Plutonium Assay By
Controlled Potential Coulometry

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ABSTRACT

A commercial multipurpose electroanalysis system has been evaluated for precision assay of plutonium by controlled potential coulometry. Instrument design necessitated the use of electronic digital integration of electrolysis current instead of the more common capacitance type integration. Precision of individual results was 100 ± 0.15 percent at the 95 percent confidence level.

INTRODUCTION

The purpose of this paper is twofold. The first purpose is to report results of an evaluation of Beckman's Electroscan 30 as a controlled potential coulometer. The second is to describe the general procedure as adapted to this instrument for the controlled coulometric analysis of plutonium.

Controlled Potential Coulometry has been documented by previous investigators. (1)(2) Initial investigation of the use of Controlled Potential Coulometry to perform plutonium assay was demonstrated at Hanford by Scott and Peekema (3) as well as Shults (4) at Oak Ridge. Through their work, Controlled Potential Coulometry is now a primary assay technique at a number of AEC installations, such as Livermore, Oak Ridge, and Hanford.

One of the functions of Atlantic Richfield Hanford Company's Plutonium Finishing Analytical Laboratory is to assay all forms of plutonium. In past years, Plutonium Finishing Laboratory has performed assays by use of a Titanous reduction and Ceric Sulphate oxidation titration. (5) This method has existed as a "workhorse" assay method on a variety of plutonium samples matrices. However, the time necessary in preparation of plutonium nitrate solutions and mixed plutonium-uranium oxide makes it difficult to obtain a significant throughput of samples.

Plutonium nitrate solutions must be fumed to dryness to destroy nitrate ions that will interfere with the titration. Mixed plutonium-uranium oxide samples must undergo a preliminary chemical separation to remove interfering uranium in addition to being fumed. A pressing need for a faster and more efficient method than the ceric sulphate titration became apparent with the emphasis by the government on fast breeder reactors. Fast breeder reactors utilize fuel elements consisting of varying percentages of uranium and plutonium oxide. Alternate methods of assay considered were X-ray fluorescence, differential spectrophotometry amperometric titration and isotopic dilution. Methods depending on the X-ray fluorescence of plutonium with gross quantities of uranium present are inherently incapable of delivering precisions greater than 1%. (6) Differential spectrophotometry routinely delivers a precision reliability of $\approx \pm 0.2\%$, a "state of the art" spectrophotometer must be used. Amperometric titration of plutonium with ferrous species is capable of a reliability well within $\pm 0.1\%$. However, amperometric titrations require a fuming step with sulfuric acid to remove nitrate interferences. (8) Isotopic dilution techniques are capable of $\pm 0.2\%$ with weighed aliquot dilutions, but require lengthy analyses and require the use of the already burdened mass spectrometers of the Plutonium Finishing Laboratory. (9)

Controlled Potential Coulometry describes by its name one of its prime advantages as an assay technique. With this method, one can accurately select and control the specific potential of an electrode in a titration, thus eliminating interfering ions. Uranium and iron, which are prime interferences in the chemical assay procedure, can be easily accommodated with controlled potential coulometry. Uranium is effectively eliminated in a titration since its redox couple is $\approx 700\text{mv}$ below that of plutonium. (Table I) The interferences of iron, whose couple is nearer to that of plutonium's, can be minimized by judicious selection of supporting electrolyte and working electrode potential. Scott described techniques in which titrations are prevented from reaching complete oxidation. He thereby completely eliminated iron as an interference.

TABLE I
FORMAL REDOX POTENTIALS OF Pu^{III} - Pu^{IV} (10)

Medium	Conc. <u>M</u>	E ^o volt vs. S.C.E.		
		Pu^{a}	Fe^{a}	U^{b}
HClO_3 HCl	1.0	0.715	0.465	
	0.1	0.76	0.51	
	0.25	0.75	0.49	
	1.0	0.72	0.45	
HNO_3	0.5	0.69	0.48	
	1.0	0.69		
	1.5	0.65		
H_2SO_4	0.25	0.50		
	0.5	0.49	0.45	
	1.0	0.48	0.45	-0.15v
AlCl_3 HCl	0.2	0.72	0.48	
	0.2			
AlCl_3 HCl	0.5	0.71	0.47	
	1.0			

