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Progress Report

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Analytical Methods for Fissionable Material Determinations in the Nuclear Fuel Cycle

October 1, 1978—September 30, 1979

University of California

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Compiled by
Glenn R. Waterbury

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ANALYTICAL METHODS FOR FISSIONABLE MATERIAL DETERMINATIONS IN THE NUCLEAR FUEL CYCLE
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ABSTRACT

Work continues on the development of dissolution techniques for difficult-to-dissolve nuclear materials, the development of methods and automated instruments for plutonium, uranium, and thorium determinations, and the preparation of plutonium materials for the Safeguards Analytical Laboratory Evaluation (SALE) program and distribution by the National Bureau of Standards (NBS) as standard reference materials (SRMs). We are measuring the longer plutonium isotope half-lives, evaluating the isotope correlation techniques and the chemistry involved in the mass-spectrometric ion-bead techniques, and analyzing the SALE uranium materials.

Completed subtasks include evaluations of various Teflon materials to recommend those acceptable for the dissolution apparatus developed at the Los Alamos Scientific Laboratory, investigations of laser-enhanced dissolution of refractory materials, determinations of diverse ion effects on the microgram-sensitive method for determining uranium, fabrication of the first automated controlled-potential coulometric analyzer for determining plutonium, preparation of a ^{244}Pu material for distribution by NBS as a SRM, and determination of the half-life of ^{239}Pu. Work has been started on a spectrophotometric method for determining microgram quantities of plutonium, a microcomplexometric titration method for determining uranium, the use of new reagents for separations of plutonium, the preparation and packaging of a new lot of high-purity plutonium metal for distribution by NBS as a plutonium chemical SRM, and determination of half-lives of other plutonium isotopes.

I. INTRODUCTION

Safeguards control of uranium, thorium, and plutonium in the nuclear fuel cycle requires inventory confirmation by adequate sampling and reliable analyses. Precise and accurate measurements of the amounts of these elements and their isotopic compositions are required for widely diverse nuclear materials, including pure products, reactor fuels having complex chemical compositions, and many types of scrap materials. Dissolutions and analyses of materials containing highly refractory components and of multiphase scrap are particularly difficult.

[redacted]

uranium, plutonium, and thorium are: (1) mineral acid reactions at elevated temperatures in

260°C in the nickel-shell apparatus.

B. Gas-Solid Reactions (M. E. Cournoyer, D. D. Jackson, and J. E. Rein)

We continued the investigation of reacting refractory nuclear fuel materials with gases at elevated temperatures to attain solubilization of uranium and thorium in refractory materials. Two mechanisms are involved. In one, volatile uranium or thorium species are condensed as materials readily soluble in mineral acids. In the other, refractory materials are converted to forms in which the uranium or thorium is readily leached by mineral acids. The materials are reacted in a closed fused-silica tube in a temperature-controlled, resistance-heated furnace. The tube is designed to provide a controllable atmosphere and an effective recovery of the uranium or thorium. Prior effort was centered on apparatus development and application to uranium materials. In this period, we investigated thorium materials and one particularly dissolution-resistant uranium material. In addition, an operational improvement was made in using the apparatus.

Reactions with chlorine gas and especially carbonyl chloride are effective for volatilizing uranium. For example, 0.1 g of U_3O_8 volatilizes completely with carbonyl chloride in 0.5 h at 1000°C and in 1 h at 800°C. Previously, uranium in a calcined ash material produced in the LASL waste-recovery facility had been solubilized completely by reaction with carbonyl chloride at 1000°C. Most of the uranium had volatilized and that left in the unvolatilized residue was leached readily by hot HNO_3. A different calcined ash material tested this period was a Zr-Nb matrix with less than 1% uranium, which, following calcination, had been heated with a 10*M* HF-1.6*M* HNO_3 solution to leach uranium and then filtered after addition of diatomaceous earth as a filter aid. This ash had a composition that defied further solubilization of uranium by acid treatments at ambient pressure. Reaction with carbonyl chloride at 1000°C followed by reaction of the unvolatilized residue with a HNO_3-HF mixture in the Teflon-container, metal-shell apparatus at 200°C solubilized 89% of the uranium. Reversing the treatment order increased solubilization of uranium to 95%. The 5% uranium remaining in the final residue was assayed by gamma counting. The overall relative standard deviation was 1.1% for a uranium assay of this material, using 1% relative standard deviation for a chemical analysis of the solubilized 95% fraction and 10% relative standard deviation for the gamma assay of the 5% residual fraction. The elapsed dissolution time was less than 24 h.

The feasibility of the technique for solubilizing thorium is being evaluated using a sample of refractory, 1200°C calcined ThO_2. Because thorium halides have low boiling or sublimation temperatures, emphasis is being placed on chlorine- and bromine-containing gases. Thorium can be expected to be more difficult to volatilize than uranium because the boiling points of $ThCl_4$ and $ThBr_4$ are higher than those for UCl_4 and UBr_4.

The amounts of thorium volatilized in chlorine-containing gases and bromine during 1 h at 1200°C (Table I) were determined from the weight loss of the reacted ThO_2. Only small quantities were volatilized with HCl, Cl_2, and Br_2, with Br_2 being better than Cl_2, in agreement with the lower boiling point of $ThBr_4$. Volatilizations with chlorine- and carbon-containing gases were significantly larger, reaching 36% for carbonyl chloride. The unvolatilized fraction remaining from all reactions was as resistant to dissolution in heated 12*M* HCl and in heated 15.7*M* HNO_3 as the initial ThO_2 itself.

