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Issued: October 1974

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Analytical Methods for Fissionable Materials in the Nuclear Fuel Cycle

Program Status Report June 1973 to June 1974

LOS ALAMOS NATIONAL LABORATORY
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UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

This work performed under the auspices of the U.S. Atomic Energy Commission's Division of Safeguards and Security, Program A241.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy $4.00 Microfiche $1.45

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ANALYTICAL METHODS FOR FISSIONABLE MATERIALS IN THE NUCLEAR FUEL CYCLE

Compiled by

Glenn R. Waterbury

ABSTRACT

Progress was made on the development of methods for the dissolution of difficult-to-dissolve materials, the determination of plutonium and uranium for nuclear safeguards applications, the preparation of well-characterized plutonium materials for SALE Program samples and for NBS reference materials, the analysis of IAEA and special inventory-surveillance materials, and the analysis of HTGR fuel materials. Improvements were made in a Teflon-container metal-shell apparatus used for acidic dissolution of samples at elevated temperature, and its application to a variety of difficult-to-dissolve samples was evaluated. Gamma-assay measurements for ^{235}U and ^{239}Pu were investigated for uranium-plutonium mixtures. A procedure was developed to obtain homogeneous precipitates of uranium and plutonium oxalates to serve as calibration materials for gamma assay. An advanced automated spectrophotometer, designed for the determination of plutonium and uranium, was constructed and sent to the AEC's New Brunswick Laboratory for application studies. The preparation of plutonium-containing materials for the SALE Program included plutonium nitrate solutions with > 99% Pu^{4+}. A high-temperature oxidation-chlorination system, followed by an anion exchange separation and titrations, was developed for the determination of uranium and thorium in HTGR fuel. SALE uranium materials were analyzed on a monthly basis. A batch of highly pure plutonium metal was prepared, characterized, and packaged for use as a future NBS CRM. An inter-AEC-laboratory program was initiated to measure the half-lives of long-lived plutonium isotopes with high accuracy.

I. INTRODUCTION

The major objectives of the program are: (1) the development of faster dissolution techniques than now are available for uranium- and plutonium-containing samples, with emphasis on scrap-type and difficult-to-dissolve materials, (2) the development of fast analytical methods for uranium and plutonium and the development of automated apparatus for use with these methods, (3) the preparation of well-characterized, plutonium-containing materials for use in the Safeguard Analytical Laboratory Evaluation (SALE) Program, (4) the preparation of well-characterized, highly pure plutonium metal chemical standards for distribution by NBS, and (5) the chemical characterization of HTGR fuels and of special samples for safeguards inventory-surveillance purposes. Recently we have begun to participate in a joint project with other AEC laboratories to measure the half-lives of the longer-lived isotopes of plutonium.

A primary concern in the chemical characterization of nuclear fuel cycle materials is the measurement of uranium and plutonium. The nuclear fuel cycle materials include nonuniform

scrap and mixtures of highly refractory compounds. The philosophy behind the analysis of these materials has been total dissolution, followed by highly precise chemical analyses. Time-saving methods are an economic necessity because of the ever-increasing numbers and types of materials, many of which are heterogeneous.

The assay schemes under development are based on relatively fast dissolutions of 90% or more of the uranium and plutonium, followed by chemical analyses of the dissolved fractions and gamma-counting assay analyses of the residue fractions. The overall relative standard deviation of these assays is no greater than 1.5% when the relative standard deviations of the chemical method and gamma-counting measurements are 1% and 10%, respectively.

II. DISSOLUTION OF FUEL CYCLE MATERIALS

A. Teflon-Container Metal-Shell Apparatus

(G. C. Swanson, G. S. Dow, S. F. Marsh, H. J. Kavanaugh, J. E. Rein)

Investigation continued into the use of a dissolution apparatus[1] consisting of a Teflon container in a metal shell. The apparatus permits use of acid mixtures at temperatures to 280°C and pressures to 34 MPa (5000 psi). It has similarities in operation to the sealed, fused-silica tube developed at NBS[2] with additional advantages of capability of using HF as a solvent, ease of handling, reusable containers, and containment of the sample in a container suitable for subsequent chemical treatments.

The metal shells are machined from 347 stainless steel or from nickel 200 alloy to permit use of various mixed-acid solvents.[1] The Teflon container has a modified long taper[1,3] with a slightly rounded and thickened edge to ensure that the seal is maintained for as many as 20 reuses.

A rupture-disc system incorporated in the metal-shell design provides safe venting in case of overpressures. A 9.5-mm-diam hole is made in the base of the shell and is covered by a 0.25-mm-thick rupture disc. When a vent-equipped metal shell was pressurized by heating weighed amounts of dry ice, the system vented between 37 and 41 MPa (5500 and 6000 psi). When the vent system was proof-tested by heating HNO_3 and silicone oil in the shell, there was rapid venting without distortion of the shell or hazard to personnel or equipment. An additional 0.05-mm disc placed between the Teflon container and the 0.25-mm disc prevents corrosion and possible weakening of the latter by acid fumes diffused through the Teflon.

Once the final design of the apparatus was satisfactory,[4] bids for construction were requested from commercial vendors. The Paar Instrument Co. was commissioned to make several units for LASL's use. The LASL design was modified slightly by Paar to attain decreased machining time and lower cost. Modifications include removal of the flange at the base of the shell and several minor alterations in the shapes of the internal shell components. The changes will not affect the pressure limitations of the metal shells.