- a) Potential at Pt electrode
b) Potentials at Hg electrode

In the late 1950's, when Controlled Potential Coulometry was receiving increased attention as an analytical method, work was begun at Plutonium Finishing Analytical Laboratory to utilize the technique in plutonium assay. This work was subsequently abandoned because of potentiostat instability. Re-evaluation of the instrument used in initial work indicated that failure could be attributed to poor instrument design. No further work was done until the present when the previously described needs prompted re-investigation. The analytical technique utilizing Controlled Potential Coulometry has become fairly standardized and instrumentation

is readily available that satisfies requirements for high current capacity, rapid response, stable potential control, and high sensitivity.

DISCUSSION

The Electroscan was designed as a multi-purpose instrument and as such, design compromises were made to insure stability in all modes of operation.

Dr. Booman in his paper, "Electroanalytical Controlled Potential Instrumentation," describes the measurement of the transfer function or output to input signal ratio of the electrochemical cell and amplifier systems used in a controlled potential coulometer to design appropriate compromises into the cell and instrument. Ideally, these measurements will result in modifications that will mate the electrolysis cell to the coulometer while maximizing system stability and sensitivity.

"The require bandwidth or usable frequency range for a potentiostat depends on the following factors: the response time desired for the external input signal; the measuring electrode potential that can be tolerated; the frequency amplitude characteristic of the potential disturbance generated by geometry and concentration gradients in the cell; and cell resistance or other caused by variations in cell current." (11)

To generate the necessary stability in an operational amplifier configuration, gain decreases as frequency increases.

The Electroscan's open loop response or ratio of output voltage to error voltage can be described by the following terms:

1. Rolloff from $5H_z = 8\text{db}$ per octave, this describes the amplifiers decreasing gain as a function of frequency, i.e., a change from $5H_z$ to $10H_z$ results in a loss in gain of 8db.
2. Unity gain crossover at 50KHz (Figure I). Most wide band operational amplifier, configurations have unity gain crossovers of 1MHz or beyond. The importance of high gain at high frequencies is seen in the requirement for fast response of the potentiostat to error signals. High gain in this instance is equated with fast response. Slewing speed or voltage response of the Electroscan is 2 volts per millisecond when system current is 400 μ a through a cell of 5000 Ω . This is a relatively slow response time for amplifiers systems that may respond as fast as 250 volts per microsecond to error signals. (12)

For cells using solid electrodes, noise which can result from area changes during anodic dissolution, gas bubble formation, electropolishing effects, erosion of rough spots, and other possible geometry changes affect bandwidth requirements of the potentiostat. For this work, I have used Scott's trident configuration cell which utilizes a helium sparge for forced agitation. Undoubtedly, this type of mixing was adversely affecting the available bandwidth of the instrument. Measurement of the closed loop gain of the system

or the gain of the potentiostat with the negative feedback of the electrolysis cell confirmed this; closed loop gain was 2.5 or 7.5db. This results in an extremely small available bandwidth of 11 KHz.

The loop gain of a system is defined as the ratio of the open to closed loop response of a system at a particular frequency. Note, in Figure I, the high loop gain at 4000 at DC signal; note also, at 2KHz how the loop gain has fallen to 4. The sparse rate of the cell makes it extremely likely that error corrections must be made at or near 1000 Hz and the voltage response of this system can be expected to be characteristically slow.

When in operation, only three controls are manipulated on the instrument for controlled potential analyses: the current span, initial voltage, and electrolysis switch. The current span control selects the appropriate load resistor to adjust recorder output and sensitivity. There is no allowance made in the construction of the instrument for constant potentiostat operation between titrations. Instead, the potentiostat must be disabled and oxidation or reduction potentials reset by use of the 10 turn, 5 volt, "initial voltage" potentiometer. As much as ± 1 mv error can be introduced to the correct redox potential setting through the inherent imprecision of the potentiometer.