The increased volatilization obtained with chlorine- and carbon-containing gases, coupled with the reported formation of UCl_4 and $ThBr_4$ by reaction of the oxides with halogen gases plus carbon,[1] prompted as evaluation of reactions with Cl_2 and carbon of various forms. The results of Table II show a marked increase in the volatilization, becoming greater than 95% with two different charcoals at 1000°C for 1 h. Experiments to assess the carbon/ThO_2 ratio effect indicate that volatilization increases with an increasing ratio with a plateau

TABLE I

VOLATILIZATION OF 1200°C CALCINED ThO_2 IN 1 H AT 1200°C

Gas	ThO_2 Volatilized (%)
HCl	0.2
Cl_2	0.6
Br_2	3
NOCl	2
Cl_2-CO(1 to 1)	8
Cl_2, trace CCl_4	33
$COCl_2$	36

TABLE II

VOLATILIZATION OF 1200°C CALCINED ThO_2 IN 1 H AT 1000 AND 1200°C IN CHLORINE (CARBON/ThO_2 RATIO$\geq$ 0.13)

Carbon Form	Percent ThO_2 Volatilized	
	1000°C	1200°C
Boneblack	Insig	---
Lampblack	45-50	> 95
Graphite	72-77	75-80
Activated charcoal	> 95	> 95
Vegetable charcoal	> 95	> 95

reached at about 0.13. A reaction with carbonyl chloride and carbon for 1 h at 1000°C gave > 95% volatilization.

Measurement techniques are being refined to assay the unvolatilized residue for its thorium content to measure the percent volatilization as it approaches 100%. It may be that a significant fraction of the unvolatilized residue consists of impurity element oxides initially present in the ThO_2. An evaluation of bromine-plus-carbon reactions is under way.

An operational improvement was to evacuate and backfill the reaction tube, rather than flush with the reactive gas to replace air. This effectively removes all air and high volatilization of thorium is attained.

C. Laser-Enhanced Dissolution Studies (M. E. Cournoyer, S. F. Marsh, and J. E. Rein)

The evaluation of laser energy to enhance the dissolution of refractory materials in aqueous acidic media has been completed. It was generally concluded that laser energy did not provide practical advantage relative to simple heating. A 425-kW, pulsed, neodymium glass laser was evaluated; use of a higher intensity laser was impractical because of steam flashing of solution. In addition to the 425-kW neodymium glass laser, a 5-W, continuous-wave (CW), argon-ion laser and two lower intensity lasers were tested. The 425-kW neodymium glass laser was operated at a rate of two 0.1-ms, 42.5-J pulses per minute.

Low absorption of the laser light in the liquid medium in which the sample is immersed is necessary to provide effective transmission of energy to the sample without steam flashing of the solution. Transmittances measured previously for various acid media at 400 to 700 nm, the wavelength range of the 5-w, CW argon-ion laser, were essentially 100% except for a 3/1 HCl/HNO_3 mixture.[2] Transmittances in HCl, HF, HNO_3, HBr, and Cl_2 aqueous media were measured this period in the near-infrared region for application to the 425-kW, pulsed, neodymium glass laser. They were essentially 100% at the laser wavelength of 1064 nm.

The test refractory materials have been Al_2O_3 powder, ZrO_2 powder, and crushed pieces of a zirconia crucible. Test conditions have been laser irradiation of weighed quantities of materials immersed in the various media in glass containers at room temperatures at reflux temperature. The quantity of material dissolved was established by chemically analyzing the solution for aluminum or zirconium, and in the case of the zirconia crucible, for impurity elements.

Experiments with the 5-W, CW argon-ion laser were terminated after negligible dissolution in various acid media and negligible vaporization in air using a 4-mm-diam spot focused on the specimen. Dissolution and vaporization also were negligible using an unfocused 25-mm-diam spot of the 425-kW, pulsed, neodymium glass laser. The volatilization rate of the three test materials in air was about 1 mg/pulse using a focused beam of 1 GW/cm^2. Defocusing to irradiate a larger sample area decreased the overall volatilization rate. Solutions defocused the beam, shown by irradiating a stack of 1-mm-thick steel plates in air and in water. At the focal point, beam diameter increased from > 0.1 to 3 mm and beam penetrations of the steel plates decreased about 20-fold from 6 mm to about 0.3 mm. Net absorption of beam power in a 1.5-cm path length of various solution media was about 20% with neither bubble formation nor significant temperature rise.

Results for the dissolution of the three test materials at ambient 20°C in HNO_3, HCl, and HBr are given in Table III. The three conditions used were the laser beam focused on (1) the material surface through a 3-mm solution depth, (2) a paste mixture of the powder materials and solution, and (3) the solution surface of a stirred suspension of the powder materials. The highest dissolution rates of

TABLE III

DISSOLUTION RATES IN ACID MEDIA (425-kW PULSED, NEODYMIUM GLASS LASER)

Reaction Condition	Material	Material Dissolved Per Pulse (mg) 15.7*M* HNO_3	12*M*HCl	9*M* HBr
Focused beam on solid through 3-mm solution depth	Al_2O_3 powder	0.27	0.28	0.22
	ZrO_2 powder	0.28	0.25	0.08
	Zirconia crucible	Negl	Negl	Negl
Paste mixture of solid and solution	Al_2O_3 powder	Negl	Negl	Negl
	ZrO_2 powder	Negl	Negl	Negl
Stirred suspension	Al_2O_3 powder	0.14	0.16	0.21
	ZrO_2 powder	0.04	0.04	Negl

the Al_2O_3 and ZrO_2 powders, obtained by the focused beam through 3 mm of solution, were about one-fourth of the vaporization rate in air. However, the heat generated at the sample surface by each pulse caused violent bubble formation and the need for a 5- to 10-min wait before the next pulse. This lengthens the reaction time unacceptably. The negligible dissolution rates of paste mixtures is attributed to insufficient material-solution interfacial contact.

