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**IMPROVED LABORATORY ASSAYS OF Pu AND U FOR SRP
PURIFICATION AND FINISHING PROCESSES**

by

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IMPROVED LABORATORY ASSAYS OF Pu AND U FOR
SRP PURIFICATION AND FINISHING PROCESSES

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ABSTRACT

Significant improvements have been made in routine assay techniques for uranium and plutonium as part of an effort to improve accountability at the Savannah River Plant (SRP). Emphasis was placed on input/output accountability points and key physical inventory tanks associated with purification and finishing processes. Improvements were made in existing assay methods; new methods were implemented; and the application of these methods was greatly expanded. Prior to assays, samples were validated via density measurements. Digital density meters precise to four, five, and six decimal places were used to meet specific requirements. Improved plutonium assay techniques are now in routine use: controlled-potential coulometry, ion-exchange coulometry, and Pu(III) diode-array spectrophotometry. A new state-of-the-art coulometer was fabricated and used to ensure maximum accuracy in verifying standards and in measuring plutonium in product streams. The diode-array spectrophotometer for Pu(III) measurements was modified with fiber optics to facilitate remote measurements; rapid, precise measurements made the technique ideally suited for high-throughput assays. For uranium assays, the isotope-dilution mass spectrometric (IDMS) method was converted to a gravimetric basis. The IDMS method and the existing Davies-Gray titration (gravimetric basis) have met accountability requirements for uranium. More recently, a Pu(VI) diode-array spectrophotometric method was used on a test basis to measure plutonium in shielded-cell input accountability samples. In addition, tests to measure uranium via diode-array spectrophotometry were initiated. This rapid, precise method will replace IDMS for certain key sample points.

INTRODUCTION

The Savannah River Plant uses the Purex process¹ in the 200-F Area to produce plutonium metal from SRP reactor targets and offsite receipts. Enriched uranium from reactor fuel assemblies used for plutonium and tritium production is purified for recycle using the HM process².

The Laboratories Department provides analytical support for these and other processes. Routine analytical measurements are required for

essential materials, process control, accountability, and product quality. In addition, the department develops and evaluates analytical methods to meet in-house needs. The department also receives support in these areas from the Savannah River Laboratory (SRL).

Analytical methods originally selected for process support over 30 years ago were limited by existing technology and preceded desires for material safeguards through accurate and precise analytical measurement. A comprehensive program is now in place in the Laboratories Department to improve analytical measurement reliability and to assist in ensuring the reliability of samples submitted for analyses.

ACCOUNTABILITY

The facets of materials control and accountability discussed will be limited to those areas applicable to the analytical methods development described herein. Accountability requires the accurate measurement of reliable samples from receipts, shipments, and key physical inventory tanks to ensure detection of diversion and to avoid analytically generated shipper/receiver differences.

Within a facility or process, accountability is most dependent upon the quantity of material moved through input and output points. Systematic error at input/output points causes either a gain or loss trend proportional to the amount of material processed through the point, unless a cancellation of systematic errors from several input/output points occurs. Characteristically, analytical methods of choice should be sufficiently precise to detect/correct for measurement bias and, thus, aid in minimizing gain/loss trends. Accuracy, precision, timeliness, complexity, and specific application must be considered during the method selection process.

Physical inventory provides a vehicle for monitoring the accuracy of input/output measurements because the measured quantity of in-process material should equal the inventory calculated from input-output data and the previous physical inventory. The reliability required at each process point is a function of the quantity of material present. Key physical inventory points are where the majority of the material is

found and where the greatest concentration of effort is required to minimize measurement error. Again accuracy, precision, timeliness, complexity, and specific application must be considered in method selection. However, systematic errors during physical inventories do not cause long-term gain/loss trends, as observed for input/output measurements.

Reliable accounting of materials requires accurate calibration of process tanks and precise measurement of the quantity of solutions in those tanks. Tank agitation, sampling equipment, and sampling procedures must provide representative samples for analysis. Analyses must be precise and accurate, and data from all sources must be properly handled.

