Analytical Methods for

Fissionable Materials in the Nuclear Fuel Cycle

Program Status Report June 1972 to June 1973

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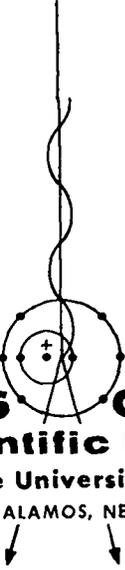
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Compiled by

Glenn R. Waterbury

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ABSTRACT

Progress was made on the development of methods for the dissolution of materials and the determination of plutonium and uranium for nuclear safeguards application, the preparation of well-characterized plutonium-containing materials as SALE samples and as NBS standards, and the analysis of special inventory-surveillance materials. The Teflon-container, metal-bomb apparatus for the acid dissolution of samples at temperatures to 280°C and pressures to 5000 psi was used in dissolution of the HTGR-fuel, made of microspheres of U-Th carbide with coatings of pyrolytic carbon and silicon carbide. A pressure venting mechanism is being added to this apparatus. Conditions have been established for a gamma assay of ^{235}U in uranium-thorium mixtures. An automated spectrophotometer has been built and applied to the analysis both of plutonium and uranium. An advanced model of this instrument is nearing completion. Well-characterized uranium-plutonium mixed oxide pellets and powders and plutonium dioxide powders were prepared for the SALE Program. A second series of plutonium nitrate solution materials is nearing completion. Five hundred highly pure plutonium metal standards were prepared for NBS. Several special samples were analyzed for inventory-surveillance purposes.

I. INTRODUCTION

The major objectives of this program are: (1) the development of fast dissolution techniques and analytical methods for the determination of Pu and U with emphasis on scrap-type and difficult-to-dissolve materials, (2) the design and construction of automated apparatus for the determination of Pu and U, (3) the preparation of well-characterized Pu-containing materials for use in the SALE Program, and (4) the preparation of well-characterized, highly pure Pu metal chemical standards for distribution by NBS.

A primary concern in the chemical characterization of nuclear fuel cycle materials is the measurement of U and Pu. The materials include non-uniform scrap and mixtures of highly refractory compounds. The past general philosophy guiding the analysis of these materials has been total dissolution followed by highly precise chemical analyses. The use of methods that are less time-consuming is an economic necessity with ever-increasing numbers and types of materials, many of which are heterogeneous.

An assay scheme being developed uses a relatively fast dissolution of 90% or more of the Pu and U followed by a chemical analysis of the dissolved fraction and a gamma counting assay analysis of the residue fraction for these elements. The overall relative standard deviation of these measurements is no greater than 1.5% when the relative standard deviations of the chemical method and gamma counting measurement are 1% and 10%, respectively.

II. Dissolution of Fuel Cycle Materials
(G. C. Swanson, J. E. Rein)

Development of a dissolution apparatus consisting of a Teflon container in a metal bomb was continued. This apparatus (Fig. 1) permits use of acid mixtures at temperatures to 280°C and pressures to 5000 psi. It has similarities in operation to the sealed, fused-silica tube developed at NBS[1]
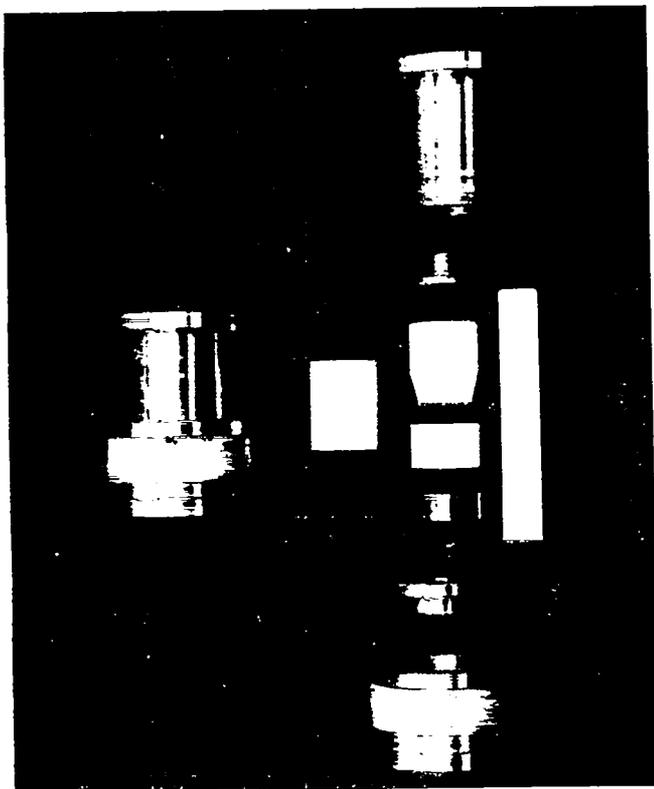
Fig. 1. High Temperature Acid Dissolution Bomb.

with added advantages of capability to use HF as a solvent, (2) ease of handling, (3) reusable containers, and (4) quantitative containment of the sample in a container suitable for subsequent chemical treatments if desired.