The stirred suspensions had low dissolution rates but could be irradiated continuously at the 2-pulse/min rate without violent bubble formation. The final test consisted of irradiating stirred suspensions of the Al_2O_3 or ZrO_2 powders in HNO_3, HCl, or HBr that were heated to refluxing temperatures for up to 8 h. The results, summarized in Table IV, show only a slight increase in dissolution rates compared to reflux heating alone.

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

Diverse cation and anion effects have been determined for the microgram-sensitive uranium method using the LASL-automated spectrophotometer. The instrument now is operational for its original function of determining milligram levels of uranium and plutonium and microgram levels of uranium. The instrument was effectively applied to the determinations of the uranium content of a series of aluminum-uranium alloy samples and evaluated for determining microgram levels of uranium in a series of NBL-supplied samples. Detailed information about the instrument has been provided to a commercial company that is considering its manufacture.

Fabrication of a controlled-potential coulometric analyzer for determining plutonium has been completed. It incorporates improvements in instrumental operations and in the chemical method developed over the past year. Testing shows that design specifications are being met.

A versatile automated titration apparatus has been developed that now is being used for development of a micro-complexometric titration method for determining uranium. Development of a microgram-sensitive spectrophotometric method for determining plutonium is under way with an objective of applicability to the LASL-automated spectrophotometer. A separation procedure has been developed for trace uranium in plutonium metal applicable to a variety of uranium assay methods. A new reagent, useful for liquid-liquid extraction or as part of a chelating resin, appears promising for the separation of plutonium. Selective complexometric titration procedures are being evaluated for the determination of thorium in nuclear fuel cycle materials.

TABLE IV

DISSOLUTION OF STIRRED SUSPENSIONS UNDER REFLUX HEATING (30-s PULSED, 425-kW NEODYMIUM GLASS LASER)

		Percentages Dissolved in Acid Media of					
		$15.7M$ HNO_3		$12M$ HCl		$9M$ HBr	
Material	Reaction Time (h)	Without Laser	With Laser	Without Laser	With Laser	Without Laser	With Laser
Al_2O_3	1	5.0	6.1	5.1	6.4	5.4	6.7
	2	5.7	7.5	5.4	8.0	7.1	7.9
	4	9.2	9.3	8.8	9.6	9.2	9.4
	8	10	12	9.9	13	11	13
ZrO_2	1	0.2	0.2	0.2	0.2	0.1	0.1
	2	0.2	0.2	0.2	0.3	0.2	0.2
	4	0.2	0.3	0.3	0.3	0.2	0.2
	8	0.3	0.4	0.3	0.4	0.2	0.3

A. Automated Spectrophotometer (D. D. Jackson, N. M. Saponara, and J. E. Rein)

1. **Microgram-Sensitive Method for Determining Uranium.** The automated spectrophotometer[3] was modified last year[2] to use a microgram-sensitive uranium spectrophotometric method developed for the purpose.[4] The method consists of extracting the colored U(VI)-benzoyltrifluoroacetone complex into butyl propionate from a solution that contains a Mg(II)-cyclohexanediaminetetraacetic acid-masking agent to provide high selectivity, and hexamethylenetetramine and triethanolamine to provide high buffering capacity. The effect of the acidity level of samples was investigated in detail and reported.[2] This year, a detailed evaluation of the tolerances of metal and nonmetal ions was completed. Because the acidity may affect the tolerances, they were measured at 1 meq of acid (as HNO_3) and 8 meq, near the upper tolerance level of acidity for measurements. Aliquots of the diverse ion solutions were added individually to tubes containing 35 μg (0.15 μmole) of uranium and 1 or 8 meq of HNO_3. If a change significant at the 95% confidence level was obtained relative to uranium alone, the experiment was repeated with less of the diverse ion. The results for metal cations are summarized in Table V and VI and for anions in Tables VII and VIII. The tolerances for impurities generally present in uranium-containing scrap materials are high. Increased acidity greatly decreases the tolerance for bromate and chromate from a 1000/1 to < 1/1 mole ratio relative to uranium. It appears that these oxidants, as well as permanaganate, oxidize the organic chromogenic agent. This supposition is supported by a decreased effect when sulfite is added to destroy the strong oxidants.

2. **Analysis of Uranium-Aluminum Alloy Samples.** Quadrant portions of 14 aluminum-uranium alloys fabricated by the Savannah River Plant (SRP) were analyzed for their uranium content to provide calibration values for the Shuffler, a LASL-developed nondestructive analyzer. Other quadrant portions were analyzed at SRP. We dissolved the 100- to 165-g portions in hydrochloric acid and analyzed the three weighed aliquots with the automated spectrophotometer in the milligram-sensitivity mode. We also analyzed aliquots using a potentiometric titration method and isotope-dilution mass spectrometry.

