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Analytical Methods for Fissionable Materials in the Nuclear Fuel Cycle

July 1, 1975—September 30, 1976

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ANALYTICAL METHODS FOR FISSIONABLE MATERIALS IN THE NUCLEAR FUEL CYCLE

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ABSTRACT

Progress continued on development of dissolution techniques for difficult-to-dissolve nuclear materials, development of methods and automated instruments for determinations of plutonium and uranium, preparation of plutonium-containing materials for the Safeguards Analytical Laboratory Evaluation (SALE) program, analysis of SALE uranium materials, and measurement of plutonium isotope half-lives. Gas-solid reactions at elevated temperatures using reactive gases such as chlorine continue to show promise for separating uranium from refractory materials. An extensive study of nonaqueous solvents for the dissolution of refractory materials is in progress. An extraction-separation procedure, highly specific for microgram amounts of uranium, has been developed, and its adaptation to the Los Alamos Scientific Laboratory (LASL) automated spectrophotometer is being evaluated. Development of an electrometric analysis method for plutonium is nearing completion, and design of an automated instrument using the method has been started. Batches of plutonium oxide and mixed uranium-plutonium, intended for issue as Secondary Reference and Calibration Test Materials, are being recharacterized for assay and isotopic contents. The half-life of ^{239}Pu has been determined by isotope-dilution mass-spectrometric measurement of ^{235}U grow-in as a function of time.

I. INTRODUCTION

Adequate levels of safeguard control of uranium and plutonium require confirmation by adequate sampling and analyses of inventories in the nuclear fuel cycle. Isotopic composition as well as the total amounts present of these two actinides must be measured precisely in widely diverse types of nuclear materials, including highly pure products, reactor fuels having complex chemical compositions, and many types of scrap materials. Dissolutions and analyses of highly refractory alloys, oxides, and scrap materials containing uranium, plutonium, or both are particularly difficult.

The objectives of this project are (1) the development of fast dissolution techniques and analytical methods for plutonium and uranium determination, with emphasis on difficult-to-dissolve materials, (2) the design and construction of automated apparatus for plutonium and uranium determination, (3) the preparation of well-characterized, plutonium-containing materials for use in the Safeguards Analytical Laboratory Evaluation (SALE) program, (4) the preparation of well-characterized, highly pure plutonium metal standards for distribution by the National Bureau of Standards (NBS), (5) participation in, and the preparation and characterization of the materials for, an inter-ERDA laboratory program established to measure the half-lives of the longer lived plutonium isotopes, and (6) the chemical characterization of special lots of nuclear materials as requested by the Energy Research and Development Administration (ERDA).

II. DISSOLUTION OF FUEL CYCLE MATERIALS

A difficult and time-consuming operation in chemical analysis of nuclear fuel cycle materials is their dissolution before assay or isotopic measurement. The rapid dissolution of fuel cycle materials or solubilization of uranium and plutonium are being investigated. Currently included in this investigation are mineral acid reactions at high temperatures in pressurized containers, reactions with reactive gases at high temperatures, and reactions with nonaqueous acid and reactive organic solvents, and later, reactions with various media abetted by laser energy input will be investigated.

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

A dissolution apparatus consisting of a Teflon container in a pressure-supporting metal shell permitted acid dissolutions at temperatures to 270°C and pressures to 320 atm (5 000 psi). The use of this apparatus is far-reaching, including uses for geological samples, metals, and most other inorganic materials, and the nuclear industry from mining and milling through nuclear fuel fabrication. The design of the LASL-developed apparatus was made available to industry, and the Parr Instrument Company now markets a slightly modified version.

In late fiscal year 1975, Parr-supplied Teflon containers experienced an unusually high number of failures, both at the New Brunswick Laboratory (NBL) and at the Los Alamos Scientific Laboratory (LASL). Teflon containers fabricated at LASL were tested under conditions causing failures with Parr containers and shells. The LASL-fabricated containers did not fail; in fact, the safety rupture diaphragm distorted only slightly, indicating low-to-moderate internal pressures.

We notified Parr Instrument Company of our test results, along with speculation that the Teflon lot used to fabricate the Parr containers might have contained reactive organic components or was unusually porous. Porosity permits excessive transpiration of acid vapors at the operating temperature and consequent corrosion and failure of the safety rupture diaphragm. Specifications and supplier of the Teflon in use at LASL were supplied to Parr. To date, Parr has not responded.

B. Gas-Solid Reactions (D. D. Jackson, R. M. Hollen, J. E. Rein)

The investigation of gas-solid reactions with the objective of converting refractory plutonium and uranium materials to more readily soluble compounds was continued, with emphasis on reacting uranium-containing materials with chlorine gas. As previously reported,[1] reaction of chlorine gas with uranium oxides (UO_2, UO_3, and U_3O_8) and UC_2 at 1000°C for 12 h in a quartz-tube furnace produced complete volatilization of the uranium. The technique has been applied successfully to scrap material samples as well.

NBL-supplied scrap materials known to contain zirconium, probably as uranium-zirconium cermet fuel, were reacted with chlorine gas at temperatures to 1000°C in the quartz-tube furnace. For a 1-g sample, 8-h reaction time, and 0.2 atm chlorine pressure, about 40 wt% of the total sample and >95 wt% of the uranium volatilized. The quartz tube was specially fabricated to provide controllable atmosphere and effective recovery of the volatilized sample fraction by dissolution with HNO_3.