In order to allow the method to be competitive with the precisions obtained with amperometric and potentiometric titrations, two types of data collection were considered.

1. Capacitance integration of current.
2. Digital integration.

Current integration on most coulometers is generally performed by an operational amplifier-capacitance integrator.⁽¹³⁾ Inspection of the Electroscan's circuitry showed that this type of integration was undesirable because of its floating output. While an integrator could be easily built with inputs above ground, it was felt that undue strain would be placed on the potentiostat causing possible instability.

An alternate method of integration, which fits this application, was the use of voltage to frequency conversion of current through a voltage drop as described by Bard and Solon.⁽¹⁴⁾ The voltage to frequency converter (VFC) that was used was designed for floating operation with a high impedance input. Initial expense for this type of integration is relatively high, $\approx$ \$1,000 as compared to \$100-200 for capacitance integration. The added usefulness as a precise, time averaging, mobile, digital integrator for many instruments in the laboratory helped to justify the added cost.

Nominal output of the Hewlett-Packard MOD-2212 VFC KHz for a 1 volt input. A factory modification was requested allowing the converter to overrange inputs by as much as 3.5 times.

The converter is calibrated for operation by shorting the reference and auxiliary electrodes and placing a calibrated precision resistor, 50-150 Ω across the working and reference electrode. The potentiostat is placed in

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FIGURE 1

operation and an appropriate voltage is generated across the resistor to drive the pen movement to full scale for the particular current span being used, i.e., 70ma span, 700mv is generated across a 10Ω resistor. The output frequency of the converter then corresponds to full scale output of the potentiostats electrometer.

Through appropriate setting of the converter's range control, the readout of accumulated counts can indicate directly micro equivalents or milligrams of sample. Although the voltage to frequency converter is designed to work with resistances of $1,000\Omega$ or less, it can also handle signals with resistances of greater than $1,000\Omega$. However, zero frequency drift at higher source resistances significantly derates the performance of the system.

Source resistances of 200Ω or less correspond to 7-14ma current ranges. Titration of 40-400 μg plutonium may be carried out with fair precision on the 7ma range. This range must be specifically calibrated to the VFC and the instrument is then limited to the 40-400 μg range. Rather than limit the precision available to the system by use of a small sample size, the converter is calibrated to the instruments 70ma range and samples of 4mg plutonium are titrated. Maximum current limitations of the instrument, along with cell design, limit titrations to less than 8mg.

Figure II shows a block diagram representation of the coulometer system, Cut off current was experimentally established for each set of operating conditions. Current was monitored by both the recorder chart and by a frequency meter placed in parallel with the VFC. Titrations of $\text{Pu}(\text{NO}_3)_4$ and plutonium metal dissolutions were terminated at $10\mu\text{a}$ or less; plutonium oxide dissolutions were terminated when residual current reached $20\mu\text{a}$ or less. When output of the VFC reaches 4Hz, residual current in the cell is $20\mu\text{a}$. A response of 4Hz for 60 seconds corresponds to $1\mu\text{gm}$ of plutonium..

The instruments supplied by Beckman was procured with a disc integrator. The disc movement integrates area under the electrolysis curve. When pen movement is at full scale, the integrator pulses an electronic accumulator at 140 pulses/second. Mechanical integration has been found by previous investigators to be incapable of the precision and speed necessary for controlled potential coulometry. Titrations were carried out on 1-2mg of Fe to test the operation of this integrator. Results were $\pm 0.4\%$ at the 95% limit, which is within the error expected from this type of integration.

INTERFERENCES

Due to the nature of preparation of plutonium products, samples are almost free of interferences. The major interference in plutonium titrations is generally iron. In this procedure, Fe interferes only when Pu:Fe ratios of less than 50:1 are reached. In extreme cases, the ratio of Pu:Fe in $\text{Pu}(\text{NO}_3)_4$ solutions would never approach less than 100:1.