The results of the automated spectrophotometer analyses agreed with our isotope-dilution mass-spectrometric results as well as with the average of results obtained by SRP using four methods. Our potentiometric-titration results were biased high, caused by unexpected interfering metal impurities in the alloys. For the automated spectrometer

TABLE V

LEVELS OF METAL CATIONS TOLERATED IN MICROGRAM-SENSITIVE URANIUM METHOD USING THE AUTOMATED SPECTROPHOTOMETER AT AN ACID LEVEL OF 1 MEQ

Mole Ratio Relative to Uranium					
1000/1	500/1	100/1	50/1	10/1	1/1[a]
Ag Li	Sr	Be La	Al In	Au Sc	Pd
B Mo		Ca Mg	Bi Mn	Ce^{3+} Se	Sb
Ba Na		Co Ni	Cd Sn	Ce^{4+} Tl	
Cs Pt		Fe Pb	Cu Th	Cr V	
Ge Rb		Hf Y	Ga Zn	Ru Zr	
K			Hg		

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[a] Te interferes at a 1/1 mole ratio.

TABLE VI

LEVELS OF METAL CATIONS TOLERATED IN MICROGRAM-SENSITIVE URANIUM METHOD USING THE AUTOMATED SPECTROPHOTOMETER AT AN ACID LEVEL OF 8 MEQ

Mole Ratio Relative to Uranium					
1000/1	500/1	100/1	50/1	10/1	1/1[a]
Ag La	Al	Ce^{3+}	Se	Au Sb	Ga
Ba Li	B	Fe		Be Sn	
Bi Mg	Co	Ni		Cr Te	
Ca Mo	Cu	Pb		Hf V	
Cd Na		Pt		Mn Zr	
Cs Rb		Sc		Ru	
Ge Sr		Th			
Hg Tl					
In Y					
K Zn					

---

[a] Ce^{4+} and Pd interfere at 1/1 mole ratio.

TABLE VII

LEVELS OF ANIONS TOLERATED IN MICROGRAM-SENSITIVE URANIUM METHOD USING THE AUTOMATED SPECTROPHOTOMETER AT AN ACID LEVEL OF 1 MEQ

Mole Ratio Relative to Uranium				
1000/1	500/1	100/1	50/1	10/1[a]
BrO_3^-	NO_2^-	Br^-	EDTA	$C_2O_4^{2-}$
$C_2H_3O_2^-$		CSN^-	I^-	
Cl^-		IO_3^-		
ClO_4^-				
$Cr_2O_7^{2-}$				
F^-				
$NH_2SO_3^-$				
S^{2-}				
SO_3^{2-}				
SO_4^{2-}				

---

[a] MnO_4^- and PO_4^{3-} interfere at 1/1 mole ratio.

TABLE VIII

LEVELS OF ANIONS TOLERATED IN MICROGRAM-SENSITIVE URANIUM METHOD USING THE AUTOMATED SPECTROPHOTOMETER AT AN ACID LEVEL OF 8 MEQ

Mole Ratio Relative to Uranium			
1000/1	100/1	50/1	10/1[a]
Br^-	CSN^-	F^-	$C_2O_4^{2-}$
$C_2H_3O_2^-$			EDTA
Cl^-			I^-
ClO_4^-			
IO_3^-			
$NH_2SO_3^-$			
NO_2^-			
S^{2-}			
SO_3^{2-}			
SO_4^{2-}			

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[a] BrO_3^-, $Cr_2O_7^{2-}$, MnO_4^-, and PO_4^{3-} interfere at 1/1 mole ratio.

analysis, aliquots of a dissolved NBS primary calibration material (SRM 950a U_3O_8) were processed concurrently and sample results were computed relative to the values for the calibration material. The random error, computed from the triplicate sample results, was 0.16% relative standard deviation.

3. **Instrument Evaluation for NBL-Supplied, Low-Level Uranium Samples.** A series of 32 solutions, containing low microgram/milliliter uranium concentrations, was supplied by NBL to evaluate the applicability of the automated spectrophotometer in the microgram-sensitive mode. At NBL, such samples are analyzed by pellet fluorophotometry, which is a highly sensitive but not precise method. The automated spectrophotometer in the microgram-sensitive mode has a range of about 2.5 to 100 μg of uranium in a maximum aliquot volume of 1 ml. The NBL-predicted uranium concentrations for 20 of the 32 samples were below the lower limit of 2.5 μg/ml. Nevertheless, all but seven samples were analyzed by dispensing larger aliquots, as necessary, into the spectrophotometer tubes, evaporating to dryness, and dissolving the residues in 1 ml of 9 M HNO_3. The dispensing of large aliquots followed by evaporation requires insignificant additional labor, but can be technically undesirable. For samples with high concentrations of impurities, the residue formed may not dissolve completely to cause low uranium results. Also, large amounts of some impurity elements may interfere, often by forming suspensions that cloud the organic phase.

Duplicates of each of the 25 samples were analyzed. Because the acid concentrations of the samples were not known, all aliquots were evaporated to dryness in the spectrophotometer tubes, then dissolved in 1 ml of $9M$ HNO_3. Aliquots of a dissolved NBS primary calibration material (SRM 950a U_3O_8) in $9M$ HNO_3 were analyzed concurrently and the results for samples were calculated using the calibration equation computed from the calibration material data. For three samples, suspensions formed. Smaller aliquots were analyzed successfully.

