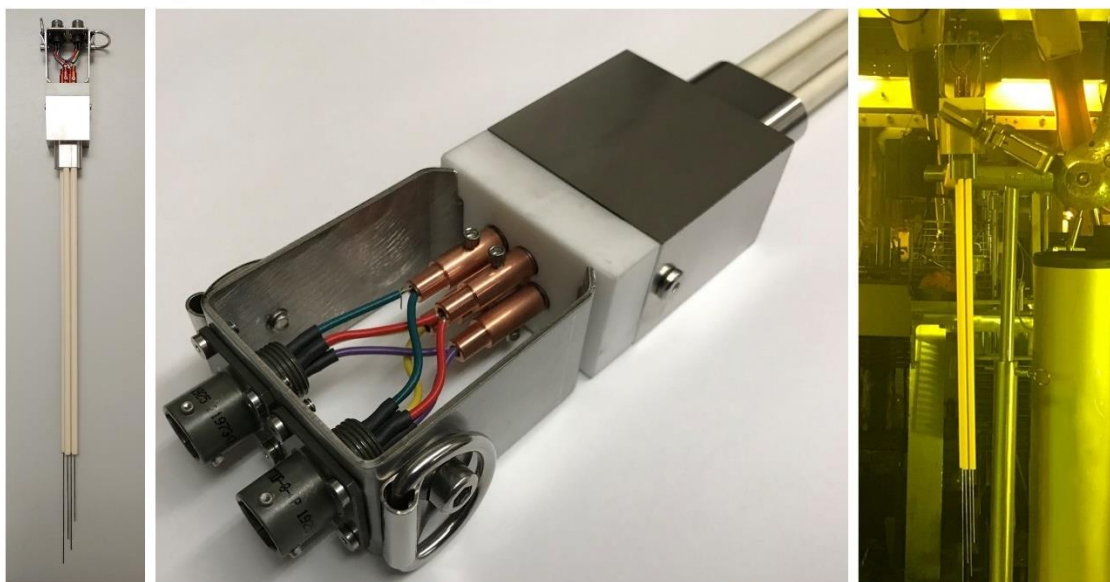
An alternate approach under consideration is split stream sampling.<sup>37</sup> This could be a viable approach for molten salt reactors if reliable metering valves can be developed, but inhomogeneity due to entrained fines must still be considered since the dynamics of particle flow can lead to partitioning and non-representative samples. A representative distribution of entrained fines such as  $\text{UO}_2$  and  $\text{PuO}_2$  in a sample, along with measurement techniques that account for these fines, will likely be important for accurate accountancy. The fact that electrochemical sensors cannot detect these precipitated species is another reason why a multimodal combination of sensor technologies will be needed for complete material accountancy.

### **Electrochemical In-Process Monitoring**

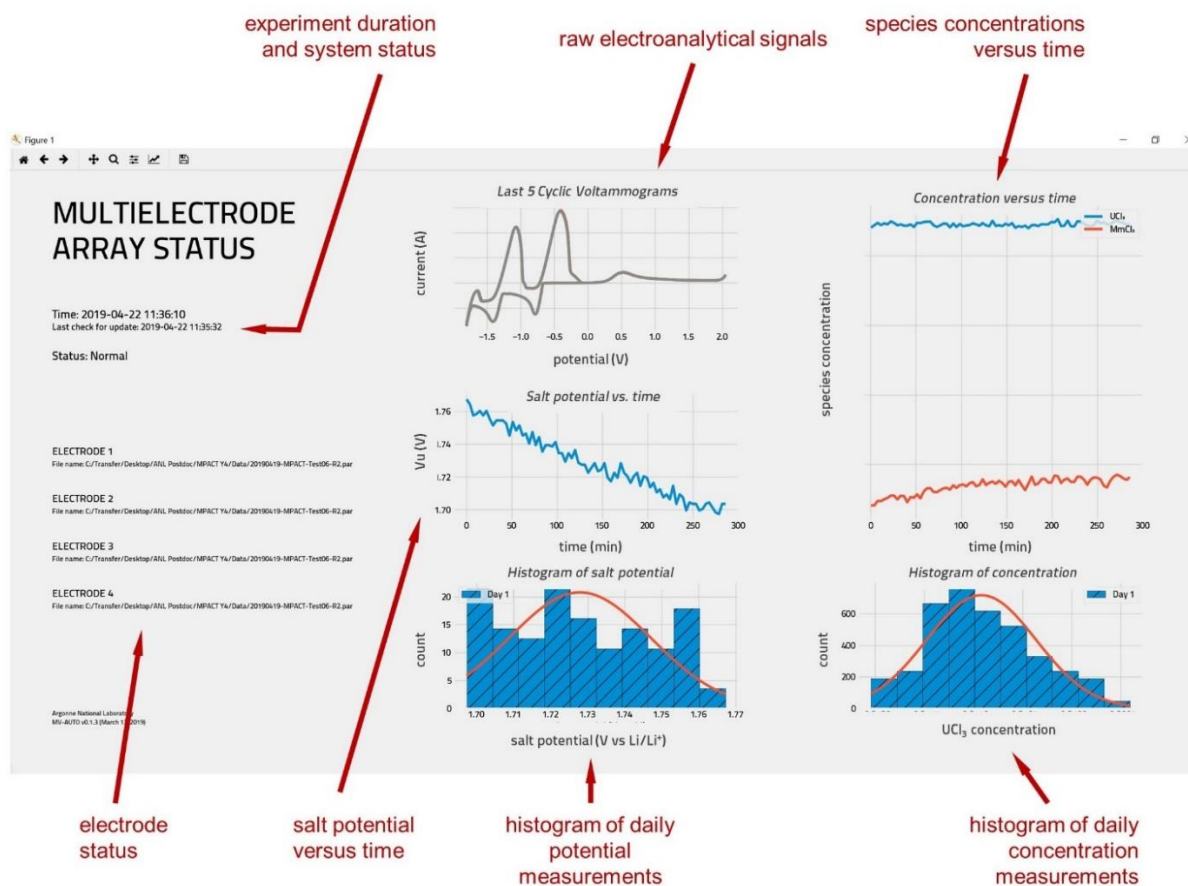
The objective of Argonne's electrochemical sensor development within the MPACT program is to integrate multifunctional voltammetry sensors into the operations of electrorefiners. Precise measurements of the electrorefiner salt are crucial as electrorefiners typically contain the bulk of the transuranic inventory in any electrochemical processing facility. To support these measurements, Argonne has developed voltammetry sensors based on a multielectrode array to take measurements of actinide concentrations, the salt level, and the salt potential. The concentrations and salt level measurements provide an overall inventory of dissolved actinide species in the salt, while the salt potential provides a signature that can be used to indicate off-normal performance.