The metal bombs are machined from 347 stainless steel and from nickel 200 alloy to provide corrosion resistance to acid vapors that diffuse through the Teflon containers. Corrosion is slight for the 347 stainless steel bomb when used with oxidizing acids such as concentrated HNO_3, H_2SO_4, HNO_3-H_2SO_4 mixtures, and HNO_3-H_2SO_4-HF mixtures. The nickel bomb is used for concentrated HF, concentrated HCl, and HF-HCl mixtures with or without small amounts of oxidizing acids.

The Teflon container has a long taper[2] for tight sealing. Spring tension applied to the container top maintains the seal as the Teflon contracts upon cooling. Containers fabricated from TFE Teflon (trademark, E. I. du Pont de Nemours, Inc.) have been reused up to twenty times although they slowly and irreversibly shrink from an initial volume of 30 cc to a final volume of approximately 10 cc.

The design operational pressure of the stainless steel bombs is 5000 psi, with an ultimate

yield at 30,000 psi; the nickel bombs are rated at 4000 psi and 24000 psi respectively. At $280^{\circ}C$, acid systems alone generally generate less than 3000 psi, however, gaseous products produced by acid-sample reactions may generate pressures higher than 5000 psi. A pressure-readout bomb previously fabricated to allow determination of pressures generated by various sample - acid systems recorded a pressure pulse > 10,000 psi in one experiment. Examination showed that the Teflon liner had severely decomposed (Fig. 2), a result of an exothermic reaction between HNO_3 and the bomb silicon oil transducing medium which triggered the thermal decomposition of the Teflon container. Teflon chips have not reacted with either concentrated HNO_3 or concentrated $HClO_4$ at $450^{\circ}C$ in sealed quartz tubes.

Because of the possibility that a pressure pulse generated by an exothermic reaction between an oxidizable component in a sample and HNO_3 (or $HClO_4$), studies using oxidizing acids have been discontinued, and design was undertaken on a system to protect bombs from high pressure pulses. Stainless steel bombs distort at pressures greater than 10,000 psi and probably would fracture at pressures greater than 30,000 psi.

Protective devices that have been tested include: (1) A spring-loaded vent designed to release at 7500 psi and (2) a pressure release rupture disc. In testing the spring loaded vent, exothermic reactions between HNO_3 and silicone oil produced a reaction so vigorous in two test bombs
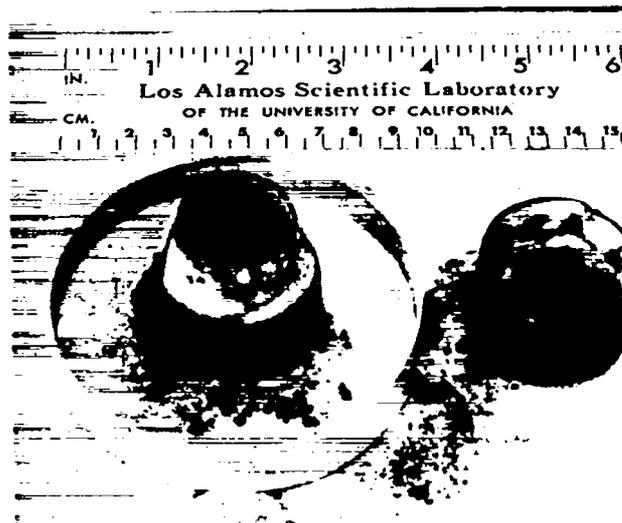

Fig. 2. Partially Decomposed Teflon Container.

that they were distorted before venting occurred (Fig. 3). Proof testing of a 0.010-in. stainless steel rupture disc, which vented at 5000 psi CO_2 pressure, showed that the vigorous reaction between HNO_3 and silicone oil caused a slight distortion of the bomb before the disc ruptured. Further changes in the design are in process to produce more rapid venting action.