The Laboratories Department's accountability objectives at SRP are to focus on key accountability points for input/output and physical inventory, to implement and monitor a comprehensive sample validation program, and to develop and maintain a collection of analytical techniques to meet the required measurement reliability.

SAMPLE VALIDATION

A sample-validation program is needed to ensure representative sampling. A validation program involves a quick and easy measurement, typically solution density, to ensure receipt of reliable samples before continued processing. Correlation between density range and assay measurement results has been demonstrated on numerous occasions. The sample validation program implemented at SRP is particularly effective for replicate samples where precise density measurements can detect small differences between sample solutions. As a result, accountability errors can be properly attributed to sampling and/or measurement error.

In addition to sample validation, accurate density measurements are required to obtain the exact volume of solution in process/accountability tanks. Tanks are calibrated using water. The response of the process gauge is related to the specific gravity of the process solution. Corrections are applied to the tank calibration equations to permit direct application of the sample solution density at 25°C.

A detailed review of developmental activities, capabilities, and applications of solution density meters for sample validation at SRP was presented by S. L. Maxwell at these proceedings.³ The suite of four-, five-, and six-place density meters in routine use provides the required precision and accuracy to detect a nonrepresentative sampling.

ASSAY METHODS

Concentration measurements for plutonium and uranium should be made using a method well suited to the sample matrix, and traceable to the national measurement system. Alternate methods should be available and confirmation measurements made on some periodic basis. Measurements on a mass basis are generally preferable to a volume basis for achieving the best reliability.

As appropriate, each method review will include purpose, application, improvements, and reliability. Program plans for future activities will be discussed separately.

Plutonium Assay

Total Alpha -- The determination of plutonium concentration by measurement of alpha particles from radioactive decay was selected initially for process control measurements because of its applicability to all concentration ranges of interest, its relative simplicity, limited alternative methodology, and satisfactory accuracy and precision relative to requirements. The reliability of routine total alpha measurements is approximately 5 - 10%, and is satisfactory for process control. Although significant refinements have been made in alpha measurements, the technique is not suitable for routine accountability assays.

Controlled-Potential Coulometry -- Controlled-potential coulometry was recognized as having the capability to achieve improvements in accountability measurement reliability and as providing reference method capabilities in support of accountability related activities.

During 1978, the coulometric technique was selected for implementation and applied to pure plutonium product from the Purex process. Commercially available Princeton Applied Research (PAR) Potentiostat/Coulometer/Cell Assemble with platinum working electrode for use in 1 *N* sulfuric acid supporting electrolyte was procured and installed. Data collected from 1980 to mid-1984 indicated that the method was achieving a reliability of 0.4% to 1.0% (RSD) with occasional periods of poorer reliability.

Since the latter half of 1984, improvements in electrode conditioning, stirring, reagent preparation, system calibration, weight aliquot preparation, and increased training and experience level of analysts have resulted in improved reliability (Tables I and II). Reproducible electrode conditioning was obtained by flaming the working and counter electrodes to a bright red at the end of each day of usage. The electrodes were then air-cooled and stored in 8 *M* HNO₃ until their next use. When conditioning, as described, failed to achieve proper electrode response, the electrodes were cleaned in aqua regia, then thoroughly rinsed and stored in 8 *M* HNO₃. Aqua regia cleaning is not generally required for periods of several months. An S-shape stirrer with flat top has replaced the PAR paddle stirrer. The supporting electrolyte is prepared from Ultrex^R sulfuric acid and demineralized water. The system is calibrated electrically and the linearity of the integrator is evaluated from 100 mA to 50 μ A. System operation is limited to experienced chemists and three qualified/experienced analysts. Anion-exchange purification was employed to expand the applicability of the technique. Controlled-potential coulometric determination with prior anion-exchange purification has been applied to special Purex processing campaigns, to the evaluation of other assay measurement methods, and to evaluation programs (Tables III-IV).

