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SRS Controlled-Potential Coulometer

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Abstract

The Savannah River Site has the analytical measurement capability to perform high-precision plutonium concentration measurements by controlled-potential coulometry. State-of-the-art controlled-potential coulometers were fabricated by the SRS Engineered Equipment and Systems Department and installed in the Analytical Laboratories' process control laboratory. The Analytical Laboratories uses coulometry for routine accountability measurements of pure plutonium from the PUREX process and for verification of standard preparations used to calibrate other plutonium measurement systems routinely applied to process control, nuclear safety, and other accountability applications. The SRS Coulometer has a demonstrated measurement reliability of ~0.05% for 10 mg samples. The system has also been applied to the characterization of neptunium standard solutions with a comparable reliability.

The SRS coulometer features: a patented current integration system; continuous electrical calibration versus Faraday's Constants and Ohm's Law; the control-potential adjustment technique for enhanced application of the Nernst Equation; a wide operating room temperature range; and a fully automated instrument control and data acquisition capability. The system has been operated for 10 years with minimal equipment failures and downtime. The coulometer and instrument controller have been periodically upgraded to remain current with available high-precision potential control and current integration components. A stability of ± 0.0015% RSD for the electronic calibration factor has been demonstrated. Most recently the system was converted from an Hewlett Packard computer platform to an IBM Computer / Windows based system.

SRS Coulometers were installed at the Tokai-mura Reprocessing Facility in Japan in February 1999 and at the Mayak Production Association in Ozersk Russia in October 1998.

Introduction

The Savannah River Site (SRS) has been building Controlled-Potential Coulometer for 15 years. The work has been completed by a team from two site departments, the Engineering Equipment and Systems Department (part of the Savannah River Technology Center) and the Analytical Laboratories Department (part of the Technical Services Division). 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. Throughout this period, the system electronics, computer hardware, software and cell design have undergone improvement. Between 1985 and 1995, two systems were built for the site Analytical Laboratories, one system for Rocky Flats, and one system for the IAEA. This paper will focus on the two systems most recently delivered in January 1999 to the Tokai-mura Reprocessing Facility in Japan. This paper contains drawings of the JNC system and results from testing at SRS and JNC. The hardware required to convert the system from a Hewlett Packard to a IBM/Windows platform is covered. New features of the control software as well as the method used for measuring and calibrating key system components is covered. The system delivered to the Mayak Production Facility in Ozersk Russia is essentially the same as the JNC systems except all components including the computer hardware were rack mounted.

Hardware

In 1997 Hewlett Packard stopped making their scientific computers running HP Basic. The interface boards such as the IEEE-488 and GPIO which plugged into their computer bus were also discontinued. As a result, the Mayak and Tokai-mura systems required a switch to an IBM platform using EISA bus interface cards and running a new product HP Basic for Microsoft Windows. The Hewlett Packard frequency counters used in the IAEA system were replaced with an EG&G Ortec Model 974 Quad Counter. This counter fits into a 2 width standard NIM opening. Figure 1 shows a diagram of the system.

The Ortec 974 Counter has four channels. Channel one is a timer with 0.1 sec resolution and is not used during automatic operation. Channels 2,3 and 4 totalize counts from the Digital Integrator. A key feature of this counter is that all channels can be read on the fly without the loss of any counts. The counter requires DC voltages of +/- 6 VDC and + 12 VDC. An option with standard NIM Bin's is three dual output supplies which include; +/- 6 VDC, +/- 12 VDC and +/- 24 VDC. The 12 and 24 Volt supplies are used in the Potentiostat Module and these voltage must be completely isolated from Digital Ground. This includes the ground for the counter. The 6 Volt supply is wired internally with the 12 and 24 Volt supplies. Therefore, a completing isolated 6 and 12 Volt supply was needed.

The HP 34907A unit is the size of a half rack voltmeter. It has three slots for interface boards. One slot contains the digital output board which replaces the GPIO interface and the second slot contains a multiplexer for use with the internal digital voltmeter.

Some special features incorporated into the Tokai-mura system included a four channel RS232 Interface (see drawing EES-22686-L6-002 in the appendix) to communicate with other exiting devices. Also, due to space limitations, the two coulometer systems shared a common screen/keyboard/mouse using a Black Box switching unit.

The Mayak system was installed into a standard 19 inch rack (see drawing EES-22562-L0-001 in the appendix). All hardware including the computer, monitor and keyboard were rack mounted. This arrangement allowed for easy maintenance from the rear and minimized cable length.