Dissolution studies of various U-containing materials using nonoxidizing acids with nickel bombs are continuing. A typical advantage provided by the high temperature bomb operation was demonstrated by complete dissolution of a fuel consisting of uranium-zirconium oxides in a metallic zirconium matrix using HCl at 275°C. Refluxing of the same material in HCl at atmospheric pressure gave no reaction.

A fuel that has been the subject of countless hours of dissolution studies in many laboratories is the HTGR type, consisting of microspheres or beads of U-Th carbide coated with successive layers of pyrolytic carbon, silicon carbide, and pyrolytic carbon. The only successful treatment reported in the literature to date[3] for these fuels involves a series of combustions at 850°C in oxygen and reaction at 1100°C in chlorine. A study

Fig. 3. Stainless Steel Bomb Shell Distorted by Reaction between HNO_3 and Silicone oil.

has been undertaken to apply the bomb to the dissolution of this fuel. Samples of the uncombusted fuel were subjected to attack at 275°C with various acids, including HF, HCl, HNO_3, H_2SO_4, and mixtures of these acids. Complete decomposition of 100 mg of fuel was achieved in a 36-h reaction with 22$\underline{M}$ HF-3$\underline{M}$ HNO_3-0.3$\underline{M}$ $HClO_4$. The product is a clear uranium solution and a precipitate of ThF_4. This product can be fumed directly in the Teflon container with $HClO_4$ to solubilize the Th. Further studies are in progress to optimize the system for larger sample quantities.

A study of the applicability of the bomb is continuing for a series of U-containing calcined ash materials supplied by NBL. Samples of 2 to 4 grams are subjected to the bomb treatment using various acids. The resulting products are passed through a membrane filter, the filtered residue is gamma counted for a ^{235}U assay (see Section III), and the filtrate is analyzed for uranium with the automated spectrophotometric prototype (see Section IV). Sequential treatments of the ash materials with HF, HCl, and HNO_3 in the bombs dissolved about half of the solids in the ash samples. Several hours after filtration, copious precipitates high in Nb content formed in the filtrates and interfered with the spectrophotometric determination. As the usual complexants to hold Nb in solution also complex U and Pu, these additives were not used. Near-complete precipitation of the Nb before filtration appears necessary.

A recent report[4] on the dissolution of high-fired $^{238}PuO_2$ in HNO_3-HF at 150°C in the Teflon-lined Paar bomb shows the utility of the Teflon-metal bomb for Pu materials. The report unfortunately does not stress the importance of not exceeding the design limitations of such systems. The Paar bomb is designed for use at temperatures to 150°C and pressures to ~ 2000 psi. Two years ago a Paar-type bomb which we were applying to dissolution of nonradioactive material failed when carried to temperatures and pressures beyond its design limits. The effect of the failure was minimized by precautions which had been taken in anticipation of such an event. The use of these types of dissolution devices with Pu-containing materials dictates strict adherence to the respective bomb design limits for both pressure and temperature.

The LASL-developed bomb will be applied to the dissolution of various Pu-containing materials when the pressure release system being developed for the stainless steel bombs has been successfully proof tested.

III. Gamma Assay of Uranium and Plutonium
(S. F. Marsh, M. R. Ortiz, J. E. Rein)

The major objective of this phase of the project is to develop gamma assay techniques for the determination of U and Pu, mainly in the residues obtained from the Teflon-container, metal bomb dissolution treatment. Emphasis is being placed on developing a series of counting conditions that provide 10% or better reliabilities tailored to the sample composition and stressing simplicity of operation and low-cost equipment. In this measurement a residue is collected on a 25-mm-diam membrane filter using a filter chimney apparatus, the filter with air-dried residue is mounted on an aluminum plate and covered with cellophane tape, and the gamma counts are recorded for ^{235}U or ^{239}Pu. These nuclides were selected for measurement because they are the major fissionable isotopes in most nuclear fuel cycle materials, and hence, most important from the safeguards standpoint. The conversion to total U and Pu requires isotopic abundance data that usually are routinely measured by mass spectrometry for all samples analyzed in safeguards laboratories.

The major effort this year was the development of advanced techniques for the gamma assay of ^{235}U. The gamma assay of ^{239}Pu was reported last year and was an easier task, mainly attributable to the use of higher energy gamma photons.

