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Electronics Upgrade to the Savannah River National Laboratory Coulometer for Plutonium and Neptunium Assay

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ABSTRACT

Implementing plutonium Material Control and Accountability (MC&A), safeguards measurements, material characterization, and standards certification requires analytical instrumentation that is reliably calibrated and traceable to the international measurement system with minimal measurement uncertainty and easy to operate.

Savannah River Site (SRS) has used controlled-potential coulometric assay for select key accountability measurements, external exchange program measurements, and secondary standards characterization. These applications required the highest plutonium assay reliability available at the SRS Analytical Laboratory. The present vintage automated controlled-potential coulometer used at the SRS was designed by the authors and fabricated at the Savannah River National Laboratory's Research and Development Engineering organization in the early 90's. The 90's vintage system used custom electronics installed in NIM modules with switches and dials. Many of the original components are now obsolete.

To ensure long term viability of the SRS and external customer systems, a complete electronics and data acquisition system upgrade has been completed. All electronics have been combined on a large multilayer pc board with individual isolated ground and power planes. All switches, knobs and batteries have been eliminated in favor of floating high resolution digital to analog converters. The HT Basic software used to control the coulometer has been updated with new features and drivers to accommodate the electronics and data acquisition hardware. The details of the electronics and software upgrades will be presented.

INTRODUCTION

The Savannah River Site (SRS) has been building Controlled-Potential Coulometers for 25 years. The work has been completed by a team from SRNL and the site's Analytical Laboratories. The SRS system is based on work originally completed at New Brunswick Laboratory. In 1984 with the arrival of Michael Holland, one of the key developers at NBL to SRS, work began on coulometry upgrades. Throughout this period, the system electronics, computer hardware, software and cell design have undergone significant improvements. Between 1985 and 1995, two systems were built for the SRS Analytical Laboratories, one system for Rocky Flats, and one system for the IAEA. The latest upgrade of the coulometer electronics was in 1992. This system consisted of two potentiostats, one for oxidation and one for reduction, a digital integrator module, a four channel counter and an automation module. The modules were built in the standard NIM Module format, using the NIM backplane for DC buses and interconnection between modules. Several coax cables were also used for interconnection to the modules and the data acquisition system (DAS). This paper will focus on the electronics and data acquisition upgrades completed for the new IAEA system delivered in May 2011. As of the writing of this paper, two additional new systems have been built and are undergoing testing. One system is being built for the Los Alamos National Laboratory (LANL) and one system for the SRS Analytical Laboratory.

BACKGROUND

Measurement uncertainty is of particular interest when performing accurate and precise measures of plutonium in support of national defense programs and international safeguards. The intrinsic value of this radioactive and fissionable element and its attractiveness to diversion for non-peace time applications necessitate that for some measurement applications, the total uncertainty of the plutonium assay or concentration measurement should be less than 0.1%. In addition to being small qualitatively, the uncertainty from the measurement method needs to be quantified so that its impact on inventory process used to safeguard this special nuclear material can be modeled and limits on inventory differences can be predicted. To ensure no significant impact on the overall measurement uncertainty, the SRS coulometer electronics is designed to achieve and maintain an electrical calibration with a two-sigma uncertainty of less than 0.01%. Uncertainty analysis has shown the actual uncertainty to be approximately $\pm 0.005\%$. Detailed uncertainty analysis will not be covered in this paper. A draft uncertainty paper has been prepared and will be issued in the future that combines the uncertainty of the measurement process with the instrument calibration uncertainty.

The existing coulometer design, before the 2010 upgrades, was based on using Nuclear Instrument Modules (NIM). The front and back panels of the NIM modules were cut out and engraved to support front panel indicators and switches while back panel contained insulated coax connectors. Custom printed circuit boards were mounted inside the modules. Using the standard back panel NIM connector, signals were routed through the back NIM wiring bus between modules. Standard linear ± 12 VDC and ± 24 VDC power supplies were used and supplemented with additional linear supplies. The system contained two potentiostats, one for oxidation and one for reduction. The potentiostats contained the high impedance voltage follower circuit for the reference electrode and the power stage for supplying the electrolysis current. In addition, a stand-alone PC board contained the high wattage 50-ohm load resistor through which the electrolysis current passed. The voltage drop from the load resistor was fed into a digital integrator module via a coax connector. An automation module contained driver chips and relays that automated the start of electrolysis, switching between the oxidation and reduction potentiostats and contained the 0.01% 100-ohm precision calibration resistor.