During December 1985, the PAR potentiostat/coulometer was replaced by a state-of-the-art coulometry system assembled/upgraded by the SRP Equipment Engineering Department, based upon the New Brunswick Laboratory's third generation system.^{4, 5} Significant improvement in integration linearity was obtained by eliminating noise generated when a computer-controlled DC signal, used to offset and adjust the control-potential output, was routed through the switching network of the automation module to the desired potentiostat module. System control software was modified to permit simultaneous and direct routing of the signal to the potentiostat modules. Instrument control problems, control-potential instability, and integrated circuit failures (linked to grounding loop problems in the mode switch and charging system electrolysis current meter in the potentiostat modules) were corrected. Additional enhancements of the coulometry system included incorporating the recently issued/upgraded Hewlett-Packard 8116A Pulse/Function Generator, 5318A Universal Counter, 59501B DAC/Power Supply, and 3456A Digital Voltmeter. The electrical calibration relative precision at 10 mA is better than 0.0005% (two-sigma), integration linearity affects electrolysis current by less than 0.005%, and the short-term stability (24 hours) is better than 0.001%. Results from the measurement of plutonium standards with the new system are shown in Table V.

In summary, our coulometry equipment is state-of-the-art, our analysts are well trained, and coulometry coupled with ion exchange, when appropriate, is used routinely for analysis of pure plutonium product, for analysis of special process samples, for validation of standards, for analysis of exchange samples, and for reference purposes.

Amperometry -- An amperometric method was evaluated to replace total alpha/PHA analyses for samples of concentrated plutonium containing americium (from a special SRP recovery process). While satisfactory for the application with respect to precision and accuracy, throughput was limited, and the method was replaced with a precise, more rapid spectrophotometric method.

Diode Array Spectrophotometry -- A Hewlett-Packard 8451A diode-array spectrometer was modified to accommodate fiber optics for remote applications⁶ and has been used extensively at SRP for plutonium assays. The system, programmed for Pu(III) measurements, was delivered and installed by SRL in April 1985. The method is rapid, and the relative precision of bias-corrected results (average of duplicates) is 1.0 - 1.7% (two-sigma).

The diode-array spectrophotometer has a built-in computer, and is interfaced to two computer terminals and disc drives. One of the terminals is removed into containment for ease of operation. In the Pu(III) method, a sample aliquot is diluted with a matrix solution containing ferrous sulfamate and sulfamic acid to convert (and maintain) the plutonium to the +3 oxidation state. All wavelengths from 190 - 820 nm are detected simultaneously by the diode array; the amount of light absorbed by the

diluted sample in the 520-635 nm region is proportional to the plutonium concentration. Multicomponent analysis is used to compare the sample spectrum with standard spectra stored in the computer's memory.

As applications of the Pu(III) spectrophotometric method expanded, additional improvements were made. A fixed-geometry flow cell was installed to facilitate measurements and improve precision. Sample aliquots were diluted on a weight basis with matrix reductant solution, and the measured densities of the sample and matrix solutions were used to calculate the volumetric dilution factor. Spectrophotometric and mass measurements were checked with quality control (QC) standard solutions, and sample results were corrected for observed bias prior to reporting. Dilutions were adjusted based upon production estimates to ensure that the diluted solutions were in the optimum range for measurement. For selected applications, a preliminary measurement was performed to determine the dilution factors to be applied to the QC synthetic (used for bias correction) and to the sample to achieve the same concentration in the diluted solutions, thereby minimizing measurement variation. Instrument control software performs all calculations and quality control checks. System referencing with water is monitored by the software and re-referencing is required after allowed intervals are exceeded.

Pu(III) spectrophotometry was initially applied to ²³⁹Pu accountability samples, to off-site scrap receipt/input accountability for a special recovery process, to recycle accountability for material transfers between finishing and purification processes, and to second plutonium cycle physical inventory samples. Test results are summarized in Tables VI, VII, and VIII. In February 1986, a second diode-array spectrophotometer for Pu(III) measurement was removed with fiber optics for routine process control to replace alpha measurements for plutonium solutions above 0.1 gPu/L, utilizing a 1-dram vial measurement cell method.⁷ Results of the technician qualification 8-week training program for personnel entering the Laboratories Department are shown in Table IX. A third spectrophotometer for Pu(III) measurement was removed with fiber optics into a glove box for accountability measurements in support of ²³⁸Pu processing. Results from the analyses of ²³⁸Pu samples are shown in Table X. The level of analyst experience required to obtain precise and accurate Pu(III) spectrophotometric measurements of plutonium (²³⁸Pu in particular) is significantly less than that for total alpha.

