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Progress Report

Analytical Methods for Fissionable Material Determinations in the Nuclear Fuel Cycle

October 1, 1977—September 30, 1978

University of California

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ANALYTICAL METHODS FOR FISSIONABLE MATERIAL DETERMINATIONS IN THE NUCLEAR FUEL CYCLE OCTOBER 1, 1977—SEPTEMBER 30, 1978

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ABSTRACT

Work has continued on the development of dissolution techniques for difficult-to-dissolve nuclear materials, development of methods and automated instruments for plutonium and uranium determinations, preparation of plutonium-containing materials for the Safeguards Analytical Laboratory Evaluation (SALE) program, preparation of plutonium materials for distribution by the National Bureau of Standards (NBS) as standard reference materials (SRMs), measurement of longer plutonium isotope half-lives, and analysis of SALE uranium materials. New tasks include the development of methods and automated instruments for the determination of thorium and uranium, and an evaluation of the ion-exchange-bead technique for the mass spectrometric measurement of uranium and plutonium isotope distributions.

Completed tasks include the measurements of ion exchange distributions of over 50 elements on cation exchange resins from nitric acid media and anion exchange resins from hydrobromic and hydriodic acid media. Using a newly developed procedure, the LASL automated spectrophotometer was modified to determine microgram levels of uranium and to determine milligram levels of uranium and plutonium. Construction of an automated controlled-potential analyzer for the determination of plutonium is nearing completion. Apparatus and procedures for the separation and complexometric titration of thorium and uranium are being developed.

I. INTRODUCTION

Safeguards control of uranium, thorium, and plutonium in the nuclear fuel cycle requires inventory confirmation by adequate sampling and reliable analyses. Precise and accurate measurements of the amounts of these elements and their isotopic compositions are required for widely diverse nuclear materials, including pure products, reactor fuels having complex chemical compositions, and many types of scrap materials. Dissolutions and analyses of materials containing highly refractory components and of multiphase scrap are particularly difficult.

Our objectives are to

- develop fast, effective dissolution techniques and analytical methods for plutonium, thorium, and uranium determinations.

- design and construct automated analyzers for determinations of the three elements.
- prepare well-characterized, plutonium-containing materials for use in the Safeguards Analytical Laboratory Evaluation (SALE) program and for distribution by the National Bureau of Standards (NBS) and the New Brunswick Laboratory (NBL).
- prepare, characterize, and distribute enriched isotope plutonium materials for a Department of Energy (DOE) interlaboratory program to measure the half-lives of long-lived plutonium isotopes and participate in the measurements of such materials.
- prepare, characterize, and provide calibration materials for the Los Alamos Scientific Laboratory (LASL) nondestructive analysis (DYMAC) system.
- evaluate correlation techniques for Safeguards control of irradiated fuels.
- analyze inventory verification samples chemically as requested by DOE.

II. DISSOLUTION OF NUCLEAR FUEL CYCLE MATERIALS

Because many nuclear fuel cycle materials are refractory in nature, their dissolution by conventional chemical techniques is difficult. Dissolution is particularly difficult for recovery process residues of fissile materials that have been incinerated and leached repeatedly with various hot acid mixtures in attempts to solubilize the uranium, plutonium, and thorium. A standard dissolution technique for such materials is unlikely because of their diverse composition.

Dissolution of nuclear fuel cycle materials being prepared for assay and isotope measurements is often the most difficult and time-consuming operation. Use of conventional techniques, such as acid reaction at ambient pressure and molten salt fusions in various combinations, often requires several days to several weeks for complete dissolution of many materials. We are currently investigating the following techniques to attain rapid solubilization of uranium, thorium, and plutonium: (1) mineral acid reactions at elevated temperatures in pressurized containers, (2) gas-solid reactions with reactive gases to decompose the material or to volatilize the uranium, thorium, and plutonium, and (3) reactions with various media using laser energy input.

A. Teflon-Container, Metal-Shell Apparatus (S. F. Marsh and J. E. Rein)

A LASL-developed Teflon container in a nickel or stainless steel metal shell has been used successfully for the dissolution of various nuclear materials. Maximum operating temperature and pressure of this apparatus were 270°C and 320 atm (5000 psi), respectively. The nickel shell was used with 3 to 29*M* HF, 3 to 12*M* HCl, and HF-HCl mixtures with or without oxidizing acids such as 0.01 to 0.1*M* HNO_3, 0.01 to 0.1*M* H_2SO_4, and mixtures of 3 to 15.6*M* HNO_3 and/or 3 to 18*M* H_2SO_4 with or without 0.01 to 0.1*M* HF. LASL offered the design of this apparatus to several manufacturers, and the Parr Instrument Company began marketing slightly modified models.

Two years ago, we verified NBL's findings that venting problems frequently occurred with the Parr stainless steel models with Parr Teflon containers when used at 270°C with mixtures of 3 to 15.6*M* HNO_3 and 0.01 to 0.1*M* HF on such materials as high-fired PuO_2 and calcined $(U,Pu)O_2$. Because the LASL-fabricated apparatus had given complete dissolution at 270°C without venting, we speculated that the ventings in the Parr apparatus were due to the Teflon undergoing a reaction at high temperature.

Six Parr containers, fabricated from another batch of Teflon, were provided to us for evaluation. All but one of these containers also vented when mixtures of 3 to 15.6*M* HNO_3 and 0.01 to 0.1*M* HF were used, even at a lower temperature of 250°C and in the absence of PuO_2 and $(U,Pu)O_2$ samples. In the one container that did not vent, the stainless steel disk was badly corroded, indicating a high permeability of the Teflon to HNO_3 and HF vapor. Tests were repeated for Parr Teflon containers with gold-plated disks. Although venting did occur, the gold-plated disks showed no corrosion, which indicated that the venting is caused by a pressure-producing reaction in the Teflon containers.