While the design has proven very reliable over the last 20 years, many parts are obsolete. In addition, the NIM architecture was not ideal since the removal and re-insertion of a potentiostat could cause a small change in the value of the load impedance due a change in contact resistance. Troubleshooting the modules required a special NIM extension cable and removing the modules from the NIM introduced noise. For most application these would not be significant issues. For the SRNL coulometer, the desired specification is to maintain the two-sigma uncertainty of the electrical calibration of the coulometer at less than $\pm 0.01\%$ to ensure no significant contribution to the overall measurement uncertainty. Another disadvantage of using the NIM module architecture is the labor cost in wiring and the cost of the modules, NIM Bin chassis and NIM Bin power supplies. With an increased focus on electrical safety, a goal of the new system was to limit all voltage in the coulometer to less than 50 volts.

HARDWARE

To eliminate interconnecting cables, the new coulometer was designed using one PC board show in figure 1. This six-layer board uses eight different floating DC linear power supplies and multiple power and ground planes. Three main grounds are used in the coulometer PC board: power analog ground, the voltage to frequency converter ground, and digital/chassis ground. All DC power supplies are located in a separate power supply chassis. The maximum voltage is 48 VDC in the coulometer chassis.

Single pole, single throw Koto™ relays were used to provide interconnection of signals. The Koto™ relay has a faraday cage around the relay with a lead that is connected to the respective ground plane minimizing any noise pickup through the relay. The relays have low contact resistance and negligible bounce making them an ideal replacement for the mercury wetted relays used on the old system. All DC power supplies connect via PC mount coax connectors. All trim potentiometers are accessible with the top of the chassis removed. Digital integrator alignment and offset potentiometers are accessible from the front panel.

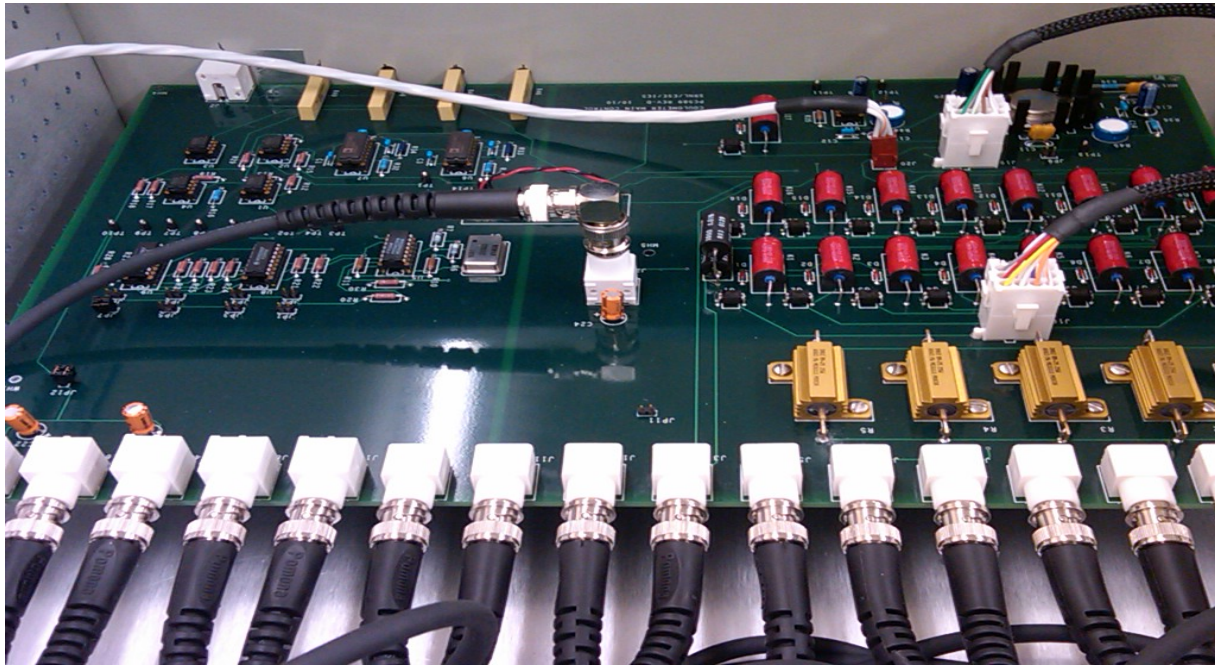


Figure 1: Coulometer 6 Layer PC Board

Multi-pin connectors were used for supplying the digital outputs from the Agilent™ 34980A data acquisition system. The digital outputs feed drivers chips and operate the coil on each Koto™ relay. Each cell electrode can be connected independently of the others, allowing for automated testing for high leakage current.

