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Cost Effective Process Monitoring using UV-VIS-NIR Spectroscopy

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Abstract. UV-VIS-NIR Spectroscopy is a simple and inexpensive measurement technology which has been proposed for process monitoring applications at reprocessing plants. The purpose of this work was to examine if spectroscopy could replace more costly analytical measurements to reduce the safeguards burden to the operator or inspector. Recognizing that the higher measurement uncertainty of spectroscopy makes it unsuited for the accountability tanks, the approach instead was to focus on replacing mass spectrometry for random samples that are taken in a plant. The Interim Inventory Verification and Short Inventory Verification (IIV/SIV) at the Rokkasho Reprocessing Plant utilize random sampling of internal process vessels and laboratory measurement using Isotope Dilution Mass Spectrometry (IDMS) to account for plutonium on a timely basis. These measurements are time-consuming, and the low uncertainty may not always be required. For this work, modeling was used to examine if spectroscopy could be used without adversely affecting the safeguards of the plant. The Separation and Safeguards Performance Model (SSPM), developed at Sandia National Laboratories, was utilized to examine the replacement of IDMS measurements with spectroscopy. Modeling results showed that complete replacement of IDMS with spectroscopy lowered the detection probability for diversion by an unacceptable amount. However, partial replacement (only for samples from vessels with low plutonium content) did not adversely affect the detection probability. This partial replacement covers roughly half of the twenty or so sampling points used for the IIV/SIV. A cost-benefit analysis was completed to determine the cost savings that this approach can provide based on lower equipment costs, maintenance, and reduction of analysts' time. This work envisions working with the existing sampling system and performing the spectroscopic measurements in the analytical laboratory, but future work could examine incorporating spectroscopy as a true on-line monitor that does not require sampling.

1. Introduction

Materials accountancy measurements at existing nuclear fuel reprocessing plants can lead to high costs for the regulator due to the time required for sampling and analytical measurements. Process monitoring measurements have been proposed as a way to augment safeguards while using less expensive plant measurements such as level measurements, flowmeters, or on-line stream monitors. The goal of this work was to examine how process monitoring measurements could save costs while still maintaining existing safeguards performance metrics in reprocessing plants. In particular, spectroscopy combined with bulk process monitoring data was examined for reducing the amount of sampling and mass spectrometry measurements required.

2. Raman and UV-Vis-NIR Spectroscopy

Various configurations of spectroscopy can be applicable to reprocessing solutions depending on the element to be measured. Raman spectroscopy can be used to measure uranium concentrations in solution. Raman spectroscopy directs a laser onto a liquid sample, and inelastic scattering of the molecules results in an energy shift of the laser photons—this shift is measured with a spectrophotometer to determine concentration. Vis-NIR (Visible-Near Infrared) spectroscopy can be used to measure plutonium concentrations in solution. Vis-NIR directs a light source onto a sample, and the collected spectra from a spectrophotometer indicates where light is absorbed by specific species. Comparison with a blank sample is used to calculate concentrations.

Spectroscopy provides concentration data at higher uncertainties than destructive analysis (DA), but the advantages are the simplicity of the measurement, low cost, and quick measurement times (on the order of seconds). Fiber optic probes are used both to deliver the light source to the sample and collect the spectra. This configuration could be used either in a laboratory or as an on-line capability with fiber optic probes entering the hot cell while keeping the instrumentation and electronics outside.

Past work at the Pacific Northwest National Laboratory [1,2,3] in the United States has provided extensive data on the use of spectroscopy for reprocessing solutions. Raman spectral measurements of uranium in nitric acid solution have determined the uranium concentration with a 0.82% relative standard deviation. Vis-NIR spectral measurements of plutonium in mixed solutions have determined the plutonium concentration with 1.7% relative standard deviation. The plutonium measurement was determined with a non-optimal experimental setup. A better-designed light source and spectrophotometer will lead to less noise and can likely determine plutonium concentrations with 1% measurement error.

3. Reprocessing Plant Monitoring Points

Spectroscopic measurements are designed for use with dissolved reprocessing solutions, so this work was focused only on the material balance area (MBA) that corresponds to the separations portion of the plant, from the input accountability tank to the output uranium and plutonium nitrate product tanks. In this paper, this area is referred to as MBA 2. The front end of the plant and the product and waste processing MBAs include solids, so spectroscopic monitoring is not appropriate.