Substitution of 316 stainless steel for 347 stainless steel in the screw cap of the shells was evaluated at the request of the Paar Instrument Co. An annular ring of 316 stainless steel, exposed to the same acid fumes that contact the screw cap during use, suffered only light corrosion. To test the effect of stress corrosion, a rupture disc of 316 stainless steel was fabricated and used in a shell with a charge of HNO_3-HF. A similarly charged shell with a 347 rupture disc was operated for comparison. A metallurgical comparison of stress-corrosion effects on the two discs was unnecessary because the 316 disc ruptured, whereas the 347 disc distorted only slightly. Therefore, 347 stainless steel will be used for the screw caps.

The degree of contamination of samples dissolved in reused Teflon containers was investigated. A UC fuel was dissolved overnight in a new Teflon container with HNO_3-HF at 275°C. After the dissolved sample was transferred and the container rinsed, HNO_3 alone was heated in the container, again overnight at 275°C. A known quantity of ^{233}U then was added to the resulting HNO_3 solution and the residual uranium that diffused from the Teflon was determined by isotope-dilution mass spectrometry. The diffused amount was 0.5 μg, equivalent to only 0.03% of the uranium in the initial sample.

B. Applications of Teflon-Container Metal-Shell Apparatus

(G. S. Swanson, S. F. Marsh, H. J. Kavanaugh, J. E. Rein)

The apparatus was evaluated for use in the dissolution of a variety of difficult-to-dissolve materials. A particularly resistant material is the HTGR fuel which consists of microspheres having UC-ThC kernels and pyrolytic carbon and SiC coats. Samples weighing 0.1 g were completely decomposed by a 2M HF-15M HNO_3 mixture overnight at 270°C in the apparatus.[5] Increase in sample size to 0.5 g resulted in venting and consequent loss of sample. A two-stage treatment, in which the outer pyrocarbon coat was removed by combustion before reaction in the shell, also resulted in venting when a 0.5-g sample was dissolved. We are now trying to establish conditions under which a sample large enough to be representative of the overall composition can be dissolved without causing venting of the dissolution apparatus.

Another difficult-to-dissolve material is an experimental U-Zr-Hf carbide fuel. Under reflux at ambient pressure, complete dissolution was not attained with HNO_3, HNO_3-HF, HNO_3-HCl, HNO_3-$HClO_4$, HNO_3-$HClO_4$-H_2SO_4, or HNO_3-H_2O_2. Complete dissolution did occur when the fuel was left in HNO_3-HF overnight at 275°C in the Teflon-container metal-shell apparatus.

The AEC's New Brunswick Laboratory (NBL) supplied uranium-containing calcined-ash samples (ash resulting from HNO_3-HF treatment at ambient pressures) which were subjected to further acid treatment in the dissolution apparatus. When 2-g samples were left overnight at 275°C in HNO_3, 72 to 90% of the uranium was solubilized, giving a soluble fraction suitable for an automated spectrophotometric determination. Solubilization of uranium was slightly greater with HCl, but the solubilization of other metals increased to a level that caused a salting interference during the spectrophotometric determination (see Sec. IV. B).

Study was begun on the applicability of the metal-shell apparatus to dissolution of plutonium-containing refractory materials. High-fired (~ 900°C) PuO_2 and sintered (1600°C) U-Pu mixed oxide dissolved completely overnight at 270°C in HNO_3-HF or HCl-$HClO_4$. NBL-supplied scrap materials, designated as brick fines, dissolver sludge, and laboratory waste, were subjected to various acids at 265°C. Dissolver sludge dissolved completely in HNO_3-HF and more than 90% in HCl-HF. Brick fines resisted both HNO_3 and HCl, as well as HCl with small amounts of HF. Acid mixtures containing large amounts of HF were more effective, but PuF_4 precipitated.

C. High-Energy Gas-Solid Reactions

(S. F. Marsh, D. D. Jackson, R. M. Hollen, J. E. Rein)

High-energy studies have begun on gas-solid reactions, with the objective of converting refractory uranium and plutonium materials to readily soluble compounds. The first studies have involved a plasma generator in which the introduced gas is excited to free radicals and other species by an rf discharge. A commercial apparatus, Plasmod (Tegal Corp.), is being used. Inert Freon-13 (trifluorochloromethane) has been tried with an NBL-supplied sample of uranium-containing calcined ash. The reaction was slight, as reflected by a negligible weight change of the sample, but the Freon-13 decomposed, as shown by fluoride attack on the Pyrex sample chamber. The reaction did not increase the solubility of the calcined ash in HNO_3. Future studies will include use of lasers or other high-energy devices.

III. GAMMA ASSAY OF URANIUM AND PLUTONIUM

(S. F. Marsh, M. R. Ortiz, J. E. Rein)

Techniques stressing operational simplicity and low-cost equipment have been developed for gamma assays of ^{235}U in uranium-containing material, and of ^{239}Pu in plutonium-containing material and in uranium-plutonium containing material. These techniques, intended for assay of residues from acidic reactions in the Teflon-container metal-shell dissolution apparatus, involve collection of the sample on a 25-mm-diam membrane filter, mounting of the filter on a suitable support, and counting over selected gamma-energy ranges using a NaI(Tl) detector. The measurement precision obtained with known solutions has been about 5%--better than the goal of 10% relative standard deviation.

Residues from the 28 NBL-supplied, calcined-ash samples remaining after reaction in the metal-shell apparatus (Sec. II. B) were gamma-assayed for ^{235}U. The relative standard deviation, computed from duplicates of two separately dissolved portions of each sample, was 11%. This poor precision is attributed to bulky residues and to heterogeneous distributions of uranium-containing materials with differing ^{235}U enrichments and differing solubilities in HNO_3.