New Teflon containers were fabricated at LASL and tested. Although their failure rate at 250°C was comparable to that of the Parr-supplied containers, there were no failures at 230°C. Therefore, we believe that 230°C will have to be the operating limit for these two supplies of Teflon containers. We have asked E. I. du Pont de Nemours & Co., manufacturer of Teflon stock material, to provide technical information for this application.

B. Gas-Solid Reactions (D. D. Jackson, J. E. Alarid, and J. E. Rein)

We continued our investigations of gas-solid reactions used to convert uranium and plutonium in refractory materials to species readily soluble in mineral acids or to volatile species that condense as readily soluble compounds in mineral acids such as HNO_3. The reactions were carried out in a closed quartz tube in a temperature-controlled, resistance-heated furnace. The quartz tube provided controllable atmospheres and effective recovery of the solubilized compounds.

We previously reported that chlorine and especially carbonyl chloride effectively volatilized uranium from uranium oxides and other nuclear materials.[1] For example, 0.1 g of U_3O_8 volatilizes completely with carbonyl chloride in 0.5 h at 1000°C and in 1 h at 800°C compared to 12 h at 1000°C required with chlorine.

Volatilities are being measured for various materials present in nuclear fuel cycle materials when reacted with carbonyl chloride at 800°C. Zirconium and niobium oxides volatilize completely in 1 h; also, >99% of stainless steel powder and >41% of aluminum powder volatilize in 1 h. A very difficult-to-dissolve, uranium-containing, scrap material from a LASL waste-recovery calcination facility was reacted with carbonyl chloride. At 1000°C, >75% of the material and >50% of the uranium volatilized in 2 h. Reaction of the residue with hot HNO_3 dissolved the remaining uranium. Thus with this treatment, the uranium was solubilized completely in several hours. In contrast, a treatment with HF-HNO_3 mixtures in the Teflon-container, metal-shell apparatus and fusion of the undissolved residue with ammonium bifluoride did not solubilize the uranium completely.

Other gases are being investigated for volatilizing uranium. Neither nitrosyl chloride (NOCl) nor an equal-volume mixture of chlorine and nitric oxide (NO) was effective. Essentially no uranium was volatilized from UO_2 or U_3O_8 in 2-h reactions at 800 or 1000°C. Tests show that nitric oxide suppresses the chlorine volatilization reaction. Mixtures of chlorine and higher oxides of nitrogen will be tested. A tube furnace being installed in a glove box will be used to investigate gas-solid reactions with plutonium materials.

C. Laser-Enhanced Dissolution Studies (M. E. Cournoyer, S. F. Marsh, and J. E. Rein)

Chemical dissolution treatments generally are enhanced by adding energy. Previously, heat has been applied to acid solutions and to fusions with molten salts. Gas-solid reactions at elevated temperatures, discussed above, are another example of energy input for chemical dissolution. It is technically advantageous to dissolve material by transferring energy directly to the material immersed in a reactive liquid or gas medium. Lasers have ample energy to vaporize materials, thereby providing a reactive interface.

Initial efforts concerning laser applications have involved acquiring safety information, making an extensive literature survey, and assembling test apparatus. There has been considerable study of the heating, decomposition, and volatilization of refractory oxides using lasers. An absorbed energy of 1 MW/cm^2 was reported as necessary to vaporize elements from oxides.[2] Directly applicable to dissolution is the laser heating of aluminum metal, immersed in a water-filled quartz cell, to >2050°C.[3]

A condition for laser-enhanced reactions is low absorption of the light energy in the medium. Transmittances over the visible wavelength range of 400 to 700 nm were measured for HCl, HNO_3, a 3/1 HCl/HNO_3 mixture, and $HClO_4$. Light was absorbed only in the HCl-HNO_3 mixture starting at 550 nm and increasing rapidly toward the ultraviolet. Preliminary evaluations are being made of three lasers: (1) a 5-W, continuous-wave (CW), argon-ion laser producing a beam of 480- and 520-nm wavelengths, (2) a 4-W neodymium glass laser with a 1.06-μm wavelength, and (3) a 100-J, pulsed, ruby laser at 694-nm wavelength. These lasers have been

TABLE I

DISSOLUTION OF ZrO_2 POWDER, Al_2O_3 POWDER, AND ZIRCONIA CRUCIBLE IN VARIOUS ACIDS UNDER VARIOUS CONDITIONS

		Percentage Dissolved in			
Condition	**Material**	**16M HNO_3**	**6M HCl**	**12M HCl**	**9MHBr**
Unheated solution	ZrO_2 powder	0.0	0.0	0.0	0.0
64-h reaction	Al_2O_3 powder	0.9	1.0	1.2	1.0
	Zirconia crucible	0.0	0.0	0.0	0.0
64-h reaction plus 0.5-h reaction in ultrasonic bath	ZrO_2 powder	0.0	0.0	---	0.0
	Al_2O_3 powder	0.9	1.0	---	1.1
	Zirconia crucible	0.0	0.0	---	0.0
Reflux heating, 24-h reaction	ZrO_2 powder	0.3	0.4	0.4	0.3
	Al_2O_3 powder	14.6	13.4	15.0	9.6
	Zirconia crucible	0.0	0.0	0.0	0.0
Teflon-container, metal-shell apparatus, overnight reaction at 250°C	ZrO_2 powder	---[a]	---	100	10.6
	Al_2O_3 powder	---	---	100	100
	Zirconia crucible	---	---	0.0	0.0

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[a] A dash indicates no test was made.

