Advances in On-Line Monitoring for Nuclear Fuel Reprocessing Streams
Dr. Amanda Lines and Dr. Samuel A. Bryan, PNNL, USA

Berta
Welcome everyone to the next GEN IV International Forum Webinar presentation. Doing the introduction today is Dr. Patricia Paviet. Patricia is the chair of the GEN IV International Forum Education and Training Working Group. She's also the National Technical Director of Molten Salt Reactor Program for the Department of Energy in the United States within the Office of Nuclear Energy. Patricia.

Patricia Paviet
Thank you very much Berta [ph]. Good morning, good evening, good afternoon everyone. It's a pleasure to have Dr. Amanda Lines and Dr. Samuel Bryan with us today from the Pacific Northwest National Laboratory. Amanda is the Chief Scientist with experience in the design and deployment of online monitoring and sensor technology. She graduated from Washington State University with a Ph.D. in analytical chemistry after earning an undergraduate degree in chemistry and chemical engineering from Purdue University.

Her work primarily focuses on the development of optical sensors for highly harsh environments, such as those common to nuclear materials processing, as well as the application of chemical data science tools to enable advanced automated data output. Dr. Sam Bryan is a laboratory fellow at PNNL in nuclear chemistry and engineering. He joined PNNL in 1990 and has over 35 years experience in optical spectroscopy, electrochemistry and separation science. Doctor Bryan's research interests involve the design and development of spectroscopic and spectroelectrochemical sensors for the measurement of actinides, lanthanides, fission products, transition metal complexes in aqueous and molten salt media. He also serves as an Adjoint Faculty member in the department of Chemistry at Washington State University. So, without any delay, I'm going to give you the floor. Amanda and Sam, thank you very much for volunteering to give this webinar. Thank you.

Amanda Lines
All right, well, thank you so much Patricia, for the invite to give a talk here. Sam and I are both excited to go through a lot of the work that we've been doing in the development of online monitoring technology. But before we really dive into the technical meat of the talk, we want to go through some background slides just to make sure we're all on the same page with terminology and really how these tools work. So,

one of the first things to note here is that when we say online or inline monitoring and variance thereof, what we're talking about is getting sensors directly onto or into a chemical process so that we can see in situ and real time what exactly is going on in that process.

This type of process, insider information, is extremely valuable and useful in a lot of ways. Many people, when they think online monitoring, their first thought is to go to operating systems at commercial scale so that they can run those processes better, faster, safer, and more cost effectively. But online monitoring has a lot of other applications as well. That includes gaining unparalleled insight into fundamentals of the chemistry of your process, allowing engineers and operators to more efficiently develop new chemical processes, and supporting engineers, operators, scientists, as they go through the scale up of a process from lab to bench to pilot to deployed scale systems.

Really, online monitoring is an incredibly valuable tool through the entire lifecycle of chemical process development to deployment. And so, we might ask a question then, how is this valuable to nuclear energy? Or really, if we think next generation reactors, and if we go right to what most people think of when they're thinking nuclear energy, which is reactor operation. When we think about GEN IV reactors, there's at least one very good example where online monitoring could be incredibly valuable, and that is molten salt reactors. Getting sensors into or onto a molten salt reactor would not only allow operators to, let's say, look at and better understand uranium three to four ratio, but it could potentially support other things, such as material control and accounting, or even safeguarding of material, so plenty of value there.

But we like to argue that if we're thinking about the future of nuclear energy, we need to be thinking about the entire fuel cycle. And online monitoring can have benefits throughout. That includes supporting fuel production to power these new reactors, fuel recycles so that we can use our resources more responsibly. And, of course, waste disposition, once we're ready to take some of those final materials into a deep geologic repository and process them into a form that's appropriate for that. So, there's a lot of applications for online monitoring through this whole cycle. And Sam and I are going to be giving you some examples of this through our talk. But before we get to that, it's worthwhile to note that there are a lot of different online monitoring tools and sensors out there.

Really, the sensor tool that you utilize is dependent on what type of information you want to get out of the process. Thermocouple for temperature and so on, right? Our team utilizes whatever sensor we need to go after the information we're most interested in. But really, one of our favorite tools out there is optical spectroscopy. And that's really because optical spectroscopy is unique in its ability to give us very detailed chemical composition information. This approach is all about getting light into your chemical process, looking at how light interacts with that material, and then gleaning that chemical composition data, information from that very simplistic, we'll say, interaction.

In this case, optical spectroscopy, is something that will let us ask and answer questions, such as, in this chemical process, is plutonium present? How much plutonium is there, what oxidation state is it in, what speciation is it exhibiting, really, what is it doing in that process? And is it behaving the way we want and need it to for that process to run smoothly?

So, optical spectroscopy is very powerful for getting that type of information, but it does have a number of other benefits as well. It's also usually a very mature technology. That means that we can go and get a lot of our components for our systems, commercial, off-the-shelf. It tends to be fairly simplistic to integrate into a chemical process, and we'll talk more about that later. But probably, the most important thing for us when we're designing online monitoring systems, is the versatility of optical spectroscopy. And it's versatile in a lot of ways. The first way to think of versatility is that we can take optical spectroscopy into a whole range of different system matrices to characterize the chemical composition of those. So, we can look at solids, liquids, gases, even molten salt.

We can also take optical spectroscopy into a wide range of system scales, everything from commercial scale. We're talking hundreds of gallons an hour, all the way down to microscale. We're talking microliters per minute, a lot of flexibility. But perhaps, the most important aspect of versatility of optical spectroscopy is our ability to go after a large number of chemical analytes that are of interest to the fuel cycle. So, that's the entire fuel cycle. And the reason we can go after so many different targets is that there are a lot of different forms or flavors of optical spectroscopy that we can utilize. So, for example, two of our favorite tend to be Raman spectroscopy and UV-vis-NIR absorption.

Now, Raman spectroscopy is a form of vibrational spectroscopy. It lets us get polyatomic species, so we can use Raman to identify and quantify targets such as oxide ions, organics, that's both solvent components as well as complexes. We can look at inorganic oxo-anions, water, acid, we can even do pH of weak acid base systems. So, there's a lot of things we can go after Raman. And UV-vis-NIR, however, probes the system a little bit differently. This is a form of electronic spectroscopy, so we can see different things such as actinides and lanthanides in multiple oxidation states, as well as various metal ligand complexes.

Now, Raman and UV-vis-NIR are not going to give us everything we need all the time. So, there are other tools that we can and have used in the past that includes things like FTIR, light scatter, optical density, and there are many, many more fluorescence and so on, and all of that to say that there are a lot of different optical tools that we can bring to bear in these different chemical processes to go after the target analytes of interest. But I want to pull this string a little bit more here. This idea that we can use optical spectroscopy to go after so many analytes and just emphasize what I think is one of the greatest strengths of optical spectroscopy, which is we can get a large number of target analytes from just one single probe or one signal technique. That means, for example, if we look at Raman, we can get one probe into a process, and we can use that one probe to identify and quantify a large number of potential targets that are in that process. And I've got just a couple here listed as examples.

What this means is we can really reduce our footprint into the chemical process, where we have a lot of hazards. It's a little bit difficult to get in there, and we can really start being a lot more efficient with how we go after information and how we pull stuff out of the process in terms of understanding. Now, some folks might look at this, and they might question whether this is truly the greatest strength. Yes, we don't have to have 20 probes here just to go after 20 analytes, but is this really all that great? When you think about a process where all of these analytes are present and all their fingerprints are going to be overlapping and your data is going to become complex, some people might look at the title of the slide and question whether this is truly a great strength in the realm of nuclear material processing, or if this is actually a weakness, since our data becomes similarly complex.

Well, Sam and I are going to show you a series of examples here coming up of applications that we've done in the past, and we're going to present an argument that this really doesn't need to be a weakness of optical spectroscopy if you take the right approach to data analysis. In fact, in the example applications we have coming up, you're going to see that we'll be addressing quite a few of the challenges that we anticipate in nuclear material processing. Many of these are actually unique to nuclear materials processing, so developing online monitoring tools to overcome them is essentially the specialty of our team. But just to give you an example of some of the challenges that we deal with, we have to deal with environments that damage our sensors in a very powerful way. So, think of highly corrosive or very high temperature systems are good examples of both of those.

We also have environments with high radiation that can cause darkening of our objects or windows or other materials that we have to compensate for and be ready to adjust for. We also tend to work with processes where the process conditions can complicate analysis. So, examples are very turbid processes or variable turbidity processes, systems where we have very sensitive matrix effects or confounded signals. And we are talking nuclear materials processing. So, one of the biggest challenges we have to face are that we have a lot of processes where frequent calibrations or probe maintenance, or think any access to that probe is just simply not realistic because it is in a hazard zone.

