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LASL Analytical Chemistry Program for Fissionable Materials Safeguards

by

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ABSTRACT

Major tasks in this program are (1) development of dissolution techniques for refractory nuclear materials, (2) development of methods and automated analyzers for determining plutonium, uranium, and thorium, (3) preparation of plutonium reference materials distributed as certified reference materials by the National Bureau of Standards, used in the Safeguards Analytical Laboratory Evaluation (SALE) program administered by the New Brunswick Laboratory, and used to calibrate nondestructive analysis apparatus at LASL, and (4) preparation and characterization of plutonium isotope materials and participation in an intralaboratory program to measure longer-lived plutonium isotope half lives. More recent and significant achievements are reported. Gas-solid reactions at elevated temperature, used previously to convert uranium in refractory forms to species readily soluble in acid, are being applied to thorium materials. A microgram-sensitive spectrophotometric method was developed for determining uranium and the LASL Automated Spectrophotometer has been modified to use it. The instrument now is functional for determining milligram amounts of plutonium, and milligram and microgram amounts of uranium. Construction of an automated controlled-potential-coulometric analyzer has just been completed. It is giving design performance of 0.1% relative standard deviation for the determination of plutonium using a method developed especially for the instrument. A method has been developed for the microcomplexometric titration of uranium in its stable (VI) oxidation state. A color probe analyzer assembled for this titration also has been used for microcomplexometric titration of thorium. The present status of reference materials prepared for NBS and for the SALE program, as well as examples of working reference materials prepared for use with nondestructive analyzers, is given. The interlaboratory measured value of the ^{239}Pu half-life is 24,119 yr. Our just completed measurement of the half life of ^{241}Pu is 14.38 yr. Measurement of the ^{240}Pu half life is in progress.

KEYWORDS: Assay of uranium, plutonium, and thorium, automated spectrophotometer, automated controlled-potential analyzer, complexometric titration of uranium and thorium, dissolution of nuclear fuel-cycle materials, plutonium reference materials, half lives plutonium isotopes.

INTRODUCTION

The primary purpose of characterizing nuclear fuel cycle materials for safeguards application is measurement of their uranium, plutonium, and thorium contents. All measurements must be accurate, with precision requirements ranging from < 0.1% standard deviation for product materials to several percent for scrap materials containing low quantities of these three elements. Many fuel-cycle materials, including scrap materials produced in calcination processes, contain highly refractory components and have multiphase, heterogeneous composition. At present, a particularly time-consuming operation in the chemical assay of such materials is their dissolution to effect solubilization of the uranium, plutonium, and thorium. In addition to fast, effective dissolution technique, automated analyzers for assaying the three elements will provide economy. The accuracy of assay measurements, whether by chemical analysis or by use of nondestructive (NDA) techniques, depends on calibration, best attained by use of proper reference materials. Accurate plutonium isotope half-life values are essential to NDA methods based on radioactive calorimetry and decay measurement, as well as for adjusting reference materials and accountable material inventories for their changing plutonium content with time.

DISSOLUTION OF NUCLEAR FUEL CYCLE MATERIALS

Techniques currently being investigated to attain rapid and effective solubilization of uranium, plutonium and thorium in refractory materials are mineral acid reactions at elevated temperatures in pressurized containers and reactions with reactive gases at elevated temperatures.

We previously developed a dissolution apparatus of a Teflon container in pressure-supporting stainless steel and nickel shells which permit reactions with various mineral acids at temperatures up to 260°C and pressures to 320 atm (5000 psi). The apparatus design was made available to industry and was adopted by the Parr Instrument Company. A stainless steel shell is used with HNO_3, H_2SO_4, and HNO_3-H_2SO_4 mixtures. A nickel container is used for HCl, HF, and their mixtures. The dissolution apparatus has been applied successfully to a variety of materials including Nb-C alloy, UO_2ZrO_2 in Zr matrix, U-Zr-Hf carbide, 1600°C-sintered $(U\text{-}Pu)O_2$, and a variety of scrap-type materials supplied by the New Brunswick Laboratory (NBL).

We verified NBL findings that the Parr Teflon containers frequently failed when used at 270°C with HNO_3-low molarity HF mixtures for the dissolution of materials such as high-fired PuO_2 and calcined mixed oxide. The Parr Company supplied Teflon containers made from new Teflon stock and we fabricated new containers. Both failed even when heated at only 250°C with a HNO_3-low molarity HF mixture and without samples.