Typical samples were subjected to this treatment and the HNO_3 solutions were analyzed for uranium using the LASL automated spectrophotometer prototype. For some samples, the organic phase was cloudy, contributing to uncertainty in the results. This cloudiness was probably caused by hydrolytic precipitation of zirconium that dispersed into the organic phase. To eliminate this effect, a two-step furnace treatment was investigated. The sample was reacted with chlorine at 500°C for 4 h, the condensate was dissolved with HNO_3, the residue was reacted at 1000°C for 8 h, and the condensate formed from this reaction was dissolved with HNO_3. The first reaction volatilized 11 wt% of the sample and no significant amount of uranium. The second reaction increased the quantity of sample volatilized to 40 wt% (based on initial sample weight) and gave 95 wt% volatilization of the uranium. Significantly, the organic phase remained clear during the uranium extraction. Because the sublimation point of $ZrCl_4$ is 331°C, the first reaction undoubtedly volatilized a majority of the zirconium.

A furnace designed to operate with the quartz reaction apparatus at temperatures to 1300°C is being installed for continued investigation using chlorine and other reactive gases. This furnace will be in a glovebox so that applicability to plutonium materials also can be studied.

C. Reactions with Nonaqueous Solvents (W. D. Spall, M. J. McLeod, S. F. Marsh, F. R. Roensch, J. E. Rein)

This year, an investigation was begun of nonaqueous acid media and organic solvents that provide increased acidity, greater oxidation-reduction potentials, and unique high reactivities. Test materials were refractory components often present in nuclear fuel cycle materials, including fused oxides of UO_2, ThO_2, ZrO_2, Al_2O_3, and SiO_2, and firebrick to simulate slag and similar components in scrap materials.

A 100-mg sample of a sieved 100-200 mesh test sample was reacted with a measured volume of the nonaqueous acid or organic solvent in a Teflon or borosilicate glass container fitted with a water-cooled cold finger. The mixture was heated for a selected time, usually 16 h, cooled, filtered, and the residue weighed. Loss of weight was taken as a measure of dissolution.

Nonaqueous acid media studied have been HI, HBr, HNO_3, H_2SO_4, and Br_2 in glacial acetic acid containing a slight excess of acetic anhydride. There was no significant dissolution of the test materials, except that UO_2 completely dissolved in HNO_3 in less than 1 h at 50°C, giving a yellow solution of UO_2^{2+} upon dilution with water. Because these media are considered to be oxidizing, and because all of the metals in the test series, with the exception of uranium in UO_2, are in their highest oxidation state, the insolubility is not surprising. Over 50% dissolution of an unground piece of zirconium-uranium carbide in HNO_3-glacial acetic acid indicated the potential applicability of such oxidizing systems to dissolution of carbide and nitride fuels.

Some refractory oxides are dissolved by reactions with reducing agents, generally as high-temperature fusions. Very strong reducing media are produced by dissolving alkali metals in low-molecular-weight amines, selected amides, and ethers. Such media studied to date include sodium and potassium metals in ethylenediamineformamide, N,N-dimethylformamide, tetrahydrofuran, p-dioxane, triethylamine, diethylamine, isobutylamine, and acetonitrile. The generally low dissolution of test materials has been attributed to the low solubilities, and hence concentrations, of sodium and potassium in these solvents. The solubilities of sodium and potassium are higher in liquid ammonia, methylamine, and ethylamine. Handling techniques must be developed for these low-boiling solvents before they can be evaluated. Other reducing media, including hydrazine hydrochloride in formamide and dimethylformamide, and sodium and potassium naphthalates in tetrahydrofuran, are being evaluated. To be studied are hydroxylamine, dimethylphosphite, triphenylphosphite, and hydrazine in amine solvents.

Free radicals formed in the high-temperature sealed-tube dissolution technique using mineral acids provide much of the reaction. Nonaqueous solvents can generate free radicals without pressure-sealing to promote high temperature. Initial attempts using sulfuryl chloride alone, and mixed with t-butylperoxybenzoate as an initiator, have given limited success. Solvents generating more energetic free radicals will require development of safe handling techniques.

In addition to the solvent types discussed above, several organic solvents known to dissolve inorganic salts are being tested, among them formamide, N,N-dimethylformamide, hexamethylphosphoroamide, acetonitrile, dimethylsulfoxide, and dibutylphosphate. Dissolution of the refractory test materials was less than 20% except for dibutylphosphate, which dissolved nearly all of UO_2 and 15-60% of the others.

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

Past efforts have produced an automated instrument for the determination of milligram amounts of both uranium and plutonium using a highly specific spectrophotometric method. Development of a more sensitive method for microgram amounts of uranium (and possibly plutonium) is nearing completion, and its adaptation to the automated spectrophotometer appears promising. An electrometric method for the determination of plutonium is being developed to serve as the basis for a high-precision automated analyzer.

A. Automated Spectrophotometer (D. D. Jackson, R. M. Hollen, J. E. Rein)

A report detailing all aspects of the instrument fabricated for NBL has been issued.[2] The main body of the report offers (1) information on chemistry aspects of determination of plutonium and uranium, including discussions of tolerances for diverse metal ions, inorganic and organic anions, and acidity, (2) a description of the instrument, component by component, and (3) data showing accuracy and precision capability. A series of appendixes gives (1) preoperational instrument adjustments and test, (2) operational procedures for the determination of uranium and plutonium, (3) details of mechanical components, including engineering drawings, (4) details of electrical control circuitry, (5) microcomputer readout system hardware, and (6) software for the readout system.