What do we do about these challenges? Our team actually goes after these challenges with two prongs of focus. We look at sensor hardening and design as one of those first prongs. So, this is really focusing on our engineering of probes, material science of probe, material choice, all of that to make sure that these probes can go into the harsh environments and survive for extended periods so think molten salts as an example. This is a big aspect of what we do, and that can overcome quite a few of these challenges that we're looking at.

But the other aspect of what we do, and this is really how we start overcoming some of those complexity and data, some of those impacts to data from things like radiation damage and so on. The other aspect of what we do is make sensors smart. Really what this means is that we build advanced algorithms that can take in the highly complex data we anticipate from a real nuclear materials process and translate that into information. And when I say information, think something like a real time readout of uranyl concentration, something that an operator can immediately understand and utilize in a decision-making process.

Now, before we get into the applications, I want to talk just a little bit about what this looks like in practice. And sensor hardening and design is probably a bit more straightforward, and you'll see some examples of that. But I do want to give you some background on this idea of making sensors smart, because, again, this is probably one of the key aspects of making sure that we can take optical spectroscopy or really a lot of sensors into a nuclear materials processing environment and get out useful, accurate and reliable information. So, it's really building that robust pathway to transform data into information.

And what we do to accomplish this is chemometric modeling. I'm going to go through some graphical examples of how this works so that we can talk about what chemometric modeling does when we work or apply it to our data. But essentially, we're talking about a form of machine learning or a form of chemical data science that lets us translate complex data. I'm going to start by going through a graphical example of what we would consider a very simplistic chemical system. What we're looking at here are the UV-Vis spectra, plutonium 4. So, this is a variable plutonium 4, as we vary the plutonium 4 concentration from 0 millimolar all the way up to 30 millimolar. And this is being done in 1 molar nitric acid.

Now, we can see that as we increase that plutonium 4 concentration, the absorbance of those bands increases. In fact, we get a really nice relationship here between the strength of the signal here and the concentration of plutonium. In this particular instance, we can actually pick our favorite wavelength and then plot the absorbance of that wavelength as a function of plutonium for concentration. And essentially what we've generated here is a single variant calibration curve, or a beer's law plot. And now forever in the future, if we run into plutonium 4 under these precise conditions, so within 0 to 30 millimolar in 1 molar nitric acid, we can use this calibration curve to quantify plutonium 4 present in solution.

Now, this is beautiful data. It's very simplistic, and it's very nice to work with. But unfortunately, in real nuclear materials processes, it's very rare that we see a system that is this clean and this easy to deal with. In fact, we tend to see data that's a little bit more complex. What we're looking at here is UV-Vis absorbance spectra of pretty much that same chemical system. What we would still consider a very simplistic chemical system that's got nothing except plutonium 4 and nitric acid in here. Except this time, we've kind of cut the deck a little bit differently. In this case, we're holding that plutonium 4 constant now at 50 millimolar, and we're varying our nitric acid from 0.5 molar all the way up to 10 molar.

And what we see here is a drastic change in that plutonium 4 fingerprint. Now, in this particular instance, it becomes very difficult to start applying that single variant tool we discussed on a previous slide here, because we have to start asking questions. We would have to ask, well, which wavelength do I want to use to quantify my plutonium? And if I'm choosing that wavelength, do I have to have a priori knowledge of nitric acid concentration? Am I supposed to assume that concentration? Am I supposed to titrate to get that concentration? All of these questions we're asking essentially translate to longer data processing. So, you're no longer talking about something that you can do very quickly. You can no longer do it in real time or near real time, and you're also talking about adding uncertainty to your measurements. So, especially if you're assuming a nitric acid concentration, you now can no longer have as great of the trust factor with your calculated plutonium for concentration. And that's certainly something we do not want.

So, instead of using that single variant calibration curve approach, what we're going to use is multivariate. We're going to use the entire wavelength range, or we're going to be using the entire fingerprint of plutonium 4. So, let's talk about what that looks like. We're actually going to zoom in on that primary response band of plutonium 4, and we'll blow it up over here on the side. And just to walk you through what happens because we change acid concentration, as we increase acid concentration, this primary band drops, scoots over, and then grows back in.

So, if we take this data and we build a chemometric model out of it, what that model is going to do is, it's going to pull out principal components, and those principal components are essentially going to rate how important signal response is at every single wavelength to quantifying our target analyte of interest. And so, that's a little bit of a mouthful. So, let's take a look graphically again about what this looks like. And what we're looking at here are the principal components from all [ph] the pulled out. In this case, our model said you really need four principal components in order to define all of the variability happening in this series of spectra.

And it shows us these principal components as a function of our loadings. Now, a loading essentially indicates how important response is in a particular wavelength. A loading of zero means not important, and a loading with magnitude means more important for quantification of plutonium 4. We're looking at these loadings as a function of wavelengths, and this is the same wavelength range as we see up here. And so, let's just give a quick example here. If we look at the wavelength range of 510 to 520 nanometers, we see this is pretty flat. We probably wouldn't really rely on this too much for quantifying plutonium or if we were making the decision.

And if we look at how our model is looking at that same region down here, it's giving it very low loading, very near to zero. So, our model agrees with us. This isn't too important for quantification. However, this region of the spectrum where we have a lot of plutonium for signal activity, we see that our model is working very, very hard to capture that down here. Now, what's a lot of fun is that if you really take a good look at these principal components that are model pulled out, and you go and read through some fun literature from the 1960s, what you see is that these fingerprints, these principal components, overlay very nicely with fingerprints of the different plutonium species. Now, this makes sense.

We know why this band shape change happens as we increase acid concentration. It's because we're changing the speciation of plutonium 4. We're going from the mono to the di, to the tetra, to the hexanenitrile species, and we see that our model is actually pulling that out. It is pulling out the chemistry of the speciation transition and using that to identify and quantify the plutonium for present. Now, what's even more fun from a chemist's perspective here in terms of the type of information we can pull out, is this little folder right here on this red band for the mononitride species [ph], right at about 470 nanometers.

That shoulder actually overlays very nicely with where you'd expect the fully aqueous [ph] species of plutonium 4 to be. So, right before that mononitride species comes in. And it's exciting that we see that at all, because our lowest concentration of nitric acid in this training set was 0.5 molar. And at that acid concentration, we had probably less than 20% plutonium 4 in the fully aqueous state within that system, and despite having only that tiny, tiny fraction of plutonium 4 in aqueous position and absolutely no signal for the fully aqueous plutonium 4 at every higher acid strength. Our model is still able to try to capture that, pull that out, and that's really powerful.

If we take this a step further, and we actually, say, let's use this model for regression now, these are the results we're looking at here. We're looking at a purity plot where we're comparing what we measured the concentration to be based on our optical spectra with the chemometric models applied to what we knew that plutonium 4 concentration to be. And I want to highlight that we're looking at a parity plot where we've got two dimensions of variability. We've got both the variability of plutonium 4 concentration so that impacts the signal strength of plutonium 4, or intensity. And we've got variability of nitric acid. So, we're really changing that fingerprint of plutonium 4 quite drastically across this range.

Now, what we're looking for on this parity plot is a one-to-one correlation between measured and known. And that's the black line here. And you can see that despite all of the variability, both concentration and matrix for plutonium 4, our data is lining up beautifully with that one-to-one correlation indicating high accuracy of measurement. Now, this is powerful. So, the next question is, what does this actually look like in practice? And so, this is really where Sam and I are going to start diving into a bunch of example applications where we go after a lot of different challenges that we expect within nuclear material processing schemes. So, that includes highly complex chemical compositions, extremely harsh environments, heavy variable processes, as well as demonstrations of real time process control. And that's both manual and automated process control.

And we'll start off with an example of manual process control supported by online monitoring. I'm going to go through a CoDCon separation example. CoDCon being the co-decontamination scheme where we take simulated dissolved [Unclear] nuclear, dissolved nuclear fuel and run it through a series of separations to produce an aqueous product that is a mixed stream of uranium and plutonium.

I'm going to be talking about some experiments we did several years ago on a bank of centrifugal contactors. We have out at PNNL in a shielded glove box. This system was used for several very exciting separation demonstrations, again a couple of years ago. But I do want to highlight this system has been utilized a lot more recently by NSP or Athena investments to do training of the next generation, as well as advance some S and T [ph] goals. But essentially what we did in this case is we wanted to make sure that we could control a separation process on a bank of centrifugal contactors in real time. And anytime you're talking about real time process control, your first thought should be online monitoring.

So, in this case, we outfitted our bank of contactors with a series of sensors on all of our inlets as well as all of our outlets. So, regardless of whatever's happening in the separation process, we could tell you everything that's going into the process and everything that's coming out of it. And for this particular demonstration, we were looking at simulated dissolved nuclear fuel. We did several runs, some of them a little bit more simplistic in terms of the feed and others as complex as really simulating dissolved nuclear fuel. That is to say, half the periodic table was in there. And so, we weren't actually trying to quantify absolutely everything in there. We had a set of target analytes that we wanted to monitor and quantify. Those were primarily our activates [ph].

