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AN AUTOMATED AMPEROMETRIC PLUTONIUM ASSAY SYSTEM

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AN AUTOMATED AMPEROMETRIC PLUTONIUM ASSAY SYSTEM

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I. INTRODUCTION

The amperometric titration for plutonium assay has been used in the nuclear industry for over twenty years (1) and has been in routine use at the Hanford Engineering Development Laboratory since 1976 for the analysis of plutonium oxide and mixed oxide fuel material for the Fast Flux Test Facility. It has proven itself to be an accurate and reliable method. The method may be used as a direct end point titration or an excess of titrant may be added and a back titration performed to aid in determination of the end point. Due to the slowness of the PuVI-FeII reaction it is difficult to recognize when the end point is being approached and is very time consuming if the current is allowed to decay to the residual value after each titrant addition. For this reason the back titration in which the rapid FeII-CrVI reaction occurs is used by most laboratories. The back titration is performed by the addition of excess ferrous solution followed by two measured aliquots of standard dichromate with measurement of cell current after each addition.

Long term precision (measured over a one year period) of the method has been improved from approximately 0.2% relative standard deviation when the method was first established in our laboratory to approximately 0.1% in the past year. To achieve this level of precision it was necessary to add all titrants gravimetrically. This required two people to perform the titration, one to perform the titrant additions, read the digital voltmeter and perform sample manipulations and one to weigh the weight burets.

The impetus to automate the titration came from the recent emphasis of efforts to reduce personnel exposure and the need to more efficiently utilize available personnel. It should be pointed out that this system automates only the titration; oxidation of the samples prior to titration is still accomplished manually.

II. SYSTEM DESCRIPTION

The system will be required to perform all of the functions that the operator would normally perform, ie., addition of reagents, turning the stirrer and rotating electrode on and off, measured addition of titrants and reading the voltmeter. The components used to perform these functions are (See Figure 1):

A. Control Unit

A Metrohm model 643 Controller operates under the control of the HP85A computer, and is programmed to open and close valves, control the stirrer, the rotating electrode and the turntable. It is linked to the computer via a GPIO interface.

B. Motor Driven Piston Buret (two)

Metrohm model 655 Dosimats are interfaced to the HP85A via a BCD interface for accurate delivery of ferrous and dichromate titrants.

C. End Point Detector

A shop made device which applies a potential across the reference electrode and indicating electrode. The reference electrode is a Metrohm mercurous sulfate electrode model EA 406. The indicating electrode is a rotating platinum disc electrode, Metrohm model EA 289, which also includes a model 628-10 Control unit and a model 628-50 drive unit. The end point detector also converts the current response to a voltage (IR drop across a standard resistor). All references to voltage readings are really converted current

values.

D. Digital Voltmeter

A Fluke model 8860A reads the end point detector voltage output and transmits the data to the HP85A via an HPIB interface.

E. Turntable

A Metrohm model 624 ten place rotatable turntable that fits easily into a glove box is used.

F. Hewlett Packard 85A Desktop Computer

Controls all peripheral equipment, the titration process and prints all titration data.

The only component not readily available was the glass titration vessel. A customized vessel was fabricated by the glass shop which allowed utilization of the standard turntable beaker. (See Figure 2) This allowed the use of the small (35 ml) volume used in the manual titration and avoided any modification to the turntable.

The cost of the system hardware was slightly under \$20,000 with an additional \$10,000 in personnel costs involved with procurement, assembly, testing and glove box installation.

III. DESCRIPTION OF OPERATION

Samples are aliquoted and oxidized with AgO in the same manner as they were prior to the use of the automated system.