A more difficult gamma-assay measurement is that for ^{235}U in mixed uranium-plutonium residues. The much lower specific activity of ^{235}U relative to ^{239}Pu and the poor resolution of NaI(Tl) detectors combine to make previously developed counting systems unsuitable. Therefore, higher-resolution detectors and more complex electronic equipment are being evaluated to find the simplest possible equipment with which to attain a precision no greater than 10% relative standard deviation.

Such an evaluation requires a series of counting references containing homogeneously distributed mixtures of ^{235}U and ^{239}Pu mounted similarly to residue samples. Preparation of these references has been difficult because of the many variable levels of uranium and plutonium isotopic abundances and the various uranium-to-plutonium ratios required. The selected preparation scheme is to mix known amounts of uranyl nitrate and plutonium nitrate standardized solutions, reduce the uranium to U^{4+} and the plutonium to Pu^{3+}, coprecipitate the oxalate salts, and filter. Sodium formaldehyde sulfoxylate ($NaHSO_2 \cdot CH_2O \cdot 2H_2O$) has been chosen as the reductant because it rapidly and completely reduces the uranium and plutonium even in 2M HNO_3. The U^{4+} and Pu^{3+} then are quantitatively coprecipitated as dense oxalates by room temperature hydrolysis of diethyl oxalate. Alpha radiography has verified homogeneity, and analysis of several supernatant liquids has verified complete precipitation.

The entire series of references was counted on a Ge(Li) gamma detector coupled to a multichannel analyzer. Resolution with this detector was insufficient in many cases to allow the 185-keV energy photopeak of ^{235}U to be distinguished from the plutonium Compton region. The references will be recounted with a recently received high-resolution Ge(Li) detector.

IV. AUTOMATED APPARATUS FOR DETERMINATION OF URANIUM AND PLUTONIUM

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

A. The Advanced Automated Spectrophotometer

The advanced model of the automated spectrophotometer[6,7] for use in the determination of uranium and plutonium was completed and delivered to NBL. A series of uranium reference solutions, prepared using NBS SRM 950 and a highly pure, depleted uranium metal from LASL, was processed. The amounts of uranium ranged from 0.004 to 0.05 mmol (approx 1 to 12 mg). The instrument was operated in the fully automated mode and produced a paper-tape output of sample-tube position, designation of filter pair selected (identifying whether uranium or plutonium was measured), and a four-digit number proportional to the quantity of uranium or plutonium in the sample. The response was essentially linear, but a more accurate calibration was that obtained by a least squares fit for a quadratic equation. The computed equation was

$$U = (2.097 \times 10^{-3}) + (1.494 \times 10^{-5})R + (2.698 \times 10^{-10})R^2 ,$$

in which

U = millimoles of uranium

R = four-digit output proportional to peak-minus-valley absorbance.

The relative standard deviation for a single measurement, determined by measuring six aliquots at each uranium level, was 0.25% at the 11- and 7-mg levels, and 2.0% at the 1-mg level. These precisions are better than those obtained with the prototype because of the improved readout system of the advanced model. The day-to-day variation for a series of uranium standards processed over a 4-wk period was not significantly different from the within-day variation.

The advanced model of the automated spectrophotometer (Fig. 1) has a 0.58-m-diam turntable which holds 24 sample tubes and rotates them into position for each operation. The maximum size of the instrument was established by the requirement that it fit into a glovebox that is 0.91 m wide, 0.79 m deep, and 0.84 m high. The analysis time was 5 min per sample, or about 2 h for a full

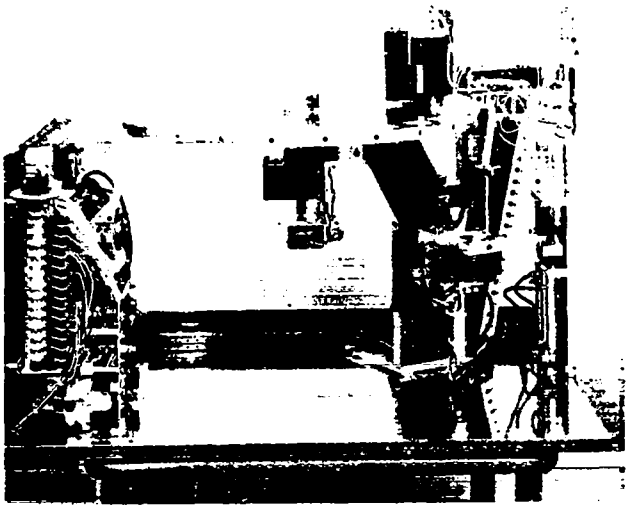

Fig. 1. Advanced automated spectrophotometer.

load of 24 samples. Analyzed samples could be removed and new samples added, and in this manner the instrument operated continuously.

The turntable is rotated by a Geneva-drive, intermittent-motion assembly which avoids rapid acceleration and provides reproducible rotational positioning. To further ensure accurate positioning of the tubes, a tapered pin driven by a pneumatic cylinder engages a hole drilled into the outer circumference of the turntable after each rotational increment. The sample holes in the turntable are numbered and this number is coded in binary as a series of small holes in the bottom of the turntable. Five roller-actuated miniature switches mounted under the turntable sense the holes and provide the information for the sample identification readout.