And in order to get all of the activates we wanted, we actually had to utilize a little bit of sensor fusion. So, we had to get multiple optical sensors into a very small footprint in our sensor. And in this case, we were utilizing UV-Vis spectroscopy to go after plutonium 3, 4 and 6 as well as uranium 4. We were using NIR spectroscopy to go after neptunium 4, 5 and 6. And we were using Raman spectroscopy to go after uranyl and nitric acid. And of course, in some of our process streams for a more complex runs, we had a slew of other fission products or simulated fission products, many of which had their own fingerprints that interfered with what we're looking at here.

And so, in this case, we had sensors on all of our inlets, all of our outlets, three forms of optical spectroscopy. There was a lot of data coming out, a lot of data processing happening. Some of this data was very complex. But really just to show you how powerful online monitoring was here, I'm going to focus on just our aqueous product stream which is actually one of our cleaner looking streams. You can see a snippet of data here. This is just the UV-Vis absorbance data from one of our runs on just the aqueous product line.

So, keep in mind, there's also the NIR and the Raman data here. But you can see here, there's a lot of band overlap. There's a lot of stuff happening. I think this is beautiful as somebody who enjoys optical spectroscopy, but our process operator didn't find this too useful. What he wanted was the real time feed [ph] of concentrations in that stream. This is what he was looking at. This is a picture of the screen that we took while we were running. You can see the uranium 4 concentration in the background here. In the foreground, you can see a real time calculation of the U to Pu ratio. And behind this, there are a bunch of tabs for all of those other actinides in the aqueous product stream as well as all of our other product stream or all of our other inlets and outlets. We replotted this just so we could show you how valuable online monitoring was for process control in this instance. And what we're looking at here is the percent composition within that aqueous product stream as a function of runtime. And for this particular demonstration, we were trying to show that we could hold a particular composition. So, 70% uranium, and 30% plutonium, that would be the horizontal dashed blue and red lines, respectively.

Now, online monitoring results are plotted here. Solid blue line for uranium, solid red line for plutonium. And you can see that after a run started and hit equilibrium, we were outside of that 30-70 goal. Based on that, our operator made a process adjustment. That's the vertical black dashed line. In fact, the operator made several manual adjustments so turning a valve based on the online monitoring output until you can see out here at the end, he really nailed that 30-70 ratio and held it within plus or minus or less than 1% variability there. This is very powerful.

While this is really fun to look at out here, I will tell you that the operator's favorite part of this graph is actually this area in here. And that's really because he was empowered to have a lot of control here. This was an interesting run because we actually started the day here. So, probably our first hot day of the spring and our air-conditioning wasn't working in our building. We started the day here at about 18 degrees Celsius, and we ended the day out here at about 30 degrees Celsius with our biggest deltas happening right in this region here.

Now, separations are exothermic processes, so when you change the temperature that much, you're going to change how that separation progresses. The operator was actually able to see that and adjust for that in real time, as well as adjusting for pumps lubricating and the other real-life factors we have in any separation process. He was really allowed to do a lot to understand control and ultimately perfect this process. That's really exciting. The other exciting thing here are the circle, squares and triangles. Those are grab samples, things that we collect, send off to analytical laboratory, get results back.

First thing to note is they agree nicely with our online monitoring output, indicating good accuracy of our measurement. But the other fun thing to note is the time differential. Those grab samples took anywhere from a couple hours to a couple months to come back, whereas the online monitoring was coming out every 30 seconds. So, every 30 seconds, our operator knew where his U was at, where his Pu was at, and he could make choices based on that. So, this is a powerful demonstration, and I think it leads nicely into our next demonstrations here, which I'll actually hand off to Sam to continue talking about.

Samuel Bryan
Yes. Thank you, Amanda. And the transition here is I'm going to be talking about some of our past applications. Now I'm going to start with one of the applications or several applications that related to the Hanford waste. I don't think I need to tell the audience here that Hanford area, which is located here in Washington state, is the location of the production of plutonium during World War 2 and also continued into the cold war. And related to that, there is a lot of processing waste that went into buried underground tanks.

This is a picture right here at the bottom that shows the tank farm area. This is a series of tanks being under construction. And each one of these tanks is about a million gallons in capacity. And there's 177 of them in the Hanford side containing various levels of fill of reprocessing waste, nuclear fuel reprocessing waste or not reprocessing, processing waste. The application for us, or the challenge for us is this waste is being destined to be immobilized in some shape or form. And we want to go ahead and put some sensors in line through the process at different locations to go ahead and measure the concentrations of the constituents efficiently.

And also, the challenge is that this is a very chemically complex environment for us to measure. In some of the past work, we have some past demonstrations related to this. Back in the early 2000s, we had a task to measure using Raman spectroscopy, the oxy-ions in the waste in a salt retrieval campaign. This is designed to go ahead and measure the salt, the salt cake that was being retrieved from a source tank.

That was going to be mobilized and run through a pipe to the vitrification plant. We designed a sensor that could measure nine analytes, the oxy-ions here in a skid [ph] that was mounted out the tank farm. It was designed for that, and it could run up to 40 gallons per minute in flow rate and measure these. In the late 2000s, we had another application where we supported the pretreatment engineering platform or the PEP platform for the waste treatment plant, where we again had a Raman system where we could measure nine analytes from graph [Unclear] that were taken from the PEP plant and sent to our laboratory.

We could analyze the nine analytes. It was these eight up here that I've mentioned before, plus oxalate. And this was a fully QA/QC HASQARD compliant procedure that we developed with a Raman probe. We could measure these and have the analysis back to the PEP plant within 24 hours period. And so, this was really good. We support that plant for about a year under while they were running that design plan. In the early 2010s, we also supported a Pilot Scale called Continuous Sludge Leaching Program where we use a Raman probe that could measure the boehmite and gibbsite dissolved in the continuous sludge leaching project where we can measure aluminum being dissolved as aluminate and hydroxide in real time. And this was 24/7 application where we ran continuously for over 2-1/2 months in giving immediate feedback to the operators as they were doing the sledge leaching in this. Some of the applications here are summarized and the techniques that we use are summarized in some of the publications I show here on the right-hand side.

The next slide shows, I mentioned we use Raman spectroscopy. This slide really shows us speaks to the reason why we use Raman spectroscopy for analyzing tank waste. This is a diagram of the waste basis inventory of all the analytes or the major analytes that are contained within all those 177 tanks out in the Hanford area. This is listed by constituent composition as a function of metric tons of each of the analytes and all of the – if you sum up the major constituents, which are sodium salts of nitrate, hydroxide, nitrite, carbonate, aluminate, phosphate and sulfate, those six or seven constituents add up to equal 95 plus percent of all the solid components in all of the tank waste out in the Hanford area. If you exclude water, 95% of what is in the tanks are Raman active sodium salts. That's why we use Raman spectroscopy, because you can measure 95% of the constituents in one spectrum.

In fact, they chose the Raman spectrum of those components that I just mentioned on the previous slide; nitrate, carbonate, nitrite, oxalate, chromate, sulfate, phosphate, aluminate. All of these species are Raman active, very strong signals. And just to mention, the peak height or peak area on each of the curve is generally proportional to concentration. These are pretty much separated quite well. In fact, using the chemometric analysis multivariate technique that Amanda had talked about previously is how we go ahead and measure these in very complicated mixtures.

This was an actual waste demo where we took AP-105, a natural waste from tank farm, AP tank number 105. This is a Raman spectrum of AP-105 waste showing the big strong band right here for nitrate, the water manifold over here that includes the hydroxide manifold. And I compare that AP-105 actual waste with a simulant waste that we designed and made based on known composition of the AP-105 and also some of the single component standards that we used in our constructing our chemometric model. You can see the [Unclear] in the red spectrum here. You can see sodium nitrate, for example, a very strong band at the same location for the AP-105 nitrate band, and so on.

We build a chemometric model using some of these single component mixtures, binary mixtures, ternary and very complex mixtures, to build a complex printing set, to go ahead and build a model. We've taken this AP-105, and we put it in one of our flow cells or in a flow loop. This is the AP-105 waste here. It's straight AP-105 waste. It's not been processed in any way except to take the cesium [Unclear] by ion exchange. We can have it contact-handled in our open phase [Unclear]. We have a pump that we're pumping it through our flow cell. This is a cuvette flow cell. We have a Raman probe. This is a fiber optically coupled back to our spectrometer. We're able to shine light into our flow cell. Measure the AP-105. The spectra of the AP-105 waste is shown here as a function of sample number, which is essentially a time axis.

We have the wave number, so we can see the water manifold here, or the hydroxide manifold here. We see the nitrate band over here. So, we start this process where we have water initially in the cuvette flow loop. Then, we transition over to AP-105 waste and measure that. Now we can go ahead and then use our chemometric models and process this spectral data and turn that into concentration data based on the model that we employed.

