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# CHEMICAL ASSAY OF PLUTONIUM FOR SAFEGUARDS

DARRYL D. JACKSON, JAMES E. REIN, GLENN R. WATERBURY

LOS ALAMOS SCIENTIFIC LABORATORY
UNIVERSITY OF CALIFORNIA
LOS ALAMOS, NEW MEXICO 87544

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# CHEMICAL ASSAY OF PLUTONIUM FOR SAFEGUARDS

BY
DARRYL D. JACKSON, JAMES E. REIN, GLENN R. WATERBURY*

LOS ALAMOS SCIENTIFIC LABORATORY
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The plutonium-containing samples analyzed for nuclear safeguards purposes range from heterogeneous scrap materials to highly pure metal. The factors governing the selection of analytical methods are the quantities of plutonium represented by the sample and the representativeness of the sample. Product-type materials generally are characterized by high plutonium contents and homogeneity whereas scrap-type materials usually have low plutonium contents and are heterogeneous. Analytical methods that provide highly reliable measurements therefore are used for product materials and less reliable methods are acceptable for scrap materials.

This paper presents analytical methodology used for plutonium assay for various nuclear fuel cycle materials with emphasis on Los Alamos Scientific Laboratory (LASL) practices. A major portion of this presentation is devoted to a system under development for scrap-type samples which involves a combination of high-temperature, pressurized, acid-dissolution attack; a gamma assay for low levels of plutonium in any resulting residue; and use of an automated spectrophotometer for measuring plutonium in the solubilized fraction. The isotopic analysis of plutonium is briefly discussed. The paper ends with a presentation of the status of physical standards for assay and isotopic measurement applications.

## ASSAY METHODS FOR PRODUCT-TYPE MATERIALS

Generally, titrimetric methods are favored for the measurement of plutonium in product-type materials using techniques of potentiometry, visual-indicator end-point detection, amperometry, and controlled-potential coulometry. The use of calorimetry is increasing for materials having accurately known isotopic composition. Gravimetry is seldom used because of the difficulty of producing a stoichiometric form and because of the handling difficulty associated with plutonium-containing powders. Differential spectrophotometry, a technique developed for the precise measurement of high concentration solutions, has been used infrequently. The spectrum of plutonium in solution is a function of the species present which are critically dependent on the plutonium oxidation states and the types and quantities of complexing ions. Hence, stringently controlled conditions are required. Spectrophotometry, in general, is more applicable to the measurement of low levels of plutonium by using chromogenic agents. The relative standard deviation obtained is 1 to 2%.

The titrimetric methods involve either the oxidation of Pu(III) to Pu(IV) or the reduction of Pu(VI) to Pu(IV), often in sulfate media. The sulfate complex of Pu(IV) is stable, thereby promoting quantitative reduction or oxidation to a single oxidation state. In the Pu(III) - (IV) oxidative titration methods, Pu(III) is first produced with a strong reductant. Iron and uranium, and some other less common elements, also are reduced and are subsequently titrated by the oxidative titrant. This interference is circumvented in the reductive titration of Pu(VI) to (IV). This scheme involves a preoxidation with Ag(II) oxide or fuming perchloric acid (potentiometric reactions 3 and 4, Table I); a titration with Fe(II) slightly past the end point which reduces Pu(VI), but not U(VI) nor Fe(III); and a final oxidative titration with Cr(VI) or Ce(IV) for the reduced Pu(III) plus the unreacted Fe(II). These methods then are somewhat more complex but are applicable to mixtures of uranium and plutonium, notably the fast reactor oxide, carbide, and nitride fuels.

Table I summarizes seven of the more popular titrimetric methods for plutonium. Methods 1, 2, and 5 use a chemical oxidative titrant of Cr(VI) or Ce(IV) with no intermediate Fe(II) reduction. These methods are used for well-characterized, highly pure plutonium products and have the advantage of using titrants with long-term stability. Four of the methods use a potentiometric endpoint, popular because the equipment is simple to maintain and is inexpensive. The photometric end point method uses a simple photometer and provides about the same relative standard deviation as the potentiometric methods. Its disadvantage is that a blank must be processed to correct for the depletion of the titrant by the added ferroin indicator. In the controlled potential coulometric method(1) a flow of current to a platinum electrode first reduces the plutonium to the (III) oxidation state; then the current is reversed to produce Pu(IV). The reduction and oxidation are done at controlled potentials of 0.31 V and 0.67 V (relative to the standard calomel electrode) to produce quantitative reactions. The integrated current for the Pu(III) - (IV) reaction is the measure of the number of plutonium ions. This technique is gaining popularity because it provides a precision comparable to the chemical titrant methods with much smaller quantities of plutonium. Other advantages are speed, variable selection of media and reaction potentials to minimize interferences, and no need of a standardized titrant. Using the conditions given in Table I, uranium is not an interference. It does require complex instrumentation but commercial equipment now is available.(*)

