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Analytical Methods for Fissionable Materials in the Nuclear Fuel Cycle

June 1974 to June 1975

Compiled by

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ANALYTICAL METHODS FOR FISSIONABLE MATERIALS IN THE NUCLEAR FUEL CYCLE

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ABSTRACT

Progress continued on method development for the dissolution of difficult-to-dissolve materials, the automated analysis of plutonium and uranium, the preparation of plutonium materials for the Safeguard Analytical Laboratory Evaluation (SALE) Program, and the analysis of HTGR fuel and SALE uranium materials. The previously developed Teflon-container, metal-shell apparatus was applied to the dissolution of various nuclear materials. Gas-solid reactions, mainly using chlorine at elevated temperatures, are promising for separating uranium from refractory compounds. An automated spectrophotometer designed for determining plutonium and uranium has been tested successfully by the New Brunswick Laboratory. Procedures were developed for this instrument to analyze uranium-plutonium mixtures and the effects of diverse ions upon the analysis of plutonium and uranium were further established. A versatile apparatus was assembled to develop electrotitrimetric methods that will serve as the basis for precise automated determinations of plutonium. Progress with the first of these methods is reported. Plutonium materials prepared for the SALE Program were plutonium oxide, uranium-plutonium mixed oxide, and plutonium metal. Improvements were made in the methods used for determining uranium in HTGR fuel materials and SALE uranium materials. Plutonium metal samples were prepared, characterized, and distributed, and half-life measurements were in progress as part of an inter-ERDA-laboratory program to measure accurately the half-lives of long-lived plutonium isotopes.

I. INTRODUCTION

The objectives of this project are (1) to develop fast dissolution techniques and analytical methods for determining plutonium and uranium with emphasis on scrap-type and difficult-to-dissolve materials, (2) to design and construct automated apparatus for determining plutonium and uranium, (3) to prepare well-characterized, plutonium-containing materials for use in the Safeguard Analytical Laboratory Evaluation (SALE) Program, (4) to prepare well-characterized, highly pure plutonium metal standards for distribution by the National Bureau of Standards, (5) to participate in an inter-ERDA-laboratory program for measuring half-lives of the longer lived plutonium isotopes, and (6) to characterize chemically special lots of nuclear materials as requested by ERDA.

A primary concern in the chemical characterization of nuclear fuel-cycle materials is their plutonium and uranium contents. The nuclear fuel-cycle materials include nonuniform scrap and mixtures of highly refractory compounds. A philosophy guiding the analysis of these materials has been total dissolution followed by highly precise chemical analyses. Faster methods of analysis are economically necessary because of the projected increasing numbers of samples to be analyzed in the various segments of the nuclear fuel cycle for safeguards purposes.

An assay scheme being developed is based on relatively rapid dissolutions of 90% or more of the plutonium and uranium followed by automated analyses of the dissolved fractions and gamma-counting assay analyses of the residue fractions. The overall precision is no greater than 1.5% when the relative standard deviations of the automated analysis and the gamma-counting assay are 1 and 10%, respectively.

II. MEETING OF ERDA, REGULATORY, BNL, NBL, AND LASL REPRESENTATIVES (J. E. Rein and G. R. Waterbury)

A meeting was held at ERDA headquarters during November 1974 to exchange technical information and to discuss analytical chemistry research programs under way at the New Brunswick Laboratory (NBL), Lawrence Livermore Laboratory (LLL), and the Los Alamos Scientific Laboratory (LASL). This meeting was considered vital to the future scope of the A241 Program at LASL, as well as to work at the other laboratories; therefore, a summary of the topics discussed, emphasizing effects on the LASL program, is included here.

It was concluded that there was not undue redundancy in the research programs of NBL, LLL, and LASL and significant changes in the programs presently under way were not proposed.

The LASL automated spectrophotometer for determining plutonium and uranium is performing well at NBL. The LASL effort to develop a second automated instrument for the highly precise determination of plutonium will use an electrometric technique. Because no method now exists with the required high precision and specificity to measure plutonium in scrap-type samples, as well as product-type samples, it was agreed that the immediate objective should be to develop such a method. A versatile apparatus now being used at LASL to evaluate various electrometric techniques for determining plutonium was discussed. This apparatus is constructed from commercial components, including an inexpensive programmable calculator.

Construction of the LLL automated titrimeter for uranium determination, which uses the NBL-modified Davies-Gray method, is expected to be completed in about 3 months. This instrument has several excellent features that are applicable to LASL's second automated instrument.

All attendees agreed that development of automated dissolution methods is a tremendously complicated task that is not economically justifiable.

BNL personnel provided interesting predictions for future throughput rates and radiation levels of nuclear fuel-cycle material, especially for fuel fabrication and reprocessing plants. The throughput rates will increase to levels where analysis uncertainties of <0.05 relative percent will be required to ensure safeguards controls. The increase in throughput rates, coupled with high radiation levels caused by increased levels of ^{238}Pu, ^{242}Pu, ^{232}U, and transplutonics, will require the use of highly precise automated methods. Widely variable isotopic compositions of uranium and plutonium will characterize future nuclear fuel-cycle materials. With wide concentration ranges of short-lived isotopes such as ^{238}Pu, ^{232}U, ^{241}Pu, and transplutonics, slight heterogeneities in the isotopic compositions of materials assayed by nondestructive techniques (particularly calorimetry and active and passive radiation measurements) will cause large errors. LASL reported that isotopic composition heterogeneity was observed with many nuclear fuel-cycle materials, even product types such as plutonium oxide and slightly enriched UO_2 powder destined as PWR fuel. Multiple samples of nuclear fuel-cycle material must be analyzed by highly precise mass spectrometry and other chemical techniques to minimize heterogeneity effects. The development of a mass spectrometer to provide high throughput rates appears to be an economic necessity.

ERDA and Regulatory personnel suggested that companies planning reprocessing and fuel fabrication plants be contacted to generate ideas (and proposals) for on-line instruments.

III. DISSOLUTION OF FUEL-CYCLE MATERIALS

A. Teflon-Container Metal-Shell Apparatus (G. C. Swanson, G. S. Dow, S. F. Marsh, H. J. Kavanaugh, and J. E. Rein)

The investigation of a dissolution apparatus consisting of a Teflon container in a metal shell was continued. This apparatus provides for acid dissolutions at temperatures to 280°C and pressures to 34 MPa (5000 psi). Its operation is similar to the sealed, fused silica tube but it is capable of using hydrofluoric acid, is easy to handle, has reusable containers, and the sample is in a container suitable for subsequent chemical treatments if desired. Its disadvantage, compared to the fused silica tube, is that it has a lower operating temperature limit.

The design of the apparatus was made available to potential manufacturers and the Parr Instrument Company now is manufacturing a slightly modified version. The 347 stainless steel shell, used with oxidizing acids, is marketed as Parr No. 4746 Acid Digestion Bomb and the nickel shell used with nonoxidizing halide acids is marketed as Parr No. 4747 Acid Digestion Bomb. Parr also provides all components, Teflon containers, stainless steel rupture disks, and the special jack and wrench used for shell disassembly. The commercial production of this equipment gives it wide availability to the many laboratories faced with the analysis of difficult-to-dissolve materials.