used for tests on three refractory oxides: Al_2O_3 powder, ZrO_2 powder, and large pieces of a crushed zirconia crucible. The effectiveness of laser-enhanced, acid dissolution is being evaluated relative to a series of progressively more vigorous reactions with the same acids. The reaction conditions are reaction at room temperature with and without ultrasonic energy, heating under reflux, and heating at 250°C in the Teflon-container, metal-shell apparatus. After reaction, the extent of dissolution was determined by measuring the dissolved aluminum and zirconium ions by complexometric titration. The results in Table I show that significant dissolution was obtained only in the Teflon-container, metal-shell apparatus. Laser bombardment, using the 4-W neodymium glass laser, of the three materials in 6M HCl and in 9M HBr was unsuccessful in causing dissolution. Direct irradiation in air did not vaporize any material, indicating inadequate energy. The 100-J, pulsed, ruby laser will be evaluated next.

III. ANALYTICAL METHODS AND AUTOMATED INSTRUMENTS FOR PLUTONIUM AND URANIUM DETERMINATION

Our past efforts produced an automated spectrophotometer[4] for determining milligram amounts of both uranium and plutonium using a highly selective method. We now have developed a method for determining microgram amounts of uranium and have modified the automated spectrophotometer for its use in addition to the original two methods. Diverse ion effects are being established for the microgram-sensitive uranium method using the automated spectrophotometer. We also developed a controlled-potential coulometric method for the selective determination of plutonium. Fabrication of the automated instrument that will use this coulometric method is almost complete. An apparatus for the complexometric titration of thorium and uranium has been assembled, and procedures for the determination of these elements are being developed. Ion exchange distribution data have been measured for 53 elements on cation exchange resins from nitric acid media and for 58 elements on anion exchange resins from hydrobromic and hydriodic acid media.

A. Microgram-Sensitive Spectrophotometric Uranium Method (S. F. Marsh, N. M. Saponara, M. R. Ortiz, and J. E. Rein)

A method, described in Ref. 5, was developed for the determination of microgram amounts of uranium. This method consists of the extraction of the colored U(VI)-benzoyltrifluoracetone (BTFA) complex into butyl propionate[5] from a solution that contains a Mg(II)-cyclohexanediamine-tetraacetic acid (CDTA) masking agent to provide high specificity and hexamethylenetetramine (HMTA) and triethanolamine (TEA) to provide high buffering capacity. The addition of a two-wavelength absorbance measurement, one slightly down from the 380-nm peak at 384 nm and the other at 400 nm for background correction, provided greater reliability without the need for a reagent blank reference.

The levels of metal and nonmetal ion tolerances for this revised method are given in Tables II and III. The uranium level for this study was 0.20 μmol (48 μg). The diverse ions were added individually to the uranium, beginning with a 1000:1 molar ratio. If a significant change at the 95% confidence level relative to uranium alone was obtained, lower molar ratios were sequentially tested. The tolerance for metal and nonmetal ions usually present in nuclear fuel cycle materials is excellent.

The absorbance response is linear for the 5- to 85-μg range of uranium, and the relative standard deviation ranges from 2.9% at 5 μg to 0.2% at 85 μg.

TABLE II
LEVELS (MOLE RATIO TO URANIUM) OF NONINTERFERING METAL CATIONS

1000:1	100:1		10:1	1:1
Ag	B	Mn(II)	Al	Ce(IV)
Cd	Ba	Ni	Au	Pd
Cs	Bi	Pb	Be	Sn
Cu	Ca	Rb	Ce(III)	Te
Ge	Co	Sr	Cr(III)	Ti
Hg	Fe	Sc	Cr(VI)	V
K	Ga	Th	Hf	
La	In	Tl	Mn(VII)	
Mg	Li	Zn	Mo	
Na			Pt	
Y			Ru	
			Sb	
			Se	
			Zr	

The correlation coefficient for a linear least squares fit of 30 measurements over the 5- to 85-μg range was 0.9998 with a relative standard deviation of the residual about the line of 0.70%.

A paper describing this method has been accepted for publication in Analytica Chimica Acta.

B. Modification of Automated Spectrophotometer for Microgram-Sensitive Uranium Method (D. D. Jackson, R. M. Hollen, and J. E. Rein)

The automated spectrophotometer, originally designed for the determination of 1 to 12 mg of uranium and plutonium, was evaluated for the determination of 0.12- to 1-mg amounts of uranium, without instrumental or procedural changes.[6,7] The standard deviation was a constant 0.013 mg over this range, which corresponds to 10.4 relative percent at the 0.12-mg lower limit.

A main application of the instrument is for analyzing uranium-containing scrap materials, most of which have low amounts of uranium and high amounts of extraneous elements. Because of a low-milligram limit and a maximum sample volume

TABLE III

LEVELS (MOLE RATIO TO URANIUM) OF NONINTERFERING ANIONS

1000:1		100:1	10:1	1:1
Acetate	Nitrate	EDTA[a]	Oxalate	Phosphate
Bromide	Sulfide	Fluoride		
Bromate	Sulfite	Iodide		
Chloride	Sulfate			
Iodate	Sulfamate			
Nitrite	Thiocyanate			

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[a] Ethylenediaminetraacetic acid.

of 0.5 mℓ, low-level uranium samples were analyzed by evaporating larger volumes in the sample tubes and dissolving the residues in 0.5 mℓ of 8*M* HNO_3. Complete dissolution may not be attained for samples containing high amounts of salt. Also, the undissolved residue may retain small amounts of uranium.