This shows the concentration in the Y-axis versus time through the process. We start with water at the very beginning. Then, we transition to AP-105 waste about half an hour into the process. And the top plot here shows the concentration of the high concentration analytes showing nitrate, nitrite, hydroxide, aluminate and carbonate. The bottom plot shows, for convenience, the lower concentration as species; sulfate, phosphate, chromate, and oxalate. We can follow the concentration in real time for nine analytes simultaneously throughout this process. And this was actual waste, which has not been conditioned any special way before analysis.

The next slide shows – Amanda mentioned that some of these solutions, since they're actual waste samples, are going to be highly turbid. And in fact, the tank waste out in the area has a lot of solids, a lot of sludge, a lot of oxides that will interfere with an optical technique. We need to go ahead and really focus on how do we go ahead and get around the high turbidity, high solid fraction, solid solutions that we measure.

The picture on this left-hand side shows a series of solutions. This is our simulant waste here with 0% solids added. And then we add, in this case, is iron oxide. We have three weight percent solids, seven weight percent, all the way up to 10 weight percent solids, very turbid solutions, and would present a problem for light scattering and an optical technique like Raman. Down below, we have a simulant sludge. In fact, the sludge was designed by some of our colleagues at Savannah River National Laboratory. And again, starting with our simulant waste, with no added solids all the way up to 10 weight percent, you can see highly turbid solution.

The trick to measure in high turbid solution is design probes that can get around some of the light scattering problems. We have several techniques that we're investigating. The top picture shows an example of one of our attenuated total reflectance probes that we're designing. This is based on an internal reflection element. This is a light guide that we shine our laser light down reflects, it bounces down the light guide, and where the light bounces against the edge of the light guide, that interfaces with the solution on the other side of that boundary, an evanescent wave is produced. And that evanescent wave, there's some attenuation of that. We do measure some attenuation from the signal, and that goes off to our detector. We can then measure the Raman spectrum based on the sample that was in solution adjacent to this September [ph] reflection element.

We also have several elements or several probes that we're designing. They have close focus design. So, this is a laser light coming through our probe, and we have an optical window that we focus the beam, laser beam right at the interface between our probe window and the solution sample. Instead of being way out in the sample, where it has scattering from some of the solids in solution, we have it right against the edge. So, we have minimized the scattering from the particles in solution. Other types of probes are Baldwin [ph] probe, again, close focus to the very edge of the surface of that element.

These probes are commercial probes down below. In fact, this probe in the middle is designed by our small business partner, Spectra Solutions, and it was developed under a small business innovative research program in collaboration with them. Using that close focus probe that shows an example of some of our variable turbidity measurements, where we have from 0% added solids to 20% weight percent added solids. These series of spectra, the black line is 0% solids, where there's no solids in solution. All the way to the bottom spectrum here is 20 weight percent solids.

You can see that the signals are attenuated as we go for higher and higher vapors and solids. They're attenuated, but they do not go to zero. So, we're able to get information from the spectrum. Even at 20 weight percent solids, the bands I just want to point out, the band I want to focus on is this bar right here at 1050 wave numbers. That's the nitrate band. And if we through preprocessing of this data, we can then see that band at 1034 wave numbers. That's a nitrate band. It still maintains very nice linearity, even at 20 weight percent solids with added nitrate.

The next slide shows some of the variable weight percent solids data. This is again sodium nitrate at 0% weighted solids, 1% weighted solids, 5% and up to 10% weighted solids. And we're looking at variable concentration of nitrate in each of these solutions. We're seeing very nice well shaped bands, so we can measure accurately the nitrate and solution. The second column shows a preprocessing step that we sometimes use, which is taking your first derivative of this curve. And what that does is really eliminate the problem of any baseline noise. It really transitions that to essentially zero. We get really nice, beautiful spectra all the way from 0 to 10 weight percent solids in this application.

And the last slide shows the signal strength as a function of nitrate concentration. The x-axis here is nitrate concentration, and from zero all the way up to 10 weight percent, we have essentially the same sensitivity of scale again, because we can do the pre-processing step of first derivative. And also, we do some normalization using that hydroxide band to normalize the spectrum.

I just want to point out the slope of these lines are about four times two [Unclear] second for each one of these applications here, from zero to 10 weight percent solids, meaning the sensitivity of this measurement has not been degraded by increasing to solids. The combination of probe design and preprocessing steps really does a really good job.

The next application I want to tak about is pH measurement using Raman technique. And what I have shown here is a series of phosphoric acid speciation as a function of pH. On the left-hand side, this is phosphoric acid or triprotic form of phosphoric acid. As you increase the pH, you can remove a proton by titration, and it goes to the diprotic form. Remove another hydrogen by going to higher pH. You go to the monoprotic form and then go to the fully deprotonated form of phosphate in this case.

And so, as a function of pH, you have a lot of speciation of phosphate. Turns out each one of these species is Raman active and has a characteristic Raman band. And this shows a spectrum of that speciation as a function of titration. This is the wave number across the x-axis here versus the intensity. And we can see that the fully protonated form of phosphoric acid has a band here. As we deprotonate, we go the diprotic form here, the monoprotic form, and then the fully deprotonated tribasic form of phosphate, and just an overhead view of that same spectra as a function of pH.

Here, you can see quite visually, the phosphoric acid bands, the diprotic form, the monoprotic form and then the fully deprotonated form. And we can use this data as a training set. We know that spectra at each pH we know the concentration. We can form a chemometric model. And when we plot that measured pH from our chemometric Raman model and as a function of titration, we can overlay that. And I'm going to just point out we have several titration curves here at variable concentration of phosphoric acid.

I'm going to focus on this red curve here, which is one more phosphoric acid. As we titrate the Raman spectrum, the Raman model is predicting the concentration or measuring the concentration of the pH. And we compare that with the light red symbols, which is the theoretical calculation for the pH in that solution. We were spot on measuring with the theoretical pH for that solution with each one of these. We can do this not just at very high concentration, but also in very dilute concentrations of phosphoric acid. We spot on with the theoretical calculation.

We can use this pH measurement in a demonstration for automated pH control. Or in this case, I'm showing a large beaker that is really our feed container where we have a citric acid weak acid solvent, which is used in a TALSPEAK separation campaign. And it's a weak acid, just like phosphoric acid is a weak acid. We can use that as a pH indicator as well. And we've built chemometric models for that. So, we can measure pH based on the Raman spectrum of that.

And right here I'm pointing out the Raman probe in solution, and we have adjacent to that some electrochemical probes, pH probes that we can measure the pH in a secondary form. So, we have a secondary form for confirmation. We also have some acid based delivery tubes that we have in solution. So, we have this setup controlled by a PLC controller. We're monitoring pH, and we're going to be adjusting the pH, and we're going to allow the PLC controller to go ahead and automatically control the pH by adding either acid or base through acid-base delivery tools; ports, tubes to go ahead and maintain the pH at the set point.

The next slide shows the results of one of our experiments. The blue line here is the pH that's measured by our Raman probe. And our set point is a pH of 2.8. We have the control zone plus or -0.1 pH units. So, at 2.9 units or 2.7 pH units, that's outside the control zone. Our PLC controller will actuate a pump to go ahead and either if the pH is too high, it will open a valve and deliver acid to drive the pH lower. If the pH is too low, then the PLC controller will open up a different pump valve and pump in some base to go and increase the pH.

We start here within the control pH zone. We spike the solution with sodium hydroxide to push it outside the control zone on purpose. At this point, the PLC controller activates. And each one of these orange lines that I have indicated here is when the PLC controller actuated and injected some acid to drive the pH lower and lower and lower and lower until we get down within the control zone and the automatic PLC controller stops delivering acid. And then it certainly does get into the control zone and stays there through the experiment.

Let me go ahead and show a series of experiments where we again start with outside the control zone. The PLC controller pushes the pH by delivering acid to push it down to the set point. We add hydroxide to push it out of the control zone. PLC controller puts it back into the control zone. We add acid on purpose to put it out outside the control zone, basis delivered to go and bring it back into the control zone. We've done this multiple times, and we recover quite nicely.

I want to point out the Raman model is in the light blue lines that are shown here. That's the real time monitoring for the Raman model with the PLC control. The pink line is electrochemical pH measurement from our auxiliary measurement. And those follow exactly on top of just spot on our Raman model. So, our confirmation is that we're tracking pH properly, and we're also controlling the pH in an automated fashion.

In this automated pH control, we also performed a mass balance during the extraction. I mentioned that the citric acid feed that we're using is used in a TALSPEAK. TALSPEAK is a separation of lanthanides from actinides process. We have a citric acid feed, and we're monitoring the UV-Vis for the metal quantification in this particular example. In the feed, in this case, it's a simulant. We have neodymium in the feed. And we want to go ahead and run the feed through a set of centrifugal contactors shown in the diagram here. The squares with circles in them that represents the centrifugal contactors. We have a bank for that we use.