Electronic Calibration and Alignment

Before using the system is used for sample measurement, the value of certain key components must be determined or their outputs calibrated. The following components must be calibrated:

1. Determine the value of the 100 ohm calibration resistor for Potentiostat #1
2. Determine the value of the load resistor for Potentiostat #1
3. Determine the value of the load resistor for Potentiostat #2
4. Calibrate the Digital Integrator clock
5. Align the Digital Integrator voltage to frequency convertors

To determine the most accurate value of the 100 ohm calibration resistor or the 50 load resistor, the resistors must be measured in place. In the case of the 50 load resistor, the true value of the load resistor (as shown in figure 2) is the equivalent impedance of the 50 [Omega] load resistor in parallel with the input impedance of the digital integrator. Since the input impedance of the digital integrator is approximately 20 k[Omega], it has a significant effect on the actual load impedance value. In the case of the 100[Omega] calibration resistor, it is easier to measure the value in place. This method will ensure that the resistance of printed circuit board traces and solder joints are included. To measure the load impedance, a cell cable was connected to the Automation module and a 100 [Omega] standard resistor was connected the cell cable as shown in figure 2. The HP3458 Digital Voltmeter was then connected across the 100 [Omega] standard resistor. The Potentiostat was turned on and current flowed through the circuit as shown. The value of the load impedance and the calibration resistor is:

To calibrate the Digital Integrator clock, the output was monitored by an Hewlett Packard 5316 frequency counter, and the frequency set to 10.00001 kHz.

To complete the Digital Integrator alignment, the offset Voltage to Frequency Converter (VFC) is set to 1600 Hz. The readout VFC, which combines the counts from the offset VFC and the actual readout counts is then calibrated with a precision voltage source, Fluke 343A, that is verified with the HP34970A. Below is the "As Left" results of the alignment of the Digital Integrator for JNC system #1.

Applied Voltage Fluke 343A as read on HP 34970A	JNC Coulometer #1 Integrator Output Units Hz	Error Hz or Counts per second	% Error of Reading
1.00000	11,599.99	0.01	0.000086 %
2.00000	21,600.07	0.07	0.00032 %
3.00000	31,600.1	0.1	0.00032 %
4.00000	41,600.2	0.2	0.00048 %
5.00000	51,600.3	0.3	0.00058 %
6.00000	61,600.4	0.4	0.00058 %
7.00000	71,600.4	0.4	0.00056 %
8.00000	81,600.3	0.3	0.00037 %
9.00000	91,600.2	0.2	0.00022 %

The calibration factor has the units of coulombs per million counts and is equal to the inverse of the load impedance multiplied by the digital integrator response. The equation is:

If the output of the digital integrator is exactly 10,000 cts/sec/volt and the calibration factor is stated in the units of coulombs per million counts, the calibration factor becomes the inverse of the load impedance multiplied by 100. This is the theoretical calibration factor. In the case of the JNC system #1, the load impedance was determined to be 49.9431 ohms. Therefore the theoretical calibration factor should be 2.00228. A typical calibration factor based on the average of 10 factors from a 500 second calibration run was 2.0022 after warm up. This factor will change slightly with temperature and correct itself for normal drift of components. The typical standard deviation for a run of 10 factors was less than 0.0005% when the temperature of the system was stable.

Software

The transformation of the existing HP Basic code to HP Basic for Windows overall went well. The drivers for the new hardware had to be updated and screens reformatted. New features were added at the request of the customers. Three files are written to on the hard drive during operation. The 1st "samples.dat", contains all sample data since the file was created. The 2nd file "calib.dat", contains all electrical calibration data since the file was created. The 3rd "linear.dat", contains all linearity testing data since the file was created. The following are examples:

In response to requests from our customers, new software options were incorporated. See flow charts 1 and 2 shown in the attachments for details.

Results and Discussion

Prior to shipping the two systems to Japan testing with samples and standards was performed at the SRS Central Laboratory. Results from acceptance testing using plutonium measurement are detailed below:

Plutonium Measurements in Advance of Visit from T. Kuno, Jnc *:

Electrolyte / Working Electrode	Coulometer System #1 Percent Recovery	Coulometer System #2 Percent Recovery
H_2SO_4 / Platinum	100.01 100.03	100.02 100.02
HNO_3 / Gold	99.97	99.96

Plutonium Measurements in Advance of Visit from T. Kuno, Jnc *:

Electrolyte / Working Electrode	Coulometer System #1 Percent Recovery	Coulometer System #2 Percent Recovery
H_2SO_4 / Platinum	99.99 100.01 100.00 100.05	99.97 99.96 99.97 100.01
HNO_3 / Gold	100.10	
HNO_3 / Platinum {Non-routine for SRS}	100.00	
H_2SO_4 / Gold {Non-Routine for SRS}	99.87	