The instrument was modified for use with the microgram-sensitive uranium method, as discussed in the previous section. The instrument may be used to determine milligram levels of uranium and plutonium using the original method and to determine microgram levels of uranium. Instrument modifications include (1) three new reagent dispensers for the microgram-sensitive uranium method, (2) a mechanism to switch the pneumatic-hydraulic system automatically between the original set of dispensers for the milligram-sensitive methods and the new set of dispensers, (3) removal of cam-actuated switches driven by a common shaft that controlled mechanical operations for the milligram-sensitive methods and expansion of the microcomputer system to provide complete controls of all mechanical and electrical operations, (4) installation of a pair of interference filters for absorbance measurements at 384 and 400 nm for the microgram-sensitive method, and (5) replacement of the 3-1/2-digit, analog-to-digital converter with a 4-1/2-digit converter to cover a larger dynamic range for the microgram- and milligram-sensitive methods. These modifications required rewiring of many instrument systems, computer hardware additions, and software additions and changes.

No change was necessary in the 1200-rpm stirring magnet mechanism. Extraction of the V(VI)-BTFA complex into the butyl-propionate organic phase was greater than 99.5% in 6 min and droplet spattering was insignificant. The aqueous and organic phases separate in less than 1 min to produce a clear organic phase. No changes were necessary for the light source and photodiode detector. Light baffles, added to the pair of filters used for the microgram-sensitive method, decreased the output signal from the photodiode to the range obtained for the milligram-level methods, thereby decreasing the dynamic range of current to be handled in the data processing system. The procedure for the microgram-sensitive uranium method is to transfer a magnet stirring bar and a maximum of 1-mℓ aliquot of sample into a tube, to place as many as 24 tubes on the instrument's turntable, to set a switch that selects instrument operation for the microgram-sensitive uranium method, and to initiate the automated operation. At the first station, a dispenser delivers 5 mℓ of a buffer-masking solution consisting of 2.15*M* HMTA, 0.75*M* TEA, and 0.08*M* Mg-CDTA complex; a second dispenser delivers 3 mℓ of a 3% BTFA-butyl propionate organic solvent; then the phases are mixed for 8 min. At the second station, 11 mℓ of a 2.8*M* HMTA solution is dispensed to raise the organic phase to a clean area of the tube. At the third station, absorbances of the organic phase are measured at 384 and 400 nm. A paper tape printout shows (1) a four-digit number, proportional to the difference of the absorbances at the two wavelengths, that is proportional to the quantity of uranium, (2) a number from 1 to 24 that identifies the tube position on the turntable, and (3) a two-digit number that designates that the microgram-sensitive uranium method was used. The throughput rate of 8 min per sample is set by the time required for mixing of the aqueous and organic phases.

Although the aqueous and organic phases disengage well, aqueous phase droplets adhere to the tube wall in the organic phase region. Raising the organic phase to a clean area of the tube provides unbiased absorbance measurements. An unexpected difficulty was finding a phase-raising solution that did not affect the absorbance of the extracted complex, but that had suitable density and viscosity for delivery control, and was inexpensive and simple to prepare. Of more than 10 solutions tested, a 2.8*M* HMTA aqueous solution met the above requirements best.

C. Investigation of Microgram-Sensitive Uranium Method with the Automated Spectrophotometer (N. M. Saponara, R. M. Hollen, D. D. Jackson, and J. E. Rein)

In the manual-operation method for determining microgram quantities of uranium, we adjust the solution pH between 5.6 and 5.7 before adding the organic solvent. Because an automated pH adjustment is difficult, the effect of acid was determined. Extensive tests of diverse ion effects are being made.

The effect of acid was determined for 0 to 12 milliequivalents (meq) of HNO_3 for 2.5 to 150 μg of uranium. Experimental acid levels used were 0, 1, 3, 6, 9, and 12 meq. We obtained the 0-meq level by evaporating uranium calibration solution aliquots to dryness and dissolving the residues with water.

For each of the six acid levels, a calibration equation was computed by a least squares fitting of the output values, which are proportional to absorbance, vs micrograms of uranium. The output response for the 1-, 3-, 6-, and 9-meq acid levels was linear for the 2.5- to 100-μg uranium range. At 12 meq of acid, the response was low and erratic. At 0 meq of acid, the response generally was 5% lower than for the 1 to 9 meq of acid for the entire uranium range. Standard deviations at the 1-, 3-, 6-, and 9-meq acid levels were similar, ranging from 0.5% above 90 μg of uranium to 3% for 5 μg of uranium. At the lower limit of 2.5 μg of uranium, the standard deviation was about 10%.

The output generally decreases with increasing acidity. Although the calibrations tend to converge at increasing uranium levels, there is only a slight difference at 100 μg. At the acidity extremes of 1 and 9 meq, the output difference equals about 1 μg of uranium from 50 to 5 μg of uranium. At higher uranium levels, the output difference decreases to <0.5 μg of uranium.

For maximum accuracy, we use a calibration equation in which the acidity level matches that of the samples. Use of an "average" calibration equation computed from the data for the 1- to 9-meq acid range gives maximum deviations of 5% for the 10- to 100-μg uranium range and 10% at 5 μg of uranium.

We are now investigating the tolerances of metal and nonmetal ions on the automated instrument analyses. Because the tolerances can be a function of acidity, they are being measured at 1 and 9 meq of acid (as HNO_3). Results obtained in the nearly complete investigation of metal cations in 1 meq of acid generally agree with those observed for the manual method (Tables II and III). The automated spectrophotometer procedure, like the manual procedure, generally is applicable to several nuclear fuel cycle materials, including scrap materials.