The reagent delivery system (Fig. 2) is similar to the one developed for the prototype.[1] The reagents are delivered by piston-displacement dispensers driven by a pneumatic-hydraulic cylinder system in which only glass, Teflon, and Kel-F contact the reagents, thus avoiding any corrosive effects on the system by the reagents. The relative standard deviation, determined by weighing dispensed quantities, was 0.014% for ten 4-ml deliveries of the $Al(NO_3)_3$ salting solution and 0.015% for ten 3-ml deliveries of the organic extractant, 2-nitropropane.

Extraction of the uranium and plutonium complexes by the organic extractant is accomplished

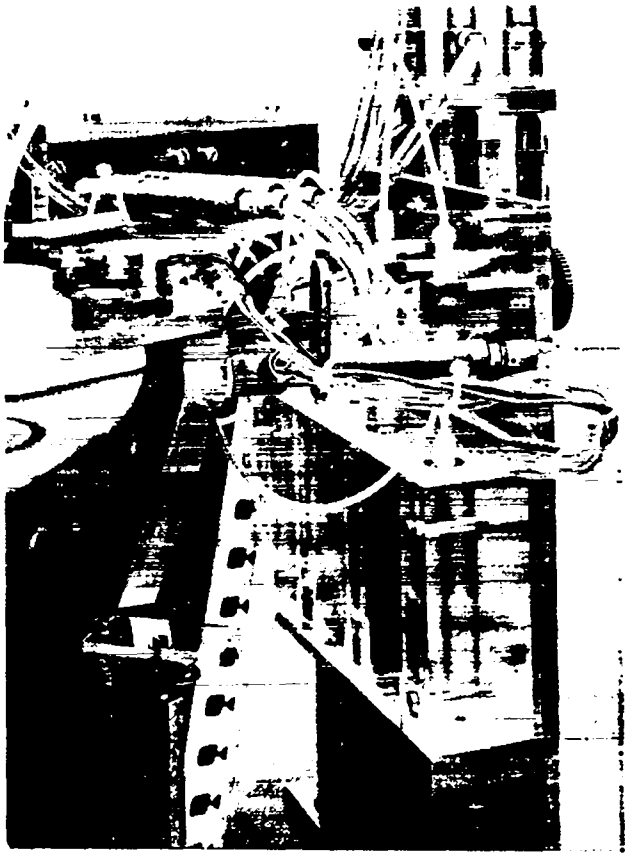

Fig. 2. Reagent dispensing system.

by mixing the solution with a Teflon-covered, cylindrical stirring bar driven by a revolving magnet (Fig. 3). To ensure dependable coupling, the driving magnet is positioned 12 mm above the bottom of the tube during the extraction and is lowered when not in use to allow the tube to pass over the magnet.

A simple, rugged spectrophotometer (Fig. 4), using narrow-bandpass interference filters as the monochromator, measures the absorbances at the very sharp peaks and at valley positions adjacent to each peak. The peak-minus-valley absorbance is the measure of the uranium or plutonium.

The monochromator (Fig. 5) contains three pairs (with transmittances at the peak and valley wavelengths) of interference filters, one for the measurement of uranium and two for the measurement of plutonium at different wavelengths. The desired peak-valley pair is manually selected by the analyst at a front panel switch. The wavelength of the absorbance peak was accurately measured

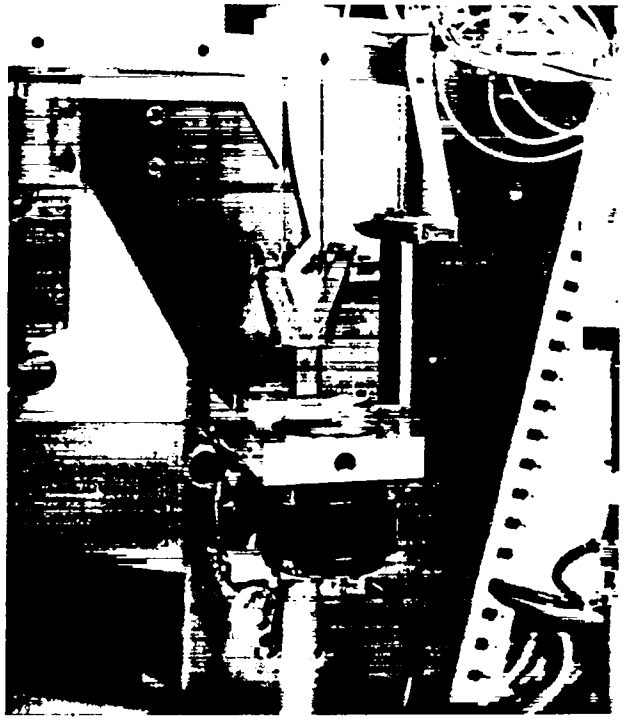

Fig. 3. Mixing-extraction system.

with a grating spectrograph as 452.5 nm for the extracted uranium complex of tetrapropylammonium U(VI) trinitrate and 501.4 nm and 807.0 nm for the corresponding plutonium complex. The molar absorbance for the most sensitive plutonium peak at 501.4 nm is about twice that for the uranium peak. The molar absorbance for plutonium at 807.0 nm is about one-third that at 501.4 nm, but the peak at 807.0 nm provides freedom from a few interferences encountered at the 501.4-nm peak.

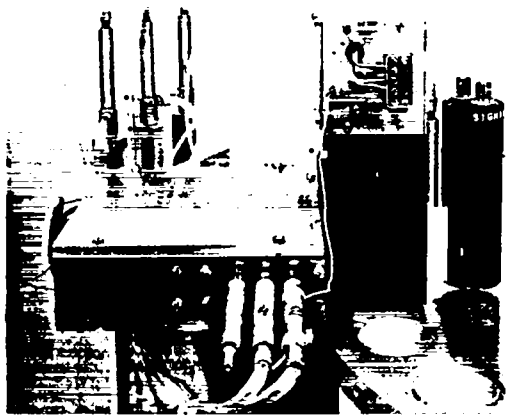

Fig. 4. Filter spectrophotometer readout system.