As described in earlier work<sup>22</sup>, the sensors make measurements using a sequence of electroanalytical waveforms applied to an array of electrodes immersed in the salt. Through analysis of the response to the applied voltage or current signals, information about the salt can be extracted. Figure 3 shows photographs of one such sensor, including an image of it inside a hot cell environment at Idaho National Laboratory. Recent work has focused on full automation of the sensor operations. Toward that end, scripts have been written to automatically adjust the applied electroanalytical signals to keep them in a stable range for measurements. Furthermore, all sensor operations have been migrated to a multi-channel configuration capable of automatic selection and sequencing of electrodes within the electrode array. For data analysis, scripts have been created to automatically analyze data taken across the array of electrodes and synthesize all of it into the desired outputs.

An example of typical sensor output is shown in Figure 4. These measurements were taken in an idle electrorefiner (i.e. when no processing was occurring). The information allows the electrorefiner operators to understand what is happening from both a safeguards and process monitoring perspective during operations. Plots showing the evolution of the salt potential and species concentrations versus time are shown, as well as histograms showing historical measurements. Statistical information for the measurements can be reported to the user, and the histograms include Gaussian fits. Off-normal conditions are indicated by a system status output.



**Figure 3.** Argonne-developed multielectrode array voltammetry sensor. The photo on the far right shows the deployment of Argonne's sensor inside a hot cell environment at Idaho National Laboratory (right).

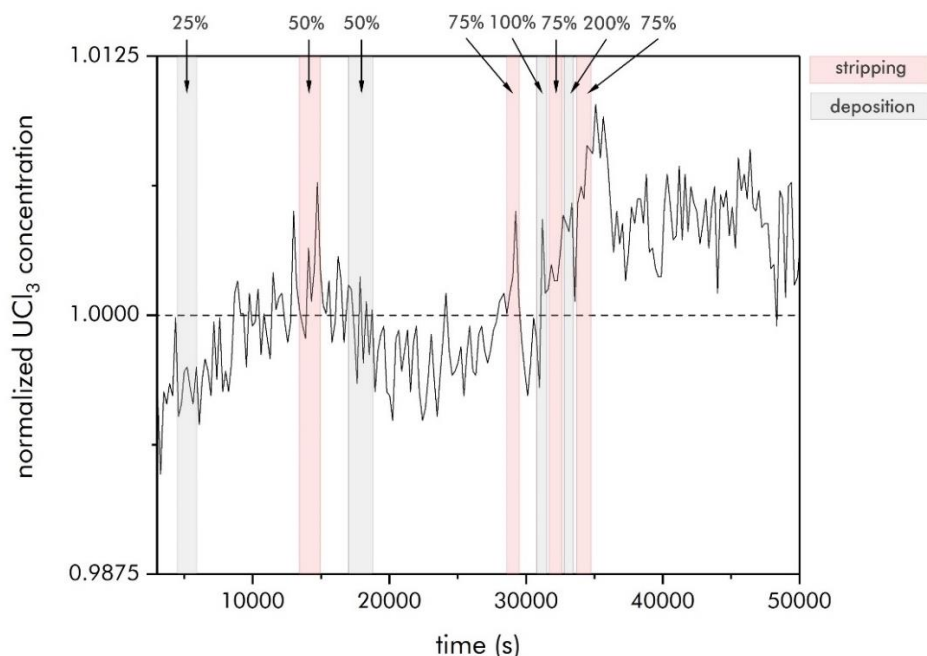


**Figure 4.** Typical sensor output for idle electrorefiner operations.

Previous work<sup>22</sup> indicated that  $\text{UCl}_3$  concentration measurements with a mean absolute error of 0.12 wt.% were achievable in salts comprised of  $\text{LiCl-KCl-UCl}_3\text{-PuCl}_3$ . Repeated measurements over the span of one day were found to have a relative standard deviation of 0.13%, while measurements taken over a 100-day testing campaign in an idle electrorefiner had a relative standard deviation of only 1.08%. The measurements, however, occurred in test cells without concurrent electrorefining operations.