We have a feed that we ran through the entrance of the centrifugal contactor and the raffinate stream coming out the other side. We have phosphorus in that, a solvent that was run through to extract the neodymium to form a loaded organic phase again in the organic phase. And the rectangles that I have shown here in blue, those represent the locations on our centrifugal bank of contactors where we had UV. There is a Raman probes to measure real-time what went into the contactor in the feed, what came out in the raffinate, what went in the solvent, and what came out in the loaded organic phase.

And what I have shown down here are the spectra that were taken in real time of the UV-Vis for the feed location, raffinate solvent in and loaded organic. As we can see at the very beginning, we start with no neodymium in the feed. But at 35 minutes into the experiment, we switched over to a feed that contained neodymium. We see immediate concentration or the bands related to neodymium increase across the UV-Vis spectrum until we stop the neodymium feed at 90 minutes into the experiment.

And then that band dropped back down again and continued on, which is solvent. And we can see in the raffinate phase, the raffinate position, as soon as we put the feed, the neodymium into the feed, we had neodymium reporting out to the raffinate position and also down in the ordered organic, we could see the neodymium bands coming in from the organic phase, from the extraction of neodymium into the organic phase. The next slide shows the results of this experiment, where at the beginning of the experiment, up to about 35 minutes into the experiment, where we probably had no neodymium in the feed at all, we were reading zero concentration. This is the axis of concentration neodymium, measured by our model at the different locations. And we're measuring zero concentration for the aqueous feed, aqueous raffinate, organic solvent, and organic product.

Then, at 35 minutes into the experiment, when we added neodymium into the feed, we saw immediate increase in the concentration at that feed location. And within a few minutes of that, we saw the concentration of the neodymium in the aqueous raffinate increase, just like we saw the spectra increase in the last slide. We're interpreting that with chemometric models, and we're seeing the neodymium coming out in the raffinate slack wise in the organic product. Now, notice here that there's a delta in time from the time we observe the neodymium going into the feed in the inlet of the contactor. And there's about 5-to 10-minute lag before we see it coming out into the raffinate in the organic stream.

That's because there's some neodymium process. It takes a while for the neodymium to work its way through the centrifugal contactor before it comes out to either the raffinate or the organic product. We see that down here. This is the plot we wanted to demonstrate mass balance. We look at a difference between what went into the contactor and what came out of the contactor. This is the delta neodymium at concentration. What we're measuring here, or what we're plotting here, is a delta of the plot 1N [ph]. That's the feed plus solvent minus the organic product. The concentration of neodymium in the organic product plus what was in the raffinate.

And so, at the very beginning, when no neodymium was in the system at all, it's zero. When we start neodymium into the feed, we see a delta. I mean, there's an offset here. And that's because we have neodymium in process. So, what went in that we're measuring it going in, but we're not measuring it coming out yet. When we get to the point that we're in steady state out here in the middle of the process, then what we're measuring going in is equal what is coming out, and we have a mass balance of zero. When we stop putting neodymium into the feed, we again see this deflection and negative deflection this time because we don't have any going into the inlet, but we still see it coming out of the inlet. And then at the end, when everything is flushed out of the system, we get to mass balance again. We were able to show and demonstrate mass balance through this experiment.

I'm going to go ahead and transition now and talk about some of the applications and molten salt reactor programs. We support several programs and two of which are the ARSS Campaign. That's the Advanced Reactor Safeguard Security Campaign under Ben Cipiti. And the other campaign is the Advanced Reactor Technology MSR

Campaign under Patricia Paviet. I'll be talking about both these examples.

In one case, we're looking at the uranium and the fuel salt. And this is a schematic of one of the GEN IV type reactors where you have molten salt fuel that's circulating through the reactor. And the idea is to put a probe in to measure the concentration of uranium in the fuel salt. And also, we're concerned about off gases coming in from fission products. We want to design probes that can measure both the salt at temperature. So, we have high temperature sensors that we're designing and also such as that can work in the highly corrosive solution, the molten salt solutions and also in the gas system.

The first slide here is showing building of the library of chemometric library, the training set library that we need to go ahead and measure uranium, different oxidation states in some of these solutions. This shows a picture of the uranium 3 in one of our cuvettes. This is a molten salt system at 700 degrees Celsius that shows the photograph of the uranium 6 in solution. And we measured variable concentrations of uranium 4, 6 or 8 mixtures. We also measure variable uranium 4 in different eutectic fluoride melts.

This shows some of the variable absorbance measurements that we use for a trimming set. And this image here shows our small scale cuvette that we use to go ahead and measure the system that we use to measure the absorbance spectra and the Raman spectra of these salts. It shows a cutaway of our furnace that we have our cuvette within the cuvette holder shown here. We have the fiber optics, light guide coming in and light guide going out to the detector here. And so, we have a cuvette, a quartz cuvette in this case that's here. And so, we can use UV-Vis for transmission. We also have ports that we can put Raman probes for light scattering and Raman measurements in this as well.

Those measurements and others were used to then produce chemometric models. As shown here are several where the measured concentration from our model is on the Y-axis and the known concentration from gravimetric analysis is shown here on the X-axis. We have models that measure for uranium 3, uranium 4, and uranium 6. In all of these we have a fairly good root mean square error of prediction in the millimolar concentration range or less.

This slide shows one of the experiments that we performed to look at the uranium 4 to uranium 6 conversion where we start with using chloride eutectic salt. This shows the concentration of uranium that we measure from our chemometric model as a function of time. And just to start out, we start with a clean eutectic with no metal involved.

We add a uranium 4 salt in different increments in the first several hours and let it sit overnight. And then we add some more uranium 4 at the end of the experiment. And shown over on the left-hand side are the UV-Vis spectra as a result of those salt additions. So, we start with green salt. We have four additions of uranium 4.

We see immediately the uranium 4 signature mid UV-Vis range. And then also we see the conversion over to the uranium 6 band over in this region here in the spectrum. And immediately when we add uranium 4, we get the signature uranium 4. We can measure the concentration with our chemometric model. And we see the uranium 4 increase. But we also see the uranium 4 decrease over the course of time under the conditions of this experiment. And what is it transition to? It transitions actually to uranium 6. And using our uranium 6 model, we're able to calculate and measure the concentration of uranium 6 throughout the experiment. And it grows in just concurrently with uranium 4 dropping out.

When we sum up those two species, uranium 4 plus uranium 6, that gives us an inventory of the total uranium in the solution. And we get a really good mass balance throughout the experiment, especially in this middle region here. If you notice, there's a discrepancy, especially at the transition periods where we add uranium to the system. We don't have exactly quantitative analysis of uranium, total uranium in the system, a bit here, here and here. We know why that is. We were able to pull up the cuvette during the experiment. And this is the cuvette, the photograph of the cuvette, right after this fourth edition. So, right when we're seeing this discrepancy, we see this nice clear solution. But we also see a lot of solid in our cuvette. So, we're able to measure the uranium quantitatively in solution using our UV-Vis spectrometer in our UV-Vis models.

But we can only measure what's in solution. If it's in the solid state, we can't measure that. When we let it sit overnight here, at the end of 20 hours period, we pulled out the cuvette again, and at this point, all the uranium dissolved in solution. We see the nice yellow color of uranyl 6 that we recognize the uranyl ion in solution. And that's where we get quantitative, because all of that metal, all that uranium phase has dissolved, and we have it all in solution. Now we're quantitative and when we add two more additions here, we filled up, and we were not seeing quantitative analysis here is because we have again a precipitate of uranium in that sample.

And this work was summarized in the Industrial Engineering Chem Research Paper shown here on the left-hand side.

The next slide is application over in molten salt reactor off gas stream. And this work was supported under Patricia Paviet's campaign. And we're demonstrating in the off gas system, the measurement of the fission gas iodine being produced. And it can be evolved either as I2 or chloride salt. It can come out as ICL. We're also looking at sensors to measure hydrogen isotopes. We're starting with hydrogen and deuterium, and we're moving toward measurement of tritium. I just want to point out this is a collaboration with team members at ORNL as well, and Joanna McFarlane and her team at ORNL. And there's a nice publication here at the bottom that talks about some of our planning for this campaign and some of the work we've done in this campaign.

The first slide I want to talk about the measurement of I2 with one of our gas sensors. This is I2 gas. And just to set this up, this is a gas tube filled with iodine gas. This is a Raman probe that we put up adjacent to our gas cell. And this is using 532 light excitation mean. And we were intending to measure the Raman spectrum in which we did. But also, I'll just want to point out, this is a video we can see that we get a really nice fluorescent spectrum, fluorescence being generated, and it's pulsating actually, which is pretty interesting. We saw that, we said, oh, this is really, really great. What we intended to do is measure the Raman measurement of this I2. But what we got in addition to the Raman measurement is also this very sensitive fluorescence band coming out.