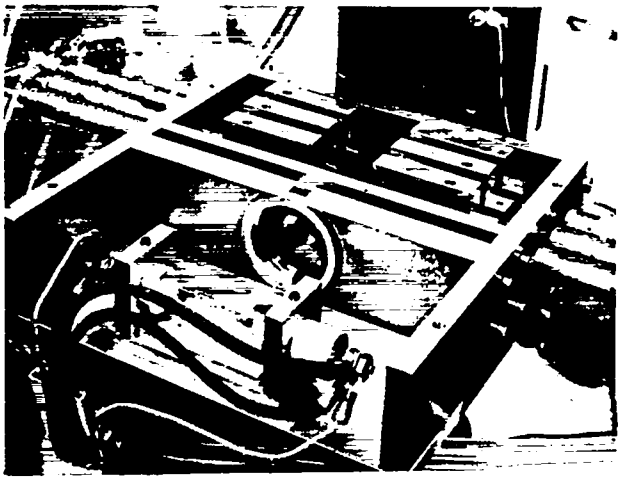

Fig. 5. Monochromator, showing light source, collimating lens, and three pairs of interference filters.

The bandpass width of all interference filters is less than 1.4 nm and the peak transmittances are precisely matched to the absorbance peaks. Peak and valley filters are moved sequentially into the light path by a pneumatic cylinder system. The light from a 45-W quartz iodine lamp is collimated with a single lens and a slit before reaching the filters. The detector is a 929 photodiode tube.

The electronic readout system of the advanced model (Fig. 6) uses a microcomputer and programmable-read-only-memory (PROM) chips to control

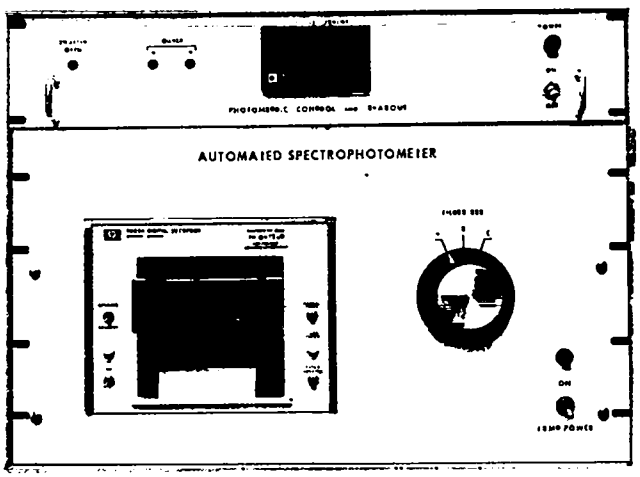

Fig. 6. Control panel for readout system.

the measurement sequence. Input data to the microcomputer include the photodiode detector current (after analog-to-digital conversion) and the turntable position of the sample tube. The microcomputer (1) controls external valves that operate the shutter and the peak-valley interference filter pair, (2) initiates the current measurements, (3) performs data manipulation, and (4) supplies signals to the digital recorder to print out on paper tape a four-digit value of the peak-minus-valley absorbance, the sample tube position, and an identification of the interference filter pair used.

The use of plug-in PROMs with readily changeable software programs coupled with the microcomputer gives a system of high flexibility. The sequence and timing of operations are accurately controlled and can be easily varied by program changes. To achieve highly reliable measurements, PROMs that allowed manual control of all operations by toggle switches were used to establish the best combination of variables. The variables evaluated were (1) the time delays between (a) shutter and dark current measurement, (b) positioning of peak filter and absorbance measurement, and (c) positioning of valley filter and absorbance measurement; and (2) the interrelated variables of the time duration of individual absorbance measurements and the number of these measurements that are integrated.

B. Development of High Sensitivity Spectrophotometric Measurements for Uranium and Plutonium

Experience with analyses of various scrap-type samples provided by NBL showed the desirability of developing a more sensitive measurement for uranium and plutonium. At present, the automated spectrophotometer has a lower limit for uranium detection of about 2 mg/ml, but many solutions resulting from acid dissolution in the Teflon-container, metal-shell apparatus have uranium levels considerably lower than 2 mg/ml. Samples are presently analyzed by evaporating a larger aliquot to dryness in the spectrophotometer sample tube and then adding 0.5 ml of 8M HNO_3. Because a usual characteristic of scrap-type samples is a high extraneous element content, voluminous salts are deposited that can inhibit the extraction of uranium. Experience with the 28 NBL-supplied, calcined-ash samples (Sec. II. B) showed that although salts did not dissolve completely in the 0.5 ml of 8M HNO_3, the uranium apparently did. A precision of 1.06% relative standard deviation for an individual determination was obtained from the results on duplicate aliquots of each soluble fraction.