The Rokkasho Reprocessing Plant (RRP) was used loosely as the basis for this work since the design is more recent, and since more information on the flow sheet was available [4]. However, detailed design information was not available and was inferred where needed. Safeguards at the RRP are based around a yearly Physical Inventory Verification (PIV) and an Interim Inventory Verification (IIV). The PIV is designed to drain material to key accountability tanks for sampling and DA at low measurement uncertainty. Both uranium and plutonium are accounted for in the PIV, and a yearly Material Unaccounted For (MUF) value is determined. The IIV occurs monthly, with an additional Short Inventory Verification (SIV) taken every ten days. Effectively, the IIV/SIV provides a plant balance once every ten days, but only plutonium is accounted for. The ten day balance period as part of the IIV/SIV was used as the basis for the modeling in this work.

MBA 2 starts with the input accountability tank that contains the dissolved spent fuel solution, and ends with the uranium and plutonium nitrate product tanks. These three tanks are sampled for precise elemental measurements using Hybrid K-Edge Densitomatry (HKED) or KED. Because of the low uncertainty needed for accountability spectroscopic measurements will not be applicable in these areas.

The internal separations operations within MBA 2 contain buffer vessels in between processes, pulsed columns where the separations occur, and evaporators for concentrating the product solutions. The existing IIV/SIV follows a random sampling pattern to draw samples from these internal vessels to verify the inventory. The pulsed columns cannot be sampled due to the variable nature of the extractions, but most of the other vessels can be. Samples are taken to a laboratory for destructive analysis, usually Isotope Dilution Mass Spectroscopy (IDMS). The goal of this work was to determine if some of these random samples could use spectroscopic measurements instead of IDMS.

4. Separation and Safeguards Performance Model (SSPM)

Modeling was used to determine how process monitoring could be used in existing plants and to provide the safeguards metrics for comparison. The Separations and Safeguards Performance Model (SSPM) was developed at Sandia National Laboratories and was used as the basis for this work. The SSPM is built in Matlab Simulink and was developed to analyze safeguards system design, test the performance of new measurement technologies, and perform diversion scenario analyses [5,6]. Various versions of the SSPM exist to represent different reprocessing concepts, but this work used a PUREX model that represents current reprocessing plants. The model is built upon open data, so specific plant design details may be different.

The Simulink model uses signals to represent the material flows between processing units. Fig. 1 shows the PUREX model. The processing units are subsystems that perform mathematical functions on the signals to represent the operations. The subsystems simulate tanks filling and emptying, and determine how the material separates into the output streams. Separations are hard assumptions that do not currently have chemistry modeling included. The inventory of material in each processing unit is tracked.