Because butyl propionate is expensive, this solvent is purified and reused. Distillation alone is not sufficient. The absorbance of the distilled butyl propionate is slightly high in the 380- to 425-nm region and causes a positive bias for uranium. Also, the reagent turns yellow soon after the BTFA is added. Satisfactory results are obtained by distillation, followed by treatment with activated charcoal and a final flow through an alumina column. Blanks and uranium samples processed in the automated spectrophotometer with reagent prepared from recovered butyl propionate are similar to those obtained using fresh reagent.

D. Development of Specific Controlled-Potential Coulometric Method for Plutonium and Construction of Automated Analyzer (D. D. Jackson, R. M. Hollen, F. R. Roensch, and J. E. Rein)

Our objective is to develop an automated plutonium analyzer whose features include high tolerance to impurity elements present in nuclear fuel cycle materials, measurement of low-milligram levels of plutonium, and measurements having only 0.1 to 0.2% relative standard deviation. A versatile instrument[8,9] used for investigating electrometric systems for determining plutonium will serve as the model for our automated instrument. It is centered around a programmable calculator that controls titration conditions and monitors pertinent variables.

A controlled-potential coulometric method developed for plutonium features high specificity, a precision of about 0.1% relative standard deviation at the 5-mg plutonium level, use of simply constructed cells, and operational simplicity for adaptation to an automated instrument.[8,9] Plutonium is reduced at 0.25 V (vs SCE) to Pu(III) in 5.5M HCl-0.015M sulfamic acid electrolyte. Diverse ions are oxidized at a potential of 0.57 V, whereas Pu(III) is not significantly oxidized. Phosphate (as Na_2HPO_4) is added to lower the Pu(III)-Pu(IV) potential, and Pu(III) is oxidized by titration to Pu(IV) at 0.68 V. Results of a detailed investigation of diverse ion effects for more than 75 metal ions and nonmetal anions are described in Refs. 8 and 9. Metal cations normally present in nuclear fuel cycle materials do not interfere at an equal mole ratio relative to 0.02 mmol (5 mg) of plutonium. Interference is defined as a change significant at the 95% confidence level relative to pure plutonium. Most potentially interfering nonmetal anions, such as fluoride, are removed by perchloric acid fuming. Because uranium often is present in plutonium-containing materials, its effect also was investigated. Five-milligram aliquots of a plutonium standard solution, with and without added uranium up to a 10 to 1 molar ratio relative to plutonium, were processed concurrently with and without an initial perchloric acid fuming. Statistical "t" tests showed no effects from the uranium at the 95% confidence level for any test condition.

During our tests we observed that for some fumed samples, a long time was required to reduce the plutonium to Pu^{3+} in the coulometric analysis and the plutonium results were low. Further investigation showed that this occurred when the samples were heated beyond "just dryness." The baked plutonium residue may still be dissolving in the 5.5M HCl-0.015M sulfamic acid electrolyte during the initial reduction. Methods for treating the fumed residue to overcome this effect are being investigated.

To characterize the plutonium content of SALE mixed-oxide materials (see Sec. V), 5-mg aliquots of a plutonium standard solution were processed daily for 6 days. The computed relative standard deviation was 0.11%.

In addition to controlling the electrolysis and data treatment, the programmable-calculator-centered apparatus will control all mechanical operations. The basic, simple design of the mechanical operation will provide long-term, trouble-free use. The analyst delivers sample aliquots into cells and places up to 24 cells on the instrument's turntable. The turntable automatically rotates the cells to one station where reagents are added and the controlled-potential electrolysis takes place. The results, along with a cell identification number, are given on a paper-tape printout. The spent sample solution is transferred to a plutonium recovery bottle, the cell components are rinsed, and the rinses also are recovered.

Most of the mechanical components for the automated instrument have been built and tested. The entire instrument, designed to fit in a sloping front glove box, is being assembled. The electronic components will be located outside the glove box, but the mechanical components, fabricated of materials to resist acid corrosion, will be inside the box. A 15° Geneva-drive mechanism provides smooth, accurate rotation of the aluminum turntable to ensure correct angular positioning. A locking mechanism driven by a pneumatic cylinder engages tapered indentations in the turntable rim at each of the 24 positions.

At the measurement station, the electrodes, stirrer, and tubes that deliver nitrogen gas, reagent solutions, and rinse solution are rigidly positioned in a Teflon support. Upon arrival, the cell is raised by a pneumatic-cylinder-driven assembly and sealed against the Teflon support. The simple and inexpensive cells are fabricated by flame-sealing a flat glass bottom onto a piece of 48-mm glass tubing.

The reagent dispensers for the HCl-sulfamic acid electrolyte and the phosphate complexant are similar to those used in the automated spectrophotometer.[4] Only the glass, Teflon, and Kel-F come in contact with the highly corrosive reagents.

The rinse solution is withdrawn by suction through a Teflon tube that is lowered through a Teflon guide tube mounted in the Teflon support. The delivery tube is driven by a pneumatic-cylinder mechanism to an exact position at the bottom of the cell, necessary for effective rinsing of the platinum gauge electrode. Preliminary tests indicate that two rinses are adequate.

Mechanical operations will be controlled by photoisolated relays actuated by the programmable calculator. These relays avoid interference of logic level signals of the calculator caused by voltage transients from the power solenoids.

E. Determination of Thorium and Uranium (S. F. Marsh, M. R. Ortiz, and J. E. Rein)

Based on techniques that were readily adaptable to automated analyzers, we developed a new method for the determination of thorium and uranium in fuel cycle materials. An attractive technique is complexometric titration to a photometric endpoint, and a low-cost apparatus was assembled for this purpose. The chemistry is simple. A metal-indicator complex, with a different color than that of the uncomplexed indicator, is titrated with a stronger complexing agent. The color changes continuously as the metal-indicator complex is converted to the uncomplexed indicator, after which the intensity of the uncomplexed indicator color remains constant.