As one of the final investigations for the automated spectrophotometer, its precision was compared to the precision of the uranium determination procedure done manually by an experienced analyst. The operations were very similar to those described for the original method,[3] except that 2-nitropropane was used as the organic extractant, and the volumes of the salting-complexing solution and the organic extractant were changed to those volumes used for the automated instrument. The analyst prepared a uranium calibration solution using a LASL-produced highly pure uranium metal. Four weight aliquots at uranium levels of 1, 6, and 10 mg were processed on each of seven alternate days to give a total of 84 measurements. The absorbance measurements were made using 1-cm cells and a Heath EU-707 recording spectrophotometer. Results were computed using both the two-wavelength calculational mode (as used in the automated instrument) and the more precise three-wavelength calculational mode. Second-order polynomials were fitted and regression lines were computed for the 84 values. The averages of the average deviations were 1.8, 0.42, and 0.55 rel% at the 1-mg, 6-mg, and 10-mg levels for the three-wavelength calculation. The corresponding values for the two-wavelength calculation were 4.0, 0.48, and 0.50 rel%. The precisions of 0.9, 0.30, and 0.27 rel% that were obtained with the automated instrument, in which the two-wavelength measurement system is used, are superior to those obtained by manual operations by the experienced analyst, especially at the 1-mg uranium level.

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, J. E. Rein)

The procedure used in the automated spectrophotometer has a lower limit of 1 mg of uranium. A major application of the instrument is the analysis of scrap samples, many of which are characterized by low uranium contents and high contents of extraneous elements. Because the automated spectrophotometer procedure is restricted to a maximum sample volume of 0.5 ml, it is necessary to evaporate larger aliquots of these samples with low uranium contents. Here, the large quantities of extraneous salts can interfere with uranium extraction and absorbance measurement. The development of a high-sensitivity spectrophotometric method compatible with the automated instrument is therefore the objective of this task. The major compatibility requirement is that all operations including the final absorbance measurement are done in a glass sample tube with no transfer of the sample.

1. Chemical Separation and Measurement Procedure. Of various procedures evaluated, one of the most promising is based on the extraction of the uranium(VI)-benzoyltrifluoroacetone complex into butyl acetate.[4] Initial experiments with this procedure showed that the degree of extraction of the complex was below the 99% level that is considered minimum to produce highly reliable measurements. Other solvents evaluated were *sec*-butyl acetate, benzyl acetate, toluene, butyl propionate, isobutyl propionate, isobutyl isobutyrate, benzyl-n-butyrate, pentyl hexanoate, isopentyl benzoate, and isopentyl hexonoate. Of these, butyl propionate gave the highest uranium extraction (>99%, based on ^{237}U tracer experiments), as well as the highest absorbance for the extracted complex. The molar absorptivity was 14 000.

The extraction of the uranium complex is relatively insensitive to pH change over the pH range 6 to 8. However, many other elements also extract under this condition. The extraction of extraneous elements can be suppressed by adding a chelon as a masking agent, ideally without suppressing the extraction of the uranium complex. Chelons investigated were ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylethylenediaminetriacetic acid (HEDTA), and cyclohexanediaminetetraacetic acid (CDTA). As expected, CDTA was the most effective. It forms particularly stable complexes with most cations; however, the UO_2^{2+}-CDTA complex is at least 100 times weaker than complexes formed with the other chelons. The effect of CDTA on uranyl ion was further minimized by adding CDTA as equimolar Mg-CDTA. The stability constant of Mg-CDTA is $\sim 10^5$ higher than for UO_2^{2+}-CDTA. Thus, CDTA remains tightly bound to Mg^{2+} in the presence of UO_2^{2+} ions. Most potentially interfering cations, however, form CDTA complexes whose stability constants are $>10^6$ higher than for Mg-CDTA. In samples containing such cations, CDTA releases from the Mg-CDTA complex to form the stronger complexes.

The initial anion interference studies, from a chloride system, demonstrated that the following anions did not interfere at a 1000:1 mole ratio to uranium SO_3^{2-}, SO_4^{2-}, F^-, NO_3^-, NO_2^-, ClO_4^-, and I^-. Phosphate did not interfere at a 1:1 mole ratio, but did at a 10:1 ratio.

Many cations are known to form highly extractable chloride complexes. For this reason, the system was modified from a chloride to a nitrate medium, and an extensive cation interference study was made of all elements commonly present in nuclear scrap materials. For pH control, a highly buffered solution of hexamethylenetetramine and triethanolamine was incorporated into the system in anticipation of automated operation that would accept 1-ml samples ranging from 1*M* HNO_3 to 8*M* HNO_3 with no pH adjustment. The effect of each cation was determined at these extremes of 1 and 8 meq of acid and at mole ratios to uranium of 10, 100, and 1000 (or until interference was apparent). Of 42 cations studied, there were no effects for 23 at 1000:1 ratios, nine at 100:1 ratios, and seven at 10:1 ratios. A few experiments remain for completion of the interference study.

Development and evaluation of this procedure for manual operation is nearing completion. At that time it will be published as a journal article or topical report.

2. Adaptation to the Automated Spectrophotometer. The above procedure, developed 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. In the automated spectrophotometer, phase mixing in the tube is attained by magnetic stirring, and a Teflon-covered magnet rotating at 1200 rpm proved effective for the new procedure. The uranium-BFTA complex extracted completely in 6 min, the phases separated in less than 1 min to produce a clear organic phase, and spattering of droplets was insignificant.

Because the absorbance peak of the extracted uranium-BTFA complex is broad and is not separated from the reagent absorbance, measurement of the complex absorbance with a single-beam instrument like the automated spectrophotometer is difficult. Absorbance by the tube's glass walls also is appreciable at the 380-nm wavelength of the complex's absorbance peak, and the measured absorbance must be corrected for variations arising from different wall thicknesses.

To investigate the conditions for measurement in a single-beam mode, a photomultiplier tube detector and a chamber to hold the glass sample tubes were constructed and attached to the exit face of a monochromator that has variable wavelength and bandwidth control. Output from the photomultiplier detector was measured with a picoammeter.

Samples containing up to 42 μg of uranium were extracted in the automated spectrophotometer for 10 min to assure complete extraction. Absorbances were measured at 384.0 nm for the peak and at three wavelengths of 400.0, 415.0, and 425.0 nm for the background correction using bandwidths up to 0.4 nm, the maximum attainable with the monochromator. Although 400 nm is on the descending slope of the UO_2^{2+}-BTFA complex peak, its use gave best precision. That the precision improved slightly with increasing bandwidth is attributed to the higher signal-to-noise ratio produced by increasing incident light intensity.