Pu(III) diode-array spectrophotometry with its precision and rapid turnaround time, ideally complements ion exchange/coulometry with its reference capabilities. These two techniques are used at SRP for all plutonium assays, excluding shielded cell samples and samples containing trace plutonium.

The more sensitive Pu(VI) diode-array spectrophotometric method is being evaluated for shielded cell samples, especially input account-

ability for the Purex purification process.* The technique is showing better than 2% (two-sigma) precision, and agreement within 2% of replicate total alpha/PHA analyses by experienced technicians. Synthetic dissolver solutions, reliable to better than 0.2% for plutonium assay and covering the normal variation of uranium, nitrate, and acid concentrations, are used to establish required calibration curves. The effect of variables is still under investigation, but routine implementation of the Pu(VI) method is expected in the very near future. The turnaround time for the Pu(VI) method will be an order of magnitude shorter than the tedious isotope dilution-mass spectrometry method.

Isotope Dilution Mass Spectrometry --

Although the Pu(VI) spectrophotometric method will shortly replace the antiquated total alpha/PHA/mass spectrometric method for the assay of plutonium in shielded cell samples, the IDMS method for plutonium is needed and is in the developmental stage at SRP.** New facilities for sample preparation/filament loading with Class 100, down-draft hoods and electroplating equipment are now operational. A MAT 260 mass spectrometer with automated sample carousel has been in routine use for several years and has been modified to provide the required stability, precision, and accuracy for Pu IDMS measurements. A relative precision (two-sigma) of less than 1% without statistically significant bias is desired for the Pu IDMS reference method. Pu IDMS technology is not new; however, at each site, the method has to be tailored to detector sensitivity, cross-contamination problems, and matrix interferences with respect to plutonium purification. At SRP, we're now resolving these problems in consultation with personnel at other sites who have implemented this technique.

Uranium Assay

Titrimetric -- The Davies-Gray uranium titration performed on a gravimetric basis is applied to enriched uranium product solutions from the HM purification process and to selected physical inventory samples. Reliable application of the titrimetric method*** combined with an improved sample validation program has virtually eliminated the contribution of SRP analytical measurements to limit-of-error estimates for SRP shipments.

The titration has been performed on a weight basis for aliquoting of sample solutions and for addition of standard dichromate solution. Data shown in Tables XI and XII for blind standards supplied by the SALE program from 1978 and for NBL Evaluation Program Samples from 1985 are typical for quality control standards and routine samples for output accountability, physical

inventory, and shipper measurements of enriched uranium product from the HM process.

Gravimetric -- The gravimetric determination of uranium in depleted UO₃ product by conversion to stoichiometric U₃O₈ has been in use at SRP for many years. The method is accurate to better than 0.25% based upon quality control standards and participation in the SALE program. The relative precision of the technique is better than 0.05% (two-sigma).

Isotope Dilution Mass Spectrometry -- An IDMS method performed on a gravimetric basis has been in routine use at SRP for the determination of uranium in HM process input accountability samples since 1984.† The gravimetric IDMS method for accountability samples was preceded by a volumetric IDMS method and a polarographic method. Application to key HM physical inventory samples requiring shielded cell handling has been systematically expanded during the last year as part of the ongoing program to minimize variations and reduce the limit of error for the physical inventory. All key HM physical inventory samples are analyzed by IDMS or Davies-Gray.

In the IDMS method, weight aliquots of sample are mixed with predispensed ²³³U spikes in the shielded cells, and after initial purification in the cells by solvent extraction, final purification and preparation for mass spectrometry are done in a radiobench. Measurements are made on a MAT 261 thermal ionization mass spectrometer.