In the apparatus, the complexing agent titrant is delivered at a constant rate from a motor-driven, high-precision micrometer pipet. A sensing probe immersed in the solution being titrated transmits light intensity through a fiberoptics guide to an inexpensive colorimeter connected to a strip-chart recorder. The recorder and motor-driven pipet are synchronized to provide a plot of changing color intensity correlated to titrant volume.

Initial studies (see Table IV) show that 100 μg of thorium are titratable to a precision better than 1%. The indicator used is xylenol orange, the strong complexing titrant is diethylenetriaminepentaacetic acid (DTPA), and the medium is 0.05M HBr.

TABLE IV

TITRATION OF THORIUM-XYLENOL ORANGE COMPLEX WITH DTPA

Thorium Titrated (μg)	DTPA Molarity	Relative Standard Deviation (%)
5	0.0001	5.8
9	0.0001	6.1
23	0.0005	2.2
46	0.0005	1.7
70	0.0005	1.0
93	0.001	0.6
139	0.001	0.7

Separation procedures for uranium and thorium mixtures and a titration procedure for uranium are being developed. Procedures will be investigated for milligram levels of thorium and uranium applicable to unirradiated fuels and for microgram levels applicable to highly radioactive, irradiated fuels. The apparatus is well suited for shielded glove box operation.

F. Determination of Thorium in Plutonium-Thorium Materials (L. F. Walker and D. S. Temer)

A complexometric titration method was applied to the analysis of plutonium-thorium materials by separating the plutonium, which otherwise interfered in the titration. The plutonium was removed from a 12M HCl solution of the sample with BioRad (Dowex) 1 x 2 anion exchange resin while the thorium passed through. Perchloric acid was added to the eluant solution, which then was fumed to dryness to remove HCl and some organics. The residue was dissolved in water and the thorium was titrated with tetra-sodium EDTA standardized solution. The pH was maintained at 2.5 ± 0.1 during the titration; the color indicator was xylenol orange. Studies of the effects of several other ions on the determination of thorium are being made using 1 and 0.1% of the foreign ion relative to the thorium. Iron removed with the plutonium on the resin column did not interfere at the 1% level. Phosphate, sulfate, zirconium, and cerium, which do not interfere at the 0.1% level, are being tested at the 1% level relative to thorium.

G. Ion Exchange of the Elements in Hydrobromic Acid, Hydriodic Acid, and Nitric Acid (S. F. Marsh, J. E. Alarid, C. F. Hammond, M. J. McLeod, F. R. Roensch, and J. E. Rein)

References 10 and 11, respectively, present cation-exchange distribution data for 53 elements between 3 and 12*M* HNO_3 and three strong acid resins having 8%, 4%, and macroporous cross linkages and anion-exchange distribution data for 58 elements between 0.1 and 8.7*M* HBr and between 0.1 and 7.4*M* HI and three strong base resins having the same percentage of cross linkages. Separations applicable to the chemistry of nuclear fuel cycle materials are described.

IV. EVALUATION OF THE MASS-SPECTROMETRIC, ION-EXCHANGE-BEAD TECHNIQUE (R. M. Abernathey, S. F. Marsh, J. E. Alarid, and J. E. Rein)

The mass-spectrometric, ion-exchange-bead technique, developed by the Oak Ridge National Laboratory (ORNL),[12] is being evaluated by ORNL and the International Atomic Energy Agency (IAEA) Safeguards Laboratory for the determination of uranium and plutonium in reprocessing plant input samples. Using mass spectrometers equipped with pulse-counting detectors, we can measure low-nanogram quantities of uranium and plutonium on a single ion exchange bead loaded on a single rhenium filament. We are using a thermal ionization mass spectrometer to evaluate the sensitivity of the technique. The spectrometer, made by Ion Instruments Inc., has a triple-filament source, Z-focusing, and interchangeable Faraday cup and electron-multiplier detectors. Only the more sensitive electron-multiplier detector was used.

For these evaluations, an aliquot of the sample dissolver solution is combined with about 10 beads of Dowex-1, X2, 50-100 mesh, anion exchange resin in 8*M* HNO_3. In 48 h, without agitation, about half of the plutonium and 0.05% of the uranium reportedly sorbs on the resin beads. With an initial 100/1 uranium/plutonium ratio and an appropriate amount of dissolver solution, 1 to 5 mg of plutonium and 0.1 to 0.5 ng of uranium are sorbed per bead. A single bead is transferred to a rhenium filament that is crimped, placed in the source of the mass spectrometer, and heated by current to destroy the bead. Current is increased and the plutonium spectrum is recorded. After increasing the current further, the uranium spectrum is recorded.

Our measurements showed that the sorption rate of plutonium onto 10 Dowex-1, X2, 50-100 mesh ion beads from 0.1 m*ℓ* of 8*M* HNO_3 containing 500 ng of plutonium was 30% complete in 15 min and 75% complete in 4 days. The mass-spectrometric sensitivity of ion-bead loading was compared to our normal loading technique of evaporating plutonium solution on a side rhenium filament using single ion beads on both center and side filaments. There was no significant difference between the sensitivities of the two ion-bead loading positions or with the sensitivity of our normal loading technique. A minimum loading of about 35 ng of plutonium is used to attain accurate measurements of minor isotopes. If only the major ^{239}Pu and ^{240}Pu isotopes are measured relative to an added ^{242}Pu or ^{244}Pu spike, the estimated minimum quantity of sample plutonium is 5 ng. The sensitivity of the technique used for uranium measurements is being evaluated.