As discussed previously, those methods using Fe(II) as a titrant are not subject to interference from such common metals as iron and uranium. However, the instability of the titrant caused by air oxidation of Fe(II) to Fe(III) more than outweighs this advantage and the need to use inert atmospheres and to calibrate frequently has made the system unpopular. The amperometric method,(3) has proven to be very reliable for relatively small quantities of plutonium.

## ASSAY OF SCRAP - TYPE MATERIALS

The assay of the so-called scrap materials is complicated by (1) their heterogeneity, (2) their characteristically low plutonium contents, and (3) their diverse chemical compositions including highly refractory materials. A general philosophy guiding the analysis of these materials has been total dissolution of samples, requiring tedious hours of analyst labor and lengthy periods of elapsed time, followed by highly precise chemical analyses. The use of a scheme that is less costly and time-consuming is an economic necessity with ever-increasing numbers and types of materials being analyzed for safeguards surveillance.

As part of the technical effort underway at LASL for nuclear materials safeguards, sponsored by the AEC (Division of Nuclear Materials Security), an assay scheme is being developed that involves relatively fast dissolution attack to solubilize 90% or more of the plutonium followed by automated chemical analyses of the soluble fraction and gamma counting assays of the residue fraction. The overall relative standard deviation for

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(*) Instrument manufactured by the M-T Electronics Company, 563-A Lewelling Blvd., San Leandro, Calif., 94579 is based on reference (2).

Table I. TITRIMETRIC METHODS FOR PLUTONIUM

| Reactions | Mg of Sample | Applicability | Interference | Std Dev, Rel % |
|---|---|---|---|---|
| **Potentiometry** | | | | |
| 1. Zn(Hg) → Pu(III)<br>Cr(VI) → Pu(IV) | 250-400 | Metal, Oxide, Nitride, Salts | Cr, Fe, Mo, Ti, U, V, W. | 0.03-0.04 |
| 2. Zn(Hg) → Pu(III)<br>Ce(IV) → Pu(IV) | 25 | Metal, Alloys, $PuO_2$ | Fe, Mo, Pt, Ti, U, V. W, Nitrate* | 0.06-0.2 |
| 3. AgO → Pu(VI)<br>Fe(II) → Pu(III, IV)<br>Ce(IV) → Pu(IV) | 4 | Metal, Alloys Salts, U-Pu-Th Mixtures | Cr, Ce, Hg, Mn, Mo, Nb, Ta, V | 0.1-0.2 |
| 4. $HClO_4$ → Pu(VI)<br>Fe(II) → Pu(III, IV)<br>Ce(IV) → Pu(IV) | 200-400 | Metal, Alloys, Salts, U-Pu Mixt, Nitrate Soln | Au, Cr, Mn, Pt, V, Sulfate, Phosphate | 0.03<br>0.07 |
| **Photometric Indicator** | | | | |
| Pb → Pu(III)<br>Ce(IV), Ferroin → Pu(IV) | 250 | Metal, Oxide | Cr, Fe, Mo, U, V, Nitrate* | 0.05 |
| **Amperometry** | | | | |
| AgO → Pu(VI)<br>Fe(II) → Pu(IV) | 5-20 | Metal, Oxide, Salts, Nitride, Carbide, U-Pu | Ce, Cr, Mn, V | 0.05-0.01 |
| **Cont Pot Coulometry** | | | | |
| 0.31 V → Pu(III)<br>0.67 V → Pu(IV)<br>at a Pt Electrode in Sulfate Medium | 5-10 | Metal, Oxide, Nitride, Carbide, U-Pu | Ag, Fe | .05-0.1 |

*Nitrate can be removed by prefuming with $H_2SO_4$.

he total plutonium content of the sample is no greater than 1.4% when he relative standard deviations of the chemical analysis and the gamma ssay are 1% and 10%, respectively.