The relative precision of the gravimetric IDMS method based upon the quality control standard solutions processed through the shielded cell/purification process during 1985 was 1.6% (two-sigma) for a single measurement. The relative precision of samples calculated from differences between duplicate sample analyses was 1.3% (two-sigma). Each batch of samples is corrected for systematic error prior to reporting, based upon the synthetic standard solutions processed in conjunction with the samples.

Diode-Array Spectrophotometry -- U(VI) spectrophotometry in a sulfate matrix is being evaluated for application to input accountability and physical inventory samples from both enriched and depleted uranium purification processes.†† The method is rapid, is applicable to shielded cell samples, and will provide more accurate measurements than those currently obtained for Purex process samples via calculation (from density, acid, and aluminum measurements) or volumetric titrations. The method will also replace the slow, tedious IDMS method used for the HM process. Preliminary evaluations indicate that a relative precision of better than 2% (two-sigma) is achievable.

*D. R. Van Hare and H. D. Hodgens, E. I. du Pont de Nemours & Co., Savannah River Plant, Unpublished Work.

** J. Satkowski, E. I. du Pont de Nemours & Co., Savannah River Plant, Unpublished Work.

***L. A. Overman et al., E. I. du Pont de Nemours & Co., Savannah River Plant, Unpublished Work.

†R. S. Dorsett, E. I. du Pont de Nemours & Co., Savannah River Plant, Unpublished Work

††P. E. O'Rourke, et al., E. I. du Pont de Nemours & Co., Savannah River Plant, Unpublished Work

PROGRAM PLANS

Coulometry

A second state-of-the-art coulometer system will be installed in a dedicated electrochemistry development laboratory module in a new laboratory facility under construction. Facility startup is planned for October 1986.

Diode Array Spectrophotometry (DAS)

Completion of the development/evaluation of the Pu(VI) DAS method for shielded cell Purex input accountability is projected during the fourth quarter of 1986. Assuming successful demonstration of the method's applicability, routine application of the technique to key physical inventory, ²³⁸Pu input accountability, and process control samples will

be evaluated. The fiber-optic couplers from two of the diode-array spectrometers currently devoted to the Pu(III) method will be modified for multiplexing up to three remoted measurement stations, enhancing method utilization. Evaluation of the U(VI) DAS method will receive considerable attention because of its potential to decrease analysis time and complement existing measurement methods. Additional process control applications of the diode-array spectrophotometer (e.g., percent of plutonium in the Pu(III) oxidation state, and sulfamic acid concentration) will be evaluated during 1987.

Pu IDMS

The development/evaluation/implementation plans for Pu IDMS project its routine application as a reference method during the last quarter of 1986.

TABLE I. Coulometric Analysis of Quality Control Synthetic Solutions

<u>Time Period</u>	<u>Rel. Prec. (two-sigma) %</u>
1st Q, 1983	0.7
2nd Q, 1983	0.9
3rd Q, 1983	4.5
4th Q, 1983	1.0
1st Q, 1984	1.3
2nd Q, 1984	0.4
3rd Q, 1984	0.3
4th Q, 1984	0.2
1st Q, 1985	0.3
2nd Q, 1985	0.2
3rd Q, 1985	0.3
4th Q, 1985	0.2
1st Q, 1986	0.3

TABLE II. Coulometric Measurement of National Bureau of Standards SRM 949F Plutonium Metal

	<u>1</u>	<u>2</u>	<u>3</u>
Coulometric Assay ¹	100.00	100.03	100.08
Rel. Prec. (two-sigma), %	0.21	0.16	0.20
No. of Measurements	11.00	6.00	7.00

¹ The Certified Plutonium Content Corrected for Isotopic Decay was 99.97% ± 0.1% (99% C.L.) at the Time of Analysis.