To maximize heat dissipation of the load resistors, five 100-Ohm, 25-Watt resistors were combined in parallel to create a net 20-Ohm load. For the calibration resistor two 100-Ohm Julie Research resistors were combined in parallel to create an equivalent 50-Ohm calibration resistor. The combined effect allows for linear response across the normal operating range of the instrument, with optimum performance in the 5 mA to 500 mA range. The calibration resistor is measured in circuit with an uncertainty of $\pm 0.0015\%$.

Figure 2 shows the entire coulometer system which includes:

- Uninterruptible Power Supply
- DC Power Supply Chassis
- Agilent™ 34980A Data Acquisition Chassis
- Laptop with a National Instruments™ PCMCIA IEEE-488 Interface
- Coulometer Chassis

The system is powered from 120 VAC or 230 VAC. A single triple-twisted cable connects from the coulometer chassis to the coulometer cell. The laptop communicates with only the Agilent™ 34980A chassis via the IEEE-488 card. The HT Basic software has been upgraded to Trans Era™ HT Basic V10, runs on Windows XP™ or Windows 7™. The software is generic for all users except for five configuration files:

- Method Parameters
- Cell Type
- Instrument Parameters
- DVM Calibration
- Analog Output Calibration

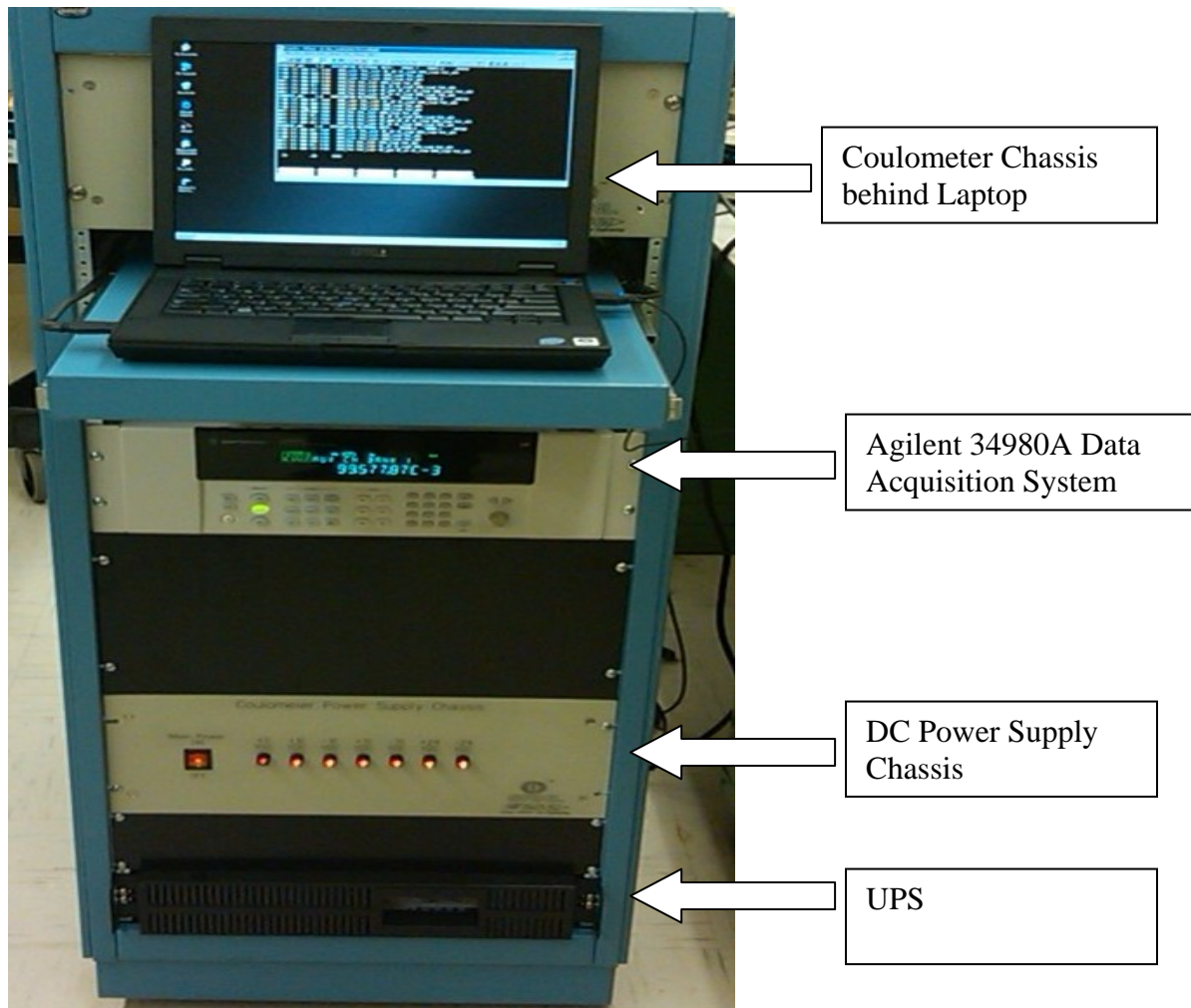


Figure 2: New Coulometer System

The Agilent™ 34980A is equipped with two digital input/output cards that control the relay operation. A multiplexer card (Agilent™ 34921A) is used to monitor the voltage across the calibration resistor, the cell voltage and the voltage across the load impedance. Each mux channel is calibrated by placing an Agilent™ 3458A voltmeter directly on the