Measurement precision was established for the above instrument conditions at four uranium levels in the range of 7 to 42 μg of uranium. The relative standard deviations, computed for six replicate measurements at each level, ranged from 0.3% at 42 μg to 0.9% at 7 μg. Without the background correction at 400 nm, precision was about tenfold worse.

C. Investigation of Electrotitrimetry for an Automated Plutonium Analyzer (D. D. Jackson, R. M. Hollen, F. R. Roensch, J. E. Rein)

The objective of this task is to develop an electrometric method for the determination of 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) measurement of low-milligram levels. A versatile coulometric apparatus consisting of commercial components has been assembled around a Princeton Applied Research Corporation 173D Potentiostat Galvonostat, a 179D Digital Coulometer, and a Hewlett-Packard 9821 Programmable Calculator. Interfaced and under control of the calculator are a scanner, a digital multimeter, a digital-to-analog converter, and a plotter. A schematic of this apparatus is shown in Fig. 1.

The calculator controls titrimetric conditions such as controlled-potential and controlled-current, and monitors the electrolysis measurements of interest, such as current, voltage, coulomb, and time. The electrolysis data can be processed on-line, decisions can be made, and conditions can be adjusted, and the data can be stored on a magnetic tape cassette for later analysis. The digital-to-analog converter permits the calculator to select any desired potential level when operating in the controlled-potential mode or the current level when operating in

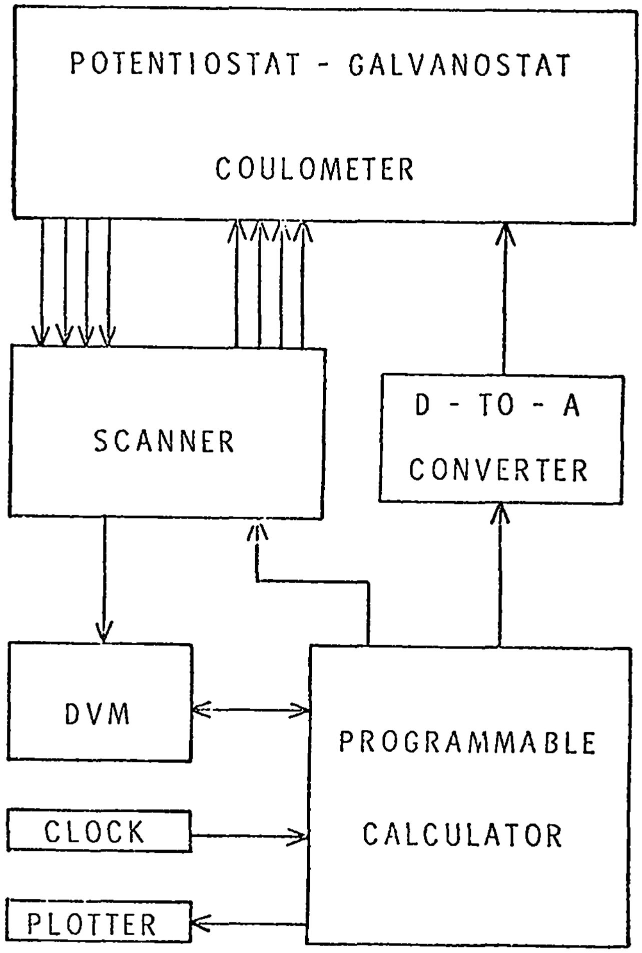

Fig. 1.
Schematic of versatile electroanalytical apparatus for the investigation of automated plutonium determinations.

constant-current mode. During all phases of an electrolysis, the on-line digital plotter can record a variable of interest, usually a plot of $\log_{10}$ current vs time or electrode potential vs time.

This apparatus has given excellent performance and will serve as the basis for the automated instrument. For example, 5-mg amounts of iron in 0.5M H_2SO_4 electrolyte were titrated with a precision of 0.05% relative standard deviation using controlled-potential coulometry and an electrolysis cell consisting of a platinum-gauze working electrode, a saturated-calomel reference electrode, a Vycor counter electrode, and a glass stirrer driven by a synchronous motor. Iron was reduced to Fe^{2+} at 0.25 V and then titrated to Fe^{3+} at 0.60 V. (All electrode potentials in this report are relative to the saturated calomel electrode.) Time for the oxidative titration was 6 min to a current end point of 30 μA.

The general system under consideration for the determination of plutonium is an initial reduction to Pu^{3+}, an oxidation in a medium in which Pu^{3+} is not oxidized but potentially interfering diverse ions are oxidized, addition of a complexing agent to lower the Pu^{3+}-Pu^{4+} potential, and oxidative titration of Pu^{3+} to Pu^{4+} using controlled-potential coulometry.

Aspects of the Davies and Townsend potentiometric method[6] are being considered as the basis for a controlled-potential coulometric method. In the Davies and Townsend method, reduction and oxidation are done with chemicals, as follows. In a medium of hydrochloric acid-aluminum chloride-sulfamic acid, excess cuprous chloride reduces plutonium to Pu^{3+}, a titration with potassium dichromate to a potentiometric end point oxidizes excess Cu^{1+} and any Fe^{2+} without oxidizing Pu^{3+} to Pu^{4+}, sulfuric and phosphoric acids are added to lower the Pu^{3+}-Pu^{4+} potential, and the Pu^{3+} is titrated to Pu^{4+} with potassium dichromate to a second potentiometric end point.

Because iron is the most troublesome diverse ion in electrotitrimetric determinations of plutonium, it is being investigated along with plutonium to establish procedure conditions.

