

Validation of Iron and Coulometry Systems at LANL's RLUOB Facility

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Abstract: In August of 2020, C-AAC successfully installed equipment at Los Alamos's Radiological Laboratory Utility Office Building (RLUOB) to perform iron analysis by UV-Vis spectrometry and high precision plutonium assay by coulometry (CPC). The systems will be replacing the instrumentation that currently supports plutonium modernization, nuclear energy, nuclear forensic, and nuclear safeguard programs in the Chemistry Metallurgical Research (CMR) facility and will need to prove that they can match the established instrumentation for precision and accuracy prior to the older systems being retired and the CMR facility closed in 2024. In addition, the work will have to meet strict standards that support 10 CFR 830.120, *Nuclear Safety Management – Quality Assurance Requirements*, DOE O 414.1D, *Quality Assurance*, and NQA-1 2008/NQA-1a-2009, *Quality Assurance Requirements for Nuclear Facility Applications*, and NAP 401.1 *Weapon Quality Policy*. The plan to validate the instruments and methods, challenges found during the qualification process, and the data used to validate the instrumentation will be discussed.

Introduction

In August of 2020, Actinide Analytical Chemistry (AAC) successfully installed equipment at Los Alamos's Radiological Laboratory Utility Office Building (RLUOB) to perform iron analysis by spectrometry and high precision plutonium assay by coulometry (CPC). The systems will be replacing the instrumentation that currently supports plutonium modernization, nuclear energy, nuclear forensic, and nuclear safeguard programs in the Chemistry Metallurgical Research (CMR) facility and will need to prove that they can match the established CMR instrumentation for precision and accuracy prior to the older systems being retired and the CMR facility closed in 2024.

Method validation for the AAC at LANL has a formal validation process which uses a graded approach to establish the validation work required. This approach is based on practices originating from the ASTM International (ASTM) [1], the International Standards Organization (ISO) [2], the International Union of Pure and Applied Chemistry (IUPAC) [3], and DOE guidance as specified in DOE-STD-1194-2019, *Nuclear Materials Control and Accountability* [4] as well as 10 CFR 830.120, *Nuclear Safety Management – Quality Assurance Requirements* [5], DOE O 414.1D, *Quality Assurance* [6], NQA-1 2008 [7]/NQA-1a-2009 [8], *Quality Assurance Requirements for Nuclear Facility Applications*, and NAP 401.1 *Weapon Quality Policy* [9]. A method validation plan and verification report are completed to document the results. Two validation plans were approved for this work, PA-PLAN 01417 *Method Validation Plan: Iron Assay by Spectrometry at RLUOB* [10] and PA-PLAN-01419 *Method validation Plan: Plutonium Assay by Coulometry* [11]. These plans establish the minimum criterion that will be used to validate the instrument and methods being validated. They cover environmental requirements, work authorizing documents (method and supplies), standards, process variables, location of work and equipment being used, personnel responsibilities, experimental details, and performance limits to evaluate against based on the established CMR facility instrumentation and methods.

Iron Method and Instrumentation: Iron is determined spectrophotometrically using an iron (II)-1,10-phenanthroline complex in an acetate buffered solution, a method that was first reported in 1938 [12]. It was adapted for use with plutonium materials in 1949 at LANL [13]. Plutonium is removed from the solution prior to measurement to prevent interference at the 510 nm wavelength. The aliquots analyzed have come from the same solution used to aliquot for the CPC method to ensure the required iron corrections are specific to the actual subsamples being analyzed. This method is one of the most stable and reliable methods performed in C-AAC and can often give results that have lower uncertainties than Inductively Coupled

Plasma-Atomic Emission Spectroscopy (ICP-AES) iron assays. However, assays for iron are extremely sensitive to environmental dust, rust particles, etc. requiring analysts to use great care to avoid contamination.

LANL chose the ThermoScientific Genesys 10S system originally at CMR as it had a small footprint allowing easy introduction into openfronts, could be equipped with a flow cell, had a wide wavelength range of 190 nm to >1100 nm, a 1.8 nm bandwidth, Xenon lamp, never would require maintenance, and can be operated manually without a computer. It uses a xenon lamp with a fundamental line at 529 nm which acts as a fundamental, first principle standard for the wavelength and is very close to the 510 nm wavelength the iron method requires. All internal tests preprogramed into the system can be traced to this. The installed RLUOB system is currently set up with a quartz 1 cm light path, sipper/flow cell, and peristaltic pump.