PC board. A calibration factor is determined such that the mux channel reads the same voltage as the Agilent™ 3458A. The calibration factor is stored in the DVM calibration file for each mux channel eliminating errors from mux relays, Koto™ relays and any voltage drop from the wiring. To ensure an accurate calibration, the Agilent™ 34980A internal DVM must be set to 10 Mega-ohms vs. 10 Giga-ohms. Otherwise the parallel combination of the Agilent™ 3458A input impedance and the Agilent™ 34980A will affect the calibration.

The Agilent™ 34980A plug in cards (Agilent™ 34950A) which contain independent counters that accumulate counts (or pulses) and can read on the fly without losing any accumulated counts. This is essential to the coulometer operation. The counters accumulate the pluses from the digital integrator and the precision 10 -kHz crystal clock. The maximum output of the digital integrator is 100,000 Hz. Testing was done to ensure that at frequencies at 100,000 Hz or less, no pulses were loss when taking multiple readings.

The Agilent™ 34980A has a four-channel 16 bit Digital to Analog Converter (DAC) card (Agilent™ 34951A) with an output of +/- 16 VDC. Each channel is floating and isolated. This allows each channel to act like a battery, so stacking voltages on each other is possible. Three channels are used on the coulometer. Channel 1 provides the offset voltage to the digital integration, channel 2 supplies the coarse voltage to the potentiostat and

channel 3 provides a fine voltage adjustment to the voltage follower amplifier on the potentiostat. By using computer controlled DAC's, and relays, all switches and dials for manual operation have been eliminated.