The redox potentials of the Fe^{2+}-Fe^{3+} and the Pu^{3+}-Pu^{4+} couples in the 1.1M $AlCl_3$-1.1M HCl-0.15M sulfamic acid electrolyte of Davies and Townsend were measured as 0.41 V and 0.67 V for a potential difference of 0.26 V. A greater potential difference was desired to decrease the small quantity of iron not oxidized at the first end point that then oxidized with and biased the plutonium result. To establish whether these half-cell potentials were sufficiently separated to permit the unbiased determination of plutonium, the oxidation levels of Fe^{2+} and Pu^{3+} were determined at various potentials. For iron, 98.0% oxidized at 0.49 V, 98.8% at 0.50 V, 99.2% at 0.51 V, and 99.5% at 0.52 V. The plutonium oxidations were 0.20% at 0.53 V, 0.32% at 0.54 V, and 0.58% at 0.55 V. Thus, at a potential of 0.50-0.51 V, 99% of the iron oxidizes with no significant oxidation of plutonium. A correction for the small amount of iron that would not have been oxidized at 0.50-0.51 V and that would then oxidize with the plutonium could be computed, based on the coulombs measured at 0.50-0.51 V. However, the accuracy of this correction will depend on the relative quantities of other diverse ions that oxidize at the first end point.

The precision for the determination of 5 mg of iron in the $AlCl_3$-HCl-sulfamic acid electrolyte, using reduction and oxidation potentials of 0.25 V and 0.60 V, was 0.46% relative standard deviation, considerably poorer than that obtained in 0.5M H_2SO_4 electrolyte. Also, electrolysis times were 2 min longer, requiring 8 min for the oxidation.

Hydrochloric acid, lithium chloride, and mixtures of the two were evaluated as electrolytes. Advantages, compared to the HCl-$AlCl_3$-sulfamic acid electrolyte, would be high purity and an ability to obtain high chloride concentration levels coupled with low viscosity. A disadvantage appears to be the inability to complex fluoride, expected to be present in many samples. This could be overcome by using a fluoride complexant such as H_3BO_3.

The half-cell potentials of the Fe^{2+}-Fe^{3+} and Pu^{3+}-Pu^{4+} couples in various combinations of hydrochloric acid and lithium chloride are given in Table I. These potentials were measured by sweeping the electrode potential rapidly over the region of interest while measuring the instantaneous current. Scans were made with increasing and decreasing electrode potential, starting, respectively, with the reduced and oxidized species in the electrolyte. The intersection of the two curves on a plot of electrode potential vs instantaneous current yields the half-cell potential. These half-cell potentials were confirmed by controlled-potential coulometric determinations.

According to Table I, the half-cell potentials for both the Fe^{2+}-Fe^{3+} and the Pu^{3+}-Pu^{4+} couples decrease with increasing chloride concentration. This is expected because the chloride complexes of the higher oxidation states are stronger than the complexes of the reduced states. At a constant total chloride level, the half-cell potential for iron decreases as the HCl/LiCl ratio increases, whereas there is little effect on the half-cell potential for plutonium. Thus, the electrolyte preferred to obtain largest differences in the iron and plutonium half-cell potentials is hydrochloric acid without lithium chloride.

The half-cell potentials of over 0.6 V for the Pu^{3+}-Pu^{4+} couple require greater than 0.8 V for complete oxidation of Pu^{3+} to Pu^{4+}. At this high potential, hydrochloric acid undergoes electrolysis and the likelihood increases that diverse ions will oxidize and interfere. The effect of sulfate, selected as a complexant to lower the half-cell potential of the Pu^{3+}-Pu^{4+} couple, was determined for the hydrochloric acid-lithium chloride electrolyte combinations (Table I). The decrease was only about 0.1 V for up to 2*M* H_2SO_4, which is not adequate (discussed later). There was even less effect upon the half-cell potential of the Fe^{2+}-Fe^{3+} couple, and the previously oxidized Fe^{3+} remained stable.

TABLE I

HALF-CELL POTENTIALS OF Fe^{2+}-FE^{3+} AND Pu^{3+}-Pu^{4+} COUPLES IN HYDROCHLORIC ACID-LITHIUM CHLORIDE-SULFURIC ACID ELECTROLYTES[a]

	Half-Cell Potentials Without H_2SO_4			Half-Cell Potentials After Addition of H_2SO_4		
Electrolyte	Fe^{2+}-Fe^{3+}	Pu^{3+}-Pu^{4+}	Difference	Molarity H_2SO_4[b]	Fe^{2+}-Fe^{3+}	Pu^{3+}-Pu^{4+}
2.5*M* LiCl	0.47	0.68	0.21	1	0.43	0.53
				2	0.42	0.51
				3.4	0.38	0.50
1.5*M* LiCl-1*M* HCl	0.44	0.67	0.23	1	0.42	0.53
				2	0.41	0.52
2.5*M* HCl	0.42	0.68	0.26	1	0.41	0.54
				2	0.40	0.52
5 *M* LiCl	0.42	0.65	0.23	1	0.40	0.51
4 *M* LiCl-1*M* HCl	0.41	0.69	0.28	1	0.39	0.53
3 *M* LiCl-2*M* HCl	0.39	0.69	0.30	1	0.38	0.54
				2	0.38	0.52
5 *M* HCl	0.37	0.67	0.30	1	0.36	0.56
				2	0.35	0.53
				3.4	0.34	0.50
4.5*M* LiCl-3*M* HCl	0.35	0.65	0.30	1	0.34	0.54
				2	0.32	0.51
7.5*M* HCl	0.31	0.63	0.32	1	0..31	0.57
				2	0.29	0.51
				3.4	0.28	0.50

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[a] Potentials vs SCE. Measured with 2*M* H_2SO_4 in reference compartment; therefore, includes a liquid junction potential.