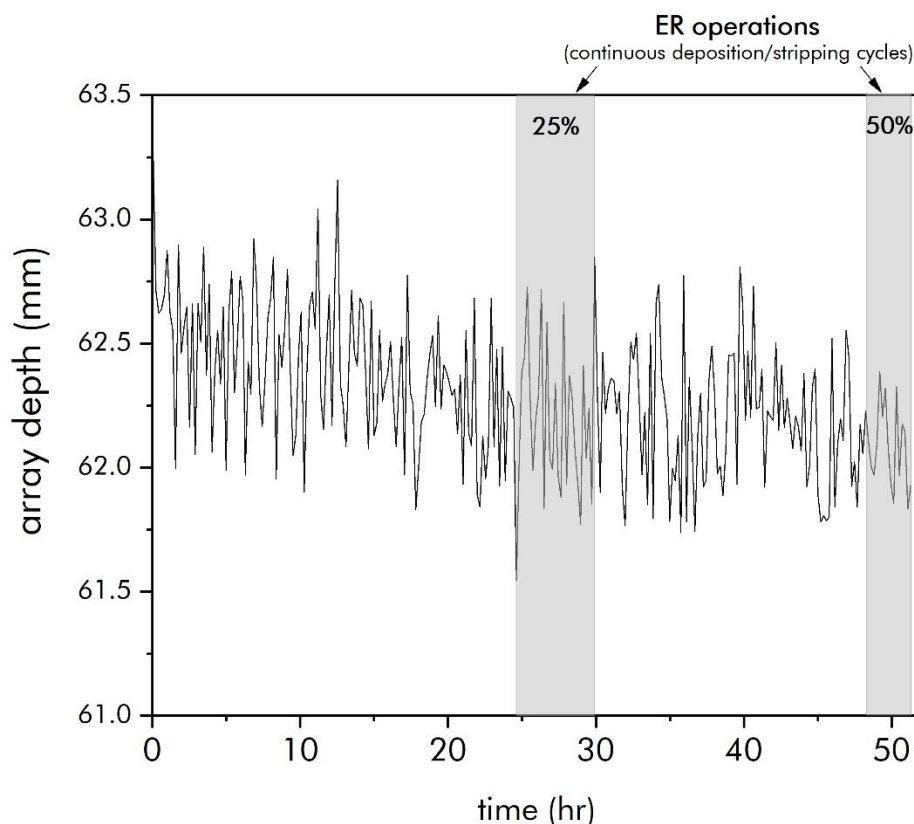
To fully integrate the voltammetry sensors with electrorefiner operations, tests of the electroanalytical measurements had to be taken while current was being passed between the electrorefiner anodes and cathodes to ensure monitoring could be achieved during material processing. The large currents that are applied to the salt during processing steps can lead to disruption of electroanalytical signals, but through proper sensor design and emplacement the effects on the resulting measurements can be minimized. Concentration gradients can be formed near the anodes and cathodes of the process equipment during operations, but temperature-induced convection serves to minimize any large-scale inhomogeneity.

Concurrent measurements were first attempted in a series of stripping and deposition cycles in which the electrorefiner current was incrementally increased. This series of cycles is not representative of an actual processing run, but serves to allow a rapid assessment of the sensor when subject to a full range of background currents. Results for  $\text{UCl}_3$  concentration measurements taken during one such sequence are shown in Figure 5. Deposition to the cathodes was begun at 25% of the electrorefiner's typical operating current, then increased to 200% in stages. As shown in the figure, the  $\text{UCl}_3$  concentration remained highly stable over the duration of the run, regardless of the electrorefiner's operational level. This invariance is expected as the electrorefiner test consisted solely of U metal stripping and deposition at the anodes and cathodes, respectively, with no net change in the  $\text{UCl}_3$  content of the salt. Measurements of the electrode array immersion depth (which can be readily translated into the salt level) were also taken during a variety of concurrent electrorefiner operations and were found to be stable and immune to disruption from background currents, as shown in Figure 6. Overall, the performance of the sensor was completely satisfactory, indicating that continuous use during processing runs is achievable.



**Figure 5.** Normalized  $\text{UCl}_3$  concentration versus time during typical electrorefiner operational assessment.





**Figure 6.** Electrode array depth during typical electrorefiner operational assessment.

A statistical analysis of the measurements taken during the complete testing campaign of combined electrorefiner operations was also conducted. Tables 1 and 2 show a summary of some of the principal statistical properties of measurements taken during the different operating regimes. For the sake of the analysis, differences in the measured values over the duration of testing were assumed to result exclusively from error associated with the sensor — the assumption was made that the electrorefiner had perfectly fixed salt conditions throughout the testing protocol. The analysis therefore represents an upper bound on the statistical performance of the sensor as minor variations in the electrorefiner salt can be expected to arise over long durations due to mass transport inhomogeneities and other kinetic factors.

The raw concentration values in Table 1 have been normalized by the mean concentration measured when the electrorefiner was off. Overall, the differences in the measured concentrations are under 1% across all regimes. Similarly, the standard deviation of the concentration measurements within any specific operational regime are also under 1%. A *t*-test of the  $\text{UCl}_3$  concentration measurements indicated the existence of a statistically significant difference between the mean of the measurements taken with and without concurrent electrorefiner operations. However, as the arithmetic means of the measurements differed by less than 0.2%, the small difference is considered acceptable. A *t*-test of the array depth measurements also indicated a statistically significant difference for active operations compared to idle operations, but, again, because the means of the sampled measurements differed by only 0.5% the difference is also considered acceptable.



**Table 1.** Statistical Analysis of  $\text{UCl}_3$  concentration measurements during combined electrorefiner operations at indicated current level.

	ER Off	ER On	Deposit (25%)	Strip (25%)	Deposit (50%)	Strip (50 %)
<b>Normalized <math>\text{UCl}_3</math> Concentration</b>	1	1.001	0.992	1.001	1.003	1.002
<b>Relative standard deviation</b>	0.15%	0.15%	0.06%	0.11%	0.13%	0.17%
<b>95% confidence interval (norm)</b>	0.00007	0.0002	0.0001	0.0002	0.0004	0.0004

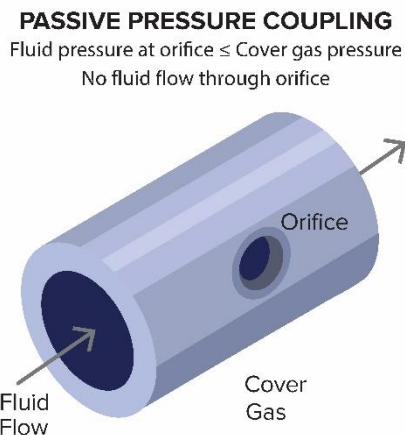
**Table 2.** Statistical Analysis of array depth measurements during combined electrorefiner operations at indicated current level.