Over 25 years experience with the sealed quartz-tube, acid-dissolution echnique(4, 5) has demonstrated its usefulness for the difficult-to-dissolve efractory materials. In this technique, samples and mineral acids, ypically a hydrochloric acid-perchloric acid mixture, are sealed in a eavy-wall quartz tube which is placed in a metal shell and heated to emperatures of 325°C or more. At temperatures substantially higher than he ambient-pressure boiling points of about 100° C, the dissolution rates ncrease abetted by the production of very reactive acid-decomposition pecies such as nascent chlorine.

An apparatus, consisting of a Teflon container in a metal shell, has een developed for acid dissolutions up to 285°C. This apparatus provides he capability to use hydrofluoric acid, an effective dissolvent for many efractory plutonium compounds. It is comparatively easy to assemble and isassemble, the Teflon container is reusable, and further chemical treatnents of the dissolved sample can be made in the container, thereby bviating transfers.

The operating temperature is limited to 285°C above which Teflon ndergoes plastic flow. As this temperature is approached, Teflon becomes permeable to low molecular weight gases. The advantage of coninuous pressure release is somewhat offset by corrosion of the metal shell. As shown in Fig. 1, stainless steel and nickel shells are used, the former for oxidizing acid solvents and the latter for halide acids. The stainless steel shell incorporates a rupture-disc venting mechanism to release overpressure that may develop as a result of an energetic reaction between organic material in a sample and an oxidizing acid. The design pressures for the stainless steel shell are 68MPa (10,000 psi) for distortion and 205 MPa (30,000 psi) for fracture. The corresponding pressures for the nickel shell, machined to the same dimensions, are about 20% lower. The combination of a 0.25-mm stainless-steel rupture disc combined with a 9.5-mm vent hole in the base of the stainless steel shell gives a foolproof, safe pressure release at 42MPa.

The Teflon container is based upon a National Bureau of Standards design.(6) A feature of this design is a long taper fit of the container lid which maintains a tight seal although the Teflon undergoes irreversible

Photo Neg No. 7311522

Fig. 1. Components of the Teflon-container metal-shell dissolution apparatus.

shrinkage. The tight seal is gained by a spring pressure and the design provides for reuse of Teflon containers which shrink from a volume of 30 ml to 10 ml after ten to twenty uses at 285° C.

The apparatus has been applied successfully to the dissolution of a variety of scrap-type nuclear materials, mainly containing refractory uranium compounds. An installation of an oven in a glove box has been completed recently for use with plutonium-containing materials. Another achievement with this apparatus has been dissolution of the Gulf-General-Atomic High-Temperature Gas Reactor (HTGR) fuel. This fuel consists of microspheres of a core of uranium and thorium carbides covered sequentially with coats of pyrocarbon, silicon carbide, and pyrocarbon. Acid dissolutions of this fuel at reflux temperature are ineffective and complex fusion procedures have given limited success. A satisfactory procedure, but one requiring considerable equipment, involves a series of sequential gas reactions with oxygen at 850°C, chlorine at 1100°C, and oxygen at 850°C to remove the three coats, followed by a nitric acid - hydrofluoric acid dissolution of the resulting Th-U oxide.(7) Using the Teflon-container, metal-shell apparatus, an overnight reaction at 275° C with a nitric acid - hydrofluoric acid mixture completely decomposes the fuel to give a soluble uranium fraction and a $ThF_4$ residue. Subsequent treatment with fuming perchloric acid in the Teflon container solubilizes the $ThF_4$.

Many laboratories have developed assay procedures for plutonium based on gamma photon counting, some using sophisticated apparatus for highly precise measurements. As a relative standard deviation as large as 10% is adequate in the measurement for the residues from the acid attack in the Teflon-container, metal-shell apparatus, we were able to stress operational simplicity and the use of low-cost equipment.

The residue is collected on a 25-mm-diam membrane filter, mounted on an aluminum plate, and covered with cellophane tape. A NaI(Tl) detector is used to count the 375-keV gamma photons of $^{239}$Pu. This isotope is measured because it is the major fissionable isotope in nuclear fuel cycle materials. The conversion to total plutonium uses isotopic abundance data routinely measured by mass spectrometry for safeguards samples. A window of 392-472 keV, above the 375-gamma photon, is used to minimize positive bias from the 332-keV gamma photon of 6.7-day $^{237}$U, in equilibrium with its $^{241}$Pu parent. This gives a sensitivity decrease of threefold compared to a lower energy cutoff of 291-keV. Plates containing

0.5 to 30 mg of plutonium of three different isotopic compositions (given in Table II) were counted to an integrated value ranging from 700 to 70,000 counts with a relative standard deviation of 3%. At the 392-472 keV window, a correction for absorption is not necessary. The gamma photon attenuation is less than 1% with a Pb/Pu ratio of 32/1.