[b] Sulfuric acid was added to the electrolyte to give the indicated molarity.

The half-cell potentials of the two couples in hydrochloric acid media were determined in detail to establish the concentration level at which the difference between the two half-cell potentials is greatest. This level would be used as the electrolyte in conjunction with a complexant (other than sulfate) for plutonium. As shown in Table II, the difference of 0.32 V is essentially maximum and constant over the range from about 5 to 7.4*M* HCl, and both half-cell potentials decrease with increasing hydrochloric acid concentration. At a 0.32-V difference, the Nernst equation predicts that 99.6% of the iron can be oxidized with oxidation of less than 0.1% of the plutonium. This is considered satisfactory. The apparent advantage of using a high hydrochloric acid concentration to attain lower oxidation potentials is more than offset by an increased background current and an increased measurement imprecision caused by electrolysis of the hydrochloric acid. Based on the above, 5.5*M* HCl was selected as the electrolyte.

Complete (>99.9%) oxidation of Pu^{3+} in 5.5*M* HCl would require a potential of almost 0.87 V which is not feasible because hydrochloric acid oxidizes and more diverse ions may interfere. Therefore, another complexant, phosphate ion, was investigated to decrease the Pu^{3+}-Pu^{4+} half-cell potential. The measured potentials as a function of phosphate molarity in 5.5*M* HCl (Table III) show that in 1*M* phosphate, the Pu^{3+}-Pu^{4+} half-cell potential is lowered to almost 0.50 V, and greater than 99.9% of the Pu^{3+} is calculated to be oxidized to Pu^{4+} at 0.68 V. At this potential, the oxidation of hydrochloric acid is negligible. The Fe^{2+}-Fe^{3+} half-cell potential was little affected by phosphate, decreasing from 0.36 V at 0.56*M* phosphate to 0.34 V at 1.33*M* phosphate. Therefore, the previously oxidized iron remains oxidized upon addition of phosphate.

Two sources of phosphate, H_3PO_4 and NaH_2PO_4, were investigated. Neither contained measurable quantities of impurities that oxidized or reduced in 5.5*M* HCl over the 0.2-0.7 V potential range. Phosphoric acid, which can be added as a more concentrated solution than NaH_2PO_4, was investigated first. After several months of successful use, unexplained erratic potentials and increased electrolysis times and background currents began occurring. Use of NaH_2PO_4 for long periods of time had none of these adverse effects, and all subsequent data were obtained with it.

With 5.5*M* HCl established as the electrolyte, and with NaH_2PO_4 added to lower the Pu^{3+}-Pu^{4+} couple, detailed experiments were conducted to establish "optimum" potentials for the preliminary oxidation of iron (and presumably other diverse ions) and the

TABLE II

MORE DETAILED MEASUREMENTS OF THE HALF-CELL POTENTIALS OF Fe^{2+}-Fe^{3+} AND Pu^{3+}-Pu^{4+} COUPLES IN HYDROCHLORIC ACID[a]

HCl conc (*M*)	**Half-Cell Potentials[b]**		
	Fe^{2+}-Fe^{3+}	**Pu^{3+}-Pu^{4+}**	**Difference**
2.5	0.446 ± 0.0026	0.705 ± 0.0080	0.259 ± 0.0084
4.7	0.397 ± 0.0015	0.701 ± 0	0.304 ± 0.0015
5.5	0.372 ± 0.0021	0.686 ± 0.0013	0.314 ± 0.0025
5.8	0.371 ± 0.0017	0.686 ± 0.0015	0.315 ± 0.0023
6.6	0.343 ± 0.0021	0.662 ± 0.0010	0.319 ± 0.0023
7.0	0.332 ± 0.0015	0.649 ± 0.0006	0.317 ± 0.0016
7.4	0.323 ± 0.0010	0.640 ± 0.0017	0.317 ± 0.0020

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[a] Potentials vs SCE.

[b] The associated uncertainty is the standard deviation for a single measurement, calculated from n = 3 measurements.

TABLE III

Pu^{3+}-Pu^{4+} HALF-CELL POTENTIALS IN 5.5*M* HCl-PHOSPHATE MEDIA

Phosphate (*M*)	Potential (V vs SCE)
0.56	0.54
0.83	0.52
1.08	0.50
1.33	0.48

TABLE IV

PER CENT OXIDATIONS OF IRON AND PLUTONIUM AT THE PRELIMINARY AND OXIDATIVE TITRATION POTENTIALS

Preliminary Potential (V)	Per Cent Oxidized		Per Cent Oxidized at 0.68 V	
	Fe	Pu	Fe	Pu
0.54	99.89	<0.01	0.11	100.
0.55	99.93	0.012	0.07	99.98_8
0.56	99.97	0.037	0.03	99.96_3

titrimetric oxidation of plutonium. Variables evaluated included the preliminary oxidation potential, the end-point current, and the effect of time for both the preliminary and titrimetric oxidations.

In general, experimental conditions were as follows: equal-mole quantities of 1 mg iron and 5 mg plutonium, 10-ml volume of 5.5*M* HCl, nitrogen flow through the cell for 10 min before and then during electrolysis, preliminary reduction at 0.25 V to an end-point current of 50 μA, preliminary oxidation at a selected potential to a selected end point (current and/or time), addition of 2.5 ml 5*M* NaH_2PO_4, and oxidative titration at 0.68 V to a selected end point (current and/or time).

To attain high precision and accurate coulometric titration, proper background correction is important. In these experiments, background correction coulombs are established at both potentials by electrolyses of the electrolyte alone for times equal to those used for the iron and plutonium oxidations.

The per cent oxidations of iron and plutonium at preliminary potentials of 0.54, 0.55, and 0.56 V, and the oxidative titration at 0.68 V are given in Table IV. The end point current for all titrations was 50 μA.