TABLE III. Rocky Flats Metal Sample Exchange Program

<u>EXCHANGE</u>	<u>METAL</u>	<u>IE/COULOMETRY</u>		<u>100%-IMPURITIES</u>		<u>SRP ASSAY vs.</u>
		<u>Assay, %</u>	<u>RSD %</u>	<u>Purity, %</u>	<u>Uncertainty, %</u>	<u>100%-IMPURITIES, RD, %</u>
JUNE 1984	C81	99.54	0.2	99.50	± 0.15	+ 0.04
	A84	99.91	0.2	99.85	± 0.10	+ 0.06
SEPT 1984	A84	100.01	0.1	99.86	± 0.10	+ 0.17
	B81	99.91	0.1	99.85	± 0.10	+ 0.06
DEC 1984	C81	99.60	0.3	99.67	± 0.15	- 0.07
	A84	99.96	0.1	99.86	± 0.10	+ 0.10

TABLE IV. Coulometric Analysis of Evaluation Program Samples

Date of Analysis	Sample Number	SRP Assay vs. NBL Prepared Value, RD, %	Daily Mean RD, % ¹
7/30/85	24, 25	- 0.12, + 0.34	+ 0.11
8/15/85	27, 29	- 0.10, + 0.04	- 0.03
8/19/85	26, 28	+ 0.04, - 0.07	- 0.02
11/6/85	18, 19	- 0.02, - 0.11	- 0.07
11/14/85	20, 21	+ 0.07, + 0.13	+ 0.10
12/3/85	17, 22	- 0.27, + 0.06	- 0.10
12/4/85	23, 30	0.00, - 0.08	- 0.04
	MEAN	- 0.01	- 0.01
	Rel. Prec. (two-sigma), %	0.29	0.16

¹ Mean value simulates SRP's routine duplicate sample measurement practice.

TABLE V. Evaluation of the State-of-the-Art Coulometer

Technical Analyst	n	Rel. Prec. (two-sigma), %	Pu Assay vs. Reference Value, RD, %
A	5	0.07	+ 0.05
B	5	0.16	- 0.02
C	3	0.09	- 0.05

TABLE VI. Plutonium Assays of Special Recovery Accountability Samples

Duplicate Sample Pairs	Ion Exchange & Coulometry		Amperometry			Diode Array Spectrophotometry			Total Alpha/Pulse Height Analysis		
	gPu/L	RD, %	gPu/L	RD, %	REC, %	gPu/L	RD, %	REC, %	gPu/L	RD, %	REC, %
A	76.4	0.8	77.6	0.4	101.6	76.6	1.9	100.3	80	4	105
B	92.4	0.6	92.4	4.7	100.0	93.0	0.7	100.6	98	1	106
C	29.0	0.8	28.9	0.1	99.7	28.8	0.8	99.3	36	3	(124)
D	34.1	1.1	34.1	0.9	100.0	33.9	0.3	99.4	36	0	106
E	30.4	0.8	30.7	2.8	101.0	30.1	0.2	99.0	33	3	109
F	25.3	1.6				25.3	0.6	100.0	27	6	107
			MEAN		100.5	MEAN		99.8	MEAN		107
			2 RSD, %		1.6	2 RSD, %		1.3	2 RSD, %		3

TABLE VII. Plutonium Assay of Finishing Line Recycle Samples

Spectrophotometric Assay, gPu/L	IE-Coulometric Assay gPu/L	Spectrophotometry vs. Coulometry, RD, %
7.63	7.67	- 0.5
7.52	7.62	- 1.3
6.74	6.73	+ 0.2
7.83	7.85	- 0.2
12.43	12.49	- 0.5
10.52	10.56	- 0.4
8.41	8.40	+ 0.1
3.79	3.72	+ 1.9
7.25	7.30	- 0.7
7.80	7.84	- 0.5
	MEAN	+ 0.2
	2 RSD, %	1.7

TABLE VIII. Plutonium Assay of Purex Process Second
Plutonium Cycle Physical Inventory Samples