Because of the strong complexing action of sulphate on Pu^{IV} and the resultant shift in redox potential, only small amounts of sulphate can be tolerated. Sulphate concentration is closely monitored in process streams and products

BLOCK DIAGRAM
ELECTROSCAN-30

FIGURE 2

because of the insolubility of $\text{Pu}(\text{SO}_4)_2$ and its effect on extraction efficiencies. Sulphate concentration in concentrated $\text{Pu}(\text{NO}_3)_4$ rarely exceed 1,000 ppm. Sulfate concentrations at this level would result in a negative of $\approx 0.4\%$.

Free fluoride, even in trace amounts, cannot be tolerated. Fluoride can be removed from solutions by a H_2SO_4 fuming step or complexing with Al^{III} . H_2SO_4 cannot be used because of the previously described sulphate interferences.

Only two other interferences are important, zirconium and organic materials. Both of these interferences foul or poison platinum electrodes. Zirconium may be removed from samples by ion exchange and organic materials must be removed by fuming.

PROCEDURAL DETAILS

The method used in this paper is essentially that described by Shults in which Pu^{III} is generated through a reduction step and then oxidized to Pu^{IV} at a suitable potential. Supporting electrolytic media varies for the three types of plutonium samples analyzed. Plutonium metal is dissolved in 6M HCl, and aliquots are placed into 1M HCl which is used as the electrolyte. Shults recommends the use of 1M Perchloric acid because of the ease of maintenance of the working electrode. Perchloric acid was not used because of the potential danger of explosion between wastes and organic material used in plutonium solvent extraction columns. An alternative electrolyte considered was sulphuric acid. In the titration of uranium, sulphuric acid has a distinct advantage over other electrolytes because of its high overpotential, but in the titration of plutonium, it has a distinct disadvantage. In 1M H_2SO_4 , plutonium's formal redox couple is 0.48V vs. SCE while that of iron's is 0.45V vs. SCE. In 1M HCl, the formal couple of plutonium is 0.72V vs. SCE while that of iron's is still 0.45V vs. SCE. The difference between the formal potentials of iron and plutonium is therefore 0.17V in HCl and only 0.03 volts in H_2SO_4 . If 1N H_2SO_4 is used as a supporting electrolyte, it is easy to see that for oxidations and reductions 200mv away from the formal couple of plutonium, a correction must be made for the contribution of iron reduction or oxidation current. In 1M HCl the couples are sufficiently far apart to minimize any effect from the electrolysis current of iron. All titrations are preceded by analyses of a reagent blank to determine the equivalent plutonium concentration to be subtracted from the sample titration as a result of "cell current."

OXIDE SAMPLES

Dissolutions of PuO_2 are generally made in conc. HCl with a trace of HF to help catalyze the reaction. Mixed oxides are dissolved in conc. HNO_3 and may or may not require HF depending upon both the percentages present of uranium and plutonium, and the temperature of formation of the mixture. In either case, the supporting electrolyte is 1N HCl-0.5N AlCl_3 . Excess fluoride is effectively complexed with aluminum. A further addition of 4 drops of 1M sulfamic acid is made to HNO_3 dissolutions to destroy nitrite ions. Samples were sparged continuously to provide deaeration and constant agitation with ultra pure helium containing less than 0.005% impurities.

Aluminum chloride lowers the surface tension of the electrolyte sufficiently to allow effervescence to occur during sparges. Tiny bubbles liberated from the electrolyte deposit a significant amount of sample, $\approx 1\%$, high in the titration cell preventing wash down. Bias corrections generated through analyses of standards were then applied to samples. A precision flow controller was installed in the helium stream in order to control the flow of sparge gas. Helium sparge rate was slowed to effect minimum splash while not extending titration times. Titration times for dissolved oxides are approximately 5-20 minutes. Lengthy pre-reduction of oxides by the addition of aluminum.

PLUTONIUM NITRATE

Plutonium nitrate solutions were titrated in 1N HCl with 4 drops of 1M sulfamic acid. Approximately 15-20% Pu^{VI} exists in freshly prepared nitrate solution. The $\text{Pu}^{\text{VI}}\text{-Pu}^{\text{IV}}$ couple is not completely reversible at the platinum electrode. Plutonium nitrate solutions that are analyzed immediately following their production must therefore undergo a chemical reduction prior to electrolytic reduction. Sample containing Pu^{VI} are easily detected by the high amount of residual current, (100 μ a) at the end of the electrolytic reduction.