One way to increase sensitivity with minimum instrumentation change is to incorporate a suitable chromogenic agent in the organic extractant. Of the agents investigated to date, dibenzoylmethane (DBM) shows the most promise. It is soluble in the organic extractant, increases the sensitivity 600 times, and is less pH-dependent than other agents. The absorbing uranium-DBM species is not formed at low pH. Because acid is extracted in the system used for the automated spectrophotometer, a pH adjustment is necessary. The addition of an organic base that is preferentially soluble in the organic phase is being tried for pH adjustment, but a successful combination of organic extractant has not been found. A major difficulty has been an insufficient wavelength separation of the absorbance peak of the uranium-DBM complex from the unreacted DBM. The measurement error, therefore, is unacceptably large for a single-beam measurement as used in the automated spectrophotometer. The investigation of additional combinations of organic bases, organic extractants, and chromogenic agents is continuing.

C. Testing of the Automated Spectrophotometer for Plutonium Determination

Determination of plutonium by the extraction-spectrophotometric method used in the automated instrument requires oxidation to the Pu^{6+} oxidation state, accomplished by reaction with a AgO pellet. Nonfragile AgO pellets of the dimensions for automatic dispensing could not be prepared even with high-pressure presses, and the use of binders was not satisfactory. Manual addition of a AgO pellet made in a small laboratory press was adopted because it required little additional effort or time. Experiments showed that the amount of AgO necessary to attain complete oxidation to Pu^{6+} depended on the oxidizing strength

of the AgO batch in use and the amount of oxidizable species in the sample. For the particular AgO batch in use, 40 mg completely oxidized up to 8 mg of plutonium in the absence of any extraneous elements. In the analysis of samples that might contain extraneous oxidizable elements, additional pellets were added until the solution remained dark brown for several seconds after the AgO dissolved. Before adding AgO, chloride was removed by two fumings after addition of 0.5-ml volumes of 16M HNO_3. The residue then was dissolved in 0.5 ml of 2M HNO_3.

The oxidative reaction produced gas and consequent solution spattering. To prevent transport of sample droplets to upper portions of the tube, it was placed in a nearly horizontal position during the oxidation. The droplets that spattered onto the opposite tube wall were at a low level and became immersed upon addition of the salting solution, the first automated operation.

The prototype spectrophotometer,[1] installed in a glovebox, was used to process a series of weighed aliquots of a plutonium nitrate solution prepared with highly pure plutonium metal. The plutonium range for the prototype is 0.6 to 8 mg, with the upper limit set by limitations of the amplifier-log converter in the readout system. The readout system of the advanced model has a greater dynamic range and is expected to have an upper limit of 14 mg of plutonium. The response was linear with a least squares fit giving the relationship:

$$Pu = (-1.095) + (2.027 \times 10^{-6})N \quad ,$$

in which

Pu = milligrams of plutonium

N = counter output proportional to the peak-minus-valley absorbance.

The relative standard deviation for a single measurement based upon six determinations at each level was 0.25% at the 7-mg plutonium level, 0.62% at the 3-mg level, and 2.0% at the 1-mg level. As with data for uranium, the day-to-day variation was not significantly different from the within-day variation.

Because of a difference in the transmittance of the pairs of interference filters used for uranium and plutonium (the transmittance for plutonium being larger), the incident light level had to be adjusted for the two elements. To avoid this adjustment, a mechanism was added that automatically sets the desired light level for the selected filter pair. A pneumatic cylinder moves a baffle into the light path to attenuate the incident light when the plutonium filter set is selected.

D. Effects of Acidity and Tolerance for Thorium in the Automated Spectrophotometric Determination of Uranium

To establish the effect of acidity on uranium measurement, 0.5-ml samples containing a constant amount of uranium but variable HNO_3 (from 1 to 7.8 mmol) were analyzed. Absorbances remained constant to acidities as high as 5.5 mmol HNO_3, then decreased continuously as the acidity was increased to 7.8 mmol HNO_3. The bias was 1% at 5.8 mmol, 2% at 6.2 mmol, 8% at 6.8 mmol, and a gel formed upon addition of the salting solution at 7.8 mmol HNO_3.

The increasing number of mixed thorium-uranium samples in the scrap from many laboratories prompted an investigation of the effect of thorium upon the determination of uranium. Thorium forms a nonabsorbing tetrapropylammonium nitrate complex, thereby competing with uranium and producing low uranium measurements. The effect is best expressed in terms of the number of millimoles of thorium plus uranium. For example, at the lower detectable uranium limit of 0.004 mmol, low bias occurs for a total of 0.05 mmol of thorium and uranium. At the upper uranium limit of 0.05 mmol, the effect becomes significant with a total of 0.07 mmol of thorium and uranium. The tolerance of the method to thorium can be increased by using a greater quantity of tetrapropylammonium nitrate, but there is a risk of extracting extraneous ions.[8]

V. PREPARATION OF PLUTONIUM-CONTAINING MATERIALS FOR THE SALE PROGRAM

(G. C. Swanson, S. F. Marsh, M. R. Ortiz, L. A. Maestas, H. J. Kavanaugh, J. E. Rein)

The SALE Program has as objectives: (1) the generation of timely data on the capabilities of AEC licensee and contractor laboratories to analyze typical uranium and plutonium materials and (2) the

preparation of well-characterized typical uranium and plutonium materials for use as working calibration test materials (WCTM) by analytical laboratories.