Table II. ISOTOPIC COMPOSITION OF THREE PLUTONIUM MATERIALS USED TO ESTABLISH GAMMA ASSAY COUNTING CONDITIONS

| | Atom Percent, for Pu Material | | |
|---|---|---|---|
| Isotope | A | B | C |
| 238 | 0.013 | 0.018 | 0.004 |
| 239 | 83.189 | 93.932 | 97.620 |
| 240 | 15.154 | 5.692 | 2.320 |
| 241 | 1.402 | 0.337 | 0.054 |
| 242 | 0.242 | 0.020 | 0.003 |

An extraction-spectrophotometric method(8) has been automated for the determination of plutonium in the soluble fraction produced in the Teflon-container, metal shell apparatus. Its attractive features for this purpose were relatively few operations and high specificity, a necessity for the widely varying compositions of scrap-type materials. The procedural sequence is:

(1) Deliver a sample into a tube

(2) Add an aluminum nitrate salting solution containing tetraproplyammonium nitrate to form the complex,

$$\left[(\text{Propyl})_4\text{N}\right]^+ \left[\text{PuO}_2\ (\text{NO}_3)_3\right]^-$$

(3) Add an organic extractant, 4-methyl-2-pentanone (or 2-nitropropane)

(4) Mix to extract the complex

(5) Separate the phases

(6) Measure the absorbance of the complex in the organic phase

A prototype of this instrument was completed about a year ago. A photograph of a just-completed advanced model is presented as Fig. 2. Samples are manually delivered into tubes made from Tru-bore tubing which are placed into position on the turntable. The automatic operation then is initiated. The tubes are rotated to stations where (1) the salting solution and organic extractant are added, (2) the phases are mixed, (3)

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Fig. 2. LASL automated spectrophotometer

additional salting solution is added to raise the organic phase where the walls of the tube are free of aqueous droplets, and (4) the tube is raised into a filter photometer for measurement of the absorbance. The significant feature of the instrument is that all operations on a sample, including the absorbance measurement, are done in the tube. This avoids the use of transfer mechanisms which are difficult to do precisely and require large solution volumes to erase memory.

The reagents are delivered with piston-displacement dispensers, driven by a pneumatic-hydraulic cylinder system (Fig. 3), in which only glass and Teflon contact the corrosive aluminum nitrate and organic extractant. The precision of delivery is better than 0.05% relative standard deviation. Mixing of the phases is accomplished by magnetic stirring. A Teflon-covered magnet is placed in the tube at the time the sample is added. At the mixing station, two magnets raise into position external to the tube and about 1 cm from its bottom. Strong coupling is maintained at the high speed of rotation necessary to form a vortex for efficient phase transfer of the plutonium complex. A 4-min extraction period gives > 99.9% transfer of the plutonium complex to the organic phase. After a programmed 2-min wait, more aluminum nitrate is added to raise the organic phase to a clear area of the tube, and the tube rotates to the photometric readout station.

The photometer features interference filters with narrow bandpasses. The instrument has separate pairs of filters for the measurement of plutonium and uranium. The extraction procedure applies equally to these elements with the complexes having unique (and different) absorbance spectra. The absorbance spectra of the plutonium complex is presented in Fig. 4. The bandpasses of the filters for the plutonium measurement are at 501.4 nm for the peak and 518 nm for the adjacent valley.

The absorbances at the peak and valley are sequentially measured for equal time periods and their difference is printed out as the measure of the plutonium. A two-wave length measurement is used because Tru-bore tubing, used for the cells, has varying wall thickness. The effect of glass thickness upon absorbance is equal at the peak and valley so that the net difference remains unaffected.