	ER Off	ER On	Deposit (25%)	Strip (25%)	Deposit (50%)	Strip (50%)
<b>Array Depth (mm)</b>	62.3	62.6	62.9	62.3	62.6	62.6
<b>Relative standard deviation</b>	0.75%	0.67%	0.31%	0.86%	0.43%	0.54%
<b>Confidence interval, 95% (norm)</b>	0.0002	0.0004	0.0004	0.0009	0.0007	0.0008

### Salt Handling Platforms to Support On-line and At-line Monitoring

While significant progress has been made in the development of analytical techniques that may be suitable for on-line or at-line analysis of molten salt, significant gaps still exist in the enabling chemical process technologies required to integrate these analytical techniques into real processes. To help fill these gaps, Argonne is developing a salt handling platform to support the integration of various measurement systems into a molten salt process sampling loop. The long-term goal of the technology is to enable the deployment of unattended monitoring systems using analytical techniques that can currently only be performed off-line.

Argonne's platform is based on an open-orifice flow cell. This cell consists of a pipe that has fluid flowing through its cross section while having one or more holes (orifices oriented axially through the pipe wall) through which fluid does not flow at steady state (Figure 7). Fluid does not flow through the orifices in the flow cell wall because the fluid pressure at the orifice is passively coupled to the cover gas pressure by employing Bernoulli's principle and gravity flow.<sup>38, 39</sup> The open orifice flow cell can be used for physical access to the salt (i.e., sample extraction) or for windowless optical access to the salt (i.e., on-line optical analysis). Both embodiments of the open-orifice flow cell are currently under development.



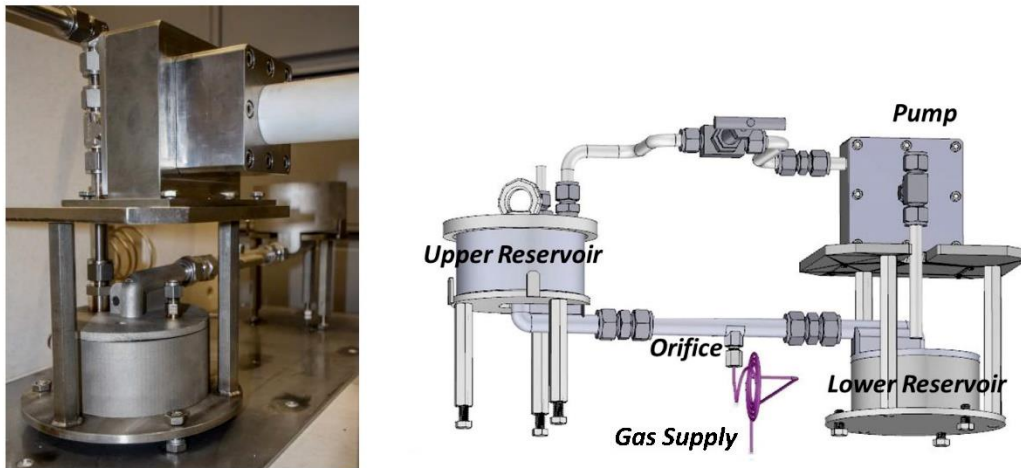
**Figure 7.** Open orifice flow cell with passive pressure coupling between the fluid pressure at the orifice and the cover gas pressure.

A successfully deployed windowless optical cell sampling loop would permit the use of a wide variety of optical techniques for on-line monitoring of molten salts systems. These techniques include Raman, UV-Vis, and laser-induced breakdown spectroscopy approaches, all of which have been extensively used for molten salts.<sup>40-47</sup> These optical techniques are at various levels of technology readiness, but most face the same technical hurdle, which is the development of a window material that can withstand the high-temperature, high-radioactivity, and highly-abrasive molten salts for more than a few hours.<sup>48</sup> While the development of a windowless optical cell flow loop is not without its own technical challenges, it has the potential to be a cross-cutting enabling technology because this single platform could provide a means of integrating multiple optical analysis techniques into an on-line monitoring system.

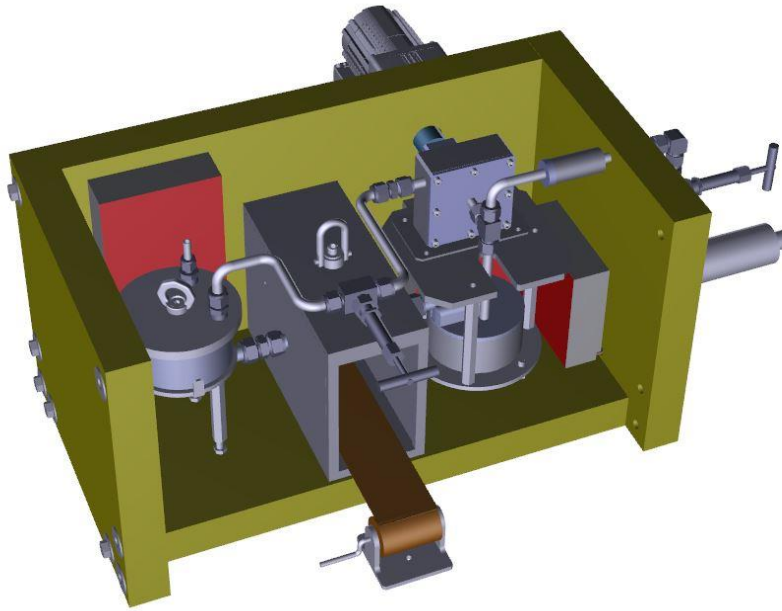
The first proof-of-concept iteration of the windowless optical flow cell system will feature Raman spectroscopy, which is a candidate for molten salt in-process elemental identification and signature monitoring.<sup>1, 49, 50</sup> Because Raman spectroscopy uses a laser light source and relies on inelastic scattering of photons, a single small aperture in a flow cell can be used for both illumination and signal collection. A custom fiber-coupled Raman spectroscopy system was fabricated for this work. The system is pumped using a 500 mW 785 nm diode laser and has a high-resolution, low-shift spectrometer that covers Raman shifts up to 1500  $\text{cm}^{-1}$ . A static cell and an acrylic prototype of the flow cell were tested with an aqueous anatase solution and a 40% glycol solution (which simulates the viscosity of a molten salt). The expected glycol and anatase peaks were observed, and, while the system requires further optimization, the first round of results indicate that optical distortion due to the dynamic liquid/gas interface will not be problematic for this method. Molten salt testing of the on-line optical analysis system and the related flow cell sample extractor system will proceed in fiscal year 2021.