A. Plutonium Nitrate Solution

A series of six plutonium nitrate solutions, each having a unique plutonium concentration and isotopic composition, was prepared for use in the SALE monthly evaluation program. Mixtures of weighed quantities of two highly pure plutonium metals with different isotopic distributions were dissolved in HBr-trace HF. The resulting solutions were added by drops to hot 12M HNO_3 to oxidize bromide to elemental bromine, which volatilized, and to oxidize Pu^{3+} to Pu^{4+}. The solutions were filtered through a membrane filter to verify completeness of dissolution. The maximum amount of undissolved plutonium was 0.01%. The final weights and volumes of each solution were measured, providing makeup values on the bases of weight (grams of plutonium per gram of solution) and volume (grams of plutonium per milliliter of solution). For all six solutions, the measured isotopic abundance data agreed with the computed makeup data. The measured total plutonium concentrations agreed for four solutions and were very slightly low for two solutions. The plutonium metals used for these two solutions had been chemically cleaned, whereas mechanical cleaning had been used in the case of the other four solutions. The chemical cleaning probably left surface contaminants which became part of the metal weights, thereby causing the slightly low biases. For these two solutions, the overcheck analysis data for the total plutonium concentration were the recommended rather than the makeup values.

One concern with sealed ampoules of plutonium nitrate solution, as used for the SALE Program, is pressure buildup from generated gases. Sources of gas are helium (alpha decay) production and radiolytic decomposition reactions. Helium production is relatively minor and does not contribute significantly to pressure buildup. For solutions containing Pu^{6+}, the radiolytic gas generation is increased by the reductive reaction of hydrogen peroxide to form Pu^{4+} plus hydrogen and oxygen. For this reason, special treatments are taken and overcheck analyses are made to ensure that the quantity of Pu^{6+} in the plutonium nitrate solutions is insignificant before the solutions are transferred to the ampoules.

Many procedures for preparing plutonium nitrate solutions from plutonium metal, including the procedure described here, produce a substantial amount of Pu^{6+}. Because Pu^{6+} undergoes radiolytic reduction in solution to form Pu^{4+} and gaseous byproducts, such solutions usually are treated to ensure that essentially all plutonium is converted to Pu^{4+} before being sealed in gas-tight containers. Since Pu^{6+} reduces spontaneously in 8M HNO_3, a study was made to determine how aging affects the oxidation states of plutonium ions in solution.

A 1-g sample of NBS SRM 949 plutonium metal was dissolved in HCl, evaporated to dryness, evaporated to dryness three times with 16M HNO_3, and the residue dissolved in 8M HNO_3 and boiled for 30 min. Past experiments have shown that boiling HNO_3 oxidizes much of the plutonium to Pu^{6+}.

The solution was analyzed for plutonium valence distribution over a 14-day period using a nitrate anion exchange column separation coupled with counting. This procedure does not distinguish between Pu^{3+} and Pu^{5+}. However, because Pu^{3+} is unlikely to occur after the evaporations with HNO_3, any plutonium not measured as Pu^{4+} or Pu^{6+} is considered to be Pu^{5+}. Table I summarizes the measured valence distributions as a function of aging time.

After 2 wk, the reduction of Pu^{5+} and Pu^{6+} in this low MWD (~ 6% ^{240}Pu) plutonium nitrate solution to Pu^{4+} was essentially complete. The radiolytic reduction process would presumably proceed at a faster rate for plutonium nitrate containing higher specific activity plutonium characteristic of the materials encountered in the nuclear industry. The general conclusion is that an aging period of 2 wk or more in 8M HNO_3 is adequate to produce only Pu^{4+}, and that special treatments to effect this conversion are not necessary.

Sealed ampoules of the first series of plutonium nitrate solutions prepared in April 1972 had been retained for a later measurement of gas pressure buildup. Several ampoules were opened with no difficulty after 1.5 yr of storage, and the gas

TABLE I
EFFECT OF AGING ON PLUTONIUM VALENCE DISTRIBUTION OF PLUTONIUM NITRATE[a] AFTER BOILING IN 8M HNO_3

Days of Aging	Pu Valence Distribution (%)		
	+4	+5	+6
0	71.0	12.3	16.7
3	86.1	3.5	10.4
5	94.4	1.0	4.6
7	97.8	1.4	0.8
10	99.0	0.0	1.0
14	99.8	0.0	0.2

[a]Plutonium concentration = 250 mg/ml.

pressure and composition of one ampoule were determined. The measured pressure was 0.53 atm above ambient, which agrees closely with a calculated value of 0.57 atm generated solely by radiolytic decomposition of water. The gas composition was 2 parts hydrogen, 1 part oxygen, and traces of helium and NO_2. The 2/1 hydrogen/oxygen ratio verifies radiolytic water decomposition alone since the ratio for hydrogen peroxide reduction of Pu^{6+} is 1/1. The glass ampoules used for the first and second series of solutions were specially fabricated with heavy walls and will withstand at least 10-atm pressure. The only precaution required, should an ampoule be retained for a long period of time, is to freeze the plutonium nitrate solution by immersing the ampoule in a dry-ice solvent or liquid nitrogen bath before opening it.

B. Plutonium Oxide

A batch of PuO_2 powder was extensively characterized for plutonium assay, plutonium isotopic distribution, and impurity element contents. A total of 500 vials, each containing 5 g of the powder, was packaged for use as WCTMs.

Two batches of PuO_2 powders, with very different plutonium isotopic distributions and intended for use as SALE monthly-QC samples, were being characterized at the end of the reporting period.

C. Uranium-Plutonium Mixed Oxide

A batch of sintered powder was extensively characterized for uranium and plutonium contents, uranium and plutonium isotopic distributions, and impurity element content. A total of 59 vials, each containing 5 g of powder, was packaged for use as WCTMs.