Single aliquots of the 25 samples also were analyzed by isotope-dilution mass spectrometry. With few exceptions, the automated spectrophotometer results agreed well with the isotope-dilution mass-spectrometric results as well as with later NBL-provided values. This agreement is considered notable because the total quantity of uranium analyzed for 13 samples was less than 5 μg, which is toward the lower limit of the method. The standard deviation of the automated spectrophotometer results, calculated from the duplicate analyses, is given in Table IX at four uranium concentration levels. The poorer precision at the 2 to 6-μg/g level is attributed to the high concentrations of impurity elements in these samples. It is likely that improved precision would have been obtained if smaller aliquots had been analyzed.

4. **Commercial Manufacture Status.** United Technical, Concord, Massassachusetts, is considering manufacture of the automated spectrophotometer. Construction information was given to a representative of this company who visited LASL.

B. Automated Controlled-Potential Coulometric Plutonium Analyzer

1. **Method Development. (D. D. Jackson, F. R. Roensch, and J. E. Rein.)** In the past year, three factors were investigated for the controlled-potential coulometric method:[2,5,8] the effect of fluoride, stability of the electrolyte, and calibration of instrument electronics to reduce day-to-day variance. In this method, plutonium is reduced at 0.25 V (vs SCE) to Pu(III) in an electrolyte of $5.5M$ HCl and $0.015M$ sulfamic acid, diverse ions are oxidized at 0.57 V where Pu(III) is not oxidized significantly, phosphate as NaH_2PO_4 is added to lower the Pu(III)-Pu(IV) potential, and Pu(III) is coulometrically

TABLE IX

PRECISION OF AUTOMATED SPECTROPHOTOMETER RESULTS AT VARIOUS URANIUM CONCENTRATION LEVELS

Uranium Concentration (μg/g)	No. of Samples	Standard Deviation (Relative %)
1	6	3.6
2-6	9	10
8-10	7	0.7
>10	3	2.0

titrated to Pu(IV) at 0.68 V. Diverse ion effects for more than 75 metal ions and nonmetal anions were measured.[5,6] Metal ions normally present in nuclear fuel cycle materials do not interfere at an equal mole ratio relative to plutonium. Nearly all interfering anions, including fluoride shown to interfere at a 5/1 mole ratio relative to plutonium, are removed by perchloric acid fuming. Many samples contain lower amounts of fluoride, which, if without effect, means that perchloric acid fuming is not required. At a fluoride to plutonium mole ratio of 0.5/1, equivalent to 10 μmol of fluoride at the usual plutonium measurement quantity of 20 μmol (5 mg), results are low by 0.5%. Fluoride should be considered an interference at all levels so that samples known or suspected to contain fluoride should be fumed before analysis.

The electrolyte of 5.5M HCl and 0.015M sulfamic acid had been prepared by separate additions of each reagent for each analysis. Use of a mixture has the advantage, especially for automated analyzer use, of requiring only one dispenser. A mixture prepared and stored for two months gave results no different from those obtained using separate addition of each reagent for samples containing 1 mmol of HNO_3.

The method is chemically calibrated daily using NBS SRM 949 plutonium metal as the certified reference material. A small but significant day-to-day variance, typically ≤ 0.04%, caused by instability of overall instrument electronics, is essentially eliminated as follows. A 100-ohm resistor is substituted for the cell and a 1-V potential from the potentiostat is applied across it. Time is measured very accurately using a timer with a time base of 10 MHz and a line-voltage stability of $< 1 \times 10^{-5}\%$ for 10% line variation. The calculator controls the coulometer and the timer. The chemical calibration factor is adjusted by the ratio of the number of coulombs measured by the coulometer to the number of coulombs calculated from the time-current measurement.

2. Instrument Construction. (D. D. Jackson and R. M. Hollen.) The first automated controlled-potential coulometric analyzer was completed this period. The instrument's performance is meeting design specifications including a measurement precision of 0.1% relative standard deviation at the 5-mg plutonium level.

The mechanical portion of the instrument is installed in a single LASL-type, sloping, open-front box that is 0.91 m wide, 0.79 m deep, and 0.84 m high. The electronic components are mounted outside the box. Waste solution of about 80 ml per analysis flows through a double tube to easily changed containers mounted outside the box.

The major electronic components of the instrument, shown in Fig. 1, are commercial, which simplifies maintenance. The Hewlett-Packard 9825 programmable calculator controls all mechanical and electrical operations, processes titration data, and outputs results on paper tape. The Princeton Applied Research Corporation 173 Potentiostat-Galvanostat and 179D Digital Coulometer, modified for calculator control, do the electrolysis. Also interfaced and under calculator control are a D to A converter, a digital multimeter, a scanner, a real-time clock, and a digital plotter. The D to A converter provides calculator capability to select electrode potentials. The digital multimeter measures electrolysis conditions of interest and serves as an A to D converter to input data to the calculator. The digital multimeter also monitors interlocks designed to protect the instrument in case of a malfunction. The scanner switches the digital multimeter to the point to be measured. The mechanical operations are controlled through the scanner by contact closure of relays. The real-time clock monitors electrolysis times and, by means of an interrupt system, terminates analyses in which the times exceed those found to affect the determination adversely. The plot of log current vs time provided by the on-line digital plotter allows a trained analyst to spot deviations indicative of a faulty analysis.