A flow cell sample extractor based on Argonne's open-orifice technology is being developed to support automated sampling-based process monitoring by generating samples of various sizes on-demand. A test loop, pictured in Figure 8, was developed to support shake-down testing of the flow cell sample extractor and windowless optical cell flow loop prototypes. In the test loop, fluid is pumped from a lower reservoir into an elevated reservoir using a custom centrifugal pump. Alternate pumping mechanisms are also being investigated including gas-lift and vacuum-lift techniques. In an industrial process, the salt could be sampled from a process tank by a variety of pumping mechanisms or could be sampled from a process line via split stream (once reliable metering valves become available). The final choice of pumping mechanism will depend on the height over which the fluid must be pumped, the radiation field, the application (optical analysis or sample extraction), and the state of development for various technologies at the time of deployment.

In the gravity flow cell sampling loop, fluid is actively pumped into the top of the elevated reservoir while fluid is draining out the bottom. The fluid is then transported by gravity through the open-orifice flow cell and back to the lower reservoir (or to a process tank in a deployed system). A slight vacuum in the flow cell relative to the cover gas prevents fluid from exiting the flow cell through the orifices during steady-state operation. A custom furnace was developed to support these experiments (Figure 9). The fluid pressure at the orifice can be raised using a variety of actuation mechanisms to extract samples from the sampling loop.<sup>38, 39</sup> In the current iteration of the system, the fluid pressure increase occurs by direct pneumatic actuation. An inert gas supply is connected to one orifice through a normally closed rapid-response solenoid valve. When the valve is opened, samples are ejected through a second, upstream orifice. In preliminary water testing of the system, samples ranging from 1 microliter to several milliliters were produced with high-precision and repeatability.<sup>22</sup>

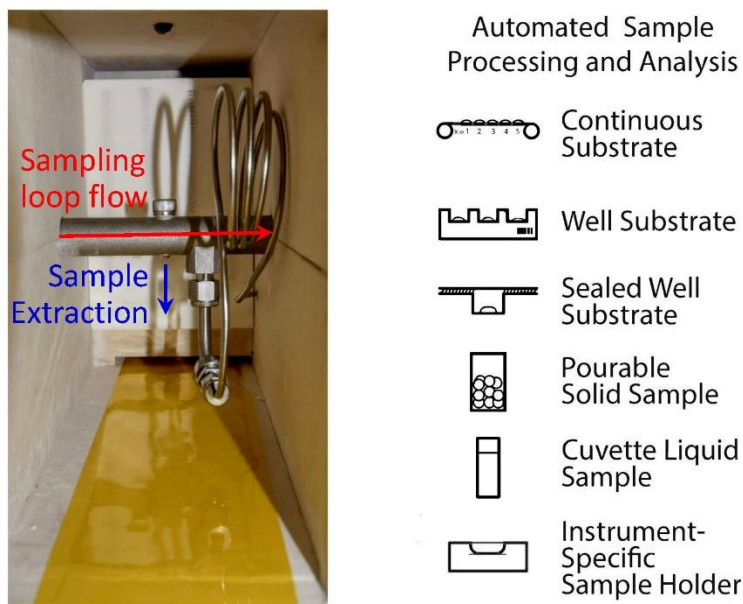


**Figure 8.** Gravity flow cell sample extractor. Left: Lower reservoir and custom centrifugal pump. Right: Flow cell sample extractor test loop. Fluid moves from the lower reservoir (which is representative of a process vessel) to the upper reservoir via active pumping, then flows through the open orifice cell back to the lower reservoir by gravity flow.



**Figure 9.** Sample extractor test loop furnace with side and lids removed. Samples are generated in an insulated inner chamber, which is heated separately and has a separate access panel to facilitate sample collection.

In a deployable system, the orifice outlet and gravity flow cell outlet would likely share a common drain back to the process to support leak containment and flushing operations. To bypass this drain and enable sample collection, a sampling substrate or vessel would be placed in the droplet path. Currently, Kapton® X-ray fluorescence spectroscopy (XRF) film (supplied from a roll) is used to collect samples for high-throughput XRF analysis (Figure 10 left). However, several other sample holder types are also possible as shown on the right side of Figure 10. Because of the versatility of the sample extractor in terms of sample size range and on-demand sample generation, a single sample extractor could be used to produce large samples (for analysis by techniques such as gamma spectroscopy) or very small samples (for analysis by techniques such as XRF). The sample extractor can also produce large quantities of samples to support high-throughput sample characterization. High-throughput sample analysis can significantly improve precision for a given measurement technique by averaging out random sampling and measurement errors, as discussed below. Similarly, sample size precision can be improved by ejecting many smaller samples to make up a single larger sample.