The du Pont Company, in response to our request, recommended two Teflon grades, molded 7A and Type 1 Premium per ASTM D-3294. Containers fabricated from both grades withstand repeated use with the HNO_3-HF mixture at 260°C. The Parr Instrument Company has changed its production to use only the molded 7A grade.

Gas-solid reactions at elevated temperatures are being investigated for converting refractory materials to soluble compounds or for forming volatile uranium and thorium compounds that condense as compounds readily soluble in mineral acids. Materials in a quartz boat are reacted in a quartz tube heated by a resistance furnace. The tube is designed to provide a controllable atmosphere and effective recovery of the volatilized compounds.

Reactions with chlorine gas and carbonyl chloride, especially the latter, are effective for volatilizing uranium. For example, 0.1 g of U_3O_8 (as well as UO_2, UO_3, and UC_2) volatilizes completely when reacted with chlorine at 1000°C for 12 h or 1200°C for 5 h. With carbonyl chloride, using the same reaction conditions for chlorine, 0.1 g U_3O_8 volatilizes completely in < 0.5 h at 1000°C and in < 1 h at 700°C. The system has been applied successfully to a variety of uranium-containing materials produced in a LASL waste-recovery calcination facility and supplied for testing by NBL. The method is effective for materials containing zirconium and niobium which, like uranium, volatilize as chlorides.

The technique now is being evaluated for thorium materials. As predicted by the relative boiling points of UCl_4 and $ThCl_4$, thorium is proving more difficult to volatilize. For example, $< 1\%$ of ThO_2, previously calcined at 1200°C in air, volatilizes during a 1-h reaction with chlorine, contrasted to about 40% for U_3O_8. Under the same conditions using carbonyl chloride instead of chlorine, uranium was completely volatilized, but volatilization of thorium increased only to 30%. The formation of volatile UCl_4 and $ThBr_4$ by reaction of the oxides with chlorine and bromine in the presence of carbon[1] prompted an evaluation of various forms of carbon. Charcoal is proving the most effective. With

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[1] G. T. Seaborg and J. J. Katz, The Actinide Elements (McGraw-Hill, New York, 1954), pp. 84, 153.

mixtures of the 1200°C calcined ThO_2 and various charcoals, at a C/ThO_2 mole ratio > 3, the thorium volatilization is $> 99\%$ in 1 h at 1000°C. The condensed thorium compound dissolves readily in mineral acids.

ANALYTICAL METHODS AND AUTOMATED INSTRUMENTS FOR URANIUM, PLUTONIUM, AND THORIUM DETERMINATIONS

Automated Spectrophotometer

The LASL Automated Spectrophotometer is designed primarily for determining uranium and plutonium in scrap materials. The method used in the original instrument[2] provides high tolerance for the many impurity elements present in scrap materials. Measurement precision is about 1% standard deviation for a range of about 1 to 14 mg of either element determined in sample portions up to 0.5 ml.

Because many scrap materials have very low uranium and plutonium contents, measurements of microgram quantities of the two elements often are required. A method, designed for use in the automated spectrophotometer, was developed.[3] It features measurement of 2.5- to 100-μg amounts of uranium and high tolerance for impurity elements present in scrap materials. The method consists of extracting the U(VI)-benzoyltrifluoroacetone complex into butyl propionate from a solution that contains Mg(II)-cyclohexanediaminetetraacetic acid masking agent to provide high selectivity and hexamethylenetetramine and triethanolamine to provide high buffering capacity.

The automated spectrophotometer, shown in Fig. 1, was modified to use this microgram-level uranium method as well as the original methods for determining low milligram levels both of plutonium and uranium. Modifications include (1) a separate reagent dispensing system for the microgram-level method, (2) a mechanism to switch the pneumatic-hydraulic system automatically between the two sets of dispensers, (3) removal of the cam-actuated switches that had controlled mechanical operations and expansion of the microcomputer system to provide complete control of all mechanical and electrical operations, (4) installation of a pair of interference filters for absorbance measurements for the microgram-level method, and (5) replacement of the 3½-digit, analog-to-digital converter with a 4½-digit converter to cover a larger dynamic range.

Output response for the microgram-level method is linear over the range of 2.5 to 100 μg of uranium. The precision ranges from 0.5% standard deviation at 90 μg to 3% at 5 μg of uranium. Under instrument operation conditions, tolerances of 48 metal ions and 17 nonmetal anions have been established.[4]

Automated Controlled-Potential Coulometer

We previously have described[5] a controlled-potential-coulometric method for plutonium developed for use in an automated analyzer. Construction of the analyzer has been completed recently. The method features high tolerance for impurities, a precision of 0.1%

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[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] S. F. Marsh, "Extraction-Spectrophotometric Determination of Microgram Quantities of Uranium with Benzoyltrifluoroacetone," Anal. Chim. Acta 105, 439-443 (1979).