<u>Spectrophotometric Assay, g Pu/L</u>	<u>IE-Coulometric Assay, g Pu/L</u>	<u>Spectrophotometry vs. Coulometry, RD, %</u>
1.264	1.268	- 0.3
1.667	1.685	- 1.1
2.488	2.481	+ 0.3
2.275	2.292	- 0.7
2.748	2.739	+ 0.3
2.394	2.402	- 0.3
2.582	2.579	+ 0.1
2.399	2.417	- 0.7
2.403	2.414	- 0.5
1.813	1.809	+ 0.2
3.186	3.184	+ 0.1
2.464	2.447	+ 0.7

MEAN + 0.2

TABLE IX. Plutonium (III) Spectrophotometry: Process
Control Qualification Measurement

<u>Technician</u>	<u>n</u>	<u>Rel. Prec. (two-sigma), %</u>	<u>Assay vs. Reference Value, RD, %¹</u>
A	9	1.1	- 0.1
B	9	1.3	+ 0.9
C	9	1.9	- 0.8
D	9	0.9	+ 1.5
E	9	0.9	- 0.2
F	9	0.9	+ 0.8
G	9	0.7	+ 0.5
H	9	1.3	- 0.2
MEAN		1.1	MEAN + 0.3

¹ Qualification performed using the same standard solution

TABLE X. Comparison of Assay Methods for Plutonium-238

<u>Replicate Samples</u>	<u>Density</u>	<u>Plutonium (III) Spectrophotometry</u>		<u>Total Alpha/PHA</u>		
		<u>gPu/L</u>	<u>2 x RSD, %</u>	<u>gPu/L</u>	<u>2 x RSD, %</u>	<u>RD, % vs. Spect.</u>
A	1.0523	5.23	2.7	5.21	9.5	-0.4
	1.0538	5.19	0.4	5.19	12.9	0.0
B	1.0559	5.71	0.4	--	--	--
	1.0559	5.55	3.0	5.64	3.0	+1.6
	1.0559	5.61	4.3	5.74	3.2	+2.3
C	1.0737	4.75	0.0	4.75	9.9	0.0
	1.0737	4.73	0.3	4.98	6.6	+5.3
D	1.0516	7.05	4.6	6.78	4.9	-3.8
	1.0506	7.22	0.4	6.91	9.8	-4.3
E	1.0444	7.38	0.3	7.86	2.1	+6.5
	1.0414	7.38	0.6	7.72	2.9	+4.6
F	1.1245	1.153	0.2	1.162	4.1	+0.8
	1.1251	1.149	0.8	1.156	2.4	+0.6
	1.1248	1.160	0.2	--	--	--
MEAN		---	1.3	--	5.9	1.1

TABLE XI. Gravimetric Davies-Gray Titration - Sale Program^{1, 2}

	<u>N</u>	<u>Rel. Prec. (two-sigma), %</u>	<u>Bias, %</u>
Technician A	28	0.14	+ 0.004
Technician B	17	0.069	+ 0.044

¹ Data were collected over a five-month period.

² Relative precision previously obtained from volumetric Davies-Gray titration was 0.35% (two-sigma).

TABLE XII. Evaluation Program Samples

<u>Date of Analysis</u>	<u>Std Sol'n</u>	<u>Aliquot Number</u>	<u>SRP Assay vs. NBL Prepared Value, RD, %</u>
7/17/85	A	1, 2, 3	+ 0.27, + 0.26, + 0.27
8/20/85	B	1, 2, 3	- 0.04, + 0.02, + 0.02
8/21/85	B	4, 5, 6	- 0.11, - 0.06, - 0.11
8/26/85	C	1, 2, 3	- 0.02, 0.00, - 0.04
9/18/85	A	4, 5, 6	+ 0.19, ---, + 0.20
9/30/85	A	7, 8, 9	+ 0.10, + 0.15, + 0.12
10/10/85	C	4, 5, 6	+ 0.03, + 0.01, + 0.01
MEAN			+ 0.06
Rel. Prec. (two-sigma), %: All Stds.			0.25
Std. Sol'n A			0.13
Std. Sol'n B			0.12
Std. Sol'n C			0.05

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