The Parr Instrument Company's stainless steel shell (No. 4746) was purchased and successfully tested under a variety of operating conditions. We do not agree with the Parr instruction that hand-tightening the shell before heating is adequate. When a wrench is not used for this purpose, there is a significant increase in corrosion, which is attributed to acid vapor leakage at the junction of the Teflon container and its lid.

The Parr No. 4747 version of the LASL-designed nickel shell, to be used with halogen acids, is not yet available for testing.

Several Parr Teflon containers were also purchased and tested. Unexpected failures of the containers occurred. NBL personnel reported a similar experience. Comparison testing of the Parr Teflon containers and LASL-fabricated Teflon containers for various samples and acid mixtures will be undertaken.

B. Applications of Teflon-Container Metal-Shell Apparatus (G. C. Swanson, S. F. Marsh, H. J. Kavanaugh, and J. E. Rein)

The apparatus has been evaluated for a variety of difficult-to-dissolve materials. A particularly resistant material is HTGR TRISO fuel microspheres that consist of a UC-ThC kernel coated with pyrolytic carbon and SiC. Past efforts have resulted in complete decomposition of 100-mg samples in 2$\underline{M}$ HF-15$\underline{M}$ HNO_3 mixtures using a 12-h heating at 270°C. Attempts to increase the sample size to 500 mg resulted in overpressurization, primarily from nitrogen gases produced from nitric acid reaction, and consequent venting. A wide variety of acid mixtures, with and without oxidants, were evaluated with the primary objective of complete solubilization of the uranium from larger samples without venting. The most successful dissolvent was a mixture of 5-ml 30% H_2O_2, 0.5-ml 29$\underline{M}$ HF, and 0.5-ml 15.7$\underline{M}$ HNO_3. In samples up to 300 mg, uranium is completely dissolved, thorium is completely released from the core and precipitates as thorium fluoride, and a residue of broken SiC shells remains. The thorium can be solubilized by fuming either with perchloric or sulfuric acid. Dissolution of the SiC shells is desirable to dispel any doubt that complete solubilization of uranium and thorium is attained. Substitution of 50% H_2O_2 for 30% H_2O_2 in the dissolvent mixture did not significantly increase dissolution of the SiC shells. An unsuccessful attempt was made to dissolve the shells, separated by filtration, by reaction with a $HClO_4$-HF mixture using a Teflon-container, nickel-shell apparatus.

Experimental 1600°C-fired pellets of $(U,Pu)O_2$ FBR-type fuel is another difficult-to-dissolve material. A commonly used dissolvent is a HNO_3-HF mixture, but many batches are incompletely dissolved even after 24 h of heating under reflux. Using the Teflon container-metal-shell apparatus, the dissolution of a whole pellet was 99.98% with 12$\underline{M}$ HCl and >99.99% with 15.7$\underline{M}$ HNO_3 in 12-h heating periods at 270°C. The complete dissolution is attained in a relatively short time and the hydrofluoric acid is not required.

C. Gas-Solid Reactions (D. D. Jackson, S. F. Marsh, R. M. Hollen, and J. E. Rein)

An investigation of gas-solid reactions was started with the objective of converting refractory plutonium and uranium materials to readily soluble compounds. A plasma generator in which the gas at reduced pressure is excited to free radicals and other species by an RF discharge was investigated using a commercial apparatus, Plasmod (Tegal Corporation). Both U_3O_8 and an NBL-supplied, uranium-containing scrap, selected as a typical difficult-to-dissolve material, were reacted with Freon-13 (trifluorochloromethane) in the Plasmod. The reaction for both materials was small, as indicated by their negligible appearance and weight changes, but the Freon-13 decomposed as shown by fluoride attack of the glass sample chamber. The reaction did not increase the solubility of the NBL scrap sample in nitric acid.

The same experiment was done with chlorine gas which provided a higher concentration of reactive gas than was provided by Freon-13 decomposition. Again, the reactions with the two materials were slight and the solubility of the NBL scrap sample in nitric acid was not increased.

Another technique being investigated is the reaction of various gases at elevated temperatures with uranium-containing materials. An NBL-supplied scrap material was reacted with chlorine-containing gases at elevated temperatures in a quartz tube furnace. The volatilized quantities of total material and of uranium were measured and the residue was subjected to solubility tests. Chlorine gas at 800°C volatilized 38% by weight of the sample. This volatile fraction, which condensed in the cooler portions of the tube, was readily soluble in nitric acid and contained 98% of the uranium initially in the sample. The unvolatilized residue was subjected to an overnight reaction with nitric acid in the Teflon-container metal-shell apparatus. The residue did not dissolve and the remaining 2% uranium was not leached. These results and results obtained with HCl gas and air are summarized in Table I.

At this point, several pure uranium compounds were reacted with chlorine gas in the quartz tube furnace at 800°C to gain an insight into the NBL sample—chlorine gas reaction. With U_3O_8 and UO_3, the weight loss was insignificant, except for the conversion of UO_3 to U_3O_8, and no uranium volatilized. With UO_2 the weight loss was great and uranium volatilized. The apparent conclusion is that the UO_2 reaction product is UCl_4 (boiling point of 792°C) and that neither UO_3 nor U_3O_8 react to form volatile chlorides at 800°C.

An x-ray fluorescence analysis of the initial NBL sample and of the volatile fraction showed much zirconium, as well as uranium. It is conjectured that the NBL sample is scrap material of zirconium-containing UO_2 fuel. Chlorine would react with zirconium or ZrO_2 to form volatile zirconium tetrachloride (sublimation point of 331°C) thereby exposing the UO_2 which then reacts to give volatile UCl_4.

With the intent of decomposing the material by subliming only the zirconium, thereby leaving the uranium in a more reactive state, portions of the NBL-scrap material were reacted with chlorine at temperatures of 400 to 600°C plus a repeat reaction at 800°C. The experimental conditions were 1-g samples, 7-h reaction time, a fairly large volume quartz tube, and a chlorine pressure of about 0.2 atm. The volatile and residue fractions were analyzed for uranium. The analysis of the residue fraction involved an overnight reaction with concentrated HNO_3 at 275°C in the Teflon-container metal-shell apparatus, followed by measurement of the uranium in the solution with the automated spectrophotometer (Sec. V) and the uranium in the undissolved residue by the previously developed gamma-assay method. As shown in Table II, material with no uranium volatilized at 400 and 500°C and the nitric acid solubility of uranium in the residue (after the reaction in the Teflon-container metal-shell apparatus) was increased. However, the increase was not sufficient for practical use. At 600°C, a third of the uranium volatilized and at 800°C, 98% volatilization again was obtained.