[4] G. R. Waterbury, Compiler, "Analytical Methods for Fissionable Materials in the Nuclear Fuel Cycle, October 1, 1978-September 30, 1979," Los Alamos Scientific Laboratory report, in press.

[5] D. D. Jackson, R. M. Hollen, F. R. Roensch, and J. E. Rein, "Highly Selective Coulometric Method and Equipment for the Automated Determination of Plutonium," in Analytical Chemistry in Nuclear Fuel Reprocessing, W. S. Lyon, Ed., Proc. 21st Conf. Anal. Chem. Energy Technol., Gatlinburg, Tennessee, October 4-6, 1977 (Science Press, Princeton, 1978), p. 51.

standard deviation for the determination of 5 mg plutonium, and operational simplicity. Plutonium is reduced at 0.2 V (vs SCE) to Pu(III) in 5.5M HCl - 0.015M sulfamic acid electrolyte. Diverse ions are oxidized at 0.57 V at which Pu(III) is not significantly oxidized. Phosphate (as NaH_2PO_4) is added to lower the Pu(III)-Pu(IV) potential and Pu(III) is titrimetrically oxidized to Pu(IV) at 0.68 V. Results of a detailed investigation of diverse ion tolerances for more than 75 metal ions and nonmetal anions have been reported.[5] Metallic elements normally present in nuclear fuel cycle materials do not interfere at equal-mole ratio relative to plutonium. Most interfering nonmetal anions are separated by fuming with perchloric acid prior to analysis.

An overall view of the instrument components is shown in Fig. 2 and its installation in a containment box is shown in Fig. 3. The mechanical portion is installed in the sloping, open-front box that is 0.91 m wide, 0.79 m deep, and 0.84 m high and the electronic components are mounted outside the box.

The major electronic components of the instrument, shown in Fig. 4, are commercial which simplifies maintenance. A Hewlett-Packard 9825 Programmable calculator controls all mechanical and electrical operations, processes titration data, and outputs results on paper tape. A Princeton Applied Research Corporation 173 Potentiostat-Galvanostat and 179D Digital Coulometer, modified for calculator control, do the electrolysis. Also interfaced and under calculator control are a D to A converter, a digital multimeter, a scanner, a real time clock and a digital plotter. The D to A converter provides calculator capability to select electrode potentials. The digital multimeter measures electrolysis conditions of interest and serves as an A to D converter to input data to the calculator. The digital multimeter also monitors interlocks designed to protect the instrument in case of a malfunction. The scanner switches the digital multimeter to the point to be measured. The mechanical operations are controlled through the scanner by contact closure of relays. The real-time clock monitors electrolysis times and by means of an interrupt system terminates analyses in which the times exceed those found to affect the determination adversely. The plot of log current vs. time provided by the on-line digital plotter allows a trained analyst to spot deviations indicative of a faulty analysis.

The mechanical assembly is designed for long-term, trouble-free operation. A turntable holding up to 24 electrolysis cells rotates them into position under a fixed Teflon support. Smooth and accurate rotation is provided by a Geneva-drive, intermittent motior assembly. Positional accuracy is further insured by a cylindrical rod, driven by a pneumatic cylinder, that engages slots in the edge of the turntable at each of the 24 positions.

The electrolysis cells are simply fabricated from 4.8-cm-diam glass tubing by flame sealing a flat bottom and grinding the top flat. The electrodes, stirring mechanism, reagent-delivery tubes, inert-gas inlet, and rinsing system are mounted in a rigid Teflon support. The cells are raised by a hydraulic-cylinder-driven assembly to form a gas-tight seal against the Teflon support and to position the various components reproducibly. The reagent dispensers for the HCl-sulfamic acid electrolyte and the phosphate complexant are similar to those used in the automated spectrophotometer.[2] Only glass, Teflon, and Kel-F contact the highly corrosive reagents.

The analyzed sample and rinse solution are withdrawn by suction through a Teflon tube. The aspiration tube is driven by a pneumatic-cylinder mechanism to an exact position at the bottom of the cell near the platinum-gauze electrode for efficient removal of the liquid. Two consecutive rinses, each with ~25 ml of 5.5M HCl, leave less than 0.01% of the previous sample.