The turntable (Fig. 2) holds up to 24 electrolysis cells that rotate to the measurement station. The turntable is rotated by a Geneva-drive, intermittent-motion assembly that provides slow acceleration and accurate positioning. Positional accuracy is further ensured by a cylindrical rod, driven by a pneumatic cylinder, that engages slots in the edge of the turntable at each of the 24 positions.

The electrolysis cells are fabricated from 4.8-cm-diam glass tubing by flame-sealing a flat bottom and grinding the top flat. The electrodes, stirring mechanism, reagent-delivery tubes, inert-gas inlet, and rinsing system are mounted in a rigid Teflon support, shown in Fig. 3. The platinum-gauze working electrode is held in the Teflon support by two 0.14-cm-diam platinum rods that also make elec-

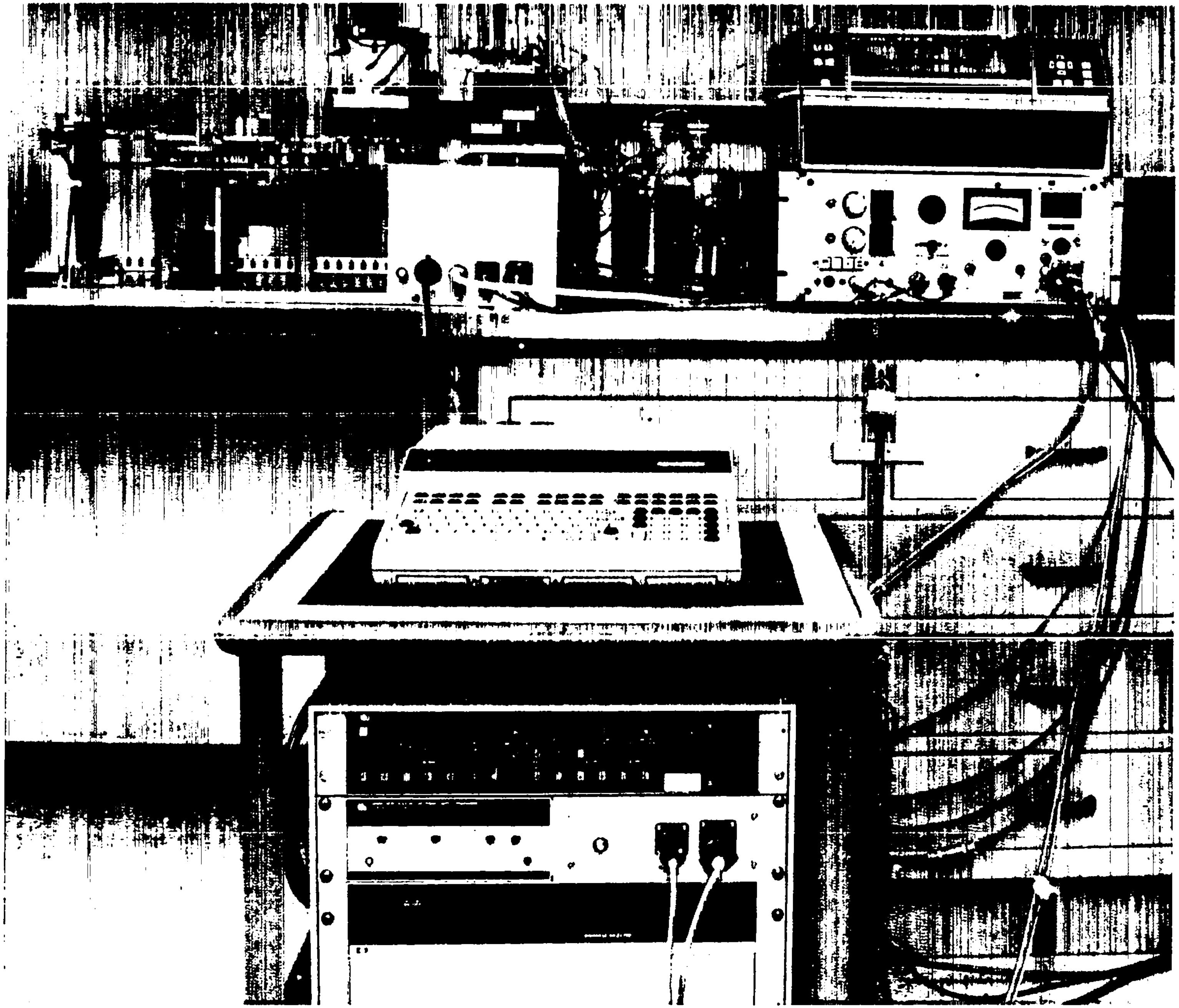

Fig. 1.
LASL-automated controlled-potential coulometer.