A different NBL-supplied scrap material was reacted with chlorine at high temperatures. This material was considered slightly more resistant to nitric acid dissolution because only 69% of the uranium was solubilized in the Teflon-container metal-shell apparatus using the same treatment conditions as for the previous material. The chlorine reaction at 800°C for 7 h volatilized 39% by weight of the material and 69% of the uranium. A further reaction with chlorine at 950°C for 5 h increased the total

TABLE I

EFFECTIVENESS OF GAS REACTIONS - NITRIC ACID TREATMENTS ON NBL SCRAP[a]

	Reaction with Gases		Post Treatment	
Gas	Weight Loss of Sample (%)	Uranium Volatilized (%)	Uranium Dissolved (%)	Uranium still in Residue (%)
No treatment	---	---	72	28
Air	3	0	54	46
HCl	23	46	0	54
Cl_2	38	98	0	2

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[a] The NBL scrap sample was reacted with various gases at 800°C and the residues were treated with nitric acid in the Teflon-container metal-shell apparatus.

TABLE II

EFFECTIVENESS OF CHLORINE GAS REACTIONS - NITRIC ACID TREATMENTS ON NBL SCRAP[a]

	Reaction with Chlorine		HNO_3 Solubilization of Uranium in the Residue	
Temperature (°C)	Weight Loss of Sample (%)	Uranium Volatilized (%)	Uranium Dissolved (%)	Uranium not Dissolved (%)
No treatment			72	28
400	13	0	81	19
500	21	0	81	19
600	29	33	50	17
800	38	98	0	2

[a] The NBL scrap material was reacted with chlorine gas at various temperatures and the residues were treated with nitric acid in the Teflon-container metal-shell apparatus.

material volatilized to 43% and, most importantly, increased the uranium volatilized to 96%.

From these experiments, the most practical application of the technique appeared to be quantitative volatilizaton of uranium, its condensation, and subsequent dissolution in acid. Uranium oxides of UO_2, UO_3, and U_3O_8, and UC_2 were subjected to the chlorine reaction at temperatures up to 1000°C. Experimental conditions were 0.1 g of compound and 0.2-atm chlorine pressure. The data presented in Table III show that the volatilization order is $UO_2 > U_3O_8 \approx UO_3$. The residue remaining after the UC_2 reaction with chlorine at 1000°C volatilized completely when heated in air at 1000°C indicating that the residue was carbon and that all the uranium had volatilized. Another sample of the UC_2 was first oxidized by heating in air at 1000°C for 4 h, then reacted with chlorine at 1000°C. The material volatilized completely in 8 h. From the use standpoint, uranium is completely volatilized from UO_2, UO_3, U_3O_8, and UC_2 at 1000°C.

The technique appears applicable to many uranium materials. The chlorine reaction can, if necessary, be preceded by an oxygen reaction to produce uranium oxide. To further evaluate the system, a quartz apparatus was constructed that provides for controllable atmosphere and for effective and fast recovery of the volatilized uranium by nitric acid dissolution. About the same reaction times are required for complete volatilization of U_3O_8 in this apparatus as in the quartz tube furnace.

The condensed uranium from the scrap samples dissolved readily in 8M HNO_3. The condensed uranium from the pure uranium compounds reacted with chlorine at 1000°C was more difficult to dissolve and it was necessary to use hot, concentrated nitric acid to remove completely the uranium from the quartz tube.

D. Acid Dissolution with Ultrasonic Energy (D. D. Jackson, S. F. Marsh, R. M. Hollen, and J. E. Rein)

An ultrasonic generator can impart much acoustic energy to a fluid, thereby generating shock waves and high shearing pressures. This phenomenon could enhance acid dissolution of samples by disrupting the surface of the solid material to provide faster leaching of the uranium. The technique was evaluated using a small, bench-top ultrasonic system. An NBL-supplied, uranium-containing scrap material was reacted with concentrated HNO_3 at 80°C for 6 h using the ultrasonic system. There was no increase in the amount of uranium dissolved compared to 62% solubilized from another portion of the material treated in the same manner but without the ultrasonic energy.

IV. GAMMA ASSAY OF URANIUM AND PLUTONIUM (S. F. Marsh, M. R. Ortiz, and J. E. Rein)

Techniques stressing operational simplicity and low-cost equipment have been developed for gamma assays of ^{235}U in uranium-containing material and of

TABLE III

VOLATILIZATION OF URANIUM COMPOUNDS WITH CHLORINE AT TEMPERATURES TO 1000°C

	Weight Percent Volatilized			
		Temperature		
U Compound	Time (h)	800°C	950°C	1000°C
UO_2	7	50	---	100
U_3O_8	7	nil	26	---
	5.5	---	---	60
	10	---	---	100
	12	---	---	100
UO_3	7	slight	---	---
	8	---	---	80
	12	---	---	100
UC_2	8	86	---	88
UC_2 After pre-oxidation in air)	8	---	---	100

^{239}Pu in plutonium-containing and mixed uranium-plutonium materials. These techniques, intended primarily for assaying residues remaining after acidic reactions in the Teflon-container metal-shell dissolution apparatus, involve collecting the sample on a 25-mm-diam membrane filter, mounting the filter on a suitable support, and counting over selected gamma energy regions using a NaI(Tl) detector. The measurement precisions obtained with uranium standards with ^{235}U enrichment ranging from natural to 93% and with plutonium standards have been about 5% relative standard deviation, about twice better than the goal of 10%.

A more difficult gamma assay measurement is that for ^{235}U in residues containing both uranium and plutonium. The much lower specific activity of ^{235}U relative to ^{239}Pu and the poor resolution of NaI(Tl) detectors combine to make previously developed counting systems unsuitable. Higher resolution detectors and more complex electronic equipment have been evaluated with the continued goal of the simplest possible equipment to attain a precision of 10% relative standard deviation.

This evaluation required a series of counting references containing homogeneously distributed mixtures of ^{235}U and ^{239}Pu mounted similarly to residue samples. A large series of counting references, having various levels of uranium and plutonium isotopic abundances at fixed uranium-to-plutonium ratios, were prepared by reducing known mixtures of uranyl and plutonium nitrate solutions with $NaHSO_2 \cdot CH_2O \cdot 2H_2O$, and precipitating U^{4+} and Pu^{3+} oxalates using ethyl oxalate.[1]

In this counting reference series, the variables are ^{235}U isotopic levels of 1, 3, 6, 11, 35, and 93%; ^{240}Pu isotopic levels of 6, 12, 16, and 20%; and total uranium plus plutonium amounts of 10, 30, and 90 mg at a constant U/Pu ratio of 3/1 to simulate FBR fuel. The total number of variable combinations was 72. Eight of the references were not used because of losses incurred during filtration or because of external contamination. The remaining 64 references were analyzed by gamma spectroscopy using a high-resolution Ge(Li) detector coupled to a multichannel analyzer. Each reference was counted for 1000 s at a 10-cm distance from the detector.

The precision of the ^{239}Pu measurement was 7.3% relative standard deviation based on simple integration of the 129-keV gamma peak. The relative standard deviation of the ^{235}U measurement, based on simple integration of the 186-keV gamma peak, was about 10% at ^{235}U isotopic levels above 6% and worsened as the ^{235}U isotopic level decreased. The fact that the specific activity of ^{235}U is 3×10^4 lower than that of ^{239}Pu accounts for small 186-keV gamma peaks and the associated larger uncertainty.