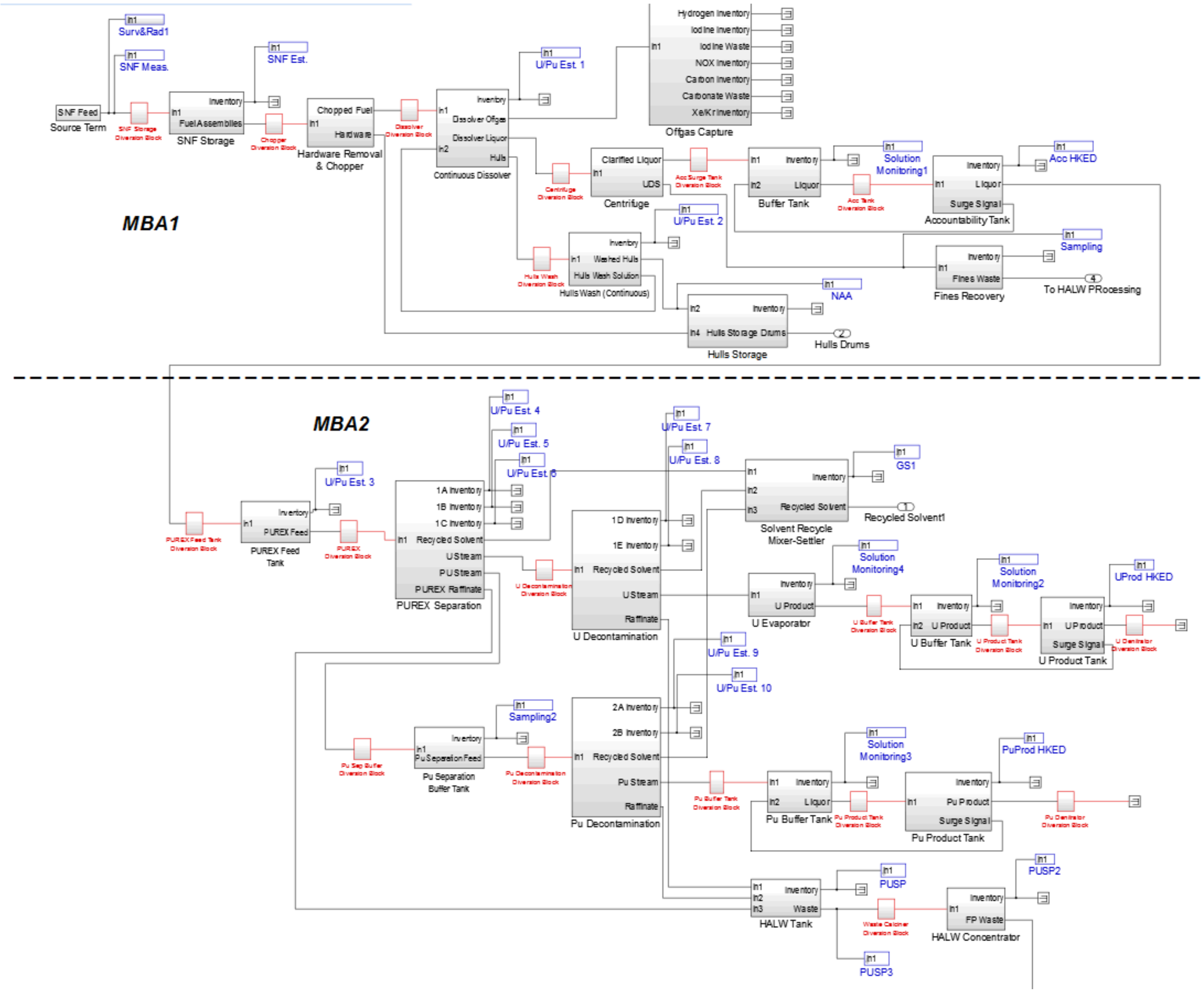

Fig. 1. PUREX SSPM

The blue blocks shown in Fig. 1 are measurement blocks that simulate what is being measured, the uncertainties, and the frequency of the measurement. Additional measurement points such as the bulk material measurements are not visible in the high-level view. The simulated measurements are used within the model to perform periodic inventory balances.

The red blocks shown in Fig. 1 are diversion points that can be turned on or off to represent material loss. The user can define when the diversion starts and stops, and the fraction of material removed. In this manner, the model is used to determine how the measurement system will respond to a material loss.

The model can be run for a single instance, and multiple graphs are available while the model is running to track material flows and the inventory balances. However, all of the measurement uncertainties have a random nature to them, so any instance will be different from another run. Multiple runs are required to determine detection probabilities. The SSPM has the capability to utilize parallel processing to decrease the run times for multiple iterations. Usually 100 iterations of a particular scenario are run in order to develop useful results.

4.1. MBA 2 Model Details

The material balance over MBA 2 starts with the measured dissolver solution from the accountability tank, which is measured once per batch (every 36 hours). Accountancy is achieved using an elemental concentration measurement from the sample multiplied by the volume of solution transferred to MBA 2—these measurements are all simulated with errors in the model.

The separations are achieved through the use of pulsed columns, as represented by the PUREX Separation, U Decontamination, and Pu Decontamination blocks in Fig. 1. At existing plants, measurements of the pulsed columns are not feasible due to the separations that are occurring, but models have been developed that can estimate the U and Pu content. The measurement blocks on the pulsed columns assume a 3% measurement uncertainty (for both random and systematic error) based on the operator models.