Coulometry Method and Instrumentation: Coulometry is a primary tool and executes work in all of DOE's missions: national security, science, material control and accountability. As a method it can be traced back to 1942 [14] in the literature and was adapted as a method for Pu in 1958[15] in a Hanford report. It became routinely performed at LANL in the 1970s as it is one of the most precise and accurate methods for plutonium content with better uncertainties for many plutonium materials than mass spectrometry techniques and less interferences than titration methods [16]. The one major interference that must be corrected for in all plutonium samples analyzed by this method is iron.

Plans for the CMR replacement project specified that SRNL would build and install a new coulometry that was the identical make and model to that installed at LANL in 2011 [17]. The CMR based system has been in near continuous operations since it's installation and has not had any major equipment. This new coulometer was installed at RLUOB in 2020 by LANL and SRNL personnel. The electrochemical cell is a custom configuration designed and assembled by LANL and Analytical Instrument Systems, Inc. personnel that is very nearly identical to the existing CMR system with platinum and calomel electrodes. This coulometer and cell configuration is compliant with both ASTM C1108, *Standard Test Method for Plutonium by Controlled-Potential Coulometry* [18], and ISO 12183, *Nuclear Fuel Technology-Controlled-Potential Coulometric Assay of Plutonium* [19] and features the ability to perform electrical or chemical calibrations, background current corrections, and control-potential adjustment capabilities.

Pu Sample and Standard Preparation: Prior to dissolution, metal samples or standards are polished to remove any surface oxide by the Sample Management team. Once cleaned each sample is split into metal subsamples. For CRM126a [20] or SRM949f [21] standards each subsample is 250-300 mg in size. For Pu metals two subsamples, approximately 0.5 gram each, are prepared per each sample. Regardless if sample or standard, these subsamples are dissolved in ~7 mL 6 M HCl and diluted to with 1 M HCl and aliquanted for use.

Plutonium oxide control materials [ref paper] are prepared by dissolutions are dissolved at the 250-300 mg subsample size using a low-pressure acid dissolution at 150 °C in sealed Savillex vessels. The dissolution acid cocktail is 5mL of 12M HCl solution plus 3 drops of 1.3M HF. Once dissolved they are diluted in 1M HCl and aliquanted for use.

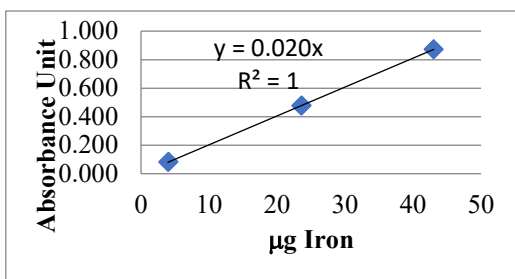
All coulometry aliquants provide 5-7 mgs of Pu from prepared standard, control material, or sample solutions for analysis. All samples were bracketed by either a calibration standard or a control material. Every sample is analyzed in duplicates: and A subsample and B subsample. Because iron can undergo oxidation at the same potential plutonium does, all samples are corrected for the iron content based on the average iron value from the spectrophotometric method. This method for iron analysis is performed on the same solution as the CPC analysis for each subsample to ensure the samples are corrected for the actual iron that exists in the analyzed CPC aliquot.

All iron aliquants provide 10-12 mgs of Pu from the prepared sample solutions. A periodic check of the calibration factor is performed using a low, low iron containing Pu matrix material that is spiked with NIST traceable and ISO GUIDE 34 iron single element solution standard. This data is used as the control chart. An ISO GUIDE 34 iron single element solution standard is also used to generate the calibration curve at the time of installation. Iron assays for samples come from two separate dissolutions and have had two replicate assays performed on each dissolution. Matrix and process blanks are subtracted out at the spectrometer.