The counting data were treated by the peak-smoothing technique of Gibbons et al.,[2] in which a third-order polynomial is fit to five channels of data using the least squares method. The equation is

$$D_i = 1/35\ (-3C_{i-2} + 12C_{i-1} + 17C_i + 12C_{i+1} - 3C_{i+2})\ ,$$

where $_i$ is the observed number of counts in channel i, and D_i is the smoothed number of counts in channel i.

The peak-smoothing routine improved the precision for an individual ^{239}Pu assay from 7.3 to 5.3 relative percent standard deviation using the results for all 64 counting references. On the other hand, the ^{235}U assay precision was not improved by the peak-smoothing technique and, in fact, worsened. It increased from 10 relative percent standard deviation for ^{235}U isotopic levels above 6% based on simple integration to 15 relative percent standard deviation using the peak-smoothing routine. Therefore, for low ^{235}U activity levels in the presence of ^{239}Pu, the goal of 10 relative percent standard deviation for the ^{235}U assay is not achieved using relatively simple counting apparatus and data processing techniques. More sophisticated data reduction routines have been developed by other laboratories that will provide this level of precision. It is considered redundant and beyond the scope of our program to evaluate these routines.

V. ANALYTICAL METHODS AND AUTOMATED INSTRUMENTS FOR THE DETERMINATION OF PLUTONIUM AND URANIUM

A. Automated Spectrophotometer

1. Status of Instrument Transferred to NBL (D. D. Jackson, R. M. Hollen, and J. E. Rein) NBL completed an evaluation of the automated spectrophotometer[3,4] transferred there last year. As the final study, the reliability of the instrument was established for the determination of uranium. Four weight aliquots of a standard uranium solution at each of 8 levels covering the range from 1 to 14 mg of uranium were processed for each of 12 days giving a total of 384 measurements. Preliminary statistical treatment of the results by NBL and LASL statistical personnel indicates that the relative standard deviation for a single determination is less than 0.5% for greater than 2 mg of uranium, increasing to about 1.5% at the 1-mg level. No major operating difficulties were reported by NBL personnel.

A detailed report of this automated spectrophotometer is being prepared.[5] Included are complete operating instructions with preoperational adjustments; chemical procedures for determining plutonium and uranium; information on tolerances for diverse ions including data from the original publications;[6,7] and details of the mechanical construction, the electrical control circuitry, and the microcomputer hardware and software.

The NBL instrument was returned to LASL, renovated for minor damage incurred in shipment, and demonstrated at the ERDA Safeguards Briefing and Demonstration, held at LASL on June 16, 1975. It also was on display for an AIF-sponsored Public relations tour June 18 at LASL.

2. Determination of Plutonium (D. D. Jackson, R. M. Hollen, and J. E. Rein)

Past experiments have shown that the instrument provides essentially equal accuracies and precisions for the determinations of uranium and plutonium. The tolerance to impurities found in nuclear fuel-cycle materials has been excellent for the uranium determination. An added step used for the plutonium determination is an oxidation with silver (II) oxide, necessary to produce Pu^{6+} because the measured spectral species is the extracted ion association complex, tetrapropyl ammonium plutonyl trinitrate. This oxidation can produce oxidized ions of impurity elements that also extract and spectrally interfere at the wavelengths used for the plutonium measurement.

A review indicated that chromium is the only impurity element likely to interfere in the above manner; therefore its effect on the plutonium measurement was investigated. For this investigation, we used the automated spectrophotometer prototype placed in a glovebox. The wavelength characteristics of the interference filters in this instrument are identical to those in the advanced model transferred to NBL, consequently the findings apply to both instruments. The spectrum of the extracted Cr^{6+} complex in the 2-nitropropane extractant has a broad peak at 450 nm with a tailing absorbance to about 580 nm. The absorbances of this complex at 501.4 nm and 518.0 nm, the wavelengths used for the peak and valley measurements for plutonium, are not equal, resulting in a positive bias. Unexpectedly, the bias was not linear with the quantity of chromium, whereas it was linear when the chromium was added as Cr^{6+} and the addition of silver(II) oxide was omitted. Precipitation of $Ag_2Cr_2O_7$, which started at about 4-mg total chromium level, caused the nonlinearity.

Because the oxidation potentials of Cr^{6+} and Pu^{6+} are nearly equal, it is not feasible to reduce chromium to nonextracting Cr^{3+} without reducing Pu^{6+}. Thus the plutonium measurement for chromium-containing samples must be made using the 806-nm peak where the extracted Cr^{6+} species does not absorb. The sensitivity for plutonium is about threefold lower at this peak than it is at 501.4 nm.

Other potential interferences with the plutonium determination are the halides, chloride, bromide, and iodide, which form an insoluble silver halide coating on the added silver oxide to prevent oxidation of the plutonium to Pu^{6+}. Two fumings to essential dryness, each with 0.5 ml of concentrated HNO_3, remove these halides. The residue is dissolved with 0.5 ml of warm $2\underline{M}$ HNO_3 and the usual operations give complete plutonium recoveries. The fumings are done in the tubes (made of Tru-bore tubing) used in the instrument so that no transfers of sample are involved.

3. Determination of Plutonium and Uranium in Mixtures (D. D. Jackson, R. M. Hollen, and J. E. Rein) As stated previously, both the prototype and the instrument constructed for NBL are equipped with identical peak-valley filter pairs for determining both plutonium and uranium. The instrument's capability to determine both elements in mixtures was investigated using a series containing weighed aliquots of standardized uranium and plutonium solutions. The normal mode of operation for plutonium analysis, including the oxidation with a pellet of silver(II) oxide, was followed.

The extracted uranium complex had no absorbance at either the peak or valley wavelengths used for the plutonium measurement. The only restriction applying to the plutonium measurement is an upper limit of 12 mg for the sum of plutonium and uranium, above which there is insufficient complexant for complete recovery.

The extracted plutonium complex absorbs at both the peak and valley wavelengths used for the uranium measurement. Fortuitously, the absorbances are essentially equal at the two wavelengths. The end effect is that the difference in peak and valley absorbances, as the measure of uranium, remains the same. The increased absorbance at both positions results in measuring a difference of two larger signals. This may cause a loss of precision that must be evaluated by additional experiments. The same restrictions of an upper limit of 12 mg for the sum of plutonium plus uranium apply.

The effect in the uranium determination of omitting the Ag(II) oxide when analyzing mixtures of uranium and plutonium was investigated. Under these conditions, the plutonium can be present primarily as the +4 oxidation state. Measurements made on mixtures of plutonium and uranium omitting the oxidation step gave low values for plutonium, as would be expected, and high bias for uranium. The oxidation with Ag(II) oxide is necessary for plutonium determinations as well as for uranium determinations in samples containing plutonium.