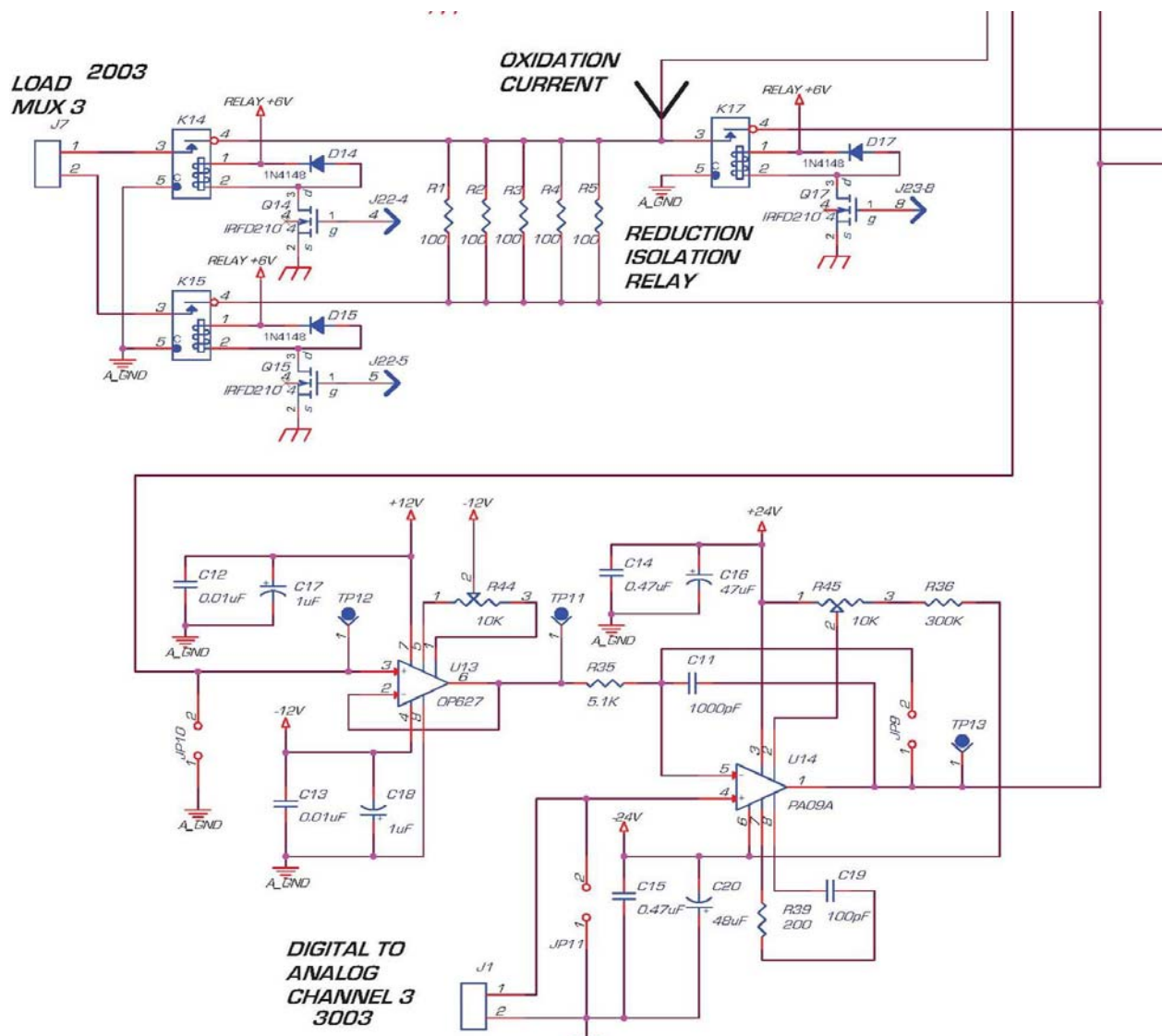


Figure 3: Potentiostat Circuit

The potentiostat circuit, located on the coulometer PC board, is a high impedance voltage follower circuit that senses the reference electrode voltage. A Burr Brown™ OPA 627 operational amplifier is used with an input bias current of 2 pico-Amps. The second stage circuit contains an RC stabilization network to minimize overshoot when the electrolysis begins. The second stage amplifier is an Apex™ PA09A with a peak current output of 2 Amps. The maximum current the coulometer is designed to integrate is 500 mA, which limited by the digital integrator design. The old integration system was limited to 190 mA.

From the output of the Apex™PA09A, current is supplied to either the cell or the calibration resistor. The amplifier circuit provides the necessary current to keep the cell voltage (or calibration resistor voltage) stable. After the current passes through the cell or calibration resistor, it is fed to the five 100-Ohm resistors in parallel shown in Figure 3. These equates to an equivalent resistance of 20-Ohms. For oxidation current (see arrow shown in the figure) the current flow results in a positive voltage which is connected to the digital integrator show in figure 4.



The offset is set from the user-defined instrument parameter file and can be easily changed. The 0.1 Volt offset is tapped from the output of the second amplifier feeding the bottom VFC and fed into a voltage summer circuit where it is added to the voltage generated by the electrolysis current dropped across the 20-Ohm load impedance. The offset pulses measured by counter#2 are subtracted in software from the pulses measured by counter#1, resulting in a highly accurate integration. To determine the conversion from coulombs to pulses from the digital integrator, the cell is replaced by a 50-Ohm precision calibration resistor. The units of the conversion factor or calibration factor, is micro-coulombs per pulse. The components and software parameters have been selected to result in a conversion factor of nominally 1.00 micro-coulomb per pulse. Table 1 shows a typical set of 10 calibration factors with a precision of 0.0002% with a stable laboratory temperature. Table 2 shows a typical

temperature response of about 0.001% per Celsius degree. Since the software performs a calibration before each sample measurement, temperature changes throughout the day will not impact results. A sudden dramatic temperature change during the measurement will result in a minor increased in measurement uncertainty.