Validation Requirements and Results

Iron: The first validation requirement for a new instrument in the iron method is that a calibration curve be linear and have a slope of 0.020 ± 0.001 absorbance unit per microgram of iron. This is only done once upon installation as it has been our experience for the last 50+ years that this curve doesn't change, and the instruments and method are exceptionally robust. It does not seem to be affected by the manufacturer of the instrument, the model of the instrument, frequency of use, or age of the instrument. The maximum amount of iron in 10 mL of solution is 50 μg , above this amount the curve is not linear. Figure 1 below show that a curve generated on December 3rd, 2021, meets the first requirement. This curve was generated at 3 concentration points performed in duplicate [see Table 1] which cover a corresponding concentration range in the Pu metal sample of 20–2500 ppm Iron. In the graph, however, the duplicate points overlaps so closely that the 2nd set of data points is not observable in the graph. The slope is exactly at 0.020 AU/ μg of Iron. Thus, this new instrument meets the calibration acceptance criteria.

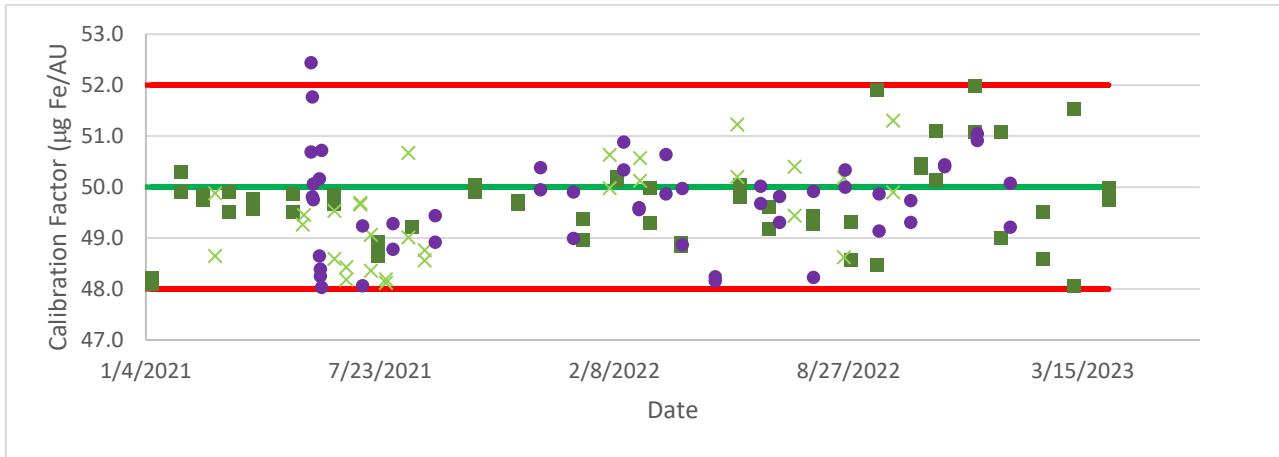
Figure 1: Calibration curve of the ThermoFisher G10S instrument. **Table 1:** Standards used to generate the curve with slope and calibration factors calibrated.



Flask #	Fe Std, μg	AU	AU/ μg	Fe $\mu\text{g}/\text{AU}$
1	3.96	0.081	0.020	48.9
2	4.08	0.082	0.020	49.7
3	23.54	0.476	0.020	49.5
4	23.62	0.479	0.020	49.3
5	43.04	0.873	0.020	49.3
6	43.04	0.871	0.020	49.4

The second requirement is that a monthly calibration factor check must be between 48–52 $\mu\text{g Fe}/\text{Abs unit}$ and show stability over at least 4 months of time. The calibration factor is just the inverse of the slope of the calibration curve (as seen in Table 1) and allows a quick check of the stability of the calibration curve without having to redo a full curve. The acceptance criteria of 48-52 $\mu\text{g Fe}/\text{AU}$ is slightly tighter/more conservative than the acceptance criteria of the calibration curve as equivalent CF for the slope limits are 47.6 to 52.6 $\mu\text{g Fe}/\text{AU}$. This helps ensure we are never outside the acceptable calibrated range. The calibration factor is tracked in a control chart over time as well to see if we see any trends or issues, see Figure 2.

Figure 2: Calibration chart comparing three facilities iron methods. Dark green squares are for the currently established CMR instrument, light green X are for PF-4 instrument, and purple circles are for the RLUOB instrument. The red solid lines are the acceptance criteria with a green center line for the midpoint.