Because it is necessary to use the oxidation with Ag(II) oxide when determining uranium in mixtures containing plutonium, the effect of Cr^{6+} on the uranium determination was investigated. Although the absorbances of the extracted Cr^{6+} species by itself are equal at 452.4 nm and 460.0 nm, the wavelengths of the peak and valley positions used for the uranium determination, Cr^{6+} caused a negative bias in the uranium determination. This effect is believed to be caused by an interaction of the extracted Cr^{6+} and U^{6+} complexes.

Unlike plutonium, Cr^{6+} can be reduced to nonextracting Cr^{3+} without reducing U^{6+}. Various reductants were evaluated of which sodium sulfite gave excellent results. For Cr^{6+}-uranium samples, a $0.3\underline{M}$ Na_2SO_3 solution is added dropwise until the color changes from orange Cr^{6+} to blue Cr^{3+}. The uranium analysis then is done in the usual manner. Other reducing agents investigated (formic acid, hydrogen peroxide, and Fe^{2+}) reduced Cr^{6+} but caused a negative bias for uranium.

In the above study, the organic extractant was 2-nitropropane. The use of methylisobutyl ketone (MIBK) was evaluated. For plutonium-chromium mixtures, the results were the same as obtained using 2-nitropropane and the 806-nm peak must be used for the plutonium measurement. For uranium-Cr^{6+} mixtures, there was no adverse effect on the uranium determination when MIBK was used as the extractant. Therefore, the reduction with sodium sulfite is not necessary.

Similarly to the case with 2-nitropropane, the extracted uranium complex in MIBK has no absorbance at either the peak or valley wavelengths used for the plutonium measurement. The same restriction of a 12-mg upper limit for the sum of plutonium and uranium applies. Unlike the situation with 2-nitropropane, the plutonium complex extracted into MIBK interferes with the uranium determination, giving a small positive bias. Mixtures covering the range of 0 to 10 mg of uranium and 0 to 8 mg of plutonium were processed to establish the bias. For the prototype instrument, the bias correction is 0.027-mg U/mg Pu.

Based on the above, the following are recommended for various combinations of uranium, plutonium, and chromium. For uranium-plutonium mixtures free of chromium, use the Ag(II) oxide oxidation, 2-nitropropane as the extractant, and measure the plutonium at the more sensitive 501.4-nm peak position. There is no effect of either element upon the other. For Cr^{6+}-uranium mixtures, use MIBK as the extractant, except for samples containing thorium.[8] When 2-nitropropane is used, a prereduction with sodium sulfite is required. For chromium-plutonium mixtures, the less sensitive 806-nm peak position must be used for the plutonium measurement either with 2-nitropropane or MIBK as the extractant. For uranium-plutonium-chromium mixtures, use the Ag (II) oxide oxidation, MIBK as the extractant, and measure the plutonium at 806 nm. Correct the uranium result for plutonium interference using the factor of 0.027 mg U/mg Pu.

4. Effect of Acidity on Uranium Determination (D. D. Jackson, R. M. Hollen, and J. E. Rein) Inorganic acids, such as nitric acid, extract into the organic phase of MIBK or 2-nitropropane. The aluminum nitrate salting solution is made basic with ammonium hydroxide thereby increasing the tolerance of the method to acid. The nitric acid content of the aluminum nitrate reagent varies among lots and the strength of ammonium hydroxide depends on its storage integrity. Also, during the preparation of the salting solution, ammonia may volatilize. Therefore, the tolerance to acid varies among salting solutions.

The acidity of a salting solution was determined by an oxalate complexing-pH titrimetric method[9] and this salting solution then was used to investigate the effect of acid on the determination of uranium. This salting solution was prepared as 2.8M $Al(NO_3)_3$, 0.025M tetrapropylammonium hydroxide, 2M NH_4OH. The determined base concentration was 1.2 N. The acid effect was measured at two uranium levels of 2.5 and 10 mg, using 4 ml of the salting solution and 0.5-ml samples with levels of nitric acid ranging from 6 to 15.8M (3 to 7.9 mmole). The absorbance was constant for both uranium levels up to 5 mmole of nitric acid, then decreased continuously with increasing acidity. At the 10-mg uranium level, the negative bias was 0.8% for 6.1 mmole HNO_3, 1.5% for 6.6 mmole, and 2.5% for 7.0 mmole. The effect was greater at the 2.5-mg uranium level being 1.9% for 6.1 mmole HNO_3, 2.3% for 6.6 mmole, 3.4% for 7.0 mmole, and 5.8% for 7.9 mmole. The effect appears to become significant when the acidity content of the sample exceeds the base content of the salting solution. For this reason, each prepared salting solution should be analyzed for its base content.

5. High Sensitivity Determinations for Plutonium and Uranium (S. F. Marsh, D. D. Jackson, M. R. Ortiz, R. M. Hollen, and J. E. Rein) Experience with analyses of various scrap-type samples provided by NBL showed the desirability of developing a more sensitive measurement for uranium and plutonium. At present, the automated spectrophotometer has a lower limit for uranium determination of about 2 mg/ml, but many solutions resulting from acid dissolution in the Teflon-container, metal-shell apparatus have uranium levels lower than 2 mg/ml. Samples are presently analyzed by evaporating a larger aliquot to dryness in the spectrophotometer sample tube and then adding 0.5 ml of 8M HNO_3. Because a usual characteristic of scrap-type samples is a high extraneous element content, voluminous salts are deposited that can inhibit the extraction of uranium.

A way to increase the measurement sensitivity without a major instrument modification is to incorporate a chromogenic agent in the organic extractant. Initial studies emphasized the use of a chromogenic agent with the existing extraction method.

Many chromogenic agents were investigated without success. Most uranium complexes having high molar absorptivities do not form at the low pH levels of the present system. Also, many require a critical pH adjustment for reproducible color development. Dibenzoylmethane (DBM), a frequently used chromogen for uranium, known to be soluble in the organic extractant, was investigated. The complex did not form at the low pH of the system. The addition of an organic base that would be preferentially soluble in the organic phase was investigated to attain pH adjustment. This was not successful.

The few chromogenic agents that gave enhanced color had insufficient separation of the wavelengths for the absorbance peak and the unreacted reagent. This caused an unacceptable large measurement error for the single-beam automated instrument.

One inorganic chromogenic agent, thiocyanate, was investigated because the colored uranium complex is formed at low pH. Instability of the reagent and the uranium complex, as well as inadequate wavelength separation of the reagent and the complex, prompted its abandonment.

The study has been expanded from finding a chromogen useful with the existing extraction system to any promising extraction-spectrophotometric method. Currently, extractants such as Alamine-336, Aliquot-336, and tridodecylamine are being evaluated with arsenazo III as the chromogen. Another system being studied is extraction of the benzoyltrifluoroacetone-uranium(VI) complex into butyl acetate.[10]

B. Investigation of Electrotitrimetry for Determining Plutonium (D. D. Jackson, R. M. Hollen, and J. E. Rein)

1. Apparatus Development. A versatile apparatus was assembled and successfully tested that provides for the investigation of a variety of electrometric titration systems. It consists of commercial components centered around a Princeton Applied Research Corporation 173D Potentiostat and 179 Digital Coulometer and a Hewlett-Packard 9820 desk-top programmable calculator. These instruments are interfaced for two-way communication. The calculator controls most functions of the potentiostat and coulometer, and receives and processes data from them. Also interfaced and under control of the calculator are a digital multimeter and a plotter.