V. PREPARATION OF PLUTONIUM-CONTAINING MATERIALS FOR THE SALE PROGRAM (J. W. Dahlby, L. C. Haynes, D. D. Jackson, S. F. Marsh, F. R. Roensch, D. J. Temer, J. E. Rein, and G. R. Waterbury)

Three batches of high-density 3/1 uranium/plutonium mixed-oxide pellets are being characterized at NBL and LASL for distribution as semimonthly SALE materials. Individual pellets, 225 from each batch, were sealed in glass ampoules under a dry argon atmosphere to attain long-term stability.

We characterized the uranium and plutonium contents using two different methods for each element. The NBL-modified Davies-Gray titrimetric method[13] and controlled-potential coulometry with sulfuric acid electrolyte[14] were used for uranium. Controlled-potential coulometry with sulfuric acid electrolyte and with hydrochloric acid electrolyte (Sec. III.D) was used for plutonium. We characterized the uranium and plutonium isotope distributions by thermal ionization mass spectrometry following ion exchange separation of the two elements.[14] Appropriate NBS standard reference materials (SRMs) were processed concurrently with the pellet samples for all analyses. The characterization results were computed relative to the results obtained for the NBS SRMs, using guidelines presented in a US Nuclear Regulatory Commission document.[15]

New batches of plutonium oxide powder are to be prepared and characterized for distribution as semimonthly SALE materials. Previous batches consisted of materials heated in air at 900°C to promote stability relative to sorption of atmospheric moisture. A study of their stability has shown that, after a 2-month exposure to atmospheres with relative humidities up to 85%, their initial compositions can be restored by heating at 110°C for 24 h. Recently, another batch of plutonium oxide heated at 950°C in air was found to sorb and desorb water when cycled in 50% relative humidity air and placed in a desiccator. Weight changes of 0.04% were obtained in 15 min. Further heating to 1250°C gave a stable material having < 0.002% weight changes. In the United Kingdom, 1250°C calcined plutonium oxide is used as a reference material with a claimed O/M ratio of 2.000 and long-term stability.[16] A disadvantage in using 1250°C calcined plutonium oxide in the SALE program is its greater resistance to dissolution than oxide calcined at lower temperatures, normally encountered in the US nuclear fuel cycle. The 1250°C calcined plutonium oxide did not dissolve completely in a heated mixture of 16*M* HNO_3 and 0.03*M* HF at ambient pressure, but it did dissolve completely in this mixture when heated overnight at 230°C in a Teflon-container, metal-shell apparatus. A 24-h reaction time was required to dissolve it in a HCl-HNO_3-HF mixture in a sealed reflux tube.[17]

Samples to be considered for preparation, characterization, and use as SALE plutonium oxide include the following.

1. Low-temperature (~550°C) calcined material, typical of US processes, can be used on a total plutonium content per container basis. Disadvantages are characterization uncertainties caused by possible heterogeneity of sorbed water, the need for the analyzing laboratory to quantitatively remove the material from its container, and the by-passing of the error component of weighing in the analyzing laboratory.
2. The past practice of using 900 to 950°C calcined material can be continued. Disadvantages are that the analyzing laboratory must heat the material to restore its original characterization composition and the uncertainty of the restoration after long storage periods.
3. Use of 1250°C calcined material, which provides long-term stability, has the disadvantage of requiring a more vigorous dissolution treatment than process material. However, its stability permits it to be packaged on both gram plutonium per gram material and gram plutonium per container bases, thereby providing a means to assess error components in the analyzing laboratories of sample weighing and of quantitative removal from the container.

VI. PREPARATION OF PLUTONIUM-CONTAINING MATERIALS FOR THE NATIONAL BUREAU OF STANDARDS (G. R. Waterbury and staff)

Batches of low ^{240}Pu (~4%) plutonium metal have been prepared, characterized, and packaged for distribution by NBS as SRM 949. Plans have been made to prepare another batch of this material. We are now preparing a ^{244}Pu SRM, to be certified for the number of ^{244}Pu atoms per container, for use in isotope-dilution, mass spectrometry (IDMS) measurements. The IDMS technique is used worldwide for the determination of uranium and plutonium. The desired isotope for addition as the spike is one present at very low levels or not at all in the sample. The usual spike for plutonium analysis is ^{242}Pu, but as plutonium is recycled and irradiated to higher burnup, the ^{242}Pu content increases and this isotope becomes less suitable as a spike.

The preferred spike, which is produced by double neutron capture on ^{242}Pu, is the heavier ^{244}Pu isotope, present only at trace levels. Its production is limited by the short, 5-h half-life of ^{243}Pu. Special high-flux irradiations in the ORNL research reactor and subsequent separation in a calutron have produced several grams of ~98% enriched ^{244}Pu. About 1 g has been allocated for distribution by NBS as a SRM, with 1 mg per container certified for the number of ^{244}Pu atoms.

Packaging of this material is in progress. A solution of the dissolved ^{244}Pu oxide was distributed by weight into 4-oz Teflon bottles, followed by oven evaporation to dryness. The Telfon bottle provides a convenient means for a laboratory to prepare the ^{244}Pu spike. The bottle with its evaporated residue is weighed, acid is added, the residue is dissolved, and the bottle with solution is weighed to provide data to calculate the atoms of ^{244}Pu per gram. The prepared solution can be distributed by weight into a series of containers for use as spikes. The assay and isotopic-distribution characterizations on random samples will be done by NBS, NBL, and LASL. The "Poly-seal"-type bottle lids consist of hollow cones of polyethylene in a bakelite screw-cap. A thin piece of Teflon, placed over the "Poly-seal," to collect any plutonium particles scattered during storage and transportation, is simply pushed into the bottle by the user. The bottles containing evaporated residue were tested by vigorous shaking and repeated 3-m falls.