In the iron control chart (Figure 2) we have data for three facilities: CMR, PF-4 and RLUOB. PF-4 data was included as a comparison for RLUOB as they are being stood up at the same time and can act as an extra check. The first apparent issue observed when starting this control chart was how much variation in the RLUOB data initially exists. Some of which exceeded the acceptance criteria. It was found that there was a severe dust issue from construction happening in the building but in a different room at that same time. When bringing new spaces up, construction dust can be present and it will take multiple cleanings to bring down blanks and cease seeing random spikes in one of the replicates. PF-4 data from at initial start up is before this chart's starting date; however, the exact same behavior was seen but more extreme and for a longer period of time. Once construction ceased in other locations in the building and after multiple wipe downs of the gloveboxes and open fronts where this method is located you ceased to see such wild swings in short timeframes. The data then stabilizes and continuously meets the acceptance criteria we typically see at CMR and at PF-4. In fact, it is often possible to see when new trainees start to report data as the scatter will increase and as they gain experience narrow down again. This can be seen in the CMR data starting in September of 2022 when two new trainees joined CMR's team. This scatter can be traced back to the skill of the trainees in doing the separation steps of the method. In Table 2 once can see the statistical evaluation of the three facilities data. They clearly overlap with each other and especially with the CMR established method once we remove the first 2 months of data when construction was still occurring. Once the RUOB facility data stabilized it has lower scatter than the CMR established method for the comparison time period. As a result, it is deemed that the RLUOB system has met the second validation requirement

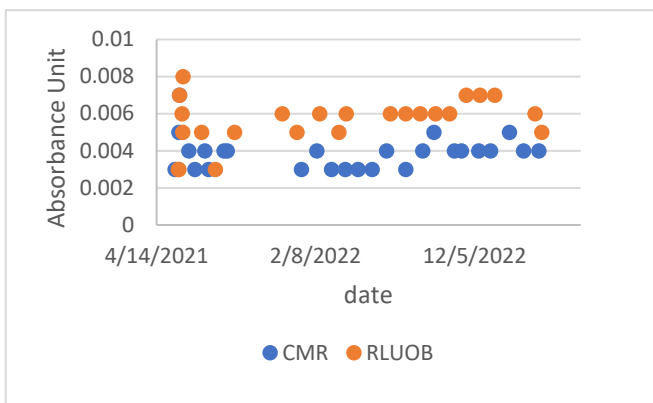
Table 2: Summary data for the iron control chart for the three facilities.

	CMR	PF-4	RLUOB (All)	RLUOB (Stabilized)	All Locations
AVG CF	49.7	49.5	49.7	49.6	49.6
SD	0.86	0.93	0.94	0.77	0.9

The iron method uses process blanks and corrects the zero point for the spectrometer first against water and then against the process blank. Once the system has been zeroed against water, the validation requirement is that the process blank be less than 0.012 AU and similar behavior to CMR process blanks. Figure 3 shows

the process blank data points relative to each other. One can see similar behavior of the blanks during the construction period as the control chart data above. Once out of that period and after the repeated cleanings, the blanks stabilize but show some stepwise behavior over time. Similar step behavior is also seen with the CMR established method. Table 3 below shows the average and standard deviations for all the monthly validation runs in the control chart for the two facilities. The two facilities have identical standard deviations and similar but not identical average blank values. Experience with the established method at CMR has shown that the hydroxylamine hydrochloride reagent can have iron contamination. It has been found that these small step behaviors over time relate to the opening of a new bottle of the hydroxylamine hydrochloride reagent. Because of this both RLUOB and CMR work authorizing documents have a requirement to obtain a certificate of analysis where the iron is less than 5 ppm OR test the reagent prior to use with sample to prove the blanks will be less than 0.012AU. Because of the similar behavior over time, equivalent standard deviations and always being <0.012AU in value RLUOB instruments have met the blank validation acceptance criteria.

Figure 3: Blanks over time for monthly verification measurements. **Table 3:** Blank statistical data.



Facility	Average (AU)	SD
CMR	0.006	0.001
RLUOB	0.004	0.001

The final validation requirement was to match the established method’s sample data. To do that the RLUOB method and instrumentation had to produce iron results on six samples that met the same within day run replicate requirements (Table 4) as the established method and be within the overall method’s relative standard deviation (RSD) of the CMR’s analysis of the same material. In addition, one exchange sample must produce data that meets within day run replicate requirements and be within the relative standard deviation of the exchange material’s mean iron value. For the samples in Table 4 below, the allowable within day range between replicates is 30 ppm and the expected RSD is 7.5%.