And what that fluorescence is due to, this is a spectrum from the literature of iodine in the gas phase of the UV-Vis spectrum of it, showing a nice vibronic progression. A lot of vibronic bands on top of this absorption band, and we're illuminating at 532 nanometers excitation right on top of a lot of vibronic progressions. And so, we're shining light, getting into an excited vibronic state, and we get light emitting and nice fluorescence bands coming out into the visible spectrum. This is our fluorescent spectrum. They also have a beautiful vibronic progression. They have multiple from vibronic progression one all the way up to. We measure them all the way up to 20, 25 vibronic progressions in any sort of fluorescent spectra, which is really pretty, but it's also very useful.

The next slide shows a series of variable pressure measurements. This is pressure as a function of temperature of measurement. This is the fluorescent spectrum as a function of both temperature and pressure. The pressure is shown here. We're measuring this with our gas manifold line. We have a Raman probe with our gas measurement cell. We have a valve system where we can measure iodine in the gas phase. We can measure that with a Baratron probe or Baratron gauge. The picture shown on the left-hand side is very busy. It's very hard to see. So, it's easy to see with the diagram here.

We have our iodine capsule here, our metering valve. We have a Raman probe and our gas manifold measurement cell Baratron gauge. And this is on a high vacuum line. We can measure easily the pressure as a function of temperature throughout this. And we have beautiful fluorescent spectra at variable temperature and pressure. We can use that data to then – blown up version of the data on the last slide. This is the spectrum on the last slide. And this is a blow up and a further blow up of that. But we have really nice strong fluorescence, weak fluorescence alternating for pulsating bands from the vibronic progressions.

When we use that, we can measure with our probe the concentration of I2 in the gas phase. We compared to the known pressure. We get nice slop of the one parity plot with both 532 nanometer excitation. We've also used red laser system for 671 nanometer excitation as well. Get really nice measurements with that. And this was summarized in the journal article Environmental Science Technology that was published just a couple of years ago.

The next application is measuring for ICL gas. In this case, ICL is actually infrared active, so we use a Fourier IR technique using an FTIR system. We measure the ICL bands as a function of pressure. We measured this not just at a function of pressure but at variable temperatures from 25 up to 75 degrees in the gas phase. And we're measuring pressures up to about 10 torr. And this plot here shows the principal component analysis of this data that I'm showing over here. On the left-hand side, the principal component in analysis of that shows that essentially two PCs are needed to go ahead and actually define all the characters in both the variable temperature and variable pressure that we see in the ICL spectra.

What PC3 and PC4 are shown here only to show essentially noise, and they can be excluded. Any PC is higher than PC2 could be excluded from forming a regression model. We use these PCs to form regression models in multivariate method. We have either partially squares method shown in the top left plot. The top right plot shows a principal component regression method. And both these have very nice, very tight error bars. You can see 95% confidence interval being plotted here. They're very tight on both of these. We can also use, as Amanda mentioned, the Beers law or univariate method. Some of my colleagues say, this is such a beautiful data, why not just use a single variate analysis, just peak height, for example, or peak area under the curve?

Well, we can do that and they form really nice models. In this case, the univariate methods will, while they work very nicely, this is the peak height versus a conscentration curve, and this uses the peak area for concentration. You can tell that the models are not quite as accurate, and they have a lot larger error bands than the multivariate method. Again, this shows that multivariate method works very nicely for this kind of data. And this work was summarized in the Journal of Physical Chemistry and published a couple of years ago.

The last application I want to talk about is looking at hydrogen isotopes. Again, we use Raman technique for this. And this is Heather Felmy, actually in the laboratory using a variable series of Raman spectrometers with variable wavelength excitation. We have Raman systems with blue, green and red excitation sources. The reason we use multiple wavelengths of light is to look for the technique that gives us the most sensitivity for the application of use.

In this case, 405 nanometer excitation gives a lot better sensitivity for deuterium and hydrogen measurement. This is the deuterium band here, about 3000 wave numbers, hydrogen band around 4000 wave numbers, very large separation between those two signals. Very nice, easy way to measure this using the Raman technique. As you go down to 532 or 671 nanometer excitation, you can tell that the scale is less sensitive as we go to longer wavelengths excitation. You can also see the ratio between the deuterium and hydrogen isotopes are much different as well. In this case, we use 405 nanometer excitation.

The next slide shows collection of some of the variable pressure measurements for deuterium. Again, doing the first derivative does a really good job at eliminating that baseline noise. And you see the baseline noise eliminated here. We use this data and others to go ahead and generate models for both deuterium. This is the measured deuterium pressure with our sensor versus the known deuterium. Same with hydrogen. We can use these models now to then predict concentrations in a variable deuterium hydrogen experiment. This shows an experiment where we start with our manifold line with two gases separated in two different chambers; hydrogen in one chamber, deuterium in another chamber. And we have our probe located at this chamber measuring the deuterium concentration in real time.

And then we open this valve. When we open that valve in the middle, the hydrogen deuterium starts mixing, and we see a decrease in the deuterium signal with time. Because we're measuring in this chamber, the deuterium escaped over the other chamber, and we see an increase in the hydrogen because hydrogen from the original chamber is now flowing back into this chamber. We see the deuterium over time. We see the hydrogen over time. This is the spectra as a function of time. We can then use our chemometric models to then predict the concentration as a function of time. And so, the composition is shown here. Deuterium decreases, the hydrogen increases over 25 minutes experiment time.

At the end of the experiment, the dotted lines here are the measured values using our mass spec, which was also associated with the gas manifold line. We can measure the concentration by mass spec, and we measure exactly what we see with the mass spec. This work was just recently in this last month appeared in analytical chemistry with the reference right here. At this point, I'm going to go ahead and transfer back over to Amanda to give some concluding and summary remarks.

Amanda Lines
All right, thanks, Sam. This slide right here is one of our final wrap-up slides, and we're talking about building bridges between fundamental and applied. But really what we're talking about here is a nod to collaboration. All of the applications that we've shown here today are either the direct result of or directly benefited from collaborations with either universities or industry. Where universities really help us narrow in and expand our understanding of fundamentals and industries really help us understand where the needs are, where the application space is, and where we can be impactful also.

We just want to give a nod and say that collaborations are extremely important to us to really advance our technologies and probably to the nuclear fuel cycle as a whole, and advanced reactors and nuclear energy in the future. And with that nod to collaborations, we'll go ahead and hit a couple of key takeaways here, which is that real time process monitoring has a diverse and wide range of applications within the future of nuclear energy. And in particular, if we're looking at optical spectroscopy applications for that chemical composition analysis, there's a lot of beneficial needs applications out in the future of nuclear energy. And in particular, if we combine optical spectroscopy both with advanced engineering of probes as well as advanced data analysis, we can really take these tools into some complex and some harsh environments.

And overall, online monitoring is the tool that we need to ensure that nuclear energy can operate better, faster, safer and more cost effectively in the future. And with that, we'll go ahead and thank all of our team members, our funding, and of course, everyone here for your time and attention, and we'll pass it back to Patricia for controlling any questions.

Berta
Thank you, Amanda. Thank you, Sam. Before we get to the Q&A portion, we just want to take a quick look at the upcoming webinar presentation. In August, we have a presentation scheduled on international molten salt research in support of MSR development. It'll be a panel session with several presenters listed there, and we look forward to that. In September and October, we have plans for overview and uptake of sodium fast reactor activities within the GEN IV international forum. In October, an overview and update of the gas cooled fast reactor activities within the GEN IV international forum.

There are several questions that have come in. I think the one that I want to start with is represented by one of the comments, and that is the love of the real-life applications. And I agree. I think that's the most exciting portion of this, is that you've reached into something that's very meaningful and directly applicable to people within the nuclear industry, and I can't echo enough that that's exciting to see. With that, I'm going to let me raise you up so you guys can see the questions as well, and then we'll just work through the list. There're several here already.

Some of these, I think, came in very early during the presentation, and as it moved along, you already addressed them. But the first one was, have you explored optical spectroscopy techniques for monitoring oxidation states of uranium and uranium fluorides?

Amanda Lines
I'll jump in there. And Sam's here and he can add in as well. So, we've used optical spectroscopy to go after oxidation state speciation for a lot of actinides, lanthanides, other fission products or corrosion products of interest. In terms of uranyl fluorides, I guess, we haven't played too much with the fluorides.

Samuel Bryan
We haven't. Although there's certainly applications and published reports in the literature that there's no trick. I mean, the trick is setting up your solution chemistry to handle fluorides. But they have been measured variable oxidation states and measurement of UV-Vis, in fluoride salts. I'll just direct you to the research out there, just the published research. There is evidence of that. We know it can be done. And we have not in our group gone into the fluorides just yet.

