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Analytical Methods for Fissionable Material Determinations in the Nuclear Fuel Cycle

October 1, 1976—September 30, 1977

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ANALYTICAL METHODS FOR FISSIONABLE MATERIAL DETERMINATIONS IN THE NUCLEAR FUEL CYCLE
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ABSTRACT

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, analysis of SALE uranium materials, preparation of certified reference material plutonium metal, measurement of longer plutonium isotope half-lives, and study of ion exchange behavior of elements in various media continued. Gas-solid reaction of carbonyl chloride with uranium-bearing materials at elevated temperature is superior to reaction with chlorine for uranium volatilization and separation. Neither reaction with a variety of nonaqueous solvents nor reaction with molten selenium oxide provides practical dissolution of refractory materials characteristic of nuclear fuel cycle materials. The LASL automated spectrophotometer has been used to determine 0.1-mg amounts without instrumental or procedural changes. A microgram-sensitive spectrophotometric method for uranium has been developed, and the automated spectrophotometer is being modified to its use. A controlled-potential coulometric method has been developed for selective determination of plutonium. An automated analyzer to use this method is being built. Uranium-plutonium mixed oxide powder, for SALE samples, has not remained stable during storage, but high-density pellets have. In a DOE interlaboratory program, the half-life of ^{239}Pu has been measured, experiments on ^{241}Pu half-life measurement are in progress, and ^{240}Pu half-life measurement is planned. Ion exchange distributions for over 50 elements have been measured to determine cation exchange in nitric acid and anion exchange in both hydrobromic and hydriodic acids.

I. INTRODUCTION

Adequate safeguard control of uranium and plutonium requires confirmation by sampling and analyses in the nuclear fuel cycle. Total amounts of these elements and their isotopic compositions must be measured accurately and precisely in widely diverse nuclear materials, including pure products, reactor fuels of complex chemical compositions, and many types of scrap. Dissolutions and analyses of materials containing highly refractory components and of multiphase scrap are particularly difficult.

The objectives are (1) to develop fast, effective dissolution techniques and analytical methods for plutonium and uranium determinations, (2) to develop automated analyzers for plutonium and uranium determinations, (3) to prepare well-characterized, plutonium-containing materials for use in the SALE programs and for NBS distribution, (4) to participate in, and prepare and characterize the materials for, a DOE interlaboratory program to measure the half-lives of long-lived plutonium isotopes, and (5) to characterize chemically special lots of nuclear materials as requested by DOE.

II. DISSOLUTION OF FUEL CYCLE MATERIALS

Dissolving nuclear fuel cycle materials in preparation for assay or isotopic measurement is a most difficult and time-consuming operation. Los Alamos Scientific Laboratory (LASL) is examining techniques for rapid dissolution of fuel cycle materials or solubilization of the uranium and plutonium. The techniques include mineral acid reactions at elevated temperatures in pressurized containers, fusion reactions, reactions with reactive gases at high temperatures, reactions with nonaqueous acid and reactive organic solvents, and reactions with various media abetted by laser energy input.

A. Gas-Solid Reaction (D. D. Jackson, J. E. Alarid, and J. E. Rein)

Investigation of gas-solid reactions for converting plutonium and uranium in refractory materials to volatile species that condense as compounds readily soluble in mineral acids such as HNO_3 continued. The reactions are carried out in a closed quartz tube in a temperature-controlled, resistance-heated furnace. The tube is fabricated to provide controllable atmospheres as well as effective recovery of the solubilized compounds. Carbonyl chloride is more effective than chlorine for volatilizing uranium from various nuclear materials.

As previously reported,[1] 0.1 g of U_3O_8 (as well as UO_2, UO_3, and UC_2) volatilized completely when reacted with chlorine at 1000°C and 1.2-atm pressure for 12 h in a quartz-tube furnace. A tube furnace designed for operation up to 1300°C was installed. As expected, the reaction time required to volatilize U_3O_8 completely decreased from 12 h at 1000°C to 5 h at 1200°C. These conditions were applied to New Brunswick Laboratory (NBL)-supplied scrap containing zirconium, previously found very resistant to mineral acid dissolution even in the Teflon-container, metal-shell apparatus.[1] Over 95% of the uranium and 40% of the 1-g sample volatilized in 8 h at 1000°C or in 4 h at 1200°C at 1.2-atm chlorine pressure. At 1200°C, the quartz tube deteriorated and had to be replaced after 25 h.

Carbonyl chloride, which decomposes into reactive chlorine species at elevated temperature, significantly increased uranium volatilization. In the same reaction conditions as for chlorine, 0.1 g of U_3O_8 volatilized completely in <0.5 h at 1000°C and in <1 h at 700°C (Table I). Uranium volatilized at even lower temperature; for example, about 99%

TABLE I

CARBONYL CHLORIDE VOLATILIZATION OF URANIUM FROM U_3O_8

Temp (°C)	Time (h)	Uranium Volatilized (%)
1000	0.5	100
800	1	100
700	1	100
650	1	89
600	1	81
500	2	99
400	2	40

volatilized in 2 h at 500°C. The condensed uranium compound dissolves more readily in HNO_3 than does the compound produced by chlorine gas reaction. Also, the volatilized uranium species produced by reaction with carbonyl chloride migrates farther in the closed quartz-tube apparatus. This fact necessitates additional rinsing of apparatus components to recover the condensed uranium completely. Several minor modifications, including cooling the quartz tube, adding baffles, and operating the tube vertically rather than horizontally, did not retard the migration significantly.