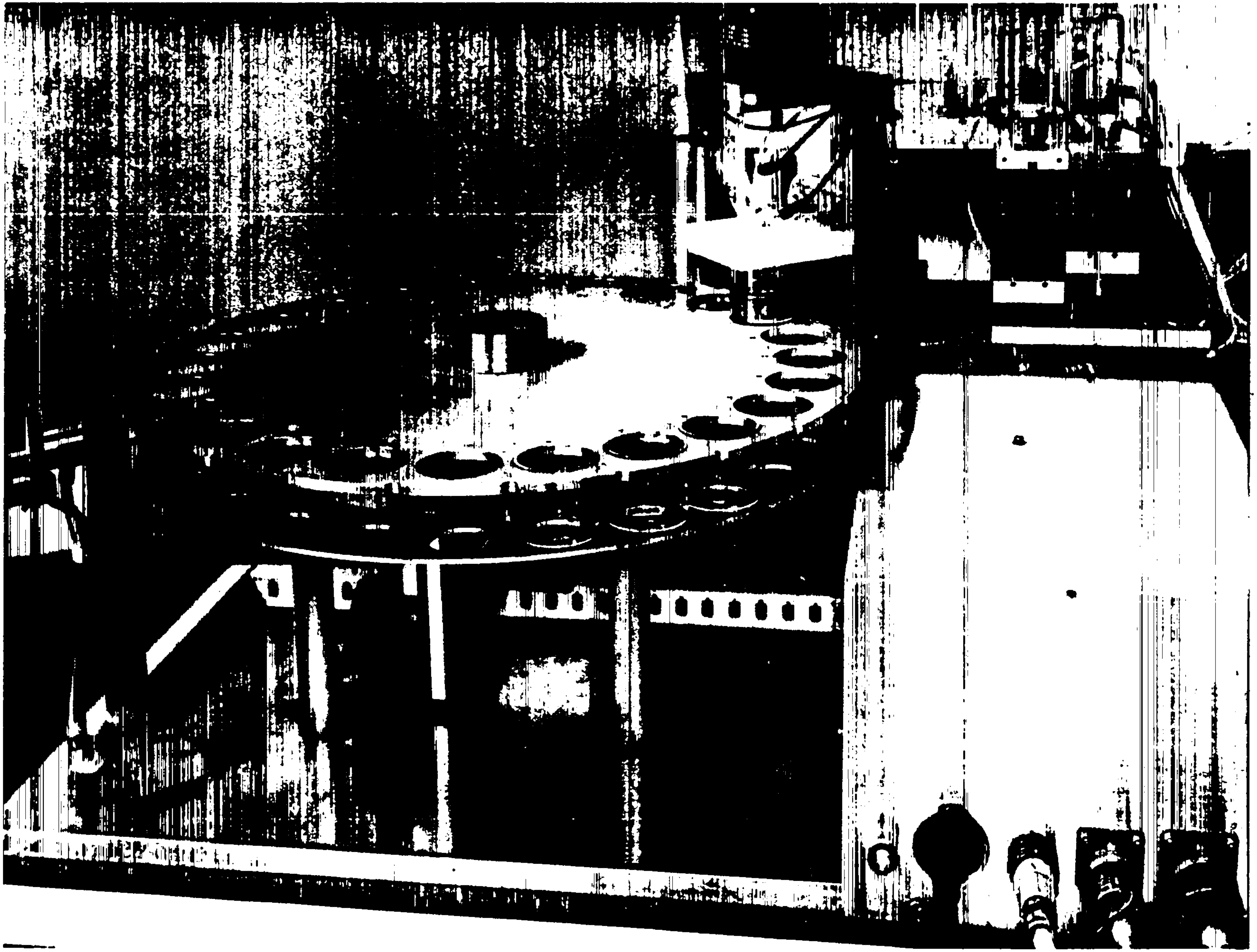

Fig. 2.
Sample transport.