MBA 2 contains several buffer vessels throughout that convert batch to continuous flow or vice versa. Other operations include the solvent recycle mixer-settler, evaporators to concentrate process solutions, and the waste tanks. All of these vessels will only be measured as part of the IIV/SIV through random sampling. The SSPM assumes that these areas are sampled once every ten days. A random sampling plan could be implemented, but this was not done since the impact on overall modeling results would have been negligible. Bulk material measurements (such as tank level) are available on all of these vessels.

The U and Pu product tanks and the waste tank collect the nitrate products and waste for accountancy purposes. Routine sampling on each batch is used for low uncertainty measurements of the U and Pu product. The waste tank or final waste form may be measured to confirm low quantities of actinides.

The actinide quantity in the tanks which would be sampled for the IIV/SIV play a key role in the interim inventory balance. Any tanks along the main Pu line will contain large quantities of Pu. However, tanks along the U line, solvent recycle, and the waste streams will only contain very small Pu quantities.

4.2. Safeguards System Modeling

The SSPM performs U/Pu balances every ten days in order to be somewhat consistent with the IIV/SIV. (In reality the IIV/SIV is only concerned with the Pu balance, but the SSPM models a U balance as well.) The input accountability tank operates on a 36 hour cycle, so several input batches go into the IIV balance. The output accountability tank operates on a five day cycle, so two batches go into the balance. A series of delays are used in order to make sure the timing of all the measurements is consistent.

The input and output accountability tanks are modeled using low uncertainty measurements that are achieved with best practices at existing plants using HKED or KED. The U/Pu content in the pulsed columns is assumed to be estimated to ± 3%. The buffer vessels are assumed to be sampled and measured once every ten days. The measurement uncertainty for these areas was changed to represent either an Isotope Dilution Mass Spectrometry (IDMS) or spectrophotometric measurement.

All of the measurements or estimates that are used for the material balance include both random and systematic errors, which are set by the user. The random error is truly random, and Simulink applies a random number generator to each measurement that will be different for each consecutive measurement. The error applied follows a normal distribution with a mean of zero and standard deviation equal to the relative random error chosen by the user. This small error, either positive or negative, is added to the true value to give a simulated measurement. The systematic error is applied differently—a random number generator is used to apply an error only once at the beginning of the run, and then this error is held constant (for each individual measurement) for the remainder of the run. This simulates the bias generated by the systematic errors.

The SSPM uses the measurement information to calculate the material unaccounted for (MUF) once every ten days and also tracks the cumulative sum of the MUF and error propagation (σ_{MUF}). Page's test is used to set alarm conditions to detect material loss. The Page's Test is a well-accepted statistical test for detecting both abrupt and protected diversions for reprocessing safeguards [7,8]. The test is designed to keep the false alarm probability below 5% while still containing enough sensitivity to detect abrupt and protracted diversions. The Page's test parameters were modified in order to maintain the appropriate false alarm probability.

Because of the random nature of the measurements, every run leads to slightly different results. During a diversion scenario, if the diversion is near the detection limits, some runs may signal an alarm using the Page's test, and some runs do not. In order to determine the detection probability, multiple runs are required. For each test case, 100 runs were completed to determine an average detection probability.

5. Modeling Results

The modeling examined material loss and the overall σ_{MUF} for three cases. The baseline case was meant to be representative of an existing plant and assumed sampling and IDMS for all internal vessels as part of the IIV/SIV. The "Full Spectroscopy" case assumed replacement of IDMS with spectroscopy measurements for all of the internal vessels. The "Partial Spectroscopy" case assumed replacement of IDMS with spectroscopy for only those vessels processing small or trace quantities of plutonium. Table 1 shows the measurement assumptions for the three cases. Current best practices were used for the measurement assumptions in the baseline case [9]. Only the highlighted rows changed between cases. Note that the SSPM is a simplified model of a PUREX plant, and many more vessels would be present than shown in the model. However, this model provides enough detail to generate useful results which could be refined for specific plants in the future.

Table 1. Assumed measurement uncertainties.