The various titration parameters (end point set voltage, time delays for voltage readings) and sample identification data are given to the computer in a menu format. When the start switch on the control unit is depressed the turntable rotates and a sample is raised to the titration head where 10 ml of 18 N-H₂SO₄ is added and the stirrer and rotating electrode are turned on. The digital voltmeter monitors the base line voltage for a preset time interval

(usually 45 sec.), then takes a reading. A strip chart recording of the titration is shown in Figure 3. An addition of 1.250 ml of ferrous titrant, approximately one half of the total, is added all at once, which significantly reduces the titration time. The remainder of the ferrous titrant is added in 50 μ l increments until the voltage reading reaches the set point ($P=5mV, +0, -1$). After a preset 25 sec. delay five readings, one per second, are taken from the digital voltmeter, averaged and the value stored in memory. Two 100 μ l aliquots of standard potassium dichromate are then added, each followed by a preset 20 sec. delay and again five readings, one per second, are taken, averaged and stored in memory. The stirrer and rotating electrode are then shut off and while the titration vessel is being lowered, the electrodes and delivery tips are rinsed with water. The computer prints out the pertinent data required for calculation of results which include sample identification, titrant volumes and voltage readings. After a suitable drip time the turntable rotates and the process is repeated. Each titration takes about 5-6 minutes depending upon the amount of plutonium in the sample aliquot. Ten to twelve milligrams of plutonium seems to be a good compromise between good accuracy and precision and a reasonable titration time.

Currently, sample calculations are performed on a larger computer following manual input of all required data. Future plans are to link the HP85A with the larger computer to allow automatic data transfer. With good coordination of sample preparation, up to fifty samples may be titrated in an eight hour work day. The turntable may also be loaded and up to ten samples titrated after lab personnel leave for the day.

IV. RESULTS

At HEDL the NBS 949 standard is used for the calibration of the titer value of the ferrous titrant. Thus all results are directly traceable to the NBS material. Typically three of four titrations are performed and the rela-

tive standard deviation must be 0.1% or less before calibration results are acceptable. Typical results are shown in Figure 4.

A reference standard is also used to measure precision over a longer time period and results are plotted on a control chart. This standard is a mixed oxide material supplied to our laboratory by LANL and is one lot of material that was used in the SALE program. Two aliquots of this material are titrated each day that plutonium samples are titrated. Average recovery on the control sample (corrected for decay) was 100.076% with a relative standard deviation of 0.11% for the ten month period prior to installation of the automated system and 100.043% with a relative standard deviation of 0.09% in the five month period since the system was put into use.

Results obtained by the automated titration system on typical mixed oxide fuel batches which are titrations on three separate pellet samples and replicate analyses on a mixed oxide quality control sample are shown in Figure 5. These data show the type of reproducibility obtainable with the system.

V. CONCLUSIONS

A very workable system (Figure 6) has been developed and implemented at a reasonable cost to perform an exacting chemical titration. All of the equipment used is readily available commercially and only minor modifications need to be made for glove box installation. Automation of the titration has improved the overall precision of the method while significantly reducing manpower requirements and the radiation exposure to the personnel performing the analysis.

VI. REFERENCE

- (1) C. J. Rodden, Editor. Selected Measurement Methods For Plutonium and Uranium in the Nuclear Fuel Cycle, TID 7029, 2nd Ed., (1972).

ASSAY SYSTEM SCHEMATIC

FIGURE 1

FIGURE 2

- A — TURNTABLE BREAKER, 250 ML
- B — POLYETHYLENE SPACER
- C — PYREX TITRATION VESSEL

TITRATION PROFILE

FIGURE 3

TYPICAL NBS DAILY CALIBRATION VALUES

3.69483	3.50899	3.47094	3.63594
3.69418	3.51270	3.46962	3.63691
3.69270	3.51159	3.46774	3.63604
3.69266		3.46961	3.63579
$\bar{x} = 3.69359$	$\bar{x} = 3.51109$	$\bar{x} = 3.46948$	$\bar{x} = 3.63617$
rsd = 0.029%	rsd = 0.054%	rsd = 0.038%	rsd = 0.014%

FIGURE 4

TYPICAL MIXED OXIDE SAMPLE REPRODUCIBILITY

<u>LOT FDOXXX-1</u>	<u>LOT FDOXXX-2</u>	<u>QC1255</u>
25.62	26.50, 26.45	23.52
		23.53
25.62	26.51, 26.48	23.53
		23.53
25.65	26.46, 26.47	23.53
		23.52
$\bar{x} = 25.630$	$\bar{x} = 26.478$	23.54
		$\bar{x} = 23.529$
rsd = 0.068%	rsd = 0.087%	rsd = 0.029%

FIGURE 5

FIGURE 6