With this apparatus, titrimetric conditions such as controlled potential and controlled current are done under control of the calculator and the electrolysis measurement of interest such as current, voltage, coulombs, and time are monitored with the calculator and plotted in any desired display. The programmable calculator uses a simple language readily mastered by personnel with no previous programming experience. Therefore, changes are easily made to provide a high level of flexibility. For example, the electrolysis data can be processed for decision-making such as decreasing the current of a controlled-current electrolysis as the end point is approached to provide highly precise results or changing the controlled potential to obtain reaction specificity. Several programs have been written for the Hewlett-Packard 9820 calculator to allow control and operation of the electrometric system in different modes. For example, one program carries out a controlled potential coulometric titration through the prereduction step, the measuring oxidation step, and then halts the electrolysis at the endpoint.

Once the electrometric conditions are established and the electrolysis is started, the operation is automatic including initial clearing of the coulometer, electrolysis to the established background current level for the reduction step, clearing the coulometer, switching to the preset oxidation potential, and electrolyzing to the established background- current-level endpoint. At the endpoint, the electrolysis is stopped and the accumulated coulombs are output. During all phases of the electrolysis, the on-line digital plotter can record a variable of interest, usually a plot of log current vs time. The electrolysis can be interrupted at any time and run manually or returned to any place in the automatic mode.

A conventional electrolysis cell was constructed having a platinum-gauze working electrode, a saturated-calomel reference electrode in a fiber-tip compartment, a Vycor counter electrode centered in the cell, and a glass stirring paddle driven by a synchronous motor. The electrolysis time is relatively short in this cell. For example, 5 mg of Fe(II) is oxidized to Fe(III) in 7 min.

The precision of the system was determined using pure iron. The relative standard deviation of a single determination of 2.5 mg of iron was 0.15%. A slight spattering of the sample was observed caused by wobble of the stirring rod which can degrade the precision. The stirring mechanism has been improved to eliminate the wobble.

2. Method Development. Investigations of electrotitration systems applicable to the determination of plutonium have been started. The objective is to develop a method that has features of (1) high specificity, (2) precision of 0.1-0.2% relative standard deviation, and (3) sensitivity of low-milligram plutonium levels to serve as the basis for an automated instrument. Unlike the situation for uranium, there is no reported electrometric method for plutonium that has the above required features.

Two systems are being considered. The first involves extraction of a plutonium complex into an organic solvent to provide specificity and an electrometric measurement of the plutonium in the organic phase without its physical separation from the aqueous phase. The second involves a preliminary reduction of plutonium to Pu^{3+}, an oxidation in a medium in which Pu^{3+} is not oxidized but potentially interfering diverse ions are oxidized, addition of complexing agents that reduce the Pu^{3+}-Pu^{4+} potential, then oxidation of Pu^{3+} to Pu^{4+}.

The first solvent extraction system evaluated was the one used for the determination of plutonium by the automated spectrophotometer. The tetrapropylammonium trinitrate complex of Pu(VI) is extracted from an aluminum nitrate salting solution into the organic phase. Various organic extractants can be used to extract greater than 99.5% of the plutonium.

In preliminary work, iron was used as a stand-in for plutonium because only one titration apparatus was available that was not yet installed for glovebox operation. Iron(III) as the chloride complex was extracted into 2-nitropropane and its electrolytic reduction to Fe^{2+} was attempted. It was not reduced although the conductance of the organic phase was adequate and the blank background current was satisfactorily low. The failure to get reduction is attributed to the strong oxidative power of nitrate in an organic medium. In aqueous medium, the reduction is not hindered by nitrate. It is concluded that an organic extraction from an aqueous nitrate medium cannot be used for this application. A chloride medium also is considered unsuitable because diverse ions, such as iron, extract and have the same oxidation potential as the Pu^{3+}-Pu^{4+} couple.

The use of higher molecular weight amines as extractants for uranium from acidic sulfate media has been reported. This separation has promise for this application because sulfate media are excellent for Pu^{3+}-Pu^{4+} titrations and sulfate should not be a strong oxidant in organic media. A literature search is under way to select specific amines suitable for the efficient extraction of plutonium from sulfate media.

Although the desired mode of an organic extraction was to do the electrometric measurement in the organic phase with no separation from the aqueous phase, thereby avoiding the difficult automated operation of transferring an exact volume of the organic phase, this latter technique was investigated briefly. After extraction of the tetrapropylammonium-iron(III) chloride complex, an aliquot of the organic phase was transferred to an electrolysis cell containing dilute sulfuric acid and the iron stripped into the sulfuric acid was determined by controlled potential coulometry with the organic phase present. With methylisobutyl ketone or 1, 1, 2, 2-tetrachloroethane as the extractant, iron(III) did not reduce. Apparently, these organics or impurities in them stripped to the dilute sulfuric acid and preferentially reduced. With 2-nitropropane or carbon tetrachloride as the extractant, the iron was determined with no difficulty.

An analytical method for determining plutonium applicable to solutions containing a wide range of metal and nonmetal ions and with a precision of 0.2% relative standard deviation has been reported recently by Davies and Townsend.[11] In this method, an excess of copper(I) chloride reduces plutonium to plutonium(III) in an aqueous solution containing hydrochloric acid, aluminum chloride, and sulfamic acid. The mixture is then titrated potentiometrically with standard potassium dichromate solution to a first end point that corresponds to complete oxidation of the excess Cu^{1+} and any Fe^{2+}. Sulfuric and phosphoric acids are added and the titration is continued to a second end point of the oxidation of Pu^{3+} to Pu^{4+}.

A study of this procedure is under way with the initial objective of adapting it to controlled potential coulometry. The results so far are promising. The redox potentials of the Fe^{2+}-Fe^{3+} couple and of the Pu^{3+}-Pu^{4+} couple in the aluminum chloride-hydrochloric acid mixture were measured as 0.41 V and 0.67 V vs a saturated calomel electrode (SCE). Electrolysis at a controlled potential of 0.30 V vs SCE should reduce plutonium to Pu^{3+} and iron to Fe^{2+} and not reduce U^{6+} nor other oxidized ion states such as Mo^{6+}. Electrolysis at a controlled potential of about 0.54 V vs SCE should oxidize Fe^{2+} to Fe^{3+} without oxidizing Pu^{3+}. Subsequent addition of the sulfuric and phosphoric acids decreases the redox potential of the Pu^{3+}-Pu^{4+} couple to a measured 0.43 V vs SCE and the plutonium should be determinable coulometrically at a controlled potential of 0.67 V vs SCE. The potential of the Fe^{2+}-Fe^{3+} couple decreases to about 0.31 V vs SCE after adding the sulfuric and phosphoric acids so the already oxidized iron should remain stable. A sample of iron was carried through this sequence with good results. The iron reduced at 0.30 V vs SCE to a satisfactory current level of 30 μA and oxidized at 0.55 V vs SCE to this same level. The number of coulombs measured agreed with theoretical based on the measured quantity of added iron. The current did not increase when the sulfuric and phosphoric acid mixture was added nor when the controlled potential was increased to 0.67 V vs SCE. Blank values measured by cycling the supporting electrolyte through the electrolysis were satisfactorily low.

