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Development of the Savannah River National Laboratory (SRNL) Controlled-Potential Coulometer and its role on International Safeguards: Past, Present, Future

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ABSTRACT

The accurate determination of plutonium (Pu) mass in nuclear materials is essential to nuclear material accountancy and international safeguard programs. Controlled-Potential Coulometry (CPC) is one of the best available analytical methods to perform such measurements. Built and certified by the Savannah River National Laboratory (SRNL), the CPC instruments are used to measure the mass fraction of plutonium in solutions and solids. This article presents a history of the development of the SRNL CPC and its role in International Safeguards.

INTRODUCTION

Plutonium controlled-potential coulometric (CPC) assay method serves an important role for many programs of both national and international importance. This method is used in many of the United States Department of Energy (US DOE) missions, for example national security, research and development, material control and accountability, and certification of standards. Many non-destructive assay instruments used throughout the US DOE complex are calibrated with matrix matched standards that were standardized against assays provided by the CPC method.

Built and certified by the Savannah River National Laboratory (SRNL), previously referred as the Savannah River Site (SRS), the CPC instrument is used to measure the concentration of plutonium in solutions. The SRNL-supplied CPC is the instrument of choice for safeguards applications. The instrument is calibrated electronically, independent of certified reference material and standards. The instrument allows for definitive measurements based upon first principles and traceable, electrical calibration of the instrument. . The metrological traceability is provided to the international measurement system (SI). Periodic measurement of primary standard plutonium metal, or equivalent reference, working standards, or exchange materials, support the demonstration of the performance of the measurement system.

BACKGROUND

In controlled-potential coulometry, plutonium is quantitatively electrolyzed at an electrode whose potential is maintained at a value that will prevent unwanted reactions. The potential is controlled by the use of a potentiostat. The measured current is directly related to the quantity of plutonium in the solution, using a form of Faraday's Law. This contributes to the technique's high precision and accuracy. Its robustness and simple operation make it the technique of choice for Pu quantification.

Precisions of 0.1 % relative standard deviation (RSD) or better are common. There are well established theory and equations relating the measured current to the quantity of plutonium in the solution. There are several options for electrolyte and electrode configurations. SRS routine method uses sulfuric acid electrolyte with a platinum electrode. In 0.5 M sulfuric acid, the Pu (III)/Pu(IV) plutonium redox couple has very few interferences - only iron. In addition, the technique is reliable, and sample preparation is simple.

PAST

Controlled-potential coulometry was introduced in the early 1940s.[1] It wasn't until the 1950s that it started to be used more extensively, as has been documented in several papers[2]. The first generation of coulometers were commercially available instruments. These instruments used analog-integrators. The precision achieved with the instruments was greater than 0.1 % RSD. The instruments required manual set-up and adjustments. Major drawbacks were capacitor leakage and dielectric absorption. In addition, they usually required long electrolysis times.

Developments in electronics and instrumentation played a key role in the improvements. The availability of digital integrators in the late 1960s prompted the development of digital-integrator coulometers. These became the second-generation coulometers. Still commercially available instruments, that claimed a precision equal to that of coulometers with analog-integrators. Other developments included the use of predictive and empirical end-point determinations in an effort to reduce electrolysis time by eliminating the need for electrolysis completion. However, the calculations were time consuming.

These improvements and developments prompted the emergence of third generation digital-integrators in coulometers specifically designed to analyze plutonium and improve the precision. The first of these instruments was developed at the US Department of Energy's New Brunswick Laboratory (US DOE NBL) by T. L. Frazzini and M. K. Holland. In 1981 they patented a digital integrator circuit design.[3] Other improvements included a non-empirical method independent of the exponential decay equation for determining plutonium assay, utilizing the Faraday constant and the Nernst equation, that allowed the calculation of 99.6 % to 99.8 % of the sample. This reduced electrolysis time by 40 % without loss of precision or accuracy. In addition, they also implemented cell modifications with increased electrode surface and improved stirring. The improved stirring minimizes the diffusion layer thickness, which in turn minimizes the analysis time.

PRESENT

In 1984, M. K. Holland, one of the key developers at US DOE NBL, started working at SRS and began collaborating with J. V. Cordaro on instrument design and method implementation. This prompted a significant expansion of the coulometry work at SRS. Throughout the years, the system electronics, computer hardware, software and cell design have undergone improvements. The SRS CPC system is based on work originally completed at US DOE NBL. The first generation of the system developed at SRS used custom electronics installed in NIM modules with switches and dials. The first system at SRS was put into operation in 1986, a second followed in 1988. A third instrument was built for the laboratory at Rocky Flats in 1989, and in 1995 a system was built was for the IAEA's Safeguards Analytical Laboratory. The instrument at SRS was used to support accountability measurements and several production campaigns where plutonium assay determinations with high precision were crucial.

The first upgrade of the SRS 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 configuration, 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).

In June 1995, a SRS coulometer was installed in the IAEA's Safeguards Analytical Laboratory (SAL) in Seibersdorf, Austria, and cold testing using iron as a surrogate for plutonium was performed by the IAEA staff. In June 1996, final hot testing was jointly performed by SRS and IAEA personnel. In 1998, an upgraded CPC was developed at the SRS for the detection of plutonium for use at SAL. The system was functionally the same as earlier systems, but all electronic circuits and printed circuit boards were upgraded with state-of-the-art components. A higher amperage potentiostat with improved control potential stability was developed. The system achieved electronic calibration accuracy and linearity of better than 0.01 %, with a precision of better than 0.001 % and a temperature stability of 0.001 % per degree Celsius. Plutonium measurement precision and accuracy better than 0.05 % RSD was demonstrated.

This coulometer featured electrical calibration of the integration system, electrolysis current background corrections, and control-potential adjustment capabilities. These capabilities allow measurements of plutonium without chemical standards, and achieve metrological traceability to the international measurement system through electrical standards and the Faraday's constant. Extensive work was also performed on a new SRS-designed coulometer cell that will allow for lower amounts of plutonium, while maintaining the same accuracy and precision.

In 1998, SRS fabricated and installed a SRS-designed Coulometer at the Mayak Laboratory, in Ozersk, Russia.

In January of 1999, two SRS coulometers fabricated for the Japan Nuclear Cycle Development Institute (JNC) were installed and tested by SRS personnel at the JNC Facility in Tokai-mura, Japan.

In 2003, the US DOE NBL (currently the NBL Program Office) acquired two SRS coulometers. These coulometers included an updated version of the HT Basic program that consisting of one instrument control software, with parameter files that that could be configured for individual needs.

In 2004, the NBL cells were upgraded to the SRS design. These instruments were used by the NBL in the characterization of CRM C126-A.

In 2010, a second upgrade of the electronics and data acquisition system was completed for a new coulometer for the International Atomic Energy Agency's Nuclear Material Laboratory (IAEA NML). The system was delivered in May 2011. Many of the original components of the instrument were obsolete or nearly so. To ensure long term viability of the SRS instrument, a complete electronics and data acquisition system upgrade was completed. All electronics were combined on a large multilayer printed circuit board with individual isolated ground and power planes. All switches, knobs and batteries were eliminated in favor of floating high resolution digital-to-analog converters. The HT Basic software used to control the coulometer was also updated with new features and drivers to accommodate the electronics and data acquisition hardware.

The same version of the instrument delivered at IAEA was delivered and installed at Los Alamos National Laboratory's Chemistry and Metallurgy Research Facility (LANL CMR) in 2011. As part of the DOE nuclear facilities upgrade process and in support of NNSA's Plutonium Production Program, Actinide Analytical Chemistry group of Chemistry division (C-AAC) is moving into new laboratory space at TA-55's Radiological Laboratory Utility Office Building (RLUOB). In 2019, SRS delivered to LANL RLUOB two instruments. The instruments were assembled, tested, and personnel were trained. In 2021, SRS personnel returned to assemble a third instrument that had been delivered in 2020.

In 2020, the SRS Analytical Laboratory became part of the Savannah River National Laboratory (SRNL). This included the consolidation of the laboratory by physically moving the Analytical Laboratory from a SRS's area to the SRNL facility. This move included the upgrade of the coulometer instrument to the new version already at IAEA and LANL laboratories.

In 2022, the HT Basic instrument control software program was replaced with LabVIEW software, funded by U. S. Department of State for implementation at the IAEA NML. The program was delivered, installed and tested at the IAEA in April 2022.

Figure 1. SRNL coulometer instrument. From left to right: first SRNL design, second design, and current instrument.

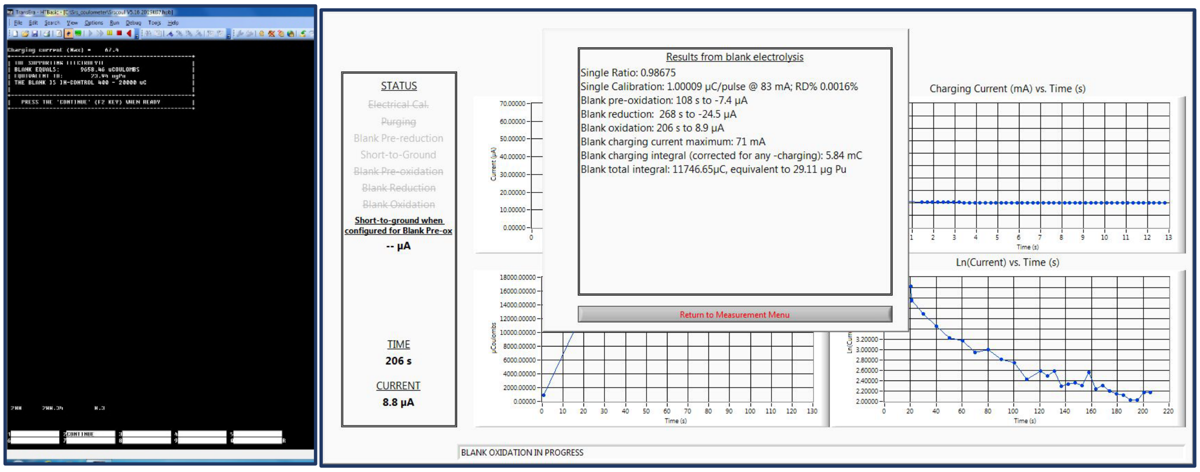

Figure 2. Output of the instrument results for blank determination. On the left output from HT Basic program, on right output from LabVIEW program.

Future

In the near future, SRNL will continue with the development of the LabVIEW program. The addition of the determination of neptunium (Np) will be of high importance for future development of a neptunium certified reference material.

SRNL will continue to adapt and update the SRNL coulometer to maintain its high precision and accuracy for plutonium assay.

Conclusions

Since its first development in the 1980s at DOE NBL, to the most recent upgrade of the program there has always been one objective; to deliver reliable and traceable results of plutonium assay with the highest precision and accuracy. The instrument has undergone electronic upgrades, software upgrades, and cell upgrades. All these upgrades together have made it possible for SRNL controlled-potential coulometry to continue being the preferred instrument in the nuclear industry.

Acknowledgments

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[1] A. Hickling, Trans. Faraday Soc., 38, 27(1942)
[2] J. E. Harrar, Techniques Apparatus, and Analytical Applications of Controlled-potential Coulometry, Electroanalytical Chemistry, A. J. Bard, Marcel Dekker, 1975, Vol. 8, Chapter 1

[3] Patent 42448001 , Jan 13, 1981,APPARATUS FOR USE IN RAPID AND ACCURATE CONTROLLED-POTENTIAL COULOMETRIC ANALYSIS