Amanda Lines
I do think we have a publication we got out in the last year or so, lead author Heather Felmy, where we actually looked at uranyl nitrate

in a system where we introduced HF. And we followed the fingerprint change in Raman spectroscopy with that particular gas [ph].

Samuel Bryan
Well, that was an ecosystem. I thought this was a molten salt application. Okay, so if you're talking about molten salt, it's done in a lot of that. You can find that literature. We've not done molten salt fluoride, but we've done aqueous solution with fluoride. Yes, that's correct.

Amanda Lines
Yeah. And that's just an example of how you can go after that type of information.

Berta
Thank you. And then the next is an observation that reads online in subloop doesn't give main loop info. You still need to back calculate what happens since the loop left the main loop. Even water reactors have to back calculate what the primary loop result would be as sampling even online requires decay of high rad before the sensors in most cases, especially optical fiber damage from high radiation levels for MSRs, where there's really no question. But do you have any thoughts on that?

Amanda Lines
Yeah, again, I'll jump in. Sam, please add. That comment is spot on. Any sensor is going to be limited to providing information based on where you've put it in your process. Now keep in mind, we do a wide range of applications from where we're talking about something on, let's say, a salt loop all the way up to something on a main line for waste processing of legacy wastes, right?

That's why we kind of interchangeably use terms like inline monitoring or online monitoring or variants there. Much of those have sub-context that indicates whether you're talking about a direct line measurement, a slipstream measurement, or if you're looking at a batch process, you are directly in that batch in some context. And so, all of those applications, we're going to be seeing what we can see from the sensor location. And of course, if you're in a slipstream or you're not on a main line, you are right. You have to back calculate what's happening in that main system. All of that to say that any information you can get into a process is going to be extremely valuable, especially if direct sampling from that process is going to be extremely costly, extremely difficult because of the hazard region, or even questionable whether or not that's going to be truly representative of what's happening in the entire loop or batch based on where you're sampling from, so fair point.

And calculation of what's going on in the main batch is something that has to be considered in, again, any sensor application. You also brought up the challenge of radiation damage. So, that was one of the challenges we highlighted early in our slides is something that we have to work around. That's something we're very familiar with. We've done experiments before, demonstrations before, where we actually intentionally damaged some of our optical windows via radiation. And we demonstrated how we can use advanced modeling to overcome that challenge. Now, really, when you radiation darken [ph] any of your windows or your optics, what you start seeing is a decay in your signal intensity as an example. There're some other effects as well.

What we can do is build in models that can handle that loss of signal intensity, because really what you're seeing is an increase in your signal to noise. And as long as you have your modeling built for that, you can start understanding, anticipating and mitigating for that impact. And really what it comes down to then is understanding when you need to get in and replace those components, when you need to get in and otherwise maintain them. And really that's determined by operator needs when they're going to set that cutoff threshold for uncertainty or error in their measurement.

Samuel Bryan
I'll add to that. One of the applications that I mentioned at the very beginning of when I started talking was that pre-treatment engineering platform that we supported, even though we could measure online, it was more valuable for our customer at that moment to have a fully QA/QC dashboard compliant procedure, which required matrix spikes added and blanks, etcetera, things that are very difficult to do online, we could do those offline. And we had our Raman measurement that could take a sample with simply no pre-treatment of the sample except for matrix spike added. We were able to measure that and get an analysis back within 24-hour period, which was much faster than any commercial laboratory. You'd have to send it off to the laboratory and get a result back. So, that supported them in a way, even though we couldn’t have done it online and had an immediate real time, 24 hours return time was adequate for them. And that's something that is even considerable for [Unclear] software. We have something that could be, again, applied that would be a sample that we've taken and with immediate response back from the laboratory.

Berta
Thank you. Another observation. Uranium solids and chloride salt is really bad.

Amanda Lines
Yes. I'll be honest, when we were running this experiment, we didn't anticipate that those solids would precipitate that way. That was actually a little bit of a surprising chemistry experience for us. And that's summarized really nicely in that journal article Sam highlighted there. First author is Shirmir Branch. But ultimately in that particular system, we were trying to understand what happens in a process where you don't have that direct and immediate redox control via either electrochemical means or chemical means, because we're really trying to see what goes on in that salt, if it's left to its own devices and you have potential interference or contaminants in there. It was a really useful exploration of the things that we need to be cognizant of and mitigate for when we're doing our chemical control of these molten salts for molten salt reactors.

Berta
Thank you. I am kind of sticking with that same. When ICL is monitored as gas, there would be a decomposition of the molecule. Is decomposition of ICL taken into consideration?

Samuel Bryan
Oh, yes, it was in fact, and I didn't point it out, sometimes I do. On the slides that I presented, you can actually see some hydrolysis products, HCL. There's some fine structure down very low wave number region, around 100 wave numbers. And below you can see the fine lines from the HCL. And so yes, we saw the hydrolysis product from ICL, as I mentioned, in the HCL. Yes, we can see the decomposition product there. I'm not sure if the questioner was asking of other products, but other products, for example, if you have other halide mixtures, certainly those would be Raman active and/or infrared active.

Berta
Thank you. Can you please expand on the internal reflection element and how it works?

Samuel Bryan
The internal reflection probe?

Berta
Yes.

Samuel Bryan
That's an attenuated total reflectance technique. And there's a lot of papers in the literature on the ATR element. In fact, we have a manuscript that is being submitted. In fact, it's under review, so it's

going to be published in the next – we anticipate within the next several months. But it describes the attenuated total reflectance. If you have a waveguide and you shine light through the waveguide at the interface between the waveguide and the medium that's adjacent to that, if there's a difference in refractive [Unclear] depending on the angle of incidence of reflection, you get an internally reflected light. At that interface where the reflected light is interacting between those two media, you get an evanescent wave being produced.

The solution, depending on the chromophore solution, it can interact with that evanescent wave, either absorb some of that light, or maybe it doesn't absorb, depending on the chromophore. And so, you're measuring the light that is – it's like an absorbance technique. It is an absorbance technique because some of that electromagnetic radiation is being absorbed by your sample. And what you're measuring is a difference in energy of the resultant wave that gets to your detector. So, of all the light that is reflected down the element, you're looking at a blank without an analyte present, and you're looking at a sample with analyte present, and you're looking at a difference of the electromagnetic, magnetic radiation that gets you detector. And it's the ratio of those two beams that gives you that transmittance of light, then you can go ahead and do the calculation to form the absorbance.

But if you're looking at what fraction of that light is being absorbed by your sample, and it's through the evanescent wave penetrating into the solution. And it summarizes better than I'm explaining it in journal articles. I can send. If somebody wants to send an email to me, I can go and let them to some literature on that.

Berta
Great. Thank you. Excellent collection of very relevant data. Have you tried applying AI to learn from this data for classification and prediction?

Amanda Lines
We'll say that the chemometric modeling that we do is a form of machine learning, machine learning being an extremely broad term that also does in some ways, include AI in there. Generally speaking, most of the modeling we approach in the chemical data science modeling realm is chemometric modeling. And we'll call that a little bit more old school in terms of how we approach data analysis. And there are reasons why we like that. We are in the nuclear field, where if we're looking at field or real-life applications, we've got a huge regulatory burden on us. There's going to be a lot of desire for, we'll say, metadata, things that quantify our uncertainty. Q residuals,

student’s t-squared residuals, all of that stuff that can tell us what our trust factor is for a given measurement, which is why we tend to utilize those older models as older algorithms, because they really have a lot of metadata that can come with them and a lot of historical trust with the model results and performance.

Now, we are secretly, not secretly, very excited about the potential to work in AI and how that can give us more flexibility and agility in some of these complex and harsh systems. But it's something we're moving into, we'll say carefully, because, again, we need to make sure that we're using algorithms that can give us that metadata, that can tell us our trust factor and that themselves are very well proven and justified out there in the literature or in practice so that folks can feel confident in the values that our assistants are giving them.

Berta
Thank you. As optical properties of fluids, molten salts, for example, change with temperature, how do you account for the temperature during the calibration?

Amanda Lines
That's a really – oh, Sam.

Samuel Bryan
Okay, I'll let you go ahead. I'll have a follow up.

Amanda Lines
Temperature impacts are a really good question. Molten salts are really good examples of an area where you're going to have larger temperature gradients. But you do have temperature gradients in a lot of other processes as well. There are multiple impacts from temperature variations that can impact our speciation. It can impact our optical fingerprint. It could even impact, as you say, maybe some of our optics performance and all of that. So, all of that is signal variation that we have to keep in mind. And when we build our chemometric models, essentially, we have to build in robustness to that variability. So, we have to, in our training sets, capture what we think those fingerprint changes, those sensing changes are going to be so that when we have our quantification tools in place, they're ready to answer that. And, Sam, I'm sure you have something to add.