VI. PREPARATION OF PLUTONIUM-CONTAINING MATERIALS FOR THE SALE PROGRAM (S. F. Marsh, M. R. Ortiz, H. J. Kavanaugh, and J. E. Rein)

The Safeguard Analytical Laboratory Evaluation (SALE) Program has the following objectives. (1) To generate timely data on the capabilities of ERDA licensee and contractor laboratories to analyze typical uranium and plutonium materials. (2) To prepare well-characterized uranium and plutonium materials for use as working calibration test materials (WCTM) by analytical laboratories.

A. Plutonium Oxide

Two batches of 900°C-fired PuO_2 powder were extensively characterized for plutonium assay, plutonium isotopic distribution, and impurity element concentrations. The homogeneity of one batch was satisfactory, whereas the other was not satisfactory even after a second sieving through a 200-mesh screen and remixing. One hundred vials, each containing 1 g of the acceptable batch of PuO_2 powder, were packaged and shipped to Allied Chemical Corporation (ACC), Idaho, for use as surveillance samples.

B. Uranium-Plutonium Mixed Oxide

Two batches of 1600°C-sintered mixed oxide powders, with differing uranium-to-plutonium ratios, were characterized for uranium and plutonium contents, uranium and plutonium isotopic distributions, and impurity element concentrations. The homogeneity level of each batch was satisfactory. Sixty vials, each containing 1 g of powder, were packaged for each batch of mixed oxide and shipped to ACC, Idaho, for use as surveillance samples.

C. Plutonium Metal

Six portions each of two different lots of high-purity plutonium metal were shipped to ACC, Idaho. Each portion was weighed in an argon-atmosphere-controlled glovebox used to prepare the plutonium metal shipped to NBS for distribution as the assay Standard Reference Material (SRM). Each portion was individually sealed in an argon-flushed, partially evacuated glass tube identical to the packaging used for the SRM plutonium metal. Complete chemical and isotopic characterizations were provided for each lot. The accurately weighed high-purity plutonium metal will be dissolved with accurately weighed high-purity uranium metal at ACC, Idaho to prepare WCTMs and RCTMs (reference calibration test materials) of mixed uranium-plutonium nitrate solution that simulate reprocessing plant dissolver solution.

VII. ANALYSIS OF HTGR FUEL (A. D. Hues and W. H. Ashley)

The analysis of monthly samples is complete for the NBL-administered Mixed Carbide Laboratory Comparison Program, Phase II. Ten sets, each consisting of two UO_2-ThO_2 samples, one BISO bead sample, and one TRISO bead sample, were analyzed for uranium and thorium. The coatings were removed from the bead samples by igniting them in oxygen or by heating them alternately in oxygen and chlorine gas.[12] After dissolution in acid, the uranium and thorium were separated by anion exchange in strong HCl, uranium was determined by a modification of the Davies-Gray method, and thorium was determined by Versene titration.[12] The pooled, relative standard deviation of the determinations, computed from the four results for each sample for each of 10 months, were 0.02% for the uranium and 0.07% for the thorium.

VIII. ANALYSIS OF SALE URANIUM MATERIALS (A. L. Henicksman, A. D. Hues, W. H. Ashley, R. M. Abernathey, and J. E. Rein)

Analyses of the SALE monthly (now bimonthly) samples of uranium nitrate and uranium oxide were continued for uranium content and isotopic distribution. There were no significant biases and the measurement precisions continued to be smaller than the averages of the participating laboratories.

The NBL-modified Davies-Gray method,[13] modified by us for determining 1-g uranium samples using a weight buret for the $K_2Cr_2O_7$ titration rather than a volumetric buret, has replaced the previously used LASL method.[14] The measurement precision is 0.008% relative standard deviation.

IX. CHEMICAL CHARACTERIZATION OF SPECIAL SAMPLES (G. R. Waterbury and Staff)

Various Safeguards Appraisal Survey samples, including aqueous, organic, and multiphase solutions with a wide range of plutonium contents were analyzed for inventory surveillance purposes. These samples were taken at ERDA-contractor facilities. Both the plutonium contents and isotopic distributions were determined. Complete conversion to single-phase solutions was accomplished before analyses.

X. PLUTONIUM ISOTOPE HALF-LIFE MEASUREMENTS (S. F. Marsh, M. R. Ortiz, R. M. Abernathey, R. K. Zeigler, G. L. Tietjen, J. W. Dahlby, J. E. Rein, and G. R. Waterbury)

LASL is participating in an inter-ERDA laboratory program to measure accurately the half-lives of longer lived plutonium isotopes. The efforts at LASL include the preparation, extensive characterization, and distribution of high-purity batches of plutonium metal from specially provided, enriched isotope materials, and half-life measurements using the technique of isotope dilution mass spectrometry for measuring the produced daughter isotope. The LASL characterization measurements include assay, isotopic distribution, metal impurities including other transuranics, and nonmetal impurities.

The plutonium isotopes in the program are ^{239}Pu, ^{238}Pu, and ^{240}Pu, and perhaps ^{241}Pu. An initial batch of ^{239}Pu metal (99.26% ^{239}Pu isotopic abundance), designated Pu-1, was prepared and characterized. This metal was sent to the Mound Laboratory for a calorimetric measurement of half-life and was then returned. Accurately weighed portions of the metal were sealed in Pyrex tubes under a dry argon cover gas and distributed to laboratories.

The goal of the LASL half-life measurement program is at least 1% relative accuracy. Based on an error propagation, an experimental program has been formulated to attain this goal using the Pu-1 metal. Six weighed portions of the metal were dissolved and separated from the grown-in and impurity uranium by ion exchange, a measured quantity of ^{233}U was added, and the growth rates of daughter ^{235}U are being measured at selected time periods by mass spectrometric determinations of the ^{235}U/^{233}U ratio. The ^{239}Pu half-life will be calculated from the fundamental decay equation, $-(dn/dt)239 = N\lambda$, where $-(dn/dt)239$ represents the loss of ^{239}Pu atoms per unit time. Because each ^{239}Pu decay produces an atom of ^{235}U (whose own half-life is ~ 3 x 10^4 times longer than ^{239}Pu), the above equation may be written $+(dn/dt)235 = N\lambda$, where $+(dn/dt)235$ represents the growth of the ^{235}U daughter per unit time. In both equations, N is the number of ^{239}Pu atoms and λ is the ^{239}Pu decay constant. Therefore

$$\lambda_{239} = \frac{^{235}\text{U formation per unit time}}{^{239}\text{Pu atoms}}\text{, and}$$

$$t_{1/2}^{239} = \frac{(\ell n2)\,(^{239}\text{Pu atoms})}{^{235}\text{U formation per unit time}}\,.$$

For this application, N, the number of ^{239}Pu atoms, is calculated from the plutonium metal weight corrected for chemical purity and isotopic distribution. The formation rate of ^{235}U is measured by isotope dilution mass spectrometry using an accurately measured initial addition of ^{233}U as the internal standard.