Table 4. Sample data summary.

Sample #	1	2	3	4	5	6
CMR Avg (PPM Fe)	406	400	398	385	394	421
RLUOB Avg (PPM Fe)	398	409	411	407	416	408
Absolute difference (PPM Fe)	-8	9	13	22	22	-14
CMR spread (PPM Fe)	7	16	20	5	6	11
RLUOB Spread (PPM Fe)	9	13	25	11	13	17
CMR RSD (%)	0.7	1.8	2.3	0.6	0.7	1.2
RLUOB RSD (%)	1.0	1.4	2.8	1.2	1.6	1.9

As can be seen every sample met the within day, 30 ppm spread for the replicates. In fact, the RLUOB and CMR spread between the highest replicate measurement and lowest measurement replicate are very similar for each sample. Showing that the two instruments are tracking each other very well. The RSD of 7.5%

means that the difference between the established CMR instrument and method and the RLUOB instrument and method should be less than 30 ppm. Each sample is within that window. In addition, we do not see a pattern of bias between the two methods and instrument. Currently the RLUOB system is meeting the first part of the sample validation requirements in matching CMR data on the same samples. The only criterion missing is running an exchange sample as that has not been provide to the RLUOB facility to run as of April 2023. Once that sample is analyzed it is expected that this method will have fully met all data acceptance criteria.

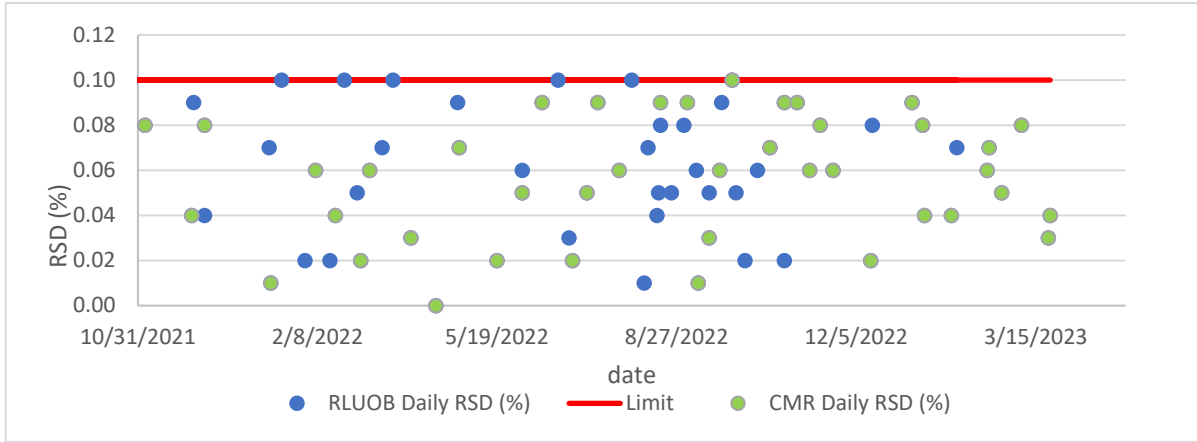
Coulometry : The first validation criteria for the RLUOB coulometry method are for blanks. Blank values must be $0.020 \text{ coulomb} \pm 0.015 \text{ coulomb}$ and two consecutive measurements of a blank on the same electrode must have a delta of $\pm 0.002 \text{ Coulombs}$. This is checked before standards and control materials are analyzed every day the coulometry is operated. In Table 5 one can see a typical run for the established method and the RLUOB method/instrument. In both cases the absolute blank value is meeting the $0.020 \pm 0.015 \text{ coulombs}$ value. But the first blank replicate delta for electrode 1 doesn't pass for either site but do pass on the subsequent measurement delta. Electrode 2 passes the first delta for the established method but not at RLUOB. The second dela RLUOB does pass. This type of behavior for blanks and different electrodes is very common and consistent with the coulometry cell conditions becoming more stable over multiple runs. RLUOB's system has lower blank measurement values than CMR, but the coulombs being measured in a blank are very dependent on things such as cell condition, electrode conditioning, electrode surface areas, general electrical noise, and how long since the last time the system was run. The similar behavior seen between the two methods and meeting the acceptance criteria mentioned above mean that the validation requirement for blanks is met.