Complexometric Titration of Uranium and Thorium

Methods are being developed for the determination of microgram and milligram levels of uranium and thorium applicable to materials produced in various stages of fuel production and ultimately for irradiated fuel analysis. A versatile, automated apparatus, shown in Fig. 5, has been assembled for this purpose. In the instrument, titrant is delivered by a micrometer buret driven by a stepping motor to provide precise increments. A probe colorimeter immersed in the solution monitors the continuously changing color. Light is transmitted to the probe tip through a flexible fiber-optic light guide. The light passes through the solution and is reflected by a mirror at the end of the probe tip back through another portion of the fiber-optic light guide to the photodiode detector. A programmable calculator controls the titrant addition, senses the approximate inflection point, processes the data, and calculates the quantity of titrant at the endpoint as the intercept of least squares fitted lines before and after the inflection point. A digital voltmeter serves as an analog-to-digital converter to transfer the measured absorbance values into the calculator. A stripchart recorder also monitors the absorbance output from the colorimeter and provides a plot of absorbance vs delivered titrant volume.

Thorium is determined by titrating the thorium-xylenol orange complex with diethylenetriaminepentaacetic acid. Over the range of 20 to 140 μg thorium, the precision is 1 μg standard deviation. Because this method is not selective, a chemical separation procedure is being developed.

A selective, complexometric titration method has been developed for determining uranium. The U(VI)-arsenazo I complex is titrated with dipicolinic acid (pyridine-2,6-dicarboxylic acid) at a pH of 4.9 attained with hexamethylenetetramine buffering. Selectivity is gained by use of cyclohexanediaminetetraacetic acid and diethylenetriaminepentaacetic acid as masking agents. Measurement precision for 30 to 180 μg of uranium is about 0.6% standard deviation. Tolerances of diverse impurities are being established.

PREPARATION OF REFERENCE MATERIALS

Reference materials, mainly containing plutonium with lesser numbers containing uranium, are prepared for distribution as NBS standard reference materials, for use in the NBL-administered Safeguards Analytical Laboratory Evaluation (SALE) program, and as working calibration materials for various nondestructive analyzers in operation at the new LASL plutonium processing facility and elsewhere. Table I summarizes the status of LASL-prepared materials prepared for NBS. The status of materials prepared for the SALE program is given in Table II. Examples of working calibration materials for nondestructive analyzers are given in Table III.

Table I. Plutonium Reference Materials Prepared by
LASL as NBS Certified Reference Materials

Composition	Designation	Certified for	Status
Pu metal	SRM 945	purity 99.9%, impurity blend matrix	present lot in ample supply
Pu metal	SRM 949	assay g Pu/g	eighth lot to be prepared in 1980
Pu-244	not assigned	atoms Pu-244 per container	prepared. characterization in progress

Table II. Reference Materials Prepared by LASL for NBL SALE Program

Composition	Certified for	Status
Pu nitrate solution	g Pu/container, isotopic	one series used in the past. Not planned for future use.
PuO_2	g Pu/g	second series of 3 lots scheduled for 1980.
$(U\text{-}Pu)O_2$ powder	g Pu/g, g U/g Pu and U isotopic	previous series of 3 lots prepared. Not planned for future use.
$(U\text{-}Pu)O_2$ pellets	as above	second series of 3 lots prepared. Characterization in progress.

Table III. Typical Reference Materials Prepared by LASL Analytical Chemistry Group for Calibration of NDA Instruments

Material	Characterization	Various Configurations
PuO_2	Pu assay, particle size, impurities	solutions
		solids
$PuCl_3$	Pu assay, isotopic	
$Pu(NO_3)_4$	Pu assay, isotopic	solids on specific substrates
$UO_2(NO_3)_2$	U assay	geometric containers
$(U\text{-}Pu)Cl_4$	U, Pu assay	

PLUTONIUM ISOTOPE HALF-LIFE MEASUREMENTS

Accurate half-life values of longer-lived plutonium isotopes are essential to nondestructive methods of analysis that measure a nuclear property associated with a disintegration rate, including calorimetry and various radioactive particle measurements, and to adjust the plutonium content and isotopic distribution values of reference materials and accountable material inventories. In an interlaboratory effort sponsored by the DOE Office of Safeguards and Security, LASL prepares and characterizes pure, enriched-isotope plutonium materials for distribution to participating laboratories, and participates in the half-life measurements.

As shown in Table IV, the intralaboratory effort has produced a precise measurement of the half-life of ^{239}Pu.[6] Our recently completed measurement of the ^{241}Pu half-life, based on mass spectrometric determinations of the decreasing ^{241}Pu/^{242}Pu ratio over a 3.6-yr time period, is 14.38 yr with a 95% confidence limit of 0.06 yr. At present, an interlaboratory effort is in progress for the measurement of the ^{240}Pu half-life

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[6] L. L. Lucas and W. B. Mann, Editor, Int. J. Appl. Radiat. Isotopes, 29 (No. 8), 479-524 (1978).