Table IV gives average results for four to eight measurements. Measurement precisions were typically 0.08% relative standard deviation for the initial iron oxidation and 0.15% relative standard deviation for the plutonium oxidation. For both oxidations, $\log_{10}$ current decreased linearly with time, in agreement with theory.

Mixtures of 1 mg iron and 5 mg plutonium were electrolyzed using the same conditions as described above. Electrolysis times and measurement precisions were the same as for the separate iron electrolysis at the three (0.54, 0.55, and 0.56 V) preliminary potentials and the plutonium electrolysis at 0.68 V. Also, the sum of coulombs for the two electrolyses did not change. There was a 0.3% increase in the coulombs at the preliminary iron oxidation, with a corresponding decrease at the plutonium oxidative titration. This was experimentally established to be a consequence of the longer electrolysis time required at the preliminary oxidation to reach the 50-μA end point current for iron and plutonium mixtures compared to plutonium alone. During this time, more plutonium oxidized. This effect will be a function of the iron-to-plutonium ratio or of any other oxidized diverse-ion-to-plutonium ratio.

Decreasing this effect will lead to better accuracy and precision for the plutonium measurement. Procedural changes being investigated are a higher potential for the preliminary oxidation and modifications in end point establishment. Following this investigation, effects of diverse ions characteristic of nuclear fuel cycle materials will be established.

A recurring problem of controlled potential coulometry using solid electrodes is instability of the working electrode, resulting in increased background currents and electrolysis times. The following treatment for the platinum gauze electrode restores its low background current and reproducible performance. Immerse the electrode in hot 16*M* HNO_3 for

1 h, rinse thoroughly with water, immerse in 12*M* HCl for ≥2 h, and cycle through the reduction and two oxidations described above using 5.5*M* HCl until the background current stabilizes. Usually, only two cycles are required. The electrode is stored in 5.5*M* HCl.

Design of the first automated instrument using electrometric titration is under way. In addition to establishing the basic electroanalytical system (see Fig. 1), mechanical components are being tested. These include reagent dispensers and cell-rinsing systems.

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

The major objectives of the Safeguards Analytical Laboratory Evaluation (SALE) program are (1) to upgrade the capabilities of US and foreign laboratories to analyze for assay and isotopic uranium and plutonium contents of nuclear fuel cycle materials, and (2) to provide uranium and plutonium Reference and Calibration Test Materials (RCTMs).

In 1973, vials containing a PuO_2 powder lot and a $(U,Pu)O_2$ powder lot were supplied to Allied Chemical Corporation, Idaho National Engineering Laboratory, for distribution as Secondary RCTMs (SRCTMs). When these two lots were characterized for their assay and isotopic values by LASL and checked by other ERDA contractor laboratories, guidelines had not been formulated for such characterizations. Since then, NRC guides have been prepared for the preparation and characterization of Working Calibration and Test Materials (WCTMs). It is proposed that the two lots be recharacterized by at least the guidelines for WCTMs by at least two laboratories. A plan is being formulated with NBL, the laboratory responsible for the SALE program, effective October 1, 1976.

A SALE program meeting, June 29-30, 1976, at NBL, was attended by more than 60 people from most of the US and foreign laboratories participating in the program. Major recommendations were to (1) expand the program to provide greater international coverage, and (2) maintain the voluntary aspects of the program, rather than use any generated information for regulatory application, to ensure the objective of technology upgrading. Five talks were presented by LASL attendees (see the Publications and Talks section).

A report[6] has been prepared that provides relationships for computing the decreasing plutonium content and changing isotopic distribution of plutonium materials for the radioactive decay of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{242}Pu to uranium daughters and of ^{241}Pu to ^{241}Am. This computation is important to the use of plutonium reference materials for calibrating destructive and nondestructive methods for assay and isotopic measurements, as well as to accountability inventory calculations. Corrections for the ^{241}Pu decay are usually made; however, the effects of the radioactive decay of the other plutonium isotopes can exceed that of ^{241}Pu decay, depending on the plutonium isotopic distribution of the material.

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

Analyses of SALE bimonthly samples of uranium nitrate and uranium oxide were continued to determine uranium content and isotopic distribution. There were no significant biases, and the measurement relative standard deviations were smaller than the averages for the reporting laboratories. A LASL-modified NBL-Davies Gray method[1] is used for the uranium determinations, and thermal ionization mass spectrometry is used for measuring isotopic distributions.

VI. 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, G. R. Waterbury)

As a part of an inter-ERDA laboratory program to measure accurately the half-lives of longer lived plutonium isotopes, 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 using the technique of isotope dilution mass spectrometry for measuring the produced daughter isotope. The LASL characterization measurements include assay, isotopic distribution, metal impurities including other transuranics, and nonmetal impurities.

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

A. Plutonium-239

Plutonium oxide of >99% ^{239}Pu was converted to high-purity metal at LASL for distribution to all participating laboratories. The chemical purity of this ^{239}Pu metal was established by measuring total plutonium assay using potentiometric titration, as well as by measuring 44 impurity elements at LASL and the Rockwell International Rocky Flats Plant using emission spectrography, thermal ionization mass spectrometry, spark source mass spectrometry, radiochemistry, spectrophotometry, inert gas fusion, and combustion chemical analysis techniques. Plutonium isotope distribution was measured by the same two laboratories using thermal ionization mass spectrometry. The individual portions of plutonium metal used in the program were weighed on the same balance used to weigh NBS SRM-949 plutonium metal.