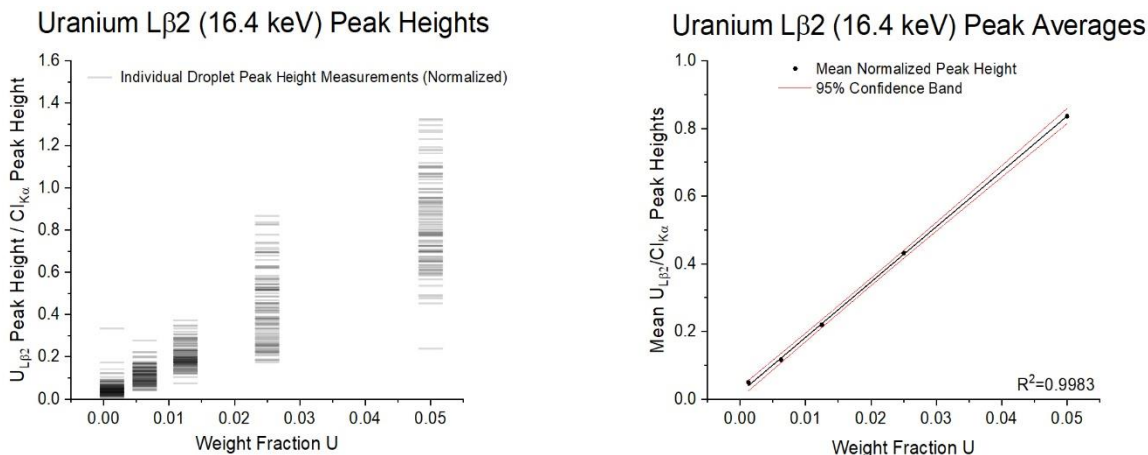


**Figure 10.** Left: Sample extractor flow cell inner chamber with Kapton® XRF film spotting substrate. Right: Alternate substrates and vessels to support the integration of sample extraction and sample analysis.

A major challenge in molten salt sampling is the potential for inhomogeneities in a salt vessel. The sampling loop sample extractor system was designed to address this issue. The system can avoid sample contamination from surface dross by positioning the sampling pipe inlet below the dross. To account for potential partitioning of entrained fines, the system is designed to circulate orders of magnitude larger volumes of salt than is ejected as samples. This will help ensure that a representative cross-section of the salt is sampled.

A third system under development is a static version of the flow cell sample extractor. It consists of a single reservoir from which samples are ejected by direct pneumatic actuation.<sup>22, 38</sup> This reservoir chamber is connected to an argon supply through a normally closed rapid-response solenoid valve. High-throughput sample generation and analysis was performed using this single reservoir system. Pressure pulses were applied to the top of the reservoir chamber by opening the solenoid valve for 20 ms to eject 40 mg molten salt samples through a 0.016 in. diameter sapphire conical vee orifice on the bottom of the reservoir chamber. The molten salt droplets were spotted onto Kapton® XRF film. A total of 500 uranium bearing LiCl-KCl salt microsamples were produced from batches of salt with five different uranium concentrations. Each sample was analyzed by a low-cost handheld XRF instrument (Olympus DELTA DS-2000). Uranium peak height measurements were normalized to the Cl peak height ( $K\alpha_1$  peak, 2.62 keV) to adjust for variable droplet positions within the inhomogeneous beam.

Figure 11 left shows individual peak height measurements, which cover a wide distribution for each weight fraction due to random sampling and measurement errors. Figure 11 right shows the average peak height values for each uranium concentration. Despite the wide distribution of individual measurements, the mean values converge into a linear calibration curve with a narrow confidence interval. These results highlight the main benefit of high-throughput sample generation and analysis, which is that random sampling and measurement errors are averaged out to improve measurement precision.



**Figure 11.** Left: XRF measurements for individual LiCl-KCl salt microsamples with uranium content ranging from 0.125 to 5.0 wt.%. Right: Mean peak height values for each uranium concentration.

## Conclusions

As part of the broader safeguards-by-design effort, Argonne is developing technologies to support multimodal in-process monitoring of molten salt compositions in electrochemical reprocessing facilities. The in-process measurement modes will include both rapid electrochemical sensing and high-precision sampling-based analysis enabled by novel salt handling platforms.

The electrochemical sensors described here have few barriers to deployment. The immunity of the sensors to background currents and the stability of the measurements over long durations indicate that the multielectrode array voltammetry sensors offer excellent capabilities for the monitoring of electrorefiners and other electrochemical reprocessing equipment. The insusceptibility of the electrochemical measurements to the operation of the electrorefiner is shown by the fact that the relative standard deviation of the concentration measurements was under 1% and the difference in the sample means was under 0.5% for conditions with the electrorefiner on or off. The minimal differences between measurements taken during active and idle operations suggest that process holds to conduct periodic accountancy checks on the electrorefiner salt will not be required. These process holds would otherwise disrupt reprocessing activities and hinder operational efficiency. Overall, the combined safeguards and process monitoring capabilities afforded by these robust, inexpensive sensors suggest that wide adoption across molten salt reprocessing facilities should be readily pursued in the near term.

Over the longer term, fully automated sampling-based analyses will likely be deployed to provide high-precision validation of electrochemical measurements. If successfully deployed, the salt handling platforms under development will enable automated on-line and at-line salt characterization using analytical techniques that can currently only be performed with manual sampling and off-line analysis. This would improve the timeliness of analysis, reduce labor costs, eliminate human error, and reduce worker access and exposure to material. This automated approach could also be used to enable high-throughput analysis, which is already widely used in other industries to improve analysis precision. However, to deploy this sampling loop technology, advances in enabling technologies for process integration will be required. Technology gaps that must be addressed include sampling pumps, metering valves, containment enclosures, and tooling for operations and maintenance (for example pneumatic reamers may be required to periodically re-bore the flow cell or orifice during long-term operation).