Table IV. Plutonium Isotope Half-Life Measurements Status

Isotope	Measurement Technique	Laboratory*	Status
238	not done	-	recommended average of 87.74 yr measured by ANL and ML
239	α-particle calorimetry mass spectrometry of U-235 daughter	ANL, LLL, NBS LLL, ML ANL, LASL, LLL	complete: 24, 119 ± 26 y
240	α-particle calorimetry mass spectrometry of U-236 daughter	LASL, NBS LLL, ML LASL	$^{240}PuO_2$ prepared. Characterization and half-life measurements in process
241	mass spectrometry of changing 241/242 ratio	LASL	complete: 14.38 ± 0.06 y

*ANL- Argonne National Laboratory
LLL- Lawrence Livermore Laboratory
NBS- National Bureau of Standards
ML- Mound Laboratory
LASL - Los Alamos Scientific Laboratory

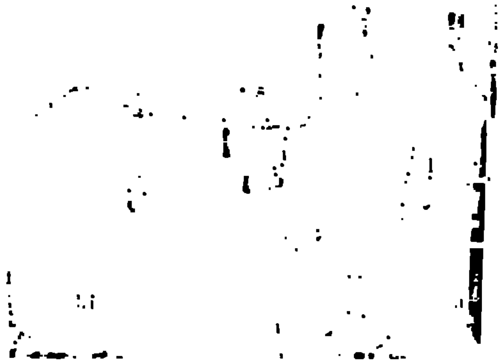

Fig. 1. Automated Spectrophotometer

Fig. 2. Automated Controlled-Potential-Coulometric Analyzer

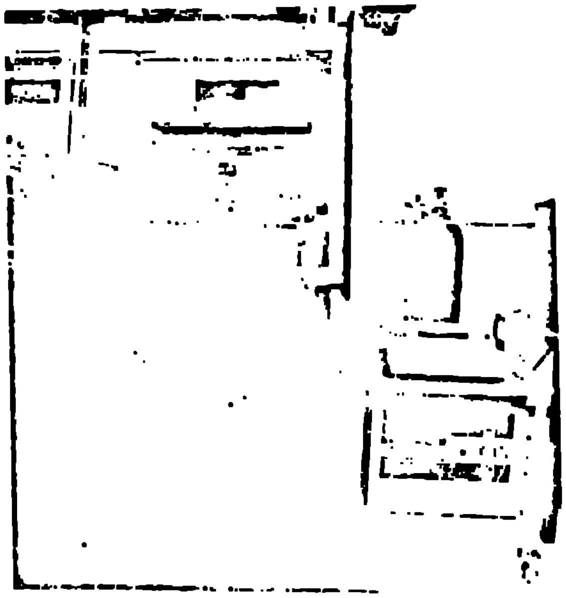

Fig. 3. Automated Controlled-Potential-Coulometric Analyzer in Box

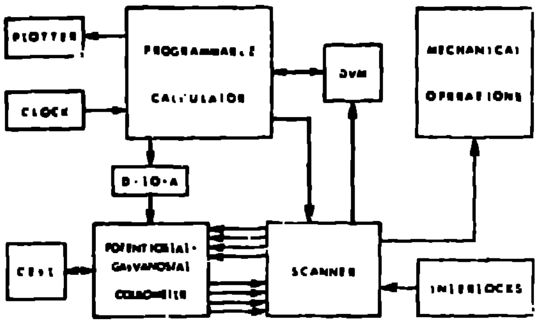

Fig. 4. Control System for Controlled-Potential-Coulometric Analyzer

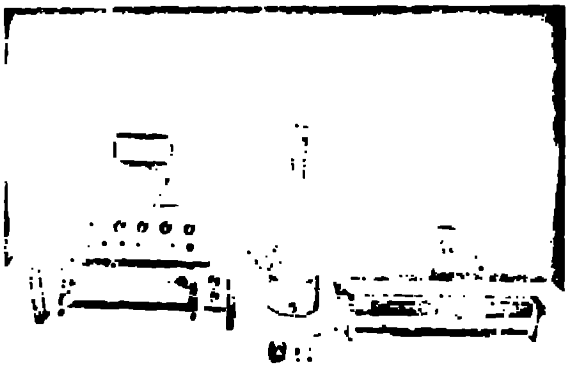

Fig. 5. Complexometric Titration Apparatus