		Baseline Case		Full Spectroscopy		Part Spectroscopy	
		σ_r	σ_s	σ_r	σ_s	σ_r	σ_s
Input Accountability Tank	HKED	0.8%	0.5%	0.8%	0.5%	0.8%	0.5%
PUREX Feed Tank	Sampling	0.2%	0.2%	1%	1%	0.2%	0.2%
PUREX Separation	Model	3%	3%	3%	3%	3%	3%
U Decontamination	Model	3%	3%	3%	3%	3%	3%
U Evaporator	Sampling	0.2%	0.2%	1%	1%	1%	1%
U Buffer Tank	Sampling	0.2%	0.2%	1%	1%	1%	1%
U Product Tank	KED	0.8%	0.5%	0.8%	0.5%	0.8%	0.5%
Pu Separation Buffer Tank	Sampling	0.2%	0.2%	1%	1%	0.2%	0.2%
Pu Decontamination	Model	3%	3%	3%	3%	3%	3%
Pu Buffer Tank	Sampling	0.2%	0.2%	1%	1%	0.2%	0.2%
Pu Product Tank	KED	0.3%	0.3%	0.3%	0.3%	0.3%	0.3%
HALW Tank	Sampling	0.2%	0.2%	1%	1%	1%	1%

The modeling results showed that the Full Spectroscopy case raised the σ_{MUF} enough to negatively affect overall safeguards performance. The reduction in detection probabilities would not be acceptable for continuing to meet the IAEA goal of the loss of 8 kg of Pu in 30 days.

On the other hand, the Partial Spectroscopy case did not negatively affect overall safeguards performance. The σ_{MUF} did not change, and detection probabilities were unaffected over a range of material loss scenarios. Therefore, the partial use of spectroscopy for the IIV/SIV would result in the same level of safeguards performance while reducing the need for as many IDMS measurements. Roughly half of the random sampling points are taken from vessels processing low or trace plutonium quantities, so there could be a cost-benefit to measuring these samples with spectroscopy instead.

6. Cost-Benefit Analysis

The cost of spectroscopy was examined to determine how increased use of spectroscopy could save costs for the regulator. KED, HKED, and Isotopic Dilution Thermal Ionization Mass Spectrometry (ID-TIMS) were compared to Spectroscopy in five areas. These included the instrument cost, maintenance cost, consumables, waste, and analyst time. Table 2 shows a summary of the results [10,11,12,13].

Specifically compared to IDMS, spectroscopy has a much lower instrument cost and maintenance costs. Consumables and wastes could be lower for an on-line monitoring approach, but measurement of samples in a laboratory would not be much different. Another significant savings is in the analyst's time. Based on the results in the previous section, the use of spectroscopy could replace IDMS for about 10 samples per month. At this rate of sampling, the yearly costs for IDMS are near $50,000 while only $6,000 for spectroscopy. The use of spectroscopy will pay for the instrument in 4-5 years.

Table 2. Summary of costs for reprocessing safeguards methods.

Method	One-time costs	Yearly costs	Costs per Sample		
	Instrument Costs, $	**Instrument Maintenance, $/Year**	**Consumables, $/Sample**	**Waste, $/Sample***	**Analysts' Time, h/Sample**
K-Edge	200,000.00	10,000.00	50.00	0.15	0:20
Hybrid K-Edge	700,000.00	15,000.00	100.00	0.30	0:20
ID-TIMS	600,000.00	30,000.00	50.00	4.00	4:00
Spectroscopic Process Monitoring	180,000.00**	2,500.00	0.00	0.00	0:05

7. Conclusion

The modeling analysis has shown that the use of spectroscopic measurements to quantify Pu for interim inventory measurements can play a role for select measurements. Using spectroscopy for inventory measurements of internal tanks that process only small quantities of Pu will not adversely affect safeguards effectiveness, while it would clearly reduce the costs of these safeguards measurements. This modeling was performed with the assumption that spectroscopy would be used in the analytical laboratory and using the current sampling systems at an existing plant. The use of spectroscopy for internal tanks or accountancy tanks that process large quantities of Pu would not be appropriate since the measurement uncertainty is high enough to adversely affect safeguards.

The cost benefit analysis showed that spectroscopic measurements have much lower overall costs in equipment cost, maintenance, and sampling costs as compared to the existing technologies including KED, HKED, and ID-TIMS. Annual cost savings will be able to pay for the new instrument in 4-5 years.

8. Acknowledgement

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