Table 5: Comparison of blanks and electrodes between facilities

Facility	Electrode	Blank replicate #	Blank (coulombs)	In range? 0.005-0.035 coulombs	within ± 0.002 ?
RLUOB	1	1	0.017	Y	-
RLUOB	1	2	0.011	Y	0.005
RLUOB	1	3	0.009	Y	0.002
RLUOB	2	1	0.013	Y	-
RLUOB	2	2	0.010	Y	0.003
RLUOB	2	3	0.010	Y	0.001
CMR	1	1	0.013	Y	-
CMR	1	2	0.019	Y	-0.006
CMR	1	3	0.018	Y	0.000
CMR	2	1	0.024	Y	-
CMR	2	2	0.025	Y	-0.001

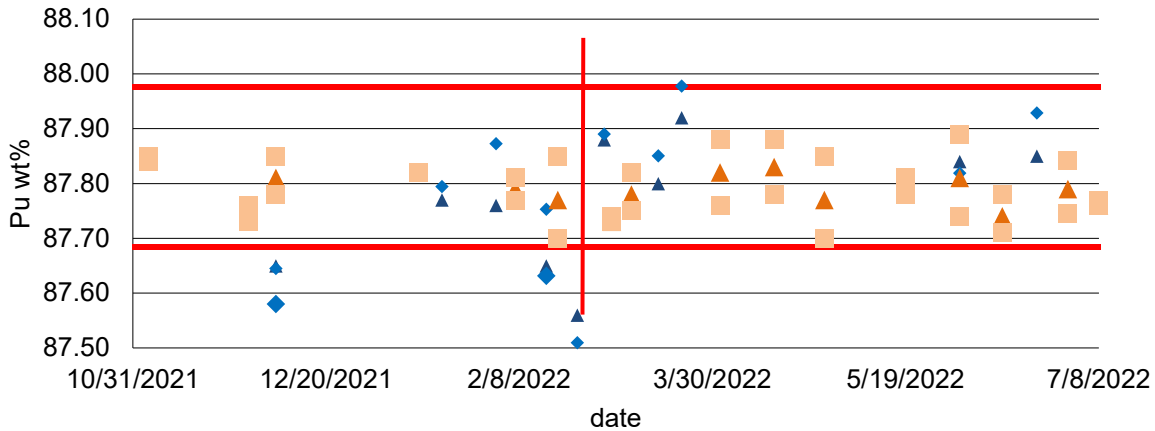
The next validation requirement for a new instrument in the coulometry method is that calibration data meets the established methods requirements and are stable over time. For the established method acceptance criteria for standards are not based on the factor (coulomb/gram) the standard provides as there is too much day-to-day variance for this to be used as a required control. A chemical standard calibration accounts for variances to the electrical system and cell environment that change daily, thus calibration factors are determined on a daily basis. The important acceptance criterion is the *precision* of the daily standard calibration factor. If the system cannot provide consistent calibration factor data on a single day, then the system is considered out of calibration and not functional. The established method requires minimum of 3 standard replicates to be run on each day of analysis. The acceptance criterion is a precision of 0.10% for all CRM material run on that day. Figure 4 shows the collected data for daily CRM RSD data for both the established method and the RLUOB system. The graph clearly shows that the new system is operating with a precision comparable to the established system at the CMR facility over multiple months. As such this validation requirement is considered fulfilled.

Figure 4: Calibration standard precision control chart.



The established method also requires that a quality control sample material be run each day the system is analyzing samples. Figure 5 shows data for a common control material between the established site and RLUOB. The acceptance criteria applied for this material is Pu assay be $88.78\% \pm 0.14\%$. It also must meet daily precision standards that are set from the historical data analysis of nearly four decades of data. The 2 sigma value that is currently used for within day replicates is 0.14 %.