Furthermore, all these new sampling technologies will require extensive testing to ensure reliable operation in relevant environments. Until these gaps are addressed, sampling-based analysis of salt systems will continue to be performed with slow and costly manual batch-wise sampling and off-line analysis. Therefore, significant continued investment to rapidly fill these gaps will likely be required if automated sampling-based approaches such as on-line optical analysis and at-line sample characterization are to be deployed as part of an integrated safeguards-by-design approach in the next generation of molten salt reactor and electrochemical reprocessing plants. If the in-situ monitoring and automated sampling-based analysis platforms are successfully deployed, these technologies will ensure rapid and accurate detection of material loss, while also providing valuable timely feedback to plant operators and process control systems.

**Keywords:** safeguards-by-design, molten salt, process monitoring, electrochemical reprocessing, voltammetry, in-situ, on-line, at-line, sampling, optical analysis

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### Acknowledgments

The authors thank Jackie Copple (Principal Software Engineer, Argonne Chemical and Fuel Cycle Technologies Division) for writing automated analysis scripts and other control software used by the multielectrode array voltammetry sensors.



This work was funded by the U.S. Department of Energy Office of Nuclear Energy MPACT Campaign. The submitted manuscript has been created by the UChicago Argonne, LLC as Operator of Argonne National Laboratory (Argonne) under Contract No. DE-AC02-06CH11357 with the U.S. Department of Energy.

## References

1. Coble, J. B., et al. 2020. Review of Candidate Techniques for Material Accountancy Measurements in Electrochemical Separations Facilities, *Nuclear Technology*, DOI: 10.1080/00295450.2020.1724728.
2. <https://www.metrohm.com/en-us/products-overview/process-analyzers/>, accessed 07/30/2020.
3. Mamantov, G. and Manning, D. 1966. Voltammetry and Related Studies of Uranium in Molten Lithium Fluoride-Beryllium Fluoride-Zirconium Fluoride, *Analytical Chemistry*, Vol. 38, No. 11.
4. Iizuka, M., et al. 2001. Application of Normal Pulse Voltammetry to On-Line Monitoring of Actinide Concentrations in Molten Salt Electrolyte, *Journal of Nuclear Materials*, Vol. 297, No. 1.
5. Randles, J. E. B. 1948. A Cathode Ray Polarograph. Part II.—The Current-Voltage Curves, *Transactions of the Faraday Society*, Vol. 44.
6. Sevcik, A. 1948. Oscillographic Polarography with Periodical Triangular Voltage, *Collection of Czechoslovak Communications*, Vol. 13.
7. Paunovic, M. 1967. Chronopotentiometry, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, Vol. 14, No. 4.
8. Lovrić, M. and Osteryoung, J. 1982. Theory of Differential Normal Pulse Voltammetry, *Electrochimica Acta*, Vol. 27, No. 7.
9. Milazzo, G. 1988. Applications of Bioelectrochemistry in Medicine, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, Vol. 253, No. 2.
10. Wang, J. 2006. *Analytical Electrochemistry*, John Wiley & Sons, Hoboken, New Jersey, United States.
11. Inman, D., et al. 1959. Electrode Reactions in Molten Salts: the Uranium + Uranium Trichloride System, *Transactions of the Faraday Society*, Vol. 55.
12. Carlin, R. T. and Osteryoung, R. A. 1989. Deposition Studies of Lithium and Bismuth at Tungsten Microelectrodes in LiCl: KCl Eutectic, *Journal of The Electrochemical Society*, Vol. 136, No. 5.
13. Serrano, K. and Taxil, P. 1999. Electrochemical Reduction of Trivalent Uranium Ions in Molten Chlorides, *Journal of Applied Electrochemistry*, Vol. 29, No. 4.
14. Nagai, T., et al. 2006. In-situ Measurement of  $\text{UO}_2^{2+}$  Concentration in Molten NaCl-2CsCl by Differential Pulse Voltammetry, *Journal of Nuclear Science and Technology*, Vol. 43, No. 12.
15. Hoover, R. O., et al. 2014. Electrochemical Studies and Analysis of 1–10 wt%  $\text{UCl}_3$  Concentrations in Molten LiCl–KCl Eutectic, *Journal of Nuclear Materials*, Vol. 452.
16. Tylka, M., et al. 2015. Application of Voltammetry for Quantitative Analysis of Actinides in Molten Salts, *Journal of The Electrochemical Society*, Vol. 162, No. 12.
17. Rappleye, D., et al. 2016. Investigation of the Effects of Uranium(III)-Chloride Concentration on Voltammetry in Molten LiCl-KCl Eutectic with a Glass Sealed Tungsten Electrode, *Electrochimica Acta*, Vol. 219.
18. Tylka, M. M., et al. 2015. Method Development for Quantitative Analysis of Actinides in Molten Salts, *Journal of The Electrochemical Society*, Vol. 162, No. 9.
19. Hoyt, N. C., et al. 2017. Communication—Quantitative Voltammetric Analysis of High Concentration Actinides in Molten Salts, *Journal of The Electrochemical Society*, Vol. 164, No. 2.
20. Lovering, D. G. and Gale, R. J. 1983. *Molten Salt Techniques*, Plenum Press, New York, United States.
21. Phillips, J., et al. 1976. Glassy Carbon Rotating Ring-Disc Electrode for Molten Salt Studies, *Analytical Chemistry*, Vol. 48, No. 8.
22. Launiere, C., et al. 2020. Safeguards By Design: Multimodal In-process Monitoring of Molten Salt Composition, *Proceedings of the 61st INMM Annual Meeting*.
23. Miller, M., et al. 2017. Material Protection, Accounting, and Control Technologies (MPACT) Advanced Integration Roadmap. OSTI Identifier: 1341846.
24. International Atomic Energy Agency, 2018. IAEA Safeguards Research and Development Plan.
25. Personal Communication, Ho Nieh (Director, Office of Nuclear Reactor Regulation, U.S. Nuclear Regulatory Commission), 08/06/2020.