For the assay of ^{235}U, two energy regions are counted, either sequentially with one single channel analyzer (SCA) or simultaneously with two SCA's. The higher energy gamma region, from 170 to 196 keV, encompasses the 185-keV photopeak of ^{235}U. The lower energy gamma region, from 130 to 155 keV, serves as the basis for correcting non-^{235}U gamma contributions to the higher energy region. The calculational relationship is:

$$mg\ ^{235}U = (K)\,[(HS - HB) - F(LS - LB)]$$

in which: K = experimentally determined factor to convert corrected count rates to weight of ^{235}U

HS = count rate of sample in higher energy region

HB = background count in higher energy region

LS = count rate of sample in lower energy region

LB = background count in lower energy region

F = ratio of (HS-HB)/(LS-LB) experimentally measured for fully depleted ^{238}U.

A 0.5-in. thick (1.5-in. diam) sodium iodide crystal used for this investigation provides better precision than thicker detectors because (1) it is less efficient for the undesirable high energy gamma rays, and (2) background readings are lower due to the smaller detector volume and lower ^{40}K content. A series of 28 standards, containing various amounts of U up to several hundred milligrams at enrichment levels of 0.72, 1.77, 3.28, 4.49, 7.86, 10.7, 32.2, and 93.1% ^{235}U was prepared and measured with this technique. The precision for a single measurement was 4.4 rel %, well within the goal of 10 rel %.

The two gamma energy regions were selected to minimize the interference of thorium and its daughters in thorium-containing samples. Measurement of a series of ThO_2 residues, free of uranium, showed that the indicated ^{235}U represented no more than 0.25% of the ThO_2. The counting system may therefore be used to measure ^{235}U in U-Th mixtures with acceptable bias.

IV. Automated Apparatus for the Determination of Plutonium and Uranium
(D. D. Jackson, D. J. Hodgkins, J. E. Rein)

An extraction-spectrophotometric method[5, 6] has been selected as the first to be automated for determining Pu and U. Some of the features which made this method attractive for automation include high selectivity for Pu and U and relatively few operations, of which only two require precise control. The main operational steps of the procedure are (1) oxidation of the Pu or U to the (VI) oxidation state, (2) addition of an $Al(NO_3)_3$ salting solution containing tetrapropylammonium nitrate, an ion association complexing agent, to the sample,

(3) addition of an organic extractant, (4) extracting the ion association complex of Pu and/or U, (5) separation of the phases, and (6) measurement of the absorbance of the complex in the organic phase at its absorbance maximum. The two operations where precise control is needed are delivery of the volume of the organic extractant and measurement of the absorbance.

A fully automated prototype instrument that performs the above operational sequence has been constructed and satisfactorily tested. An advanced model for use by NBL is nearing completion.

In the prototype instrument, the samples are hand delivered into individual tubes made of Trubore glass tubing which are then placed into holes in a turntable. The 20-in. diam turntable holds 18 sample tubes and rotates them into position for each operation. The maximum size of the instrument, and thus the maximum number of samples per load, was established by the requirement that it fit into a standard LASL-type, sloping front glovebox that is 36 in. wide, 31 in. deep, and 33 in. high. The analysis time required per sample is 5 min or about 1.5 h for a full load of 18 samples. Analyzed samples can be removed and new samples added and in this manner the instrument operates continuously. All operations on a sample including the absorbance measurement are done in the individual tubes, thus avoiding any quantitative transfer of the sample.

The major components are (1) the turntable and associated Geneva drive mechanism, (2) dispensers that add various reagents, (3) a magnetic mixer to effect the extraction, (4) a filter spectrophotometer, and (5) a control mechanism for correct sequential operation.

A precise, dependable reagent delivery system was developed for the instrument. 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 attack by the corrosive reagents.

Mixing is accomplished with a Teflon-covered cylindrical stirring bar driven by a revolving magnet. The magnet assembly is moved down when not in use to allow the sample tubes to pass over the magnet.

Before the absorbance measurement, saturated $Al(NO_3)_3$ solution is added to the tube to raise the organic phase above the area of the tube where aqueous droplets might adhere.

Inexpensive sample tubes are made from precision-bore, 0.75-in.-diam tubing to provide equal and precise light path lengths for optical measurements. This tubing diameter was experimentally determined to be the best compromise to obtain efficient mixing and phase disengagement, small error in the effective optical path length caused by differences of positioning tubes, and an appropriate optical path length.