VI. ANALYSIS OF HTGR FUEL

(A. D. Hues, A. L. Henicksman, W. H. Ashley)

A method was reported last year[1] for the analysis of HTGR fuel. High-temperature oxidation and chlorination reactions are used to destroy pyrolytic carbon and SiC coatings, uranium-thorium oxide is dissolved in HNO_3-HF, the uranium and plutonium are separated by anion exchange, and titrimetric determinations are made for each. The development of the method was completed and details were reported.[9]

VII. ANALYSIS OF SALE URANIUM MATERIALS

(A. L. Henicksman, A. D. Hues, W. H. Ashley, R. M. Abernathey, J. E. Rein)

The uranium nitrate and uranium oxide SALE monthly samples have been analyzed since 1972 for uranium content and isotopic distribution. The biases are not significant for any of the measurements, and the precisions are smaller than the average for all participating laboratories.

Uranium content has been measured by a long-standing LASL method that uses a sample aliquot containing 1 to 2 g of uranium. Major operations are: fuming with H_2SO_4 to remove nitrate, reduction of uranium to U^{3+} with zinc amalgam, air oxidation to U^{4+}, addition of a slight excess of solid $K_2Cr_2O_7$, and back titration with Fe^{2+} to a potentiometric end point. The NBL version[10] of the Davies and Gray method[11] also is being used. Apparent advantages of the NBL method include determination of smaller (25- to 300-mg) amounts of uranium and greater tolerance for extraneous elements.

VIII. CERTIFIED REFERENCE MATERIAL PLUTONIUM METAL

(C. H. Ward, G. Meadows, J. Roybal, R. G. Bryan)

A batch of highly pure plutonium metal with low ^{241}Pu abundance was carefully characterized for plutonium content and isotopic distribution. The percentage of plutonium was established by determining the low level metal and nonmetal impurities (including oxygen) and subtracting the sum from 100. The value was verified by a highly precise determination of plutonium. Weighed 0.5-g samples were sealed in glass ampoules, using a special glovebox in which the atmosphere is argon containing not more than 1 ppm of oxygen or water vapor. Each sample was inspected for plutonium surface oxidation. A detailed report describing the material and giving overcheck analysis data has been prepared to accompany the shipment of the material to the National Bureau of Standards.

IX. CHEMICAL CHARACTERIZATION OF SPECIAL SAMPLES

(G. R. Waterbury and Staff)

With the ban on plutonium handling at NBL, LASL has provided an increased service operation for the analysis of inventory surveillance samples. Most of the samples analyzed were scrap, consisting of heterogeneous phases (aqueous, organic, and suspended solids) with low plutonium content. For most samples, plutonium concentration and isotopic distribution were determined. A variety of techniques was used for the plutonium assay, including controlled potential coulometry, alpha counting, and isotope dilution mass spectrometry.

A special series of IAEA exchange samples (designated PAFEX-I) of plutonium nitrate, PuO_2, and uranium-plutonium mixed oxide were analyzed for uranium and plutonium content and isotopic distribution. The values reported by IAEA were essentially at the median of the values reported by all participating laboratories.

X. PLUTONIUM ISOTOPE HALF-LIFE MEASUREMENTS

(W. J. Maraman, G. R. Waterbury, and Staff)

In a joint program with other AEC laboratories to make accurate measurements of the half-lives of the longer-lived plutonium isotopes, LASL's major efforts are: preparation of high-purity batches of plutonium metal from enriched isotope materials; extensive chemical and isotopic characterization, with participation of another laboratory in this characterization; and distribution of samples to other AEC laboratories for the half-life measurements. The technique to be used at LASL for half-life measurements is isotope dilution mass spectrometry for measurement of the produced daughter isotope.

The isotopes to be covered in the program are ^{239}Pu, ^{238}Pu, ^{240}Pu, and perhaps ^{241}Pu. An initial batch of ^{239}Pu metal (99.3% ^{239}Pu isotopic abundance) was prepared and characterized. This metal was sent to Mound Laboratory for a calorimetric measurement of half-life and will be returned for distribution to other participating laboratories.

XI. PUBLICATIONS AND TALKS

1. D. D. Jackson, D. J. Hodgkins, and J. E. Rein, "Automated Spectrophotometer for the Determination of Plutonium and Uranium," 17th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, TN, October 23-25, 1973.

2. G. C. Swanson, G. S. Dow, J. E. Rein, and G. R. Waterbury, "Teflon Container Apparatus for Pressurized Acid Dissolutions at High Temperature," ibid.

3. D. D. Jackson, J. E. Rein, and G. R. Waterbury, "Chemical Assay of Plutonium for Safeguards," American Nuclear Society Meeting, San Francisco, CA, November 11-15, 1973.

4. G. C. Swanson, G. R. Waterbury, and J. E. Rein, SALE Program Participants Meeting, Idaho Falls, Idaho, October 10-11, 1973. Talks presented describing LASL-prepared SALE materials, assay methods for plutonium, and methods for isotopic abundance measurement of uranium and plutonium.

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

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7. D. D. Jackson, J. E. Rein, and G. R. Waterbury, "Chemical Assay of Plutonium for Safeguards," American Nuclear Society Meeting, San Francisco, CA, November 11-15, 1973. To be published in the July 1974 issue of Nuclear Applications & Technology.

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10. A. R. Eberle, M. W. Lerner, C. G. Goldbeck, and C. J. Rodden, "Titrimetric Determination of Uranium in Product, Fuel, and Scrap Materials after Ferrous Ion Reduction in Phosphoric Acid," New Brunswick Laboratory report NBL-252 (July 1970).

11. W. Davies and W. Gray, "A Rapid and Specific Titrimetric Method for the Precise Determination of Uranium Using Iron (II) Sulfate as Reductant," Talanta 11, 1203 (1964).

HK:410(60)