Variables investigated in establishing the packaging scheme were the acid medium composition of the ^{244}Pu distributed to the Teflon bottles, the means of evaporation, and the composition of the acid necessary to attain complete solubilization of the evaporated residue. The solubilization was determined by filtering to collect any undissolved plutonium, rinsing the bottle twice with the same acid medium used to dissolve the residue, and finally cutting the Teflon bottles into sections. These sections, as well as the filter, were assayed for plutonium by alpha-particle counting. The adopted scheme that gives >99.995% solubilization is an $8M$ HNO_3-$0.01M$ HF mixture as the medium of the ^{244}Pu solution distributed to the Teflon bottles, oven evaporation at 80°C, removal of trace moisture at high vacuum, and solubilization of the residue with the same $8M$ HNO_3-$0.01M$ HF acid mixture.

VII. PLUTONIUM ISOTOPE HALF-LIFE MEASUREMENTS (G. R. Waterbury and staff)

The Half-Life Evaluation Committee (HLEC), consisting of representatives from the Argonne National Laboratory (ANL), LASL, Lawrence Livermore Laboratory (LLL), Mound Laboratory-Monsanto (MLM), NBS, and the Rockwell International Rocky Flats Plant (RI-RFP), is organizing an effort to measure accurately the half-lives of longer lived plutonium isotopes. Toward this effort, LASL is (1) preparing, characterizing, and distributing batches of high-purity plutonium from specially provided, enriched isotope materials, and (2) determining the half-lives using the IDMS technique for measuring the produced daughter isotope. The LASL characterization measurements include assay, isotopic distribution, metal impurities including other transuranics, and nonmetal impurities.

Measurements of the ^{239}Pu half-life are completed and articles have been accepted for publication in a technical journal. A batch of enriched ^{240}Pu has been received, and measurements of the ^{241}Pu half-life are in progress at five laboratories. An ANL measurement of the ^{238}Pu half-life of 87.71 ± 0.03 yr agrees closely with the MLM measurement of 87.77 ± 0.03 yr. The HLEC recommends adoption of the average of 87.74, with an uncertainty of ±0.04 yr.

A. Plutonium-239

Our two papers "Preparation and Chemical Characterization of Plutonium-239 Metal Used for Half-Life Measurements"[18] and "Plutonium-239 Half-Life Determined by Isotope-Dilution Mass-Spectrometric Measurement of Grown-In Uranium-235"[19] will be published in a special issue of the International Journal of Applied Radiation and Isotopes.

B. Plutonium-240

A recent ANL measurement of the half-life of ^{240}Pu, based on alpha-particle counting, of 6569 yr[20] is much higher than the present American Nuclear Standards Institute's (ANSI) recommended value of 6537 yr.[21] The HLEC has recommended that a new measurement of the half-life of this isotope be made by the participating laboratories. A 28-g quantity of 98.3%-enriched ^{240}Pu was received and will be used in the form of the stable oxide because reduction to metal cannot be undertaken at LASL for several months. Another form considered is the stoichiometric $Pu(SO_4)_2 \cdot 4\ H_2O$,[22] but initial work will be done with the oxide. Chemical characterization provided with the material indicated a ^{241}Am content of 0.12% and a uranium content of 0.057%. Because these and other impurities would cause uncertainty in the half-life measurements determined by calorimetry, alpha-particle counting, or IDMS of daughter ^{236}U, the entire quantity of ^{240}Pu was purified.

The $^{240}PuO_2$ was dissolved in a 15.7*M* HNO_3-0.02*M* HF solution, the solution was filtered to remove a silica residue, the filtrate was adjusted to 7.2*M* HNO_3, and the plutonium was sorbed on a column containing 400 cm^3 of Dowex-1, X2 anion exchange resin.[23] The column was washed with 7.2*M* HNO_3 until the ^{241}Am and ^{237}U activities in the effluent decreased to low and constant levels, indicating equilibrium between their formation and elution. Monitoring showed that the effluent did not contain ^{240}Pu. The plutonium then was eluted with a 0.39*M* HNO_3-0.01*M* HF solution, the solution was evaporated slowly to dryness, and the residue was calcined to PuO_2 at 1250°C and blended to promote homogeneity.

Chemical analyses of the ignited and blended ^{240}Pu oxide show a total impurity content of 600 ppm. About 200 ppm consisted of iron and other stainless steel components, apparently introduced by the container used to blend the ignited ^{240}Pu oxide. The other major impurities, chloride and fluoride, were reduced to <10 ppm by pyrohydrolyzing the material. It then was reignited at 1250°C.

Plans are being made by W. Strohm of MLM and Chairman of the HLEC for the interlaboratory characterization and half-life measurements of the material. If the characterizations show that the material is satisfactory, it will be packaged accordingly and distributed to the various laboratories.

C. Plutonium-241

Three years ago, measurements were started on a mixture of highly enriched isotopes of ^{241}Pu and ^{242}Pu at a ratio of ~1.27 to 1. The ^{241}Pu half-life is being determined from the decreasing ratio of $^{241}Pu/^{242}Pu$ measured at 6-month intervals by thermal ionization mass spectrometry following chemical separation of ^{241}Am. Portions of the mixture were distributed to LLL, MLM, NBS, and RI-RFP for measurements.

Our most recent values for the ^{241}Pu half-life, using two mass spectrometers, were 14.38 and 14.41 yr. These values were computed from four different filament loadings on each instrument for four plutonium fractions of the ^{241}Pu-^{242}Pu mixture. The only data reported by other participating laboratories have been the first $^{241}Pu/^{242}Pu$ ratio measurements by MLM and very preliminary values by RI-RFP. The computed ^{241}Pu half-life, using the MLM value and our initial measurement of three years ago, is 14.4 yr.

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