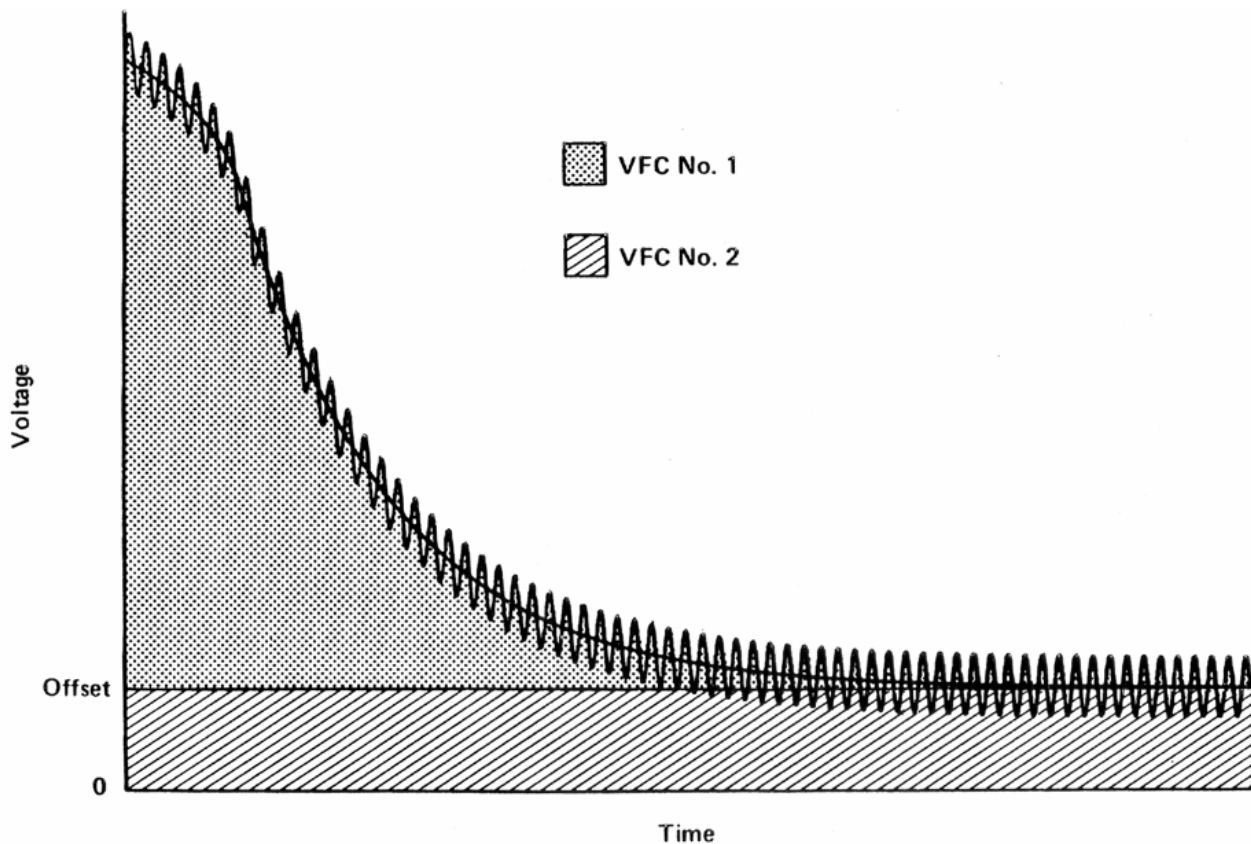
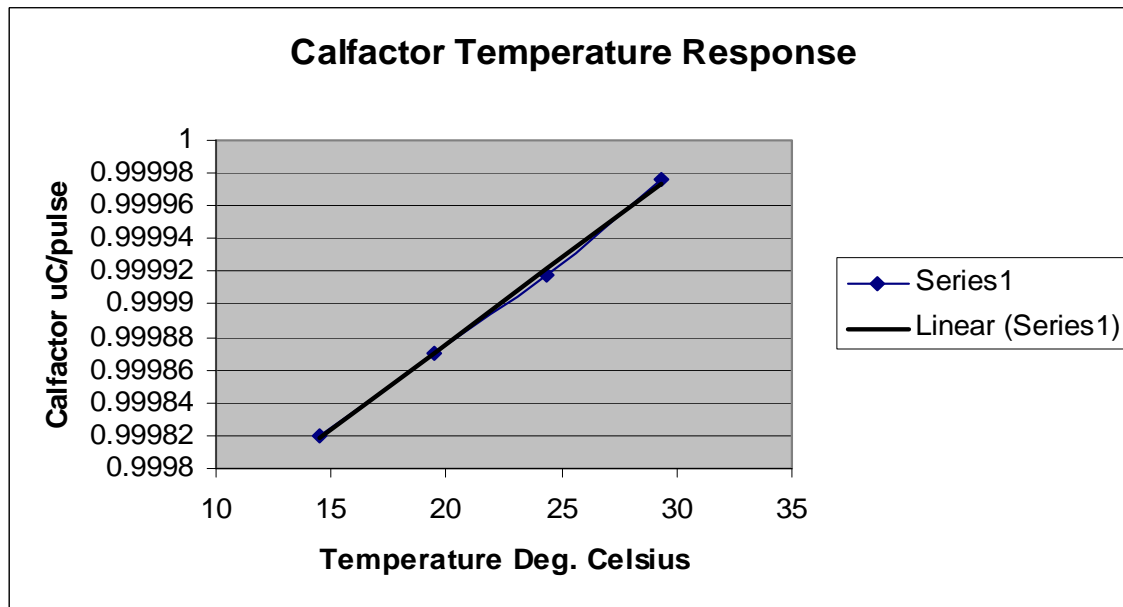