26. Williams, A. N., et al. 2018. Accurate Determination of Density, Surface Tension, and Vessel Depth Using a Triple Bubbler System, *Journal of Industrial and Engineering Chemistry*, Vol. 63.
27. Andrews, M., et al. 2015. MCNP6 Simulations of Gamma Line Emissions from Fission Products and Their Comparisons to Plutonium and Uranium Measurements, *Progress in Nuclear Energy*, Vol. 79.
28. Knowles, J., et al. 2016. A Generalized Method for Characterization of  $^{235}\text{U}$  and  $^{239}\text{Pu}$  Content Using Short-Lived Fission Product Gamma Spectroscopy, *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, Vol. 833.
29. Cipiti, B., et al. 2016. Material Protection, Accounting, and Control Technologies (MPACT): Modeling and Simulation Roadmap, OSTI Identifier: 1296697.
30. Cipiti, B., et al. 2020. The MPACT 2020 Milestone: Safeguards and Security by Design of Future Nuclear Fuel Cycle Facilities. Submitted to the Journal of Nuclear Materials Management.
31. Laidler, J. J., et al. 1997. Development of Pyroprocessing Technology, *Progress in Nuclear Energy*, Vol. 31, No. 1-2.
32. Williamson, M. and Willit, J. 2011. Pyroprocessing Flowsheets for Recycling Used Nuclear Fuel, *Nuclear Engineering and Technology*, Vol. 43, No. 4.
33. Gallaher, R. 1971. Operation of the Sampler-Enricher in the Molten Salt Reactor Experiment, ORNL-TM-3524.
34. Burris Jr, L., et al. 1967. Two Techniques Enable Sampling of Filtered and Unfiltered Molten Metals, NASA 19670000034.
35. Koger, J. 1972. Corrosion and Mass Transfer Characteristics of  $\text{NaBF}_4\text{-NaF}$  (92-8 mole percent) in Hastelloy N, OSTI Identifier: 4602933.
36. Shin, Y. J., et al. 2001. Development of Advanced Spent Fuel Management Process, KAERI/RR--2128/2001.
37. Cheatham III, J. R., et al. 2019. *U.S. Patent Application* 16/595,064, Fission Reaction Control in a Molten Salt Reactor, TerraPower LLC.
38. Launiere, C. A., et al. 2019. *U.S. Patent* 10,416,045, Method for High-Throughput Micro-Sampling Analysis of Electrochemical Process Salts, Argonne National Laboratory.
39. Launiere, C., Kozak, P.; Lichtenberger, J.; Pereira, C. 2019. *U.S. Patent Application* 16/709,520, Flow Loop Sample Generator, Argonne National Laboratory.
40. Janz, G. J. and James, D. W. 1961. Raman Spectra and Ionic Interactions in Molten Nitrates, *The Journal of Chemical Physics*, Vol. 35, No. 2.
41. Maroni, V. A., et al. 1971. Structural Studies of Magnesium Halide-Potassium Halide Melts by Raman Spectroscopy, *The Journal of Physical Chemistry*, Vol. 75, No. 1.
42. Hanson, C., et al. 2014. Temperature Effect on Laser-Induced Breakdown Spectroscopy Spectra of Molten and Solid Salts, *Spectrochimica Acta Part B: Atomic Spectroscopy*, Vol. 97.
43. Effenberger, A. J. 2009. Methods for Measurement of Heterogeneous Materials with Laser-Induced Breakdown Spectroscopy (LIBS), ProQuest ID: EffenbergerJr\_ucsd\_0033D\_10496.
44. Smith, N. A., et al. 2014. Application of Laser Induced Breakdown Spectroscopy to Electrochemical Process Monitoring of Molten Chloride Salts, *Poster presented at: International Atomic Energy Agency (IAEA) Symposium on International Safeguards*.
45. Williams, A. and Phongikaroon, S. 2018. Laser-Induced Breakdown Spectroscopy (LIBS) Measurement of Uranium in Molten Salt, *Applied spectroscopy*, Vol. 72, No. 7.
46. Williams, A. N. and Phongikaroon, S. 2017. Laser-Induced Breakdown Spectroscopy (LIBS) in a Novel Molten Salt Aerosol System, *Applied spectroscopy*, Vol. 71, No. 4.
47. Nagai, T., et al. 2004. Study on Redox Equilibrium of  $\text{UO}_2^{2+}/\text{U}^{2+}$  in Molten  $\text{NaCl-2CsCl}$  by UV-Vis Spectrophotometry, *Journal of Nuclear Science and Technology*, Vol. 41, No. 6.
48. Anheier, N. C., et al. 2013. Technical Readiness and Gaps Analysis of Commercial Optical Materials and Measurement Systems for Advanced Small Modular Reactors, OSTI Identifier: 1095436.
49. Holcomb, D. E., et al. 2018. Instrumentation Framework for Molten Salt Reactors OSTI Identifier: 1462848.
50. Singh, V. J. 2019. Nuclear Material Accountancy in High Temperature Molten Salt Using In Situ Raman Spectroscopy and Cyclic Voltammetry, <http://hdl.handle.net/11714/5772>.