The photometric detector control and readout system is schematically shown in Fig. 5. The photodiode (detector) current, proportional to the incident light (transmittance) is converted to voltage and amplified in a current-to-voltage converter. The log converter changes the value to photo neg No 7311516

Fig. 3. Control system for reagent dispensers

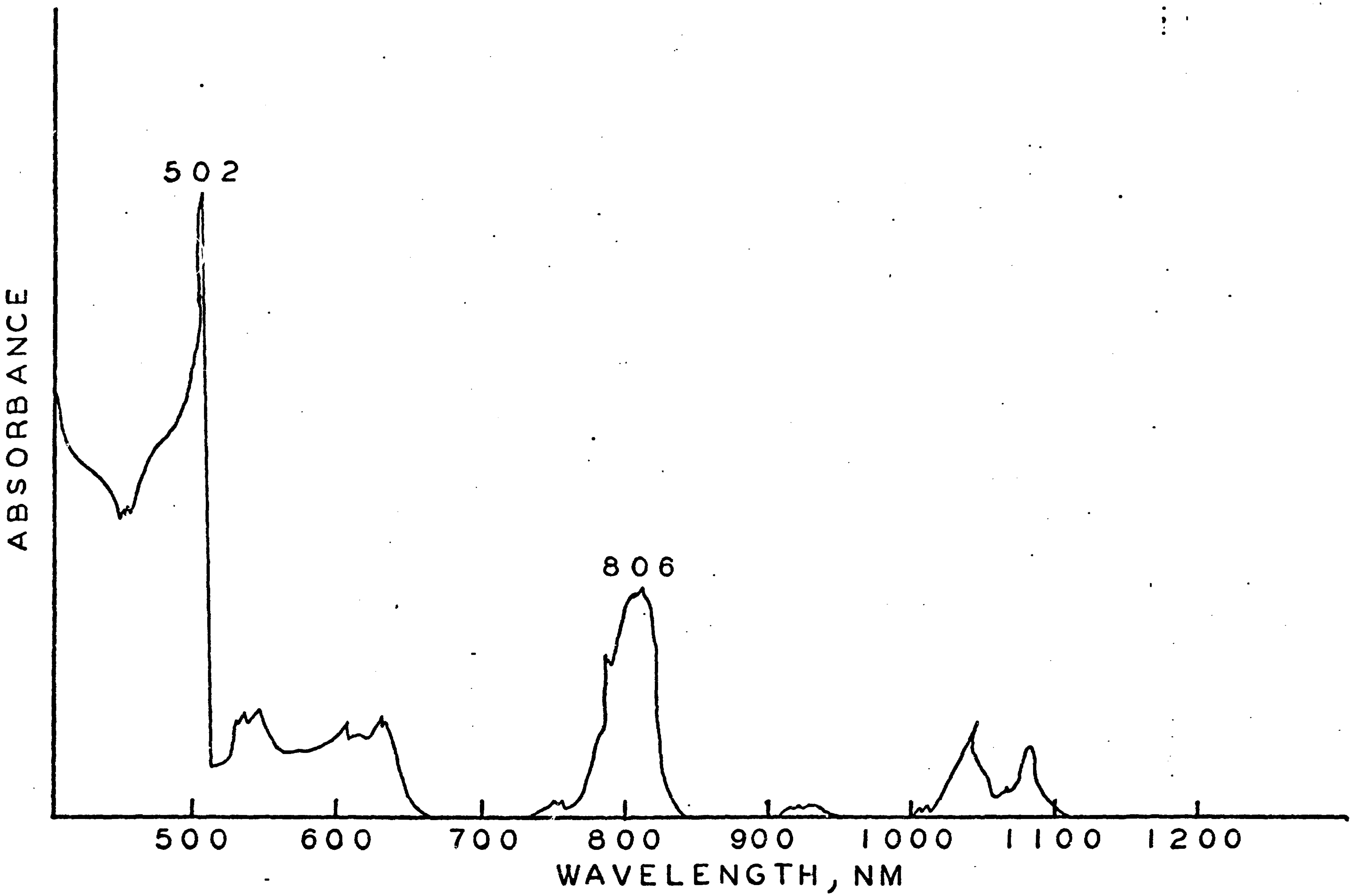

FIG. 4. SPECTRUM OF TETRAPROPYLAMMONIUM PU(VI) TRINITRATE

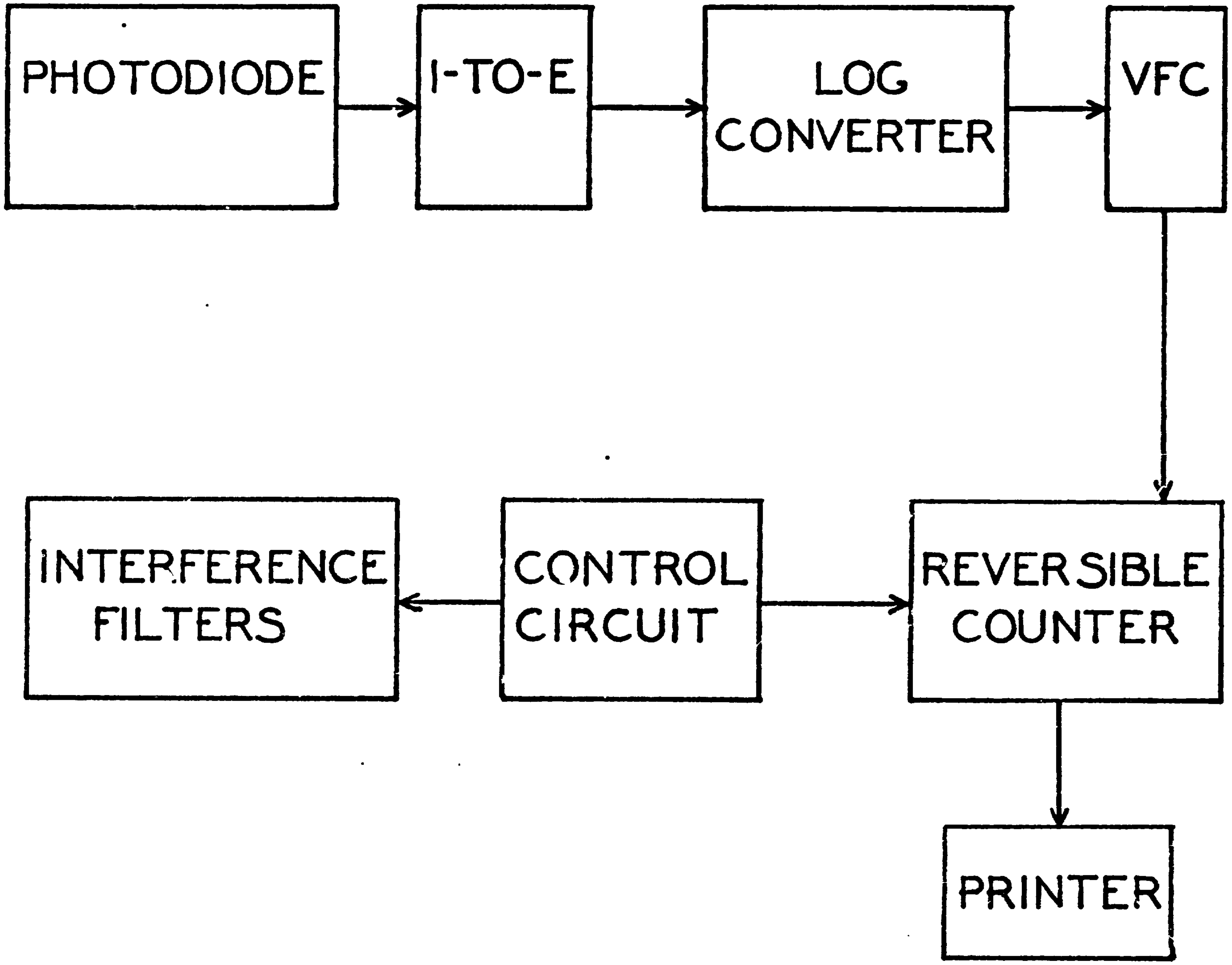

Fig. 5. Photometric detector control and readout system

log V or absorbance. The voltage-to-frequency converter changes the analog voltage input to a frequency signal which passes to the reversible counter. The control circuit, consisting of a motorized switch assembly (Fig. 6) sequentially places the peak filter and the valley filter in the light path for preselectable, equal time periods. When the valley filter is in position, the control circuit sends a logic signal to the reversible counter to subtract the frequency value from the peak frequency value. This net absorbance value is printed. The control circuit also activates and deactivates a shutter in front ot the photodiode, as well as resetting the reversible counter to zero after the absorbance of each sample is measured.

A turntable position identification number is printed along with the absorbance value. Holes are machined in the turntable in a 5-bit binary mode. Roller-actuated miniature switches relay the position number to the printer.