Scrap from a LASL waste-recovery facility and from NBL was reacted with carbonyl chloride. The volatilization was greater than that with chlorine. Typically 35-55% of the total NBL sample and >99% of the uranium volatilized in 1 h at 800°C in carbonyl chloride contrasted to 20-40% of the sample and about 95% of the uranium in chlorine at 1000° for 8 h. Carbonyl chloride volatilized >95% of a LASL material containing about 60% zirconium, and volatilized >99% of the uranium, in 1 h at 800°C. Volatilization of a material containing about 40% niobium was less; about 75% of the total material and only 5% of the uranium volatilized in 1 h at 800°C. Interestingly, the unvolatilized residue dissolved completely and readily in HNO_3. The treatment converts a refractory material to two readily soluble fractions. Raising the temperature from 800 to 900°C increased the material volatilization from 75 to 93% and the uranium volatilization from 5 to about 45%.

Another scrap material containing about 12% each of zirconium and niobium was about 85% volatilized in 1 h at 800°C, and >99% of the uranium volatilized.

Zirconium and niobium oxides alone volatilize readily in carbonyl chloride. More than 99% of Nb_2O_5 volatilized in 1.5 h at 500°C, and about 99% of ZrO_2 volatilized in 2 h at 750°C.

B. Reaction with Nonaqueous Solvents (W. D. Spall and M. J. McLeod)

The investigation of refractory, nuclear fuel cycle material dissolution in various nonaqueous media has been concluded. None of the media studied was practical. Test materials were common refractory components of nuclear fuel cycle materials. Fused oxides of UO_2, ThO_2, ZrO_2, Al_2O_3, SiO_2, and firebrick were used to simulate slag and similar components of scrap.

Nonaqueous media studied were solutions of HI, HBr, HNO_3, and H_2SO_4 in glacial acetic acid containing a slight excess of acetic anhydride; reactive organic solvents such as hydrazine, formamide, dimethylformamide, hexamethylphosphoramide, dimethylsulfoxide, and dibutylphosphate; free-radical producing compounds such as sulfuryl chloride and t-butylperoxybenzoate; the alkali metals potassium and sodium in organic solvents of methylamine, ethylamine, ethylenediamineformamide, N, N-dimethylformamide, triethyleneamine, p-dioxane, isobutylamine and acetonitrile; and two reducing agents, disodium napthalate and disodium anthracate in p-dioxane and tetrahydrofuran.

Alkali metal-amine solutions gave the greatest dissolution, which increased as the molecular weight of the amine solvent decreased. Liquid ammonia, the lowest molecular weight amine, was found impractical owing to experimental difficulties. These solutions partially reduced UO_2, ThO_2, ZrO_2, and Al_2O_3 to free metals that are soluble in aqueous acids. However, the reactions are limited both by low solubility of the alkali metals in the solvent and by metal formation on particle surfaces which blocked further reaction.

C. Reactions with Liquid Selenium Dioxide (S. F. Marsh and M. McLeod)

Molten selenium dioxide, which melts at 390°C, has 9-atm vapor pressure, and reportedly reacts with refractory metal oxides to produce soluble pyroselenates.[2] We investigated this reaction for use on nuclear fuel cycle materials. It proved cumbersome and offered no substantial advantages over more conventional dissolution techniques.

The experiments involved mixing 1.5 g of SeO_2 and 0.1 g of sample in a 5-mm-i.d. by 8-mm-o.d. borosilicate glass tube, heat-drying the mixture under vacuum, adding oxygen to 1-atm pressure, and flame-sealing the tube. The mixtures were fused overnight at 420°C. After cooling, the melt was reacted with 6*M* HCl or 8*M* HNO_3 in an ultrasonic bath. The resulting solution was filtered, and any residue was dried and weighed to compute the weight percentage of material dissolved. Any uranium in the filtrate was measured spectrophotometrically.

Materials tested were firebrick, ThO_2, ZrO_2, Al_2O_3, UO_2, UO_3, UO_4, and U_3Si_2. Dissolution of the various uranium oxides exceeded 80%, that of ThO_2 was 55%, and that of firebrick and Al_2O_3 was slight.

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

Past efforts produced an automated instrument[3] for determining milligram amounts of both uranium and plutonium by a highly specific spectrophotometric method. We investigated use of that instrument without instrumental or procedural changes to determine 0.1- to 1-mg amounts of uranium. We have now developed a more sensitive method for determining microgram amounts of uranium and are modifying the automated spectrophotometer to its use. A controlled-potential coulometric method for selective determination of plutonium has been developed for use in an automated analyzer. We are designing and building components for this instrument.