A simple, rugged spectrophotometer, using narrow-bandpass interference filters as the monochromator, measures the absorbances at the very sharp peaks, and at a valley adjacent to the peak. The difference is used as a measure of the Pu or U. An improved monochromator was constructed which contains two pairs of interference filters, one for Pu, the other for U. The control system provides for analysis of either Pu or U by using the appropriate pair of filters selected by the analyst. The wavelength of the absorbance peak was accurately measured with a grating spectrograph as 504.4 nm for the Pu complex and 452.5 nm for the U complex. The interference filters have a bandpass width less than 1.4 nm and peak transmissions a few Angstroms greater than the absorbance peaks. The transmission peak of the filters is tuned to match precisely the absorbance peak by rotating the filter slightly in the collimated light path. The two filters are moved sequentially into the light path. The light from a 45-W quartz iodine lamp is collimated with a single lens and a pair of slits before it passes through the filters. The detector is a 929 photodiode tube. The photodiode, high-gain amplifier combination has low inherent long-term drift because the primary gain is controlled by a feedback system which tends towards self-correction. Another desirable feature of photodiodes is a high degree of uniformity. The detector output is electronically converted to an absorbance output by a current-to-voltage converter, a log converter, and a voltage-to-frequency converter, and the resulting pulse train is counted by a reversible counter. The sequence of events which takes place to measure the absorbance of the Pu or U complex is (1) raise

the sample into position in the readout chamber and make the necessary light seals, (2) open the shutter to the photodiode tube, (3) measure the absorbance at the wavelength of the absorbance maximum with the proper interference filter, (4) mechanically switch to another interference filter to measure the background absorbance, (5) switch the reversible counter so it counts in the negative direction, (6) open the gate to the reversible counter for the same time period as previously used, thus subtracting the background absorbance from the previously stored value at the absorbance peak, (7) print the difference as a measure of the Pu or U, and (8) clear the reversible counter and close the shutter. A 10-position, adjustable cam switch controls the entire readout timing sequence. It seemed likely that the precision of the absorbance measurement would be improved by alternating the peak and background measurements in short intervals and integrating the differences for equal times. This form of signal averaging decreases adverse effects of short-term fluctuations. This scheme was evaluated using time intervals ranging from two 40-sec periods to twenty 4-sec periods. The measurement precision continuously improved as the time interval decreased. Due to limitations in the control mechanism, the prototype instrument measures for only two cycles (four 20-sec readings). The advanced model will use the signal-averaging technique.

Because many samples analyzed for uranium at NBL contain thorium, the effect of thorium in the automated method was investigated. Thorium forms an insoluble complex with tetrapropylammonium nitrate and competes with Pu or U for the complexing agent. In the automated instrument, the thorium complex slowly settles causing the absorbance to continuously decrease during the measurement period. The settling is not linear and because the absorbance at the peak wavelength is measured first followed by the background measurement, the overall effect is a positive bias. This problem was solved by using an organic extractant in which the Th complex and the U and Pu complexes are soluble. Of various organic solvents tested, 2-nitropropane adequately met all requirements and extracted the uranium complex to the same high level of 99.9% as did the

previously used solvent, methyl isobutyl ketone. The only adverse effect was a slight decrease of 3% in the absorbance of the uranium complex. Therefore, 2-nitropropane will be used as the extractant in the automatic instrument for all samples.

As many samples analyzed for Pu or U contain sulfate and fluoride, the tolerance of the automatic instrument for these anions was investigated. An adverse effect occurs only at combinations of high levels of sulfate or fluoride and high levels of U (or Pu). In the absence of large quantities of extraneous metals, samples can be fumed to dryness which reduces fluoride and sulfate contents to below-interference levels.

The precision of the instrument was measured over a 2-week period. Six aliquots each at U levels of 1, 8, and 11 mg were processed daily. The relative standard deviations computed from all data collected in the 2-week period were 0.5% at both the 8-and 11-mg levels and 4% at the 1-mg level. These precisions were comparable to the within-day precisions demonstrating long-term stability. The log converter used in the readout of the prototype is not highly precise so that the relative error of the output value increases disproportionately as the U level decreases. A more precise log conversion system is being developed for the advanced model.

Standard solutions prepared from NBS U_3O_8 (SRM-950) and from LASL-prepared, highly pure, depleted U metal were used to establish a U-calibration curve for the prototype instrument. The absorbance response was approximately linear over the range of 1 to 12 mg U.