Samuel Bryan
I'm glad you went first because I'll just go very specific. Now, in the example of the ICL that I showed, sometimes I don't even show this slide. But I showed it today where I showed four principal components that were pulled out of the variable ICL data. And I

mentioned that we can analyze this data with essentially two principal components. The first principal component looks almost identical to the spectrum of ICL at one temperature. The second principal component looks broader. And so, it turns out the first principal component there is really talking about the variability in concentration. The second principal component is looking at the variability in temperature. Amanda was exactly right to go ahead and have a robust sensor that uses, that can predict under variable conditions of temperature and the concentration range you're interested in, you need to have a training set that has both the variability in temperature and concentration for the conditions that you would expect that sensor to see.

If you train it only on one temperature, then your system is actually operating on variable temperature, on a different temperature, and variable temperature especially then, that's not going to be as robust as a model that was built using the variability of concentration and temperature that you have in your actual system. You need to be prepared for that and just incorporate that into your model so the model can then, through the multivariate type of analysis that we use, then can adjust for that.

Berta
Thank you. I think, as we've talked a little bit following your presentation, some of these thoughts may have already been addressed. But do you have any additional comments on what are some common strategies or technologies used to mitigate the challenges and limitations faced in optical spectroscopy, such as resolution, limitations, signal noise ratio issues and calibration errors?

Amanda Lines
I'll jump in first and let Sam add in, and I'll say that this is a real life sensor, and we're talking about extremely challenging applications. There are going to be a lot of hurdles that we have to overcome to not only get a sensor into our chemical process, but then have it survive an extended period of time and continue to provide us reliable and trustworthy and accurate data. You touched on some of those challenges, calibration being one. Ultimately, for all of our applications, we have to take a very in-depth assessment of what the challenges are for that particular application, what the lifetime is needed for that sensor, and what type of frequency we would actually be allowed for getting at, maintaining, adjusting or so on our sensor process or our models.

Ultimately, it's a little bespoke again to every application and we take into account. But I'll use calibration as one example to kind of give you some insight into some of the thinking and processing that goes on with that. So typically, let's say, we get a new instrument. What we do is, we check, we verify our calibrations. What we like to do is verify that instrument against a set calibration, set of really well characterized standards. We kind of get a fingerprint in time of what's going on with that instrument. Then, we'll train our systems. We'll make sure our probes are behaving well. We'll get the probe out into a system, and then forever through the life of that, what we're doing is, we're periodically checking how that system is performing against standards. Now, whether that's a standard you measure on your probe out in the hazard zone, that's questionable, or if that's a standard you're measuring in a secondary standard so closer to your instrument, outside of a hazard zone, that your operator can actually access. There're different games you can play with checking your instrument performance and calibration via those means.

There's also frequent check-ins or maintenance of our models. So, you can't build a model in 2020 and then make sure or feel very confident that it's still doing exactly the same thing in your process in 2024. What you have to do is check-in periodically and say, oh, man, are my pipes starting to corrode? Am I starting to see some iron in this that I need to know account for and update my model for? Has my instrument been hit a couple of times since it's out in the field? And sometimes people are clumsy and like to kick instruments. Did that impact our calibration of the instrument? Do we need to update the model, the maintenance for that? There's a lot that you have to do, you have to take care of in these systems, just like any sensor you'd have out in the field.

In terms of resolution, so that's kind of something that's set with each instrument. And again, it's something that we specialize for each application. What resolution is truly needed to give us the analytes that we're after? Hopefully that hits your question. I know that that's a very broad answer.

Berta
Sam, did you have anything that you were going to add to that? You just want to move to the next one or let me know?

Amanda Lines
Oh, I think we're ready for the next one Berta.

Berta
Okay, great. This comes in from Ivan [ph] with CMN [ph] in Spain. He's interested in knowing whether Raman's measurements of real solutions with high concentrations of radionuclides, for example, PUREX raffinate, you anticipate high fluorescence from the solution.

That could affect the accuracy of Raman analysis due to overlapping signals.

Excuse me, overlapping signals. Do you have experience on that?

Amanda Lines
Yeah, that's a fun one. We've actually looked at both simulated raffinate streams from a PUREX process as well as Sam you looked at real raffinate streams.

Samuel Bryan
Yes, we did. And this is where – I mentioned, when I talked about some of the deuterium hydrogen measurements where we look at, I mentioned we purposely look at various excitation wavelengths for our Raman technique. And the reason we do that is you can get different sensitivities based on excitation wavelength. They can also dial in if something is fluorescing. You want to go as red as possible, so you're not illuminating up into that electronic transition that you start getting fluorescence out of. You go more and more red, you tend to get less fluorescence. You tend to also get less and less sensitivity in some of your measurements. So, it's a balancing act. You want to go blue enough to get more sensitivity, but you want to go more red, so you reduce that fluorescence. We choose them judiciously to go ahead and minimize the effects of fluorescence but also getting that high enough sensitivity that we need. And in fact, for the actual raffinate that we did measure, Raman was very useful in that. And we used 671 nanometer excitation for that. And that was an article in Journal of Radioanalytical and Nuclear Chemistry. And in fact, if the questioner wants to send me an email, I'd be happy to go ahead and supply him with a couple of references of where we measured some actual pure raffinate samples.

Berta
Thank you. Another observation, we need a way to monitor for loss of U or Pu in MSRs.

Amanda Lines
I think that molten salt example that Sam went through, it provided a really good example of looking at uranium in molten salts. And that one is a lot of fun because we were following uranium in multiple oxidation states. So, we could see it in multiple oxidation states. But directly to your point, monitoring for loss, I mean, Sam directly showed in that example that we could see, we'll call it, 'loss of uranium.' Really what that was our uranium was not fully dissolved, right? We had some precipitants in there.

That's a really good example, showing that we can see a lack of dissolved uranium in your system, otherwise, indicating that some of your uranium is not where it’s supposed to be. Maybe, it's precipitated, who knows what. So, optical spectroscopy is a powerful tool for that, for sure. Regarding plutonium, we're actually just starting to dive into some plutonium work now. One of our team members, Shirmir Branch, is really leading that work. And that's under Ben Cipiti’s Advanced Reactor Safeguards and Security Campaign, and she's seen some really exciting stuff. And hopefully we'll be able to pull out a manuscript of that relatively soon and get that out in literature for folks to use.

Berta
Super. Thank you. It looks like there is another temperature can affect the results. What's the importance of temperature on those models? Do you have more thoughts on that?

Samuel Bryan
Well, I think we already hit that a little bit. But, yeah, temperature is very important. I'll just say, in general, what I didn't say before. You get band broadening generally at higher temperature. If you're looking at Raman spectroscopy, for example, you're looking at a vibronic transition. And vibrational transitions are affected by temperature. As the molecules heat up, the bonds are essentially lengthening due to temperature effects. So that affects that vibrational transition. You need to go ahead and build that variability, temperature variability, into your modeling just to capture that bond broadening or bond lengthening effect upon increasing temperature. Similarly, the electronic transitions, less so, that are also in UV-Vis, for example, electronic transitions are also affected by temperature. And so, we need to go ahead and fill that in, too.

Berta
Thank you. We've worked through most of the questions. There's one remaining observation. We need to replace the moderator, hydroxide purification for MSRs. Hydroxide being a moderator, bad for fast reactor MSRE almost had a re-criticality to having moderator on that purification system. Again, I'm not sure there's a question in there, but is there anything in there that strikes you as discussion points?

Samuel Bryan
I'll just go and just say that's outside of my area of expertise about moderators and to even offer an opinion on that. Amanda.

Amanda Lines

No, I think that that's probably a great observation, but I think that a comment would be better from a reactor or nuclear engineer.

Berta
Thank you. I think we've worked through all of the comments and questions through the list we've just passed. Well, we're into 100 minutes, so that is so fantastic. I think you can tell from the level of questions, the interest in your work, and the appreciation for your expertise, and I echo that. So, Patricia, if you have any last minute thoughts, I think we're ready to conclude and thank our presenters one more time.

Patricia Paviet
Yes Berta. We were a bit late, but it was really worth it. I would like to thank you both, Amanda and Sam, for taking the time first to prepare the presentation and to present excellent webinar. I'm really happy that we were able to capture your knowledge today. And this is being recorded, so people will be able to listen again to this webinar. Thank you again, Sam, and thank you again, Amanda. And as always, thank you very much, Berta, for moderating this webinar.

Berta
You're very welcome.

Samuel Bryan
You're very welcome, Patricia. And thank you, Berta, for moderating well and keeping us on track. Thank you very much.

Amanda Lines
Indeed. Yes, thank you.

Berta
You're very welcome. All right, that will conclude where we're at today. Thank you. Bye bye.

Patricia Paviet
Bye bye, everyone.

Samuel Bryan
Bye bye.

Amanda Lines
Thanks.

END