A. Evaluation of the Automated Spectrophotometer for Determination of Submilligram Amounts of Uranium (D. D. Jackson, R. M. Hollen, and J. E. Rein)

A need to analyze samples from various LASL uranium recovery processes in which the uranium concentrations were generally 0.05-1 mg/ml prompted evaluation of the instrument, without chemical or instrumental modifications, for lower-level uranium analysis. We processed calibration solutions containing 0.12-1.5 mg of uranium. Also, we analyzed 32 typical process solutions and compared the results with those obtained using all-manual spectrophotometry.

Six weight aliquots apiece of the calibration solutions containing 0.12, 0.27, 0.56, and 1.5 mg of uranium, and of four blank solutions were processed for 15 days during an elapsed period of almost a month. A second-order polynomial calibration equation, almost linear, was computed by least-squares fitting all the data. Then the milligrams of uranium corresponding to each output number were computed. The variances of the 90 values at each uranium level were not significantly different, indicating constant precision from 0.12 to 1.5 mg of uranium. The pooled standard deviation (for a single measurement) was 0.013 mg of uranium, which corresponds to 10.4 rel% at 0.12 mg and 0.87 rel% at 1.5 mg. There was a significant, but small day-to-day difference that is essentially eliminated by adjusting the calibration using results from four daily processed samples, two each toward the upper and lower limits of the range.

The LASL recovery process solutions, both nitric acid and sulfuric acid media, contained 0.07-0.8 mg/ml of uranium and significant amounts of various impurities. Half the samples contained <0.3 mg/ml of uranium. To get more reliable results, we evaporated duplicate 10-ml aliquots of each sample to dryness in the automated spectrophotometer tubes and dissolved the residues in 0.5 ml of 8*M* HNO_3, the maximum sample volume for analysis.

Aliquots of the process solutions also were analyzed by an experienced chemist using a well-established spectrophotometric method.[4] The algebraic grand average difference of the two sets of results from the 32 samples was an insignificant 0.0017 mg. The standard deviation of a single measurement by the automated spectrophotometer, computed from the duplicate analyses, was 0.039 mg of uranium which corresponds to 6 and 0.5%, respectively, at the 0.7- and 8-mg extremes.

A technical report[5] presents the above information in greater detail.

B. High-Sensitivity Spectrophotometric Uranium Determination and Application to Automated Spectrophotometer (S. F. Marsh, M. R. Ortiz, F. R. Roensch, R. M. Hollen, D. D. Jackson, and J. E. Rein)

A major use of the automated spectrophotometer is in analysis of scrap samples, many of which have low uranium content and high extraneous element content. The instrument was designed for 0.5-ml maximum sample volume and a precision of ~1% standard deviation in determining ≥1 mg of uranium. As discussed above, the lower limit has been extended to 0.12 mg of uranium with a standard deviation of 10%. To analyze low-concentration samples, aliquots larger than 0.5 ml are evaporated in the sample tubes, then dissolved in 0.5 ml of 8*M* HNO_3. Samples containing high extraneous salt concentrations may not dissolve completely, and the undissolved residue can retain small amounts of uranium. Development of a spectrophotometric method for determining as little as <10 μg of uranium which is compatible with the automated instrument is essentially complete. The major compatibility requirement is that all operations, including the final absorbance measurement, be done in the sample tube without transferring the sample.

1. Method Development. Few published methods had the required features. In the most promising one, the uranium(VI)-benzoyltrifluoroacetone (BTFA) complex is separated by extraction into butyl acetate;[8] this provided <99% extraction of the uranium complex, considered minimal for highly reliable measurements. We increased the extraction of the uranium complex and the tolerance for diverse ions. We evaluated 11 solvents, of which butyl propionate provided the best combination of >99.5% uranium extraction, high absorbance of the extracted complex, and efficient phase disengagement.

We got high selectivity by incorporating cyclohexanediaminetetraacetic acid (CDTA) as a masking agent. CDTA complexes most multivalent metal ions strongly while complexing uranium only weakly. The Mg-CDTA complex we use is about 10^4 times more stable than U-CDTA, but about 10^6 times weaker than most potentially interfering metal ions. As in most in-situ, extraction-spectrophotometry, extraction and color development are pH dependent. A buffer of hexamethylenetetramine is incorporated in the aqueous phase. For highly acid samples, the analyst still must make an appropriate pH adjustment before the automated analysis. This is simply done using a chromogenic pH indicator. Of 12 likely indicators evaluated, only fuchsin and m-cresolsulfonephthalein effectively neutralized the excess acid without contributing significant absorbance at the measurement wavelengths. We will evaluate these two indicators further under operating conditions with the automated spectrophotometer.

Tables II and III list the results of a systematic study of the method's tolerance for metals and nonmetals found in nuclear fuel cycle materials and processes.

2. Modification of Automated Spectrophotometer. The above method, proven for manual operation, uses inversion mixing for the extraction and a double-beam spectrophotometer with a reagent blank in the reference cell for absorbance measurements. The stirring mechanism of the automated spectrophotometer, using the existing 1200-rpm rotated Teflon-covered magnet, also gave >99.5% extraction of the uranium-BTFA complex in 6 min of stirring. The phases disengaged in less than 1 min to produce a clear organic phase, and droplet spattering was insignificant.