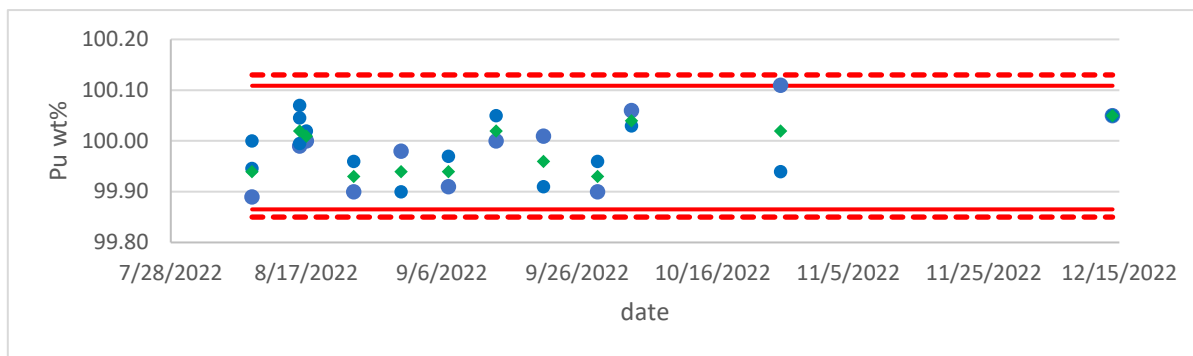
Figure 5: RLUOB control chart of common control material. Data from established method at CMR is in orange and RLUOB data is in blue. Triangles are each facility’s daily average value.



The RLUOB system clearly had issues at the beginning meeting this requirement as seen in Figure 5. Investigation found that the work authorizing documents had neglected to put in a requirement for baking out the established control material prior to use. In addition, several stir motors burned out and very long oxidation and reduction times were observed. The investigation also identified differences with the established site’s stir motor and connections. When the stir motor was looked at the established site it was found to be running at 1800 rpm using a fairly rigid plastic piece to mate the glass stir rod to the motor and very good alignment of the motor shaft to the center hold in the cell cover. This resulted in little to no flex/flair in the rod when operating and no rubbing of the rod against the cell’s Teflon covering. At that

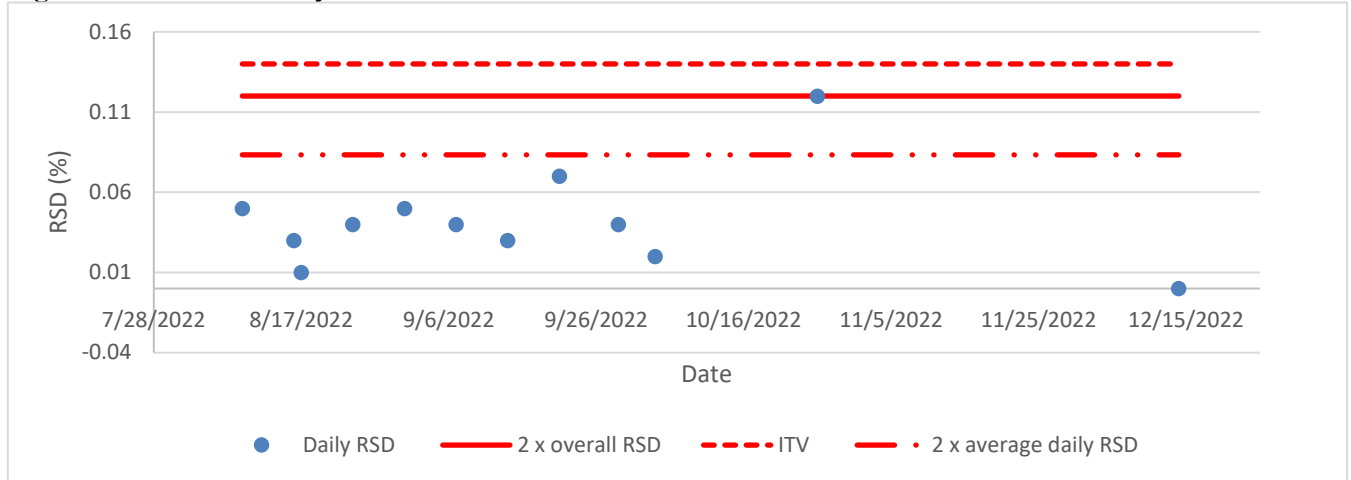
time, the RLUOB system was operating well below 1000 rpm, the motors found to be just slightly misaligned, and flexible hose used to mate the glass stir rod to the motor. This flexible connection was causing the low power, low torque motors that originally came with the cell stands to burn out when the flex/flair that happened, and made the rods rub against the central opening of the cell. New more robust motors were purchased and installed which can run the stir rods up to 1200 rpm before the flexible connections cause flair and rubbing. A request to have in house LANL machinists make a rigid connector is in process now which should allow the RLUOB system to match the established methods 1800 rpm and keep the rod aligned with the center hole so as not to rub. With new motors and higher stir rates oxidation/reduction times significantly dropped though are still longer than the established method. Once both the control material was baked at 950 °C for 8 hours and the higher stir rates were implemented the control chart started to stabilize. It was at this time that the amount of control material at the established site was restricted to ongoing validated method use only as it was becoming scarce and continued use in development and testing at the RLUOB site would deplete it faster than a replacement could be obtained. At that time, a significant stockpile of SRM949F was found in the plant and reserved for C-AAC use. A new control chart was started using this material and can be seen in Figure 6 This material has a certified value of 99.99 wt% Pu. Initial controls for acceptance were using the IAEA ITV values for coulometry on high purity material of 0.14%. Those are the dashed lines in the graph. Statistical analysis shows a 2 sigma control limit of 0.12% which are the solid red lines in the chart. Blue circles are the replicate measurements, green diamonds are the daily average.