In a cooperative program with NBL, four samples were recently analyzed for U both with the prototype instrument and by a chemical method at NBL. These samples were representative of typical material produced in the LASL incinerator waste-handling facility and are considered similar to those frequently encountered in safeguards work. Samples of the incinerator ash were subjected to the Teflon-container bomb dissolution technique (see Section II)and the solutions analyzed were the resultant soluble fraction. Duplicate aliquots of the solutions were processed on the automated spectrophotometer. The total time required for

the eight analyses was less than 1 h. The NBL and LASL results agreed within statistical limits with an uncertainty of 1% relative standard deviation assigned to the LASL results.

The prototype instrument has recently been installed in a glove box and Pu samples have been analyzed. The analysis of Pu requires oxidation to Pu(VI) before the extraction. This will be accomplished by adding a 50-mg pellet of AgO to the sample tube just prior to the $Al(NO_3)_3$ salting solution. A device for adding this pellet automatically has been designed and a prototype version has been satisfactorily tested. No difficulties were encountered in the Pu analyses. The sensitivity for Pu is about twice that for U as predicted from their relative molar absorbances. The precision for Pu analysis is predicted to be the same as for the U analyses. An investigation will be made of potential interfering ions with the Pu analysis.

Detailed engineering drawings of the advanced model of the automated spectrophotometer have been completed. Construction of the mechanical portion of this instrument is almost complete. The design and construction of the electronic readout system is expected to be complete in several months. This system incorporates modifications that are expected to improve the analysis reliability. Other improvements in the advanced model include an increase in the maximum number of samples per loading from 18 to 24 and a sample identification system which will print out an identification number matched to the absorbance value.

V. Preparation of Plutonium-Containing Materials for the SALE Program
(S. F. Marsh, G. C. Swanson, M. R. Ortiz, J. E. Rein)

Two objectives of the SALE Program, administered by Aerojet Nuclear and Allied Chemical Corporation (Idaho), are monthly evaluation of the capability of participating AEC and licensee laboratories to analyze various uranium and plutonium materials and to provide well-characterized uranium- and plutonium-containing materials for distribution as working standards for assay and isotopic measurements. LASL is supplying most of the plutonium-containing materials for this program.

A. Uranium-Plutonium Mixed Oxide

Three batches of $(U, Pu)O_2$ powder and three batches of $(U, Pu)O_2$ pellets, each with unique U/Pu ratios, were obtained from Westinghouse-Hanford for use in the preparation of both monthly evaluation and working standards. The mixed oxides were extensively characterized for U and Pu content and isotopic compositions. The O/M ratios of the mixed oxide pellets were substoichiometric when received. To ensure the long-term stability of the pellets, the O/M ratio was adjusted to 2.00 by heating the pellets to 125°C in air for 72 h. Totals of 360 mixed oxide pellets and 360 powder samples were packaged for use as monthly evaluation standards, while 750 powder samples were packaged for use as working standards. Random samples of the mixed oxide powders as well as PuO_2 powder (see following subsection) were returned to LASL from Idaho for analysis of contaminants. There was no increase in the boron and other metal impurity levels.

B. Plutonium Oxide

Three batches of specially treated PuO_2 powder, each with a unique isotopic composition, were supplied by ARHCO for use as monthly evaluation and working standards. Plutonium oxide tends to sorb atmospheric moisture. To ensure the long-term stability of the PuO_2, the three powder materials were subjected to a four-month study of stability relative to moisture sorption by exposing them to air atmospheres with three relative humidity levels of 37, 54, and 85%. The powders gained weight proportional to the relative humidity with a maximum weight gain of 0.2% at 85% relative humidity. Drying conditions which establish a reproducible "dry" base for analysis of Pu content were established and recommendations were included with the analytical data sent to Idaho. Totals of 522 samples of PuO_2 and 200 1-g PuO_2 samples were prepared for use in the monthly evaluation program and as working standards.

One of the three PuO_2 batches will be used to prepare 500 additional 5-g PuO_2 samples for working standards. The remaining lots of this material are now being analyzed. Two additional batches of PuO_2 of unique isotopic compositions have

been received from ARHCO for future use in preparation of monthly evaluation samples.

C. Plutonium Nitrate Solution

A series of Pu nitrate solutions of accurately known Pu concentration and isotopic composition are prepared as a monthly evaluation material. The starting Pu material is highly pure metal so that the final concentration values can be independent of analytical results. A previous series of Pu nitrate solutions prepared by dissolution of Pu metals in HBr followed by conversion with hot HNO_3 produced slight residues upon aging. Alternate dissolution techniques therefore were evaluated to obtain more stable solutions. Dissolution media studied included (1) fluoride-catalyzed strong HNO_3, (2) fluoride-catalyzed dilute HNO_3, (3) fluoride-catalyzed HNO_3 plus hydrazine, and (4) a variation of the HBr dissolution procedure previously used.