The turntable takes 24 tubes at a throughput rate of 5 min per analysis. The overall precision is 1% relative standard deviation over the range of about 2 to about 15 mg of plutonium decreasing to about 3% at the lower limit of about 0.5 mg. The maximum sample volume is 0.5 ml corresponding to a lower concentration limit of 1 mg Pu/ml.

## ISOTOPIC ANALYSIS

Since the primary purposes of Safeguards is control of fissionable isotopes, a combination of total element measurement and isotopic measurement is necessary. For plutonium isotopic abundance measurement, thermal ionization mass spectrometers are used almost universally. A description of the instrumentation and procedures used is beyond the scope of this paper. In essence, samples are subjected to chemical separation procedures to obtain a pure plutonium fraction which then is placed in the mass spectrometer where the relative abundances of the 238 through 242 masses are measured.

The measurement is highly precise with the absolute standard deviations ranging from $4 \times 10^{-6}$ at a fractional abundance level of $1 \times 10^{-4}$ to $2 \times 10^{-4}$ at fractional abundances above $5 \times 10^{-2}$.

## STATUS OF PLUTONIUM PHYSICAL STANDARDS

The most important characteristic of an analytical result obtained on samples analyzed for Safeguards purposes is accuracy. It therefore is

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Fig. 6. Control system for detector and readout

essential that standardized nuclear materials are commercially available for the calibration of analytical methods. At this time, six plutonium Standard Reference Materials (SRM) are available from the National Bureau of Standards (NBS) (Table III). The isotopic levels in the three isotopic standards are considered to cover adequately the range now encountered in fuel cycle materials and expected to be encountered in the forseeable future. The plutonium metal standard SRM 945 is intended to serve as the plutonium matrix for customized impurity element standards. The two assay standards of $PuSO_4 \cdot 4H_2O$ and plutonium metal are not representative of nuclear fuel cycle materials. For this reason, the AEC is planning to make available a variety of secondary standards representative of fuel cycle materials and has sent a letter to AEC contractors and licensees requesting recommendations.

Table III. PLUTONIUM STANDARD REFERENCE MATERIALS.

| SRM No. | Chemical Form | Intended Use | Pertinent Information |
|---|---|---|---|
| 946 | Sulfate | Isotopic | 12% $^{240}Pu$, 4% $^{241}Pu$ |
| 947 | Sulfate | Isotopic | 18% $^{240}Pu$, 4.5% $^{241}Pu$ |
| 948 | Sulfate | Isotopic | 8% $^{241}Pu$, 0.6% $^{241}Pu$ |
| 945 | Metal | Matrix for Impurity Standards | |
| 944 | $PuSO_4 \cdot 4H_2O$ | Assay | 47.50% Pu (Stoichiometric) |
| 949 | Metal | Assay | 99.99% Purity, Low $^{241}Pu$ |

The two plutonium metal SRMs are prepared and characterized at LASL. Highly pure electrorefined metal is used with especially low levels of $^{241}Pu$ for the assay standard. The metals are handled in an inert-atmosphere glove box installation devoted exclusively to the project. Any oxide film is removed by a file and the metal is sheared into sections. Pieces are weighed independently by two operators and transferred to glass ampoules which are sealed by electrical heating within the inert atmosphere. The weight is recorded on a label affixed to the ampoule so that the analyst can conveniently use the entire contents of an ampoule even though oxidation may occur when the ampoule is opened. The analytical characterization of the metal is very extensive. The plutonium assay value is established by subtracting the measured levels of all trace metal and nonmetal impurities. The plutonium content also is determined by two independent titrimetric methods, and the three measured values must agree within statistical limits for acceptance. The $^{241}$Am content is determined radiochemically and plutonium isotopic abundance is determined mass spectrometrically as the measure of atomic weight. The assay value, $^{241}$Am content, and molecular weight are provided as part of the NBS certification.

As a means of improving the capability of analytical laboratories to determine fissionable materials, the AEC sponsors the Safeguards Analytical Laboratory Evaluation (SALE) Program. Well-characterized uranium and plutonium materials, representative of many nuclear fuel cycle materials, are distributed at monthly intervals to AEC contractors and licensees, as well as to foreign laboratories. The coded results and statistical computations are made available to all participants. For the SALE Program, LASL has the responsibility for the preparation and characterization of the plutonium materials. To date, these materials have been plutonium nitrate solution, plutonium oxide, and mixed uranium-plutonium oxide. Batches of the latter two materials are being prepared as secondary standards for eventual commercial distribution.

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