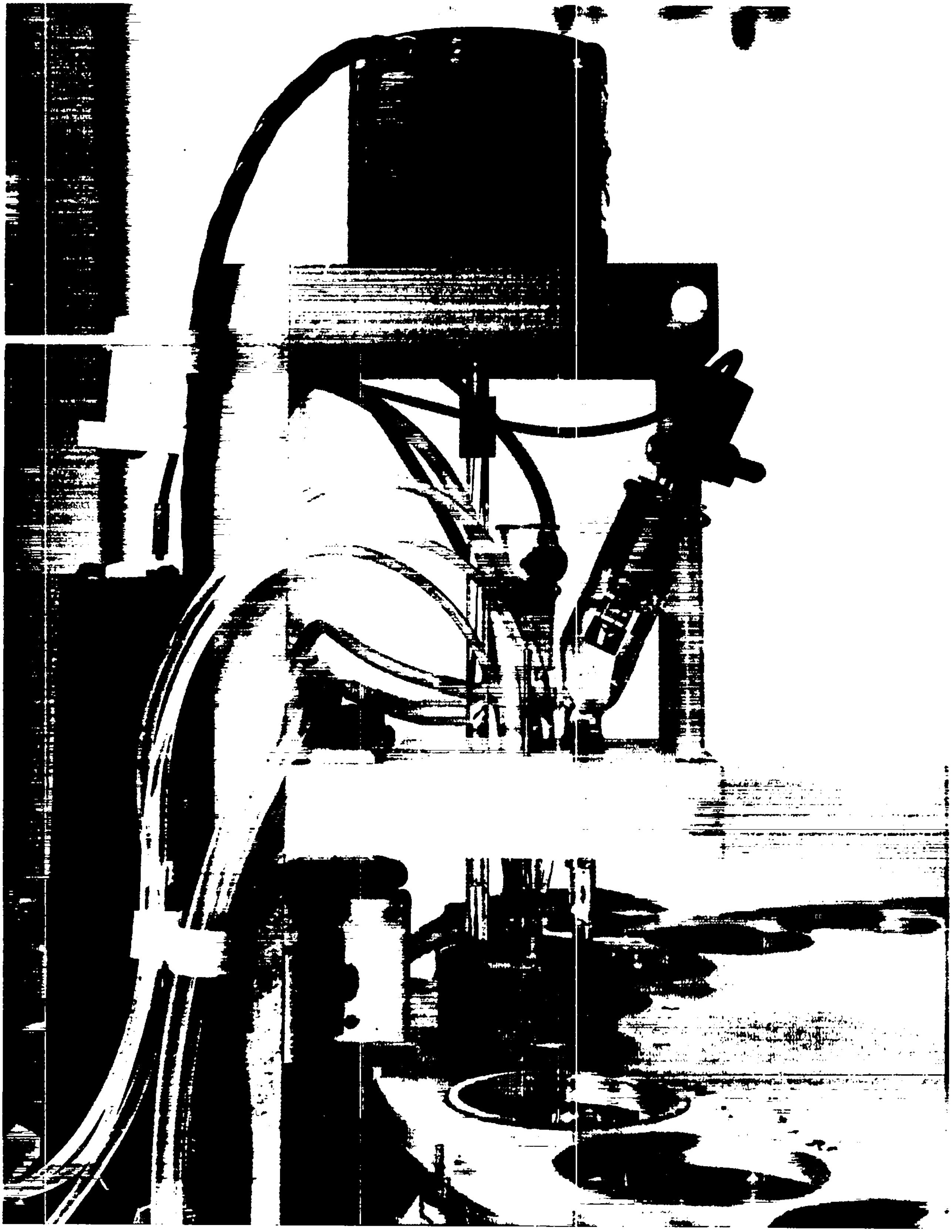

Fig. 3.
Electrolysis assembly.

trical contact. Vycor frits in both the reference electrode and counter electrode bridge tubes provide high electrical conductance with very low electrolyte flow rates. A small paddle stirring rod, made from 0.5-cm-diam glass rod rotated at 1800 rpm, effectively stirs the electrolyte to provide relatively short electrolysis times. The rod fits securely in the Teflon support to avoid eccentric rotation, which could cause splashing and consequent low results.

The electrolysis cells are raised by a hydraulic cylinder and a guide (Fig. 4) to form an airtight seal against the Teflon support and to position the various components reproducibly. A low-torque, lever-actuated switch senses when a cell is not positioned correctly and triggers an operation stop to avoid damage to the potentiostat and sample transport system.

The analyzed sample and rinse solution are withdrawn by suction through a Teflon guide tube mounted in the support (Fig. 5). The aspiration tube is driven by a pneumatic-cylinder mechanism to an exact position at the bottom of the cell near the platinum-gauze electrode for efficient removal of the liquid. Two consecutive rinses, each with about 25 ml of $5.5M$ HCl, leave less than 0.01% of the previous sample. The rinse is added by a positive-displacement pump constructed so that the corrosive acid solution contacts only inert materials.

Two reagent dispensers (Fig. 6) deliver 20 ml of the $5.5M$ HCl-$0.015M$ sulfamic acid electrolyte and 5 ml of $5M$ NaH_2PO_4. A pneumatic-hydraulic cylinder drives a gas-tight syringe in conjunction with a pneumatic cylinder that operates a three-way valve. These dispensers are patterned after those used successfully in the LASL-automated spectrophotometer.[3] The only materials contacting the corrosive reagents are glass and Teflon. Precision deliveries, determined by weighing dispensed quantities of the two solutions, are better than 0.01% relative standard deviation.

All mechanical operations of the instrument are controlled by photoisolated relays actuated by the calculator through the scanner. These relays avoid interference of logic level signals and of the potentiostat caused by voltage transients generated by the power solenoids. Figure 7 shows some of the photoisolated relays and power solenoids that control the mechanical operations.

A small scanner assembly, consisting of a light and phototransistor mounted in the same housing, detects the last cell. After the last cell is rinsed, electrolyte is added to keep the electrodes immersed in solution and the instrument is stopped.

Sensors and interlocks incorporated in the automated instrument minimize the possibility of damage or an incorrect analysis caused by a malfunction. The action taken after sensing a problem depends on the nature of the difficulty. If continued operation might damage the instrument, it is turned off; if it would only affect the sample being analyzed, that sample is bypassed and the automated operation continues. For example, if the turntable fails to rotate correctly, operation of the instrument is stopped. No reagents will be dispensed and the sample is bypassed if a cell fails to raise. Instrument operation stops if a cell fails to lower. Excessive voltage output from the potentiostat, as could result from failure of the reference electrode or a break in the cell electrical leads, turns off the potentiostat. An excessively long electrolysis time, which can affect results adversely, stops the analysis of that sample and sequences operation to the next sample.

Separate calculator programs are used for samples and for blank electrolyte measurements. The blank coulomb value at an elapsed time equal to that for each sample analysis is used in the results calculation.

Detailed engineering drawings of the mechanical portion of the automated instrument are nearly complete and drawings of the electronic portion will follow.

C. Microcomplexometric Titration of Uranium (S. F. Marsh, M. R. Betts, D. D. Jackson, and J. E. Rein)

A microcomplexometric-titration method, based on titrating the intensely colored arsenazo I - U(IV) complex with dipicolinic acid, is promising for determining microgram, as well as higher amounts, of uranium. An automated, versatile titration apparatus consisting of low-cost commercial components has been improved by addition of a programmable calculator.

Our earlier efforts to titrate the xylenol orange-(U(IV) complex with the strong complexing agent diethylenetriaminepentaacetic acid (DPTA) were not successful because a consistently reliable system was not found to reduce and hold the uranium as