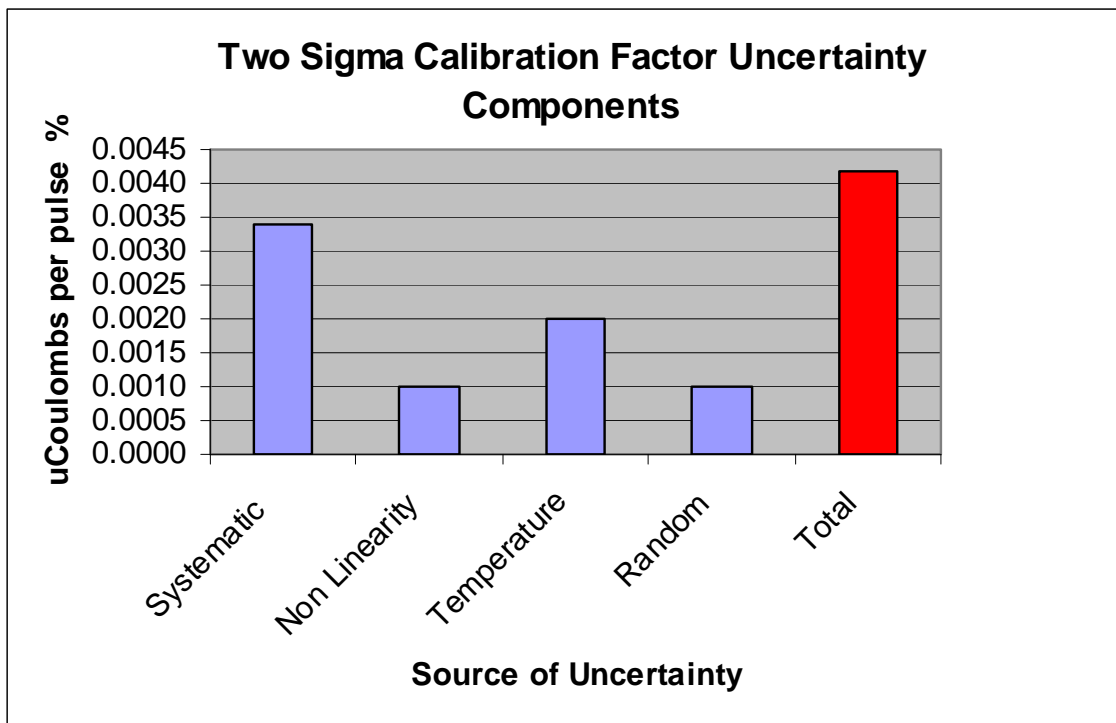
Figure 5: Voltage Signal Integrated by the Coulometer

1.00004 1.00004 1.00004 1.00004 1.00004
1.00004 1.00004 1.00004 1.00004 1.00004
LENGTH OF TIME FOR: CALIBRATION= 100.0 SEC.
Cal Temperatures:
27.0 26.6 26.9 26.7 26.2
26.3 26.5 26.9 26.8 26.3
AVERAGE CALIBRATION FACTOR: 1.000041 Temperature= 26.6
RSD: 0.0002%

Table 1: Typical Group of 10 Calibration Factors

**Table 2: Temperate Response of the Calfactor**

An estimate of the two-sigma uncertainty of the electronics has been completed and a paper drafted. Table 3 is shown for information purpose to see the relative contributors to the uncertainty of the electronics.