Figure 6: SRM 949 control chart.



Just as with the calibration, within day RSD values are part of the validation criteria. Since the control material changed in the middle of the validation process it cannot be compared directly to the established method. Instead, data will be collected over the entire testing time and LANL based statisticians will evaluate and set final control limits when the validation process is deemed complete. Figure 7 shows the within day RSD for the SRM949F material. Again, a dashed red line is shown for the IAEA ITV value, the overall 2 sigma value are solid red line and 2 times the average within day RSD are the dot-dash red line. All data is less than the IAEA ITV value. One data point is equal to the overall 2 sigma value and larger than 2 x the average within day RSD. If this pattern is continued the control chart at RLUOB will have a tighter range than that seen with the established method/control material. Because of this, the requirement of having a control chart that is stable over time is considered met.

Figure 7: SRM 949F Daily Control Chart for RSD



The final test set was to produce results on six samples that meet the same within day run replicate requirements, 0.16%, as the established method and be within two times the overall method’s RSD, 0.15%, of the CMR’s analysis of the same material. In addition, one exchange sample must produce data that meets within day run replicate requirements and be within the two times the RSD of the exchange material’s mean Pu assay value.

Table 5: Sample results for the established method and RLUOB.

CMR Avg (wt%, normalized)	100.02	100.00	100.08	100.04	100.05	99.99
RLUOB Avg (wt%, normalized)	99.98	99.87	99.97	100.17	99.92	99.81
Difference (wt%)	-0.04	-0.14	-0.10	0.13	-0.13	-0.18
CMR spread (wt%)	0.03	0.00	0.15	0.07	0.09	0.03
RLUOB Spread (wt%)	0.02	0.03	0.16	0.07	0.12	0.02
Allowed spread (wt%)	0.16	0.16	0.16	0.16	0.16	0.16

In Table 5, CMR and RLUOB instruments are observed to have the same sort of spread between A and B replicates on each sample. This indicates that the two systems are running in very similar manners. It does appear that most RLUOB samples are running slightly low compared to CMR but are not outside of statistical probability of the method. Analysts, however, would like to see slightly more variation on either side of the established method and smaller differences between the two methods especially since sample 6 clearly didn’t meet the validation criteria to be within two RSDs of the established method. Analysts feel that though these results are promising, continued issues with the stir motor alignment and not being able to stir to the same rpm values used with the established method are contributing to the small differences between the method and equipment at the two sites. In addition, an exchange sample is still need for analyses at the RLUOB location. At this time, coulometry has not quite met the last validation requirement and additional samples should be tested and compared against the established method.

Conclusion

The new iron system and associated method at the RLUOB location is fully meeting all requirements for production work. It is nearly complete in its validation for routine work and only requires an exchange

sample to finish. Analysts are confident this can be accomplished in a short amount of time. The coulometry has made significant progress in becoming qualified to run customer samples. The blanks are comparable to the established methods and control charts have been established that appear stable over significant time. Improvements to the cell set up have significantly reduced analysis time from when the system was first installed. However, until the stir motor can fully aligned to run at higher rpm, and additional samples are tested it can't be fully qualified for customer samples.

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