The fluoride-HNO_3 dissolvent containing hydrazine provided rapid dissolution of Pu metal in $4\underline{M}$ or less HNO_3, with a fluoride concentration of only $0.005\underline{M}$. However, the resulting solution contained excess hydrazine and trivalent Pu, both of which are undesirable for long-term stability of the solution. Oxidation of excess hydrazine and Pu(III) is accomplished by bubbling N_2O_3 gas into the solution to produce HNO_2 in-situ. Although this dissolution technique was successful in small scale tests, an unidentified precipitate formed before dissolution of large quantities of Pu metal was complete. It appears that the hydrazine dissolvent is suitable for preparing solutions containing Pu concentrations no greater than $0.25\underline{M}$.

The previous series of Pu nitrate solutions was prepared by dissolving Pu metal in HBr, then adding HNO_3 dropwise while heating the solution at about $85^\circ C$. The HNO_3 oxidizes bromide to bromine which distills, as well as oxidizing Pu(III) to Pu(IV). The HNO_3 is consumed as it is added until the bromide is completely oxidized. The solution acidity becomes minimum at this point, at which time Pu may have partially hydrolyzed to produce the slight residue that was observed. This should be avoided by adding the Pu-HBr solution to the HNO_3 and has been adopted to prepare a series of six Pu nitrate solutions, each with a different total Pu concentration and a different Pu isotopic composition.

Because plutonium nitrate solutions are known to generate gases through radiolysis of water as well as through reactions between Pu(VI) and radiolytic hydrogen peroxide, it is desirable to minimize the level of Pu(VI) in solutions which are to be sealed in vials. An observation that boiling $8\underline{M}$ HNO_3 solutions of Pu produced appreciable quantities of Pu(VI) led to a rate study of this reaction. The results of the study are summarized in Table I.

The study shows that little Pu(VI) forms during brief boiling in $8\underline{M}$ HNO_3, but that an appreciable quantity forms during prolonged boiling; furthermore, the rate of Pu(VI) formation in boiling $8\underline{M}$ HNO_3 is constant over a period of 1 h.

A separate study was conducted to resolve conflicting claims in the literature concerning the ability of nitrite to reduce Pu(VI) in $8\underline{M}$ HNO_3. No measurable reduction of Pu(VI) was observed with a two-fold excess of nitrite.

TABLE I

OXIDATION OF PLUTONIUM BY $8\underline{M}$ HNO_3

Treatment	Pu(VI) Formed, %
Adjust HNO_3 conc. to $8\underline{M}$: sample in 5 min	0.2
Heat just to boiling	0.4
Boil 15 min	3.9
Boil 30 min (total)	7.8
Boil 60 min (total)	15.4

VI. Analyses of HTGR Fuels

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

Successful dissolution of HTGR fuel materials was achieved using an oxidation-chlorination method for removing pyrocarbon and silicon carbide coatings from the particles. The samples were heated alternatively in O_2 at $950^\circ C$ to remove pyrocarbon, Cl_2 at $1200^\circ C$ to remove silicon carbide, and then in O_2 at $950^\circ C$ to remove the inner carbon coating. The residues were dissolved in HNO_3-HF. It was found that 15-g samples of the heads were completely stripped of their coatings in about the same treatment time, 2.5 hours, as the 100-mg samples used in early experiments.

Small amounts of uranium and thorium that were carried out of the reaction tube were collected in four water-filled traps. With samples of 6 to 15 g of beads, the traps collected as much as 400 μg of U and Th. The solutions from the first three traps were combined, treated to remove silicon as SiF_4, and the solution added to the sample. The fourth trap was treated separately and total uranium was determined spectrophotometrically as a measure of the actual loss. In about 20 analyses, many on 15-g samples, no more than 8 μg of uranium was found in this trap.

Following this dissolution, which requires a total of only 5 or 6 hours elapsed time per sample, the thorium and uranium are separated by anion exchange from hydrochloric acid media in preparation for their individual measurements. Thorium is determined by titration with versene (ethylenedinitrilotetraacetic acid), and uranium is determined by titration with ceric sulfate.