From the experimental standpoint, highly accurate values are required for (1) the initial weights of the six Pu-1 metal samples, (2) the isotopic abundance of ^{239}Pu in Pu-1 metal, (3) the characterization measurements of the Pu-1 metal for total impurities, (4) the quantity of ^{233}U added to each dissolved Pu-1 sample, and (5) the mass spectrometric measurement of ^{235}U/^{233}U ratios. The experimental goals, in terms of relative percent, are 0.01 for weighing each of the six Pu-1 samples, 0.05 for the ^{239}Pu content of the six Pu-1 solutions, 0.1 for the quantity of ^{233}U added, and 0.1 for the ^{235}U/^{233}U measurements. Any small losses of plutonium during the ion-exchange removal of uranium will be measured and the appropriate corrections applied.

Because there is no source of high-enrichment ^{233}U metal from which a known concentration ^{233}U solution can be directly prepared, the ^{233}U solution concentration was established by isotope dilution mass spectrometry using four separate uranium standard solutions. For this purpose, two solutions were prepared from NBS SRM-960 (natural U metal) and two were prepared from high-purity 93% ^{235}U metal available at LASL.

The quantity of ^{233}U added to four of the dissolved Pu-1 metal solutions was selected to equal the quantity of ^{235}U grown-in during a time period of 1.5 yr. The quantity of ^{233}U added to the remaining two solutions will provide equal amounts of ^{235}U and ^{233}U after 4.5 yr. Mass spectrometric measurement of isotope ratios is most accurate and precise at 1/1 ratios. The ^{235}U/^{233}U mass spectrometric measurements for the first four solutions will cover the time period 0.5 to 2 yr, with data then being reported. Data from the remaining two solutions should be more accurate with the threefold longer grow-in period and will serve to substantiate the earlier data. The initial and the first 6-month grow-in measurements of ^{235}U daughter have been completed. Two more 6-month grow-in intervals will be measured during FY 76.

A batch of ~90% enriched ^{238}Pu metal will serve as the test material for the ^{238}Pu half-life measurement. The packaging and distribution of this metal to the participating laboratories for characterization and half-life measurements will proceed based on agreements reached by representatives of ANL, DOW-RF, LLL, Mound, and LASL at the second meeting of the Half-Life Evaluation Committee (HLEC) at LASL, February 18-19, 1975.

PUBLICATIONS AND TALKS

1. S. F. Marsh, M. R. Ortiz, and J. E. Rein, "Coprecipitation of Uranium and Plutonium Oxalates Using Sodium Formaldehyde Sulfoxylate Reduction and Diethyl Oxalate Hydrolysis Precipitation," Los Alamos Scientific Laboratory report LA-5876-MS (March 1975).

2. S. F. Marsh, M. R. Ortiz, and J. E. Rein, "Cation Exchange Behavior of Lanthanides and Trivalent Actinides in Ethanol-Hydrochloric Acid," Los Alamos Scientific Laboratory report LA-5728 (December 1974).

3. D. D. Jackson, D. J. Hodgkins, R. M. Hollen, and J. E. Rein, "Automated Spectrophotometer for the Determination of Plutonium and Uranium," Los Alamos Scientific Laboratory report, in press.

REFERENCES

1. S. F. Marsh, M. R. Ortiz, and J. E. Rein, "Coprecipitation of Uranium and Plutonium Oxalates Using Sodium Formaldehyde Sulfoxylate Reduction and Diethyl Oxalate Hydrolysis Precipitation," Los Alamos Scientific Laboratory report LA-5876-MS (March 1975).

2. D. Gibbons, L. E. Fite, and R. E. Wainerdi, "Computer-Coupled, Automatic Activation Analysis," U.S. Atomic Energy Commission report TID-7629, pp 221-238 (1972).

3. D. D. Jackson, D. J. Hodgkins, and J. E. Rein, "Automated Spectrophotometer for the Determination of Plutonium and Uranium," 17th Conf. Anal. Chem. Nucl. Technol., Gatlinburg, TN, October 23-27, 1973.

4. D. D. Jackson, J. E. Rein, and G. R. Waterbury, "Chemical Assay of Plutonium for Safeguards," American Nuclear Society Meeting, San Francisco, CA, November 11-15, 1973. Published in Nucl. Technol. **23**, 132-141 (1974).

5. D. D. Jackson, D. J. Hodgkins, R. M. Hollen, and J. E. Rein, "Automated Spectrophotometer for the Determination of Plutonium and Uranium," Los Alamos Scientific Laboratory report, in press.

6. W. J. Maeck, M. E. Kussy, G. L. Booman, and J. E. Rein, "Spectrophotometric Extraction Methods Specific for Uranium," Anal. Chem. **31**, 1130 (1959).

7. W. J. Maeck, M. E. Kussy, G. L. Booman, and J. E. Rein, "Spectrophotometric Extraction Method Specific for Plutonium," Anal. Chem. **33**, 998 (1961).

8. G. R. Waterbury, Compiler, "Analytical Methods for Fissionable Materials in the Nuclear Fuel Cycle. Program Status Report June 1972 to June 1973," Los Alamos Scientific Laboratory report LA-5347-SR (August 1973).

9. G. L. Booman, M. C. Elliott, R. B. Kimball, F. O. Cartan, and J. E. Rein, "Determination of Free Acid in the Presence of Hydrolyzable Ions," Anal. Chem. **30**, 284 (1958).

10. T. Shigematsu, M. Tabushi, and M. Matsui, "The Solvent Extraction and Spectrophotometric Determination of Uranium using Benzoyltrifluoroacetone as the Chelating Reagent," Bull. Chem. Soc. Japan **37**, 1333-1336 (1964).

11. W. Davies and M. Townsend, "Analytical Method for the Titrimetric Determination of Plutonium Using Cuprous Chloride as Reductant," United Kingdom Atomic Energy Authority report TRG-2463 (1974).

12. A. D. Hues, A. L. Henicksman, and W. H. Ashley, "Determination of Uranium and Thorium in Carbon and Silicon Carbide-coated Uranium-Thorium Carbide Fuel Beads," Los Alamos Scientific Laboratory report LA-5429 (March 1974).

13. A. R. Eberle, M. W. Lerner, C. G. Goldbeck, and C. J. Rodden, "Titrimetric Determination of Uranium in Product, Fuel, and Scrap Materials after Ferrous Ion Reduction in Phosphoric Acid," U.S. Atomic Energy Commission report NBL-252 (July 1970).

14. G. R. Waterbury, Compiler, "Analytical Methods for Fissionable Materials in the Nuclear Fuel Cycle. Program Status Report June 1973 to June 1974," Los Alamos Scientific Laboratory report LA-5696-SR (October 1974).