**Table 3: Estimated Two-Sigma Uncertainty of the Electronics**

METHODOLOGY

Traceability of plutonium and neptunium measurements by controlled-potential coulometry

The SRS controlled-potential coulometric measurement method is recognized as a definitive method, traceable to the international measurement system through electrical and mass standards.⁸ The methodology is typically validated and the uncertainty estimated using a traceable certified reference material, such as CRM 126 plutonium metal. For the controlled-potential coulometric measurement of plutonium using procedural standard ISO12183:2005, the Savannah River Site has consistently demonstrated a measurement uncertainty on the order of 0.1% (1-sigma), or better, using this methodology.^{1,2,3,6,7,9,10}

Savannah River National Laboratory

The Savannah River National Laboratory (SRNL) organization performs numerous research and development functions as well as technical and engineering support functions for the SRS operations organizations, DOE-Headquarters programs, NNSA programs, Homeland Security programs, other DOE contractors, and international programs including support to the Department of State – International Safeguards Program Office (ISPO).

SRS Analytical Laboratories

The SRS Analytical Laboratories organization provides analytical measurement and services to the SRS operations and programmatic organizations. Measurement services include destructive and nondestructive measurements that support material control and accountability, nuclear criticality safety, process control, waste acceptance criteria, regulatory compliance, environmental monitoring, internal dosimetry (bioassay), and industrial hygiene measurements. The Analytical Laboratories staff collaborates with the SRNL staff and also provides technical support and measurement services to many of the same external customers that receive support from the SRNL.

CONCLUSIONS

SRNL and the SRS Analytical Laboratories have successfully completed a major electronics upgrade of their automated controlled-potential coulometer with improved performance, ease of calibration and troubleshooting. Circuits have been upgraded with state-of-art set of electronic components readily available. The Agilent™ 34980A data acquisition system has demonstrated excellent performance and is ideally suited for the application.

Future plans include converting the 10,000 lines of HT Basic instrument control software to National Instruments Labview™ platform to provide an enhanced user interface. The IEEE-488 bus will be eliminated and industrial Ethernet will be used to communicate with the DAS.

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REFERENCES

1. Holland, M. K., and Cordaro, J. V., 1988. U.S. Department of Energy Publication DP-1751, "An Automated Instrument for Controlled-Potential Coulometry: System Documentation.
2. Holland, M.K., Weiss, J. R., and Pietri, C. E., "Controlled Potential Coulometric Determination of Plutonium," *Anal. Chem.*, 50, 236 (1978).
3. Holland, M. K., Weiss, J. R., and Pietri, C. E., "A Reference Method for the Determination of Plutonium Using Controlled Potential Coulometry," printed in the proceedings of the 3rd ESARDA Symposium on Safeguards and Nuclear Material Management, Karlsruhe, F. R. Germany, May 6-8, 1981.
4. ISO 12183:2005, "Controlled-Potential Coulometric Assay of Plutonium"
5. American Society for Testing and Materials. 1991. Annual Book of Standards, Volume 12.01 Nuclear Energy (I), ASTM C1108-88, "Standard Test Method for Plutonium by Controlled-Potential Coulometry."
6. Frazzini, T. L., Holland, M. K., Weiss, J. R., and Pietri, C. E., "A Digital Integrator for Controlled-Potential Coulometry," *Anal. Chem. Acta*, 129, 125 (1981).
7. Holland, M. K., Cordaro, J. V., Fields, T. C., and Reeves, G. E., 1998. "Automated Controlled-Potential Coulometer for the IAEA," Proceedings from the 6th International Conference on Nuclear Engineering, San Diego, California, USA.
8. Uriano, G. A. and Gravatt, C. C. "The Role of Reference Materials and Reference Methods in Chemical Analysis," *SRS Critical reviews in Analytical Chemistry*, p361, October 1977.
9. Holland, M. K., Cordaro, J. V., Fields, T. C., and Reeves, G. E., and Kuno, T., "SRS Controlled-Potential Coulometer," Institute of Nuclear Material Management (INMM) 40th annual meeting, July 1999.
10. Holland, M. K., Nuessle, P. R., and Nichols, S. T., unpublished work. [Measurement results from routine internal quality control standards and external exchange program standards are retained in the laboratory information management system and associated quality control monitor (LIMS-QAM).]
11. Nuessle, P. R. and Holland, M. K., unpublished work. [A technical report is in preparation.]
12. ISO 7476:2003, "Determination of uranium in uranyl nitrate solutions of nuclear grade quality – gravimetric method."