A series of HTGR fuel samples and some U_3O_8-ThO_2 materials were analyzed as part of a program of comparative analyses administered by NBL. First results obtained for uranium in the U_3O_8-ThO_2 materials were precise but differed from the prepared values. No explanation for the differences has been found. Subsequent analyses of the mixed oxides were in good agreement with the prepared compositions, and the results for uranium and thorium in the HTGR fuels agreed well with those obtained by other laboratories in this program. Additional sample exchanges are planned for next fiscal year. Work on the sealed bomb dissolution of HTGR Fuels (see Section II) will also be continued.

VII.   Analyses of SALE Program Materials
(A. L. Henicksman, W. H. Ashley, R. M. Abernathey, J. E. Rein)

The uranium nitrate and oxide SALE monthly exchange samples have been analyzed throughout FY 1973 for uranium content and isotopic distribution. The uranium contents were measured precisely by a dichromate titration in which the reduced uranium solution was added to a weighed excess quantity of $K_2Cr_2O_7$, and the excess was back-titrated potentiometrically with Fe(II) solution. The isotopic distributions were measured

mass spectrometrically. The compilations of results from all laboratories showed that the LASL results were satisfactorily within precision and accuracy limits.

In addition to the monthly samples, a series of U-Pu solutions, simulating fuel processing plant dissolver solutions, and solutions of ^{233}U and ^{242}Pu were analyzed for U and Pu contents and isotopic distributions by isotope dilution mass spectrometry.

VIII.   Standard Reference Material Plutonium Metal
(C. H. Ward, G. Meadows, R. G. Bryan, J. Roybal)

Another lot of Pu for chemical standards was prepared from highly pure, low ^{241}Pu content metal purified by the LASL Plutonium Chemistry and Metallurgy Group. Extensive analyses showed that this metal contained less than 75 μg/g total impurities. Weighing and sealing of 600, 0.5 - 0.6-g samples in glass ampoules was underway in an Ar atmosphere containing no greater than 1 ppm of either O_2 or H_2O. Partial evacuation of the ampoules during sealing further reduced the O_2 and H_2O in the ampoule and provided an internal atmosphere in which the Pu metal remained essentially unoxidized.

A new, digital-readout, electronic balance is being used for weighing these standards. Following careful calibration relative to National Bureau of Standards certified weights, weighing of the 500- to 600-mg samples was started. Each weight is an average of 40 taken by the balance automatically. In sequence, the tare is weighed twice, the sample is weighed twice, the sample is placed in a glass ampoule, and the tare is weighed twice again. The standard deviation of the combination of these six weights is .017 mg; therefore, the sample weight should be precise to ± 0.03 mg at the 95% confidence level (2 σ). The two weighings reduce the chances of an erroneous weight, and a portion of sample left on the pan is immediately obvious from the second set of tare weights. The electronic balance reduces the tedious nature of the procedure and the possibility of human error. Each weight, which is certified to ± 0.05 mg, is checked and recorded by two analysts. Once sealed, the tubes are removed to room atmosphere where they are visually examined

periodically for evidence of significant surface oxidation of Pu. Defective ampoules are removed as detected.

Based upon current progress a set of 500 standards should be thoroughly checked and available for shipment to the National Bureau of Standards during the first half of FY 1974. Any remaining samples will be retained for comparison analyses on future lots and for re-analysis throughout the time the standard is being distributed.

IX. Chemical Characterization of Special Samples

A. Inventory Verification Samples

Fifteen inventory verification samples taken at the Hanford Engineering Development Laboratory were analyzed for plutonium content by controlled potential coulometry and radiochemical methods. Five of these samples were analyzed mass spectrometrically for plutonium isotopic distributions. Analyses were started on May 16, 1973, and results were reported on June 1, 1973.

B. Plant Inventory Samples to be Used as "Standards"

Five plutonium button, 3 dirty fluoride, 2 dirty green cake, 3 oxide, and 3 ash samples are being analyzed for Pu content by controlled potential coulometry, if applicable, and by x-ray fluorescence or other methods for samples containing large quantities of foreign materials. The isotopic compositions of the Pu are measured mass spectrometrically. The samples range in size from a few hundred grams to a few kilograms and contain between 100 and 2300 grams of plutonium. Dissolution is a very time-consuming operation, requiring repeated acid leaches, fusions, and other drastic operations which generate many liters of dilute solutions. Most of the dissolution is being done by the Plutonium Chemistry and Metallurgy Group. All but the ash samples have been dissolved, assayed for plutonium contents and isotopic distributions, and the data have been reported. Dissolution of the ashes is in progress.

X. References

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