**Documentation was provided to T. Kuno for all plutonium results from both the pre-visit testing and those observed by T. Kuno. During the course of testing the SRS Coulometer for JNC, several measurement results* *were excluded from the acceptance testing when the cause for the poor plutonium recovery was proven to the SRS measurement cell, which is not part of the system being supplied to JNC. Results from non-routine supporting electrolyte and electrode combinations are provided for information only. All results have been decay corrected to October 98 and fully buoyancy corrected for all weight/mass measurements.*

During the acceptance testing at SRS, the observed precision for plutonium measurements using the coulometers provided for JNC and the routine SRS measurement method in sulfuric acid at a platinum electrode was: 0.03% relative standard deviation with a mean recovery 99.99%.

As part of the task to build two systems for JNC, SRS personnel assisted JNC with measurements at the Tokai-mura facility. Plutonium measurements were performed on standards prepared by JNC Laboratory from U. S. Department of Energy, New Brunswick Laboratory's CRM-126 plutonium metal. In general, measurement results tracked extremely well with apparent electrode and electrolyte performance and conditioning. The electrode/electrolyte performance for SRS JNC Cell 2 was significantly better than JNC Cell 1. In addition, one plutonium standard measurement was performed in nitric acid supporting electrolyte (100.04% recovery). For JNC system #2, the mean plutonium recovery percent and relative standard deviation were 100.01% and 0.09%, respectively, excluding one piece of data on a statistical basis in thirteen measurements. Data from system #2 is shown below:

Measurement Results of Pu Standard Solution (System #2)

		Blank*1		**Standard*2**					**Notes**
Std. No	**Mea. Date**	**Count/mC**	**Pu/mg**	**Ref./mg**	**Pu/mg*3**	**Pu/mg*4**	**Recovery/%*5**	**Oxi./sec*6**	
29	990129	0.013	0.032	5.5633	5.562706	5.563517	100.004	741.929	
29	990129	0.013	0.032	5.5633	5.562263	5.562768	99.990	724.072	2nd Run
4-2	990202	0.01	0.025	19.6360	19.660821	19.6590	100.117	1351.143	
4-2	990202	0.01	0.025	19.6360	19.657814	19.6541	100.092	1359.81	2nd Run
3-2	990202	0.014	0.036	15.2090	15.204807	15.2169	100.052	2741.747	
3-2	990202	0.014	0.036	15.2090	15.265568	15.2660	100.375	2253.881	2nd Run
30	990203	0.012	0.030	5.5648	5.571115	5.569185	100.079	636.273	
27	990203	0.012	0.030	5.5467	5.542742	5.547927	100.022	820.698	
24	990203	0.011	0.027	5.5608	5.533562	5.552902	99.858	1211.464	
28	990204	0.012	0.030	5.5613	5.560495	5.56069	99.989	758.209	
37	990204	0.013	0.031	5.5658	5.558748	5.56293	99.948	807.475	
32	990204	0.012	0.029	5.5628	5.543414	5.554274	99.847	998.419	
18	990204	0.013	0.031	5.5708	5.51665	5.543594	99.512	1619.737	Outlier
14	990204	0.014	0.036	5.577	5.586531	5.581569	100.077	495.042	
10	990205	0.013	0.033	5.574	5.588062	5.579585	100.104	526.317	
2*7	990205	0.021	0.052	5.570	5.567655	5.572223	100.035	686.448	

*1:05.5M H2S04
*2:RPL-PuST-31 or RPL-PuST-32(1-1~4-6
*3:Cutoff Calculation (JNC Method)
*4:SRS Calculation (Recommended Method)
*5:(SRS value/Ref.value)*100
*6:SRS oxidation time
*7:In 0.8M HNO3

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Appendix A

1. Figure #1 System Block Diagram
2. Figure #2 Resistance Measurement Setup
3. Flow Chart #1 Software Main Menu
4. Flow Char #2 Software Sub Menu
5. EES-22686-L0-001, PNC Rack Arrangement
6. EES-22686-L6-002, PNC Interconnection Diagram
7. EES-22686-L8-003, Cable Wiring Diagram
8. EES-22686-L2-004, Coulometer Power Supply Chassis
9. EES-22686-L2-005, Digital I/O and Analog Output Panel
10. EES-22686-L2-006, Ortec 974/NIM Bin Wiring Mods
11. EES-22562-L0-001, Mayak Coulometer Rack Layout