The experimental program[1] formulated at LASL to attain at least 1% relative accuracy in measuring the half-life of ^{239}Pu-1 involves the following operations. The grown-in and impurity uranium was 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 are being measured at selected time periods by mass spectrometric determinations of the ^{235}U/^{233}U ratio. The ^{239}Pu half-life will be calculated from the fundamental decay equation

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

in which

$-(dn/dt)\ 239 =$ loss of ^{239}Pu atoms

per unit time, and

$+(dn/dt)\ 235 =$ growth of the ^{235}U

daughter per unit time (Ref. 1).

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

To attain the stated accuracy goals, the various operations must be accomplished within an accuracy of 0.01 rel% for weighing each of the six ^{239}Pu-1 samples, 0.05 for the ^{239}Pu content of the six solutions, 0.1 for the quantity of ^{233}U added, and 0.1 for the ^{235}U/^{233}U ratio measurements.[1] The ^{233}U spike solution concentration was established by isotope dilution mass spectrometry using four separate uranium standard solutions, two prepared from NBS SRM-960 (natural uranium metal) and two prepared from high-purity 93% ^{235}U metal. Mixtures of each calibration solution and the ^{233}U were analyzed in triplicate. The quantity of ^{233}U added to four of the dissolved ^{239}Pu-1 metal solutions was selected to equal the quantity of ^{235}U grown-in during 1.5 yr. The quantity of ^{233}U added to the remaining two solutions will provide equal amounts of ^{235}U and ^{233}U after 4.5 yr. Mass spectrometric measurement of isotope ratios is most accurate and precise at 1:1 ratios. Weighed portions of the calibrated ^{233}U solution were added to each of the six ^{239}Pu solutions to produce solutions having ^{233}U/^{239}Pu ratios known to ±0.022% relative standard deviation.

Four of the six ^{239}Pu-1 solutions were measured in quadruplicate at five different times over 20 months. Plutonium half-life values were calculated for each average quadruplicate measurement. The remaining two ^{239}Pu-1 solutions were designed to provide more accurate half-life measurements after 4.5 yr of ^{235}U daughter growth. The first scheduled measurement of these solutions, after 1.5 yr, has yielded ^{239}Pu half-life values in good agreement with the values obtained from the other four solutions.

The half-life data for the first four solutions currently are undergoing detailed statistical analysis. The preliminary ^{239}Pu half-life value is 24 150 yr with an overall relative standard deviation of about 0.15%. The stated goal of the mass spectrometric measurement technique has thus been achieved and is expected to be further improved when the 4.5-yr measurements are complete. This value is 1% lower than the currently accepted value of 24 400 yr. An error this large represents a significant bias in all nondestructive analytical techniques that use the ^{239}Pu half-life. A 1% bias in the ^{239}Pu content of the many tons of material assayed nondestructively represents a large amount of fissile material. More accurate half-life values will contribute significantly to the safeguarding of fissile material.

B. Plutonium-238

Plutonium metal of ~90% ^{238}Pu isotopic abundance has been prepared at LASL, weighed using specially developed, thermal-isolation weighing techniques, and sent to the Mound Laboratory for weight verification and calorimetric measurements. The ^{238}Pu metal was handled only in argon-atmosphere gloveboxes and sealed in an inner-welded tantalum capsule and two outer-welded stainless steel capsules for shipment. Nonetheless, the ^{238}Pu metal has apparently reacted with oxygen and perhaps nitrogen to cause the metal to be unusable. The metal will be repurified to remove the oxygen and nitrogen, and then will be resampled.

PUBLICATIONS AND TALKS

1. D. D. Jackson, D. J. Hodgkins, R. M. Hollen, and J. E. Rein, "Automated Spectrophotometer for Plutonium and Uranium Determination," Los Alamos Scientific Laboratory report LA-6091 (February 1976).

2. D. D. Jackson, S. F. Marsh, J. E. Rein, and G. R. Waterbury, "Recent Developments in the Dissolution and Automated Analysis of Plutonium and Uranium for Safeguards Measurements," International Atomic Energy Symposium, Safeguarding of Nuclear Materials, Vienna, Austria, October 20-24, 1975.

3. S. F. Marsh, W. D. Spall, R. M. Abernathey, and J. E. Rein, "Uranium Daughter Growth Must Not Be Neglected When Adjusting Plutonium Materials for Assay and Isotopic Contents," Los Alamos Scientific Laboratory report LA-6444 (November 1976).

4. Talks presented at SALE Program Meeting, New Brunswick Laboratory, June 29-30, 1976.
   a. J. E. Rein, "Preparation and Characterization of Plutonium Materials."
   b. G. R. Waterbury, "Uranium Methodology-LASL Experience with the NBL Titration."
   c. G. R. Waterbury, "Plutonium Methods Used at LASL."
   d. J. E. Rein, "Automated Spectrophotometer for Uranium and Plutonium."
   e. J. E. Rein, "Isotope Measurements at LASL."

REFERENCES

1. G. R. Waterbury, Comp., "Analytical Methods for Fissionable Materials in the Nuclear Fuel Cycle, June 1974 to June 1975," Los Alamos Scientific Laboratory report LA-6045-SR (October 1975).

2. D. D. Jackson, D. J. Hodgkins, R. M. Hollen, and J. E. Rein, "Automated Spectrophotometer for Plutonium and Uranium Determination," Los Alamos Scientific Laboratory report LA-6091 (February 1976).

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

4. T. Shigematsu, M. Tabushi, and M. Matsui, "The Solvent Extraction and Spectrophotometric Determination of Uranium Using Benzoyltrifluoroacetone as the Chelating Agent," Bull. Chem. Soc. Jpn. **37**, 133-136 (1964).

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

6. S. F. Marsh, W. D. Spall, R. M. Abernathey, and J. E. Rein, "Uranium Daughter Growth Must Not Be Neglected When Adjusting Plutonium Materials for Assay and Isotopic Contents," Los Alamos Scientific Laboratory report LA-6444 (November 1976).

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