Because the absorbance peak of the extracted uranium-BTFA complex at 380 nm is broad and not separated from the reagent absorbance, measurement with a single-beam instrument, such as the

TABLE II

LEVELS (MOLE RATIO TO URANIUM) OF METAL CATIONS THAT DO NOT INTERFERE

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

TABLE III

LEVELS (MOLE RATIO TO URANIUM) OF METAL AND NONMETAL ANIONS THAT DO NOT INTERFERE

1000 : 1		100 : 1	10 : 1	1 : 1
Br^-	I^-	F^-	$C_2O_4^{2-}$	MnO_4^-
BrO_3^-	IO_4^-	NO_3^-		PO_4^{3-}
$C_2H_3O_2^-$	$NH_2SO_3H^-$	EDTA		
Cl^-	S^{2-}			
ClO_4^-	SO_3^{2-}			
CSN^-	SO_4^{2-}			
$Cr_2O_7^{2-}$				

automated spectrophotometer, is difficult. Absorbance by the glass tube walls also is appreciable at this wavelength and must be corrected.

Peak and background correction wavelengths of 384.0 and 400.0 nm were established to give highest measurement precision, on the basis of experiments using a single beam spectrophotometer that had variable wavelength and bandwidth control. Interference filters that have these central wavelengths and 10-nm half-bandwidths have been tested successfully.

The automated spectrophotometer is being modified to operate in either the original way for uranium and plutonium or the high-sensitivity way for uranium. The additional pair of interference filters required for the high-sensitivity method has been installed at the position previously used for measuring plutonium at 807.0 nm. This wavelength was used only in analyzing samples that contained chromium at high concentrations that interfered at the more sensitive 501.4-nm plutonium peak. We will investigate chemical methods of increasing the tolerance of the plutonium determination to chromium. If necessary, we will build a new monochromator that can hold four pairs of interference filters.

Greater dynamic range is necessary to accommodate both the original and high-sensitivity methods. The 3-1/2-digit A-to-D converter is being replaced with a 4-1/2-digit converter. The light source and detector do not require change.

Dispensers required for the high-sensitivity method have been tested satisfactorily. The pneumatic-hydraulic drive system will be switched between the two sets of dispensers.

Major instrumental changes in the control system are required because of the differences in timing of the two methods. The instrument now has two independent control systems. Cam-activated switches driven by a common motor-driven shaft control the operations required to rotate the turntable, deliver reagents, stir the sample, and raise the sample tube into position for absorbance measurements. The second control system provides electronic readout, using a microcomputer and programmable read-only-memory chips to control the measurement sequence. Because of the difficulty of modifying the cam-activated time-sequencer to provide two independent time cycles, we are expanding the microcomputer system to control the instrument completely. Additional hardware, considerable rewiring, and software-program modifications are in progress.

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

We want to develop an electrometric method for determining plutonium to serve as the basis for an automated instrument that features: (1) high specificity, (2) precision of 0.1-0.2% relative standard deviation, and (3) low-milligram level sensitivity. The general technique being investigated is initial reduction of plutonium to Pu^{3+}, oxidation under conditions in which Pu^{3+} is not oxidized but diverse ions that may interfere are oxidized, addition of a complexing agent to lower the $Pu^{3+}-Pu^{4+}$ potential, and oxidation of the Pu^{3+} to Pu^{4+} as the measurement step. The versatile apparatus assembled for investigating the electrometric systems has been described.[7] A further interface was constructed and added to the system to record the number of coulombs at each reduction and oxidation. Several improved programs were written which simplify operator interaction during electrolysis and record additional data.

After extensive experiments, we selected 5.5*M* HCl containing 0.015*M* sulfamic acid to increase the tolerance to nitric acid as the electrolyte. Phosphate, as NaH_2PO_4, was selected as the complexant to lower the $Pu^{3+}-Pu^{4+}$ half-cell potential. Electrolysis conditions established were (1) initial reduction at 0.25 V vs a saturated calomel electrode, (2) initial oxidation at 0.57 V, (3) addition of the phosphate complexant, and (4) oxidation at 0.68 V as the measurement step. Each electrolysis is to a 50-μA current endpoint.

Figure 1 shows the results of a detailed investigation of more than 50 metal cations in periodic chart form. No metal cation normally present in nuclear fuel cycle material interferes (creates a change significant at the 95% confidence level relative to plutonium alone) at an equal mole ratio relative to 0.02 millimole (5 mg) of plutonium. Only four metals, antimony, gold, iridium, and selenium, interfere at a 0.1-mole ratio. These oxidize at the 0.68-V measurement potential to cause positive bias. Tungsten and thallium partially oxidize at 0.68 V, producing positive bias at an equal mole ratio but no effect at a 0.1-mole ratio.

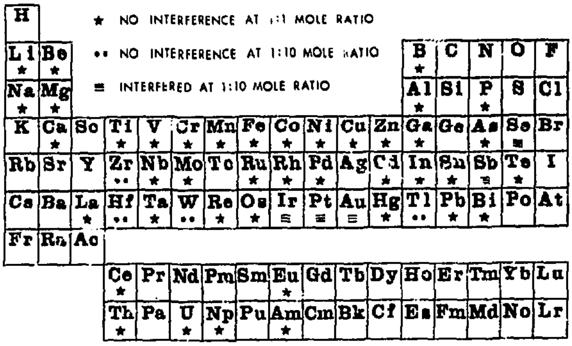

Fig. 1.
Cation interference effects.

Platinum, used as the working electrode, interfered unexpectedly. It reduced and adhered to the electrode, then stripped off and oxidized during the initial oxidation, and oxidized partially in the measurement oxidation to cause high bias. The electrode response was harmed in that subsequent plutonium electrolyses took longer to reach the 50-μA cutoff level. The electrode required chemical treatment to restore efficient operation, and, to avoid changing the response characteristics of the electrode again, we made no further tests of platinum interference at the 0.1-mole ratio. Zirconium and hafnium, precipitated as phosphates, partially occluded plutonium and caused negative bias at the equal mole ratio but no effect at the 0.1-mole ratio.

We did not test all metals in the alkali metal and alkaline earth groups for interference because they have a single, high electropositive oxidation state and are not oxidized or reduced during the various stages of the electroanalysis. Testing of representative elements in each group was adequate to show that there were no subtle adverse effects. Essentially the same is true of the lanthanides. Cerium and europium were tested as representative because only they have other oxidation states in addition to +3 (+4 for cerium and +2 for europium). Because neither interfered, we concluded that lanthanides do not interfere. Noteworthy is the fact that uranium did not interfere at ratios of at least 5/1. With this tolerance level, the method is applicable to determination of plutonium in mixed uranium-plutonium FBR fuels in which the maximum uranium-to-plutonium ratio usually is 4/1.

Table IV lists the results of the detailed investigation of anions. Each nonmetal anion was tested first at a 500-mole ratio relative to plutonium at a plutonium level of 0.02 millimole (5 mg). If the result differed significantly at the 95% significance level relative to the average for pure plutonium, the anion was considered to interfere. If there was a significant effect, we tested lower mole ratios of 50 and then 5. The three metal anions were tested at an equal mole ratio. The sulfamic acid increases tolerance to HNO_3. Without sulfamic acid, plutonium samples containing 1.0 mmole of HNO_3 acid cannot be reduced. With 0.015*M* sulfamic acid, there is no interference up to 1.0 mmole or less of HNO_3, the highest level tested because of possible degradation of the platinum electrode by a HCl-HNO_3 mixture. We will test higher HNO_3 levels later.

As expected, fluoride, which preferentially complexes Pu^{4+} and thereby reduces the potential of the $Pu^{3+}-Pu^{4+}$ couple, interfered because some Pu^{3+} was oxidized during the initial oxidation. At a concentration of 1.0 mmole of fluoride, 68% of the plutonium was oxidized. Unexpectedly, neither borate nor aluminum completely eliminated the fluoride interference. At levels of 1.0 and 0.1 mmole of fluoride, 2.0 mmole of boric acid decreased the Pu^{3+} oxidized to 2.6 and 0.8%, respectively. Aluminum was somewhat more effective, but still did not eliminate the fluoride interference. With 2.0 mmole of aluminum and 0.1 of fluoride, about 0.4% of the Pu^{3+} oxidized. Therefore, fluoride must be removed before electroanalysis by fuming with perchloric acid containing some nitric acid. The nitric acid ensures that the plutonium oxidizes to at least Pu^{4+}. Moderate fuming with perchloric acid alone can leave some Pu^{3+}, depending on the sample composition, which forms insoluble PuF_3 to prevent complete volatilization of the fluoride. The perchloric acid fuming increases tolerance to many nonmetal ions. Fuming effectiveness has been demonstrated for Br^-, BrO_3^-, ClO_3^-, F^-, H_2O_2, I^-, IO_3^-, NO_3^-, S^{2-}, SO_3^{2-}, and SCN^-.

Electrolytic reduction of Pu^{6+}, which can occur in samples, is said to be slow and incomplete in mineral acids other than sulfuric acid.[9] However, its reduction to Pu^{3+} at 0.25 V in the 5.5*M* HCl-0.015*M* sulfamic acid electrolyte is rapid and complete. The method, therefore, is directly applicable to determination of plutonium in all its oxidation states.

The versatility of the apparatus was well demonstrated in the Pu^{6+} reduction study. The interface for recording the number of coulombs needed for the reduction, initial oxidation, and measurement oxidation allowed us to compute the effective oxidation state of the initial plutonium, as well as to determine the various reaction rates. The on-line digital plots of log current vs time for Pu^{6+} reduction gave two slopes, one for reduction of Pu^{6+} to Pu^{4+} and the other of Pu^{4+} to Pu^{3+}.

In studying interference effects, we processed aliquots of plutonium calibration solutions containing 0.02 mmole (5 mg) of plutonium on a daily basis to get reference values. Over a 3-month period, the relative standard deviation computed for these calibration aliquots was 0.2%. Shorter-time bases, such as would be used for routine analyses, can be expected to improve this measurement precision to about 0.1% relative standard deviation.

The system, including the electrodes, has remained stable for the approximately 9 months required for the above investigations. The anion effect study subjected the platinum gauze electrode to rough treatment. The sulfur-containing anions, sulfide and thiosulphate, produced reduction products that affected electrode characteristics, but not seriously. Importantly, the residual background current remained satisfactorily low. The adverse effect was an increase in electrolysis times, particularly the time for the plutonium measurement oxidation at 0.68 V, which about doubled. The electrode is restored to normal performance by a simple cleaning treatment. It is immersed in hot 16*M* HNO_3 for 1 h, rinsed thoroughly with water, immersed in 12*M* HCl for at least 2 h, and cycled through the reduction and two oxidations using 5.5*M* HCl until the background current stabilizes. Usually only a few cycles are required.

TABLE IV

ANION INTERFERENCE EFFECTS

Nonmetal Anion	Highest Noninterfering Mole Ratio[a] Tested	Nonmetal Anion	Highest Noninterfering Mole Ratio[a] Tested
Acetate	500	I^-	50
Borate	500	IO_3^-	<5
Br^-	5	NO_3^-	50[b]
BrO_3^-	<5	Oxalate	<5
Citrate	500	PO_4^{3-}	<25
Cl	500	S^{2-}	<5
ClO_3^-	<5	SO_3^{2-}	<5
ClO_4^-	500	SO_4^{2-}	50
EDTA	500	$S_2O_3^{2-}$	<5
F^-	<5	$S_2O_8^{2-}$	5
Formate	500	SCN^-	<5
H_2O_2	50	Tartrate	50

Metal Anion	Highest Noninterfering Mole Ratio[a] Tested
MnO_4^-	1
MoO_4^{-2}	1
VO_3^-	1

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[a] Mole ratio relative to plutonium; plutonium level = 0.02 millimole (5 mg). A <5 value means interference at this level.

[b] Not tested at 500-mole ratio to avoid degradation of the platinum electrode by the HNO_3–HCl mixture.

Design and construction of components for the automated instrument are progressing well. A 49-cm-diam aluminum turntable that holds 24 electrolysis cells will rotate them sequentially into position for reagent addition and electrolysis. A 15° Geneva-drive mechanism will provide smooth, accurate rotation. To further ensure correct angular positioning, a locking mechanism will engage tapered indentations in the turntable rim. The turntable and its support mechanism have been constructed.

The electrolysis cells are simple glass cylinders. After rotation, a cell is lifted by a pneumatic cylinder to form an air-tight seal against a stationary Teflon support. This support rigidly holds the electrodes, a stirrer, and tubes that deliver reagents, rinsing solution, and nitrogen gas. A prototype cell-raising mechanism has been tested satisfactorily. Two methods for stirring the electrolyte were investigated, and a rotating glass paddle was chosen over magnetic stirring, which generated high electrical noise. The paddle, rotated by an 1800-rpm motor, extends through a close-fitting hole in the stationary Teflon support. The seal adequately excludes air from the cell, and the paddle rotates smoothly without splashing electrolyte.

Reagent dispensers for adding the hydrochloric acid-sulfamic acid electrolyte and the phosphate complexant have been constructed and tested satisfactorily. They are patterned after those in the automated spectrophotometer[8] in which only glass, Teflon, and Kel-F touch the highly corrosive reagents.

A prototype rinsing system has been constructed, and initial testing is satisfactory. Immediately after completion of analysis, a small-diameter Teflon tube descends to the bottom of the cell through a close-fitting hole in the Teflon support. The sample is aspirated and then the electrodes, stirrer, and cell are rinsed with 5.5*M* HCl. Two rinses appear sufficient. For the system to be effective, the Teflon tube must be positioned carefully relative to the platinum gauze electrode and cell.

IV. PREPARATION OF PLUTONIUM-CONTAINING MATERIALS FOR THE SALE PROGRAM (S. F. Marsh, F. R. Roensch, J. E. Rein, and G. R. Waterbury)

The major objectives of the SALE program, administered by NBL, are (1) to upgrade the capabilities of United States and foreign laboratories for analyzing nuclear fuel cycle materials to determine their uranium and plutonium assay and isotopic contents, and (2) to provide uranium and plutonium Reference and Calibration Test Materials (RCTMs). To meet the former objective, NBL distributes characterized nuclear fuel cycle materials every 2 months for laboratories to test on a voluntary basis. The statistical computations showing accuracies and precisions of the analytical results are transmitted to individual laboratories as soon as they are available and are published (with the laboratories coded) every 2 months. Our major function is to prepare plutonium-containing nuclear fuel cycle materials, both those distributed at 2-month intervals and those used to calibrate assay and isotopic analytical methods.

Three batches of 3/1 (U/Pu) mixed oxide powder, packaged in 1-g amounts per glass vial 4 yr ago for distribution as the bimonthly samples, have not remained stable. The uranium and plutonium concentrations have decreased, and the powders continuously gain weight when heated at 110-120°C. These same instability characteristics, as well as an O/M ratio increased to 2.04 from an original value of 2.00, apply to archive material of two of the three batches in storage at LASL.

The suspected cause of instability is fracturing of the $(U,Pu)O_2$ crystal structure by self-radiation to produce reactive UO_2. The UO_2 reacts with atmospheric moisture and oxygen, tending to U_3O_8. This instability and the fact that the materials cannot be heated to constant weight preclude their use in the SALE program.

The stability of three batches of high-density, 3/1 (U/Pu) mixed oxide pellets, stored under the same conditions as the powders, is superior. The weight gain of pellets from the three batches, heated for 8 h at 115°C, is ≤0.02%. The O/M ratios increased slightly from 1.992 to 1.994. To ensure continued storage stability, pellets will be sealed individually in glass ampoules that have a dry, inert argon atmosphere. Random samples will be characterized as to plutonium and uranium assay and isotopic contents, both at NBL and LASL, using guidelines for Working Calibration and Test Materials proposed to the Nuclear Regulatory Commission.[9]

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

Analyses of bimonthly SALE uranium nitrate and uranium oxide samples for assay and isotopic distribution continued. Biases were insignificant, and the standard deviations were smaller than the averages from the reporting laboratories.

VI. CERTIFIED REFERENCE MATERIAL PLUTONIUM METAL (G. R. Waterbury and staff)

The remaining 250 units of NBS-SRM-949 plutonium metal standard, that LASL had stored for the National Bureau of Standards, were sent to them at their request. Increases in sales and a low inventory (about 20 units) at NBS necessitated shipping all the units of this lot. We will start procurement, purification, and characterization of another batch of high-purity, low-^{241}Pu metal. Preparation and packaging of another lot of 500 units from this extensively analyzed batch of metal is tentatively scheduled for next fiscal year.

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

The Half-life Evaluation Committee (HLEC), consisting of representatives of 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 guiding an effort to measure the half-lives of long-lived plutonium isotopes accurately. LASL is (1) preparing, extensively characterizing, and distributing high-purity batches of plutonium metal from specially provided, enriched isotope materials, and (2) determining the half-lives by using isotope dilution mass spectrometry to measure the produced daughter isotope. The LASL characterization measurements include assay, isotopic distribution, metal impurities including other transuranics, and nonmetal impurities.

The ^{238}Pu half-life measurements are complete. A recent ANL measurement of the ^{238}Pu half-life agrees closely with a past MLM measurement. The HLEC recommends adoption of the average and no further measurements. Plans are under way to start ^{240}Pu measurements. The ^{241}Pu half-life is being measured at five of the laboratories.

A. Plutonium-239

Plutonium oxide of >99.2% ^{239}Pu enrichment was converted to high-purity metal at LASL for distribution to all participating laboratories. The chemical purity of the metal was established by measuring total plutonium assay through use of potentiometric titration, as well as by measuring 44 impurity elements at LASL and RI-RFP through use of emission spectrography, thermal ionization mass spectrometry, spark source mass spectrometry, radiochemistry, spectrophotometry, inert gas fusion, and combustion chemical analysis techniques. ANL, LASL, and RI-RFP measured plutonium isotope distribution by thermal ionization mass spectrometry. The individual portions of plutonium metal were weighed at LASL on the same balance used to weigh NBS SRM-949 plutonium metal.

LASL work on measuring the half-life of ^{239}Pu involved the following operations. The grown-in and impurity uranium were separated from six samples by ion exchange, a measured quantity of ^{233}U was added as the internal standard, and the growth rates of daughter ^{235}U were measured at selected times by mass spectrometric determinations of the ^{235}U/^{233}U ratio. The ^{239}Pu half-life was calculated from the fundamental decay equation

$$-(dn/dt)\,239 = (dn/dt)\,235 = N\lambda \quad ,$$

in which

$-(dn/dt)\,239$ = loss of ^{239}Pu atoms per unit of time and

$+(dn/dt)\,235$ = growth of the ^{235}U daughter per unit of time.

In this equation N is the number of ^{239}Pu atoms and λ is the ^{239}Pu decay constant. The ^{235}U formation rate is measured by isotope dilution mass spectrometry using an accurately measured initial addition of ^{233}U as the internal standard. The loss of ^{233}U by radioactive decay is negligible.

The ^{233}U spike solution concentration was established by isotope dilution mass spectrometry using four uranium standard solutions, two prepared from NBS SRM-960 (natural uranium metal) and two from high-purity 93% ^{235}U metal. Mixtures of each calibration solution and the ^{233}U were analyzed in triplicate. The amont of ^{233}U added to four of the dissolved ^{239}Pu−1 metal solutions was selected to equal the amount of ^{235}U grown-in during 1.5 yr. The ^{233}U added to the remaining two solutions will provide equal amounts of ^{233}U and ^{235}U after 4.5 yr. Mass spectrometry of isotope ratios is most accurate and precise at 1:1 ratios. Weighed portions of the calibrated ^{233}U solution were added to each of the six ^{239}Pu solutions to produce solutions whose ^{233}U/^{239}Pu ratios were known to ±0.022% relative standard deviation.

Four of the six ^{239}Pu-1 solutions were measured in quadruplicate initially and after grow-in times of 1.4 and 1.7 yr, when the ^{235}U/^{233}U ratio brackets the optimum ratio of unity for mass spectrometry. The ^{239}Pu half-life calculated from these measurements is 24 164 yr with 95% confidence limits of 34 yr.

The remaining two ^{239}Pu solutions, which contain three times as much added ^{233}U standard, are now two-thirds of the way to 4.5 yr, when grown-in ^{235}U will equal ^{233}U. Then, further mass spectrometry of these solutions is expected to confirm and improve the precision of the half-life value.

The HLEC met at NBS on May 16-17, 1977, to review completed ^{239}Pu half-life measurements and to formulate plans. The results from all participating laboratories are scheduled for publication in a single issue of the International Journal of Applied Research and Isotopes. The papers on chemical characterization of the ^{239}Pu-1 metal and the LASL mass spectrometric half-life measurement have been written and submitted to the journal.[10,11]

B. Plutonium-238

A scheduled half-life measurement had been that of ^{238}Pu. A recent ANL measurement of 87.71 yr, presented by A. Jaffey at the November 8-9 HLEC meeting, agrees with an MLM value of 87.77 yr. The Committee decided that further measurements would not give a value better enough to merit the effort and expense.

C. Plutonium-240

The HLEC has decided that measurement of the ^{240}Pu isotope half-life is warranted. ANL recently completed a measurement based on alpha-particle counting. Their 6571 yr is considerably higher than the American Nuclear Standards Institute recommended value of 6537 yr.

We have ordered 28 g of 98.3% $^{240}PuO_2$ (lot 274A) from Oak Ridge and will reduce it to the metal early in 1978. Tentative plans for characterization of the metal by the various laboratories were formulated at the May meeting.

D. Plutonium-241

The HLEC decided at its May meeting that the complexity (and cost) of measuring the half-lives of two ^{241}Pu materials, one freshly produced in a reactor and one aged, to resolve the controversy about existence of a short-lived isomer, would be excessive.

We have prepared a mixture containing aged ^{241}Pu and ^{242}Pu in an ~1.1/1.0 ratio and are measuring the decreasing ^{241}Pu/^{242}Pu ratio by thermal ionization mass spectrometry at 6-month intervals. Results over a 1.5-yr period give a value of 14.45 yr.

Measurements over a 5-year span are considered necessary for high reliability.

The HLEC has sanctioned this measurement technique and concurred with our suggestion to have other laboratories join in the measurement. We have distributed portions of the mixture to LLL, MLM, NBS, and RI-RFP.

VIII. ION EXCHANGE BEHAVIOR OF ELEMENTS IN HYDROBROMIC ACID, HYDRIODIC ACID, AND STRONG NITRIC ACID

(S. F. Marsh, J. A. Alarid, M. McLeod, C. F. Hammond, F. R. Roensch, and J. E. Rein)

Because ion exchange systems have proven very valuable to nuclear operations, we investigated three systems not previously studied: (1) cation exchange in nitric acid, (2) anion exchange in hydrobromic acid, and (3) anion exchange in hydriodic acid. For each system, the distributions of 53, 58, and 58 elements, respectively, were measured on three types of resin: macroporous, 4% cross-linked divinylbenzene (DVB), and 8% cross-linked DVB. Cation exchange measurements were made at 3, 6, 9, and 12*M* HNO_3. Anion exchange measurements were made at 0.1, 1, 3, 6, and 8.7*M* HBr and at 0.1, 1, 3, 5.7, and 7.4*M* HI. Batch contacts of 16-18 h on a Khan-type mechanical shaker were made. Most of the distribution data were determined by alpha, beta, or gamma counting radionuclides either obtained by thermal neutron activation of the natural elements or purchased. Elements without suitable radionuclides were measured by atomic absorption or chelometric titration.

The observed anion exchange behaviors of the 58 elements, relative to their behaviors in HCl, are affected by (1) the reduction of many elements to their lower oxidation states by the HBr and HI, (2) differing tendencies to form anionic complexes with bromide and iodide, (3) differences among the macroporous, 4% DVB, and 8% DVB resins, and (4) the lower maximum 8.7 and 7.4*M* aqueous acid concentrations of HBr and HI, respectively, contrasted to 12*M* HCl. Relative sorption by the resins generally is MP-1 > 4% DVB > 8% DVB. This is particularly true from HI systems that have very large among-resin differences.

Noteworthy ion exchange behavior includes sorption of barium from strong HBr, sorption of technetium from HBr but not HI, sorption of iron (presumably Fe^{2+}) from HI, high sorption of polonium from all concentrations of both acids, and lack of sorption of the actinides in the series through americium. Americium is 70% sorbed on MP-1 resin from 0.1*M* HBr or 0.1*M* HI, indicating an anionic complex in dilute acid.

Cation exchange distribution of the 53 elements in 3-12*M* HNO_3 showed that many were sorbed more highly from strong HNO_3 than from low to moderate concentrations. This observation agrees with the cation exchange behavior in $HClO_4$ and HCl which Nelson et al.[12] reported.

Two papers have been submitted for publication in a technical journal.

PUBLICATIONS AND TALKS

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2. R. M. Hollen, D. D. Jackson, and J. E. Rein, "Evaluation of the LASL Automated Spectrophotometer for Uranium Determination at Submilligram Levels," Los Alamos Scientific Laboratory report LA-6867 (July 1977).

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11. S. F. Marsh, R. M. Abernathey, R. J. Beckman, R. K. Zeigler, and J. E. Rein, "Plutonium-239 Half-Life Determined by Isotope Dilution Mass Spectrometric Measurement of Grown-In Uranium-235," submitted for publication in Int. J. Appl. Res. and Isotopes.

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