Two methods of chemical reduction can be used. The first must be completed before sample dilutions are completed. Hydroxylamine hydrochloride is added in an equal-molar relationship for plutonium. The mixture is heated at 80° C for 25 minutes to insure complete reduction of Pu^{VI} and destruction of any excess reductant. The dilution is then carried through the regular $\text{Pu}(\text{NO}_3)_4$ procedure.

In the second reduction, ferrous chloride is added in approximately a 1:50 relationship for the plutonium sample. Iron.II is used as a reductant for Pu^{VI} in many reduction titrations.

The iron reduction has the advantage of being available after samples have been diluted and aliquoted to the cell, and also because of its specific nature for Pu^{VI} . The hydroxylamine hydrochloride reduction has the advantage of not introducing a possible interference into the sample, but has the disadvantage of requiring added manipulation of samples.

Table II summarizes the results of analyses on a variety of plutonium samples.

TABLE II

	N	Recovery	σ	95%
NBS 949b	25	99.99%	.073%	0.15%
Pu^0 Ingot	14	(a)	.065%	0.14%
Mixed U- PuO_2	10	100.22%(b)	.124%	0.344%
$\text{Pu}(\text{NO}_3)_4$				
ARHCO STD 250g/1	16	100.01%	.068%	0.14%

(a) No significant difference between C.A.-CPC at 99% confidence level.

(b) Pu content of mixed oxides was 5-20%; recovery based on multi-lab exchange.

CONCLUSIONS

The Electroscan must be evaluated by the following criteria: Initial cost, versatility, speed, sensitivity, reliability, ease of servicing, convenience of use.

Initial cost of the instrument is $\approx$ \$4300 equipped with a disc integrator and $\approx$ \$3500 without. This expense compares favorably with the cost of instruments designed solely for CPC. If the disc integrator is ordered with this instrument, an additional expenditure must be made for an electronic counting instrument. In view of the effectiveness of the disc, its value to the investigator with the Electroscan is questionable when in the controlled potential mode.

The Electroscan is extremely versatile, being able to function as a recording pH meter or to complete analyses using controlled current or voltage modes. It functions most effectively as either a training tool for electroanalysis or as a development instrument. A voltametry procedure may be developed for a particular element; an inexpensive instrument using operational amplifiers may be constructed to then run the analyses, freeing the Electroscan for further investigations.

An improvement to the versatility of the instrument would be the addition of a compensation network to effect bandwidth shaping for mercury or platinum electrolysis cells. Addition of such a network in the present design would be difficult and would probably result in instability. In the controlled potential mode, both speed and sensitivity are a function of the electrolysis cell and integration system. Response of the instrument is somewhat slow due to the relatively narrow bandwidth caused by the interaction of the cell with the instrument's modest open loop gain.

To date, the Electroscan has been generally reliable. The repair of intermittent shorts somewhere in the instrument chassis, which was causing double pulsing of the frequency accumulator inconvenienced by the necessity of removing the instrument face and disabling RF shields to gain accessibility to the chassis. Instrument circuitry is on printed circuit boards and can be difficult to service for shorts of this type.

A source of confusion in the operation of the instrument may be found in Beckman's terminology for the control's regulating instrument modes. The "initial voltage" control sets the oxidation and reduction potentials for a titration and also sets the voltage for the start of linear sweep voltametry.

While the instrument is versatile, the control of some of the modes is awkward. Cyclic voltametry sweeps are controlled by means of a potentiometer attached to the chart movement and are reversed by manually reversing the chart movement. For this Laboratory's particular purpose, the Electroscan is not well suited for operation by semi-technically skilled analysts.

In summary, a multipurpose electroanalysis system has been evaluated to complete assays of plutonium samples. The unit as evaluated performed favorably in spite of the handicaps presented by the electrolysis cell. The modest success attained with the instrument along with the pure esthetic satisfaction of using controlled potential coulometry merit further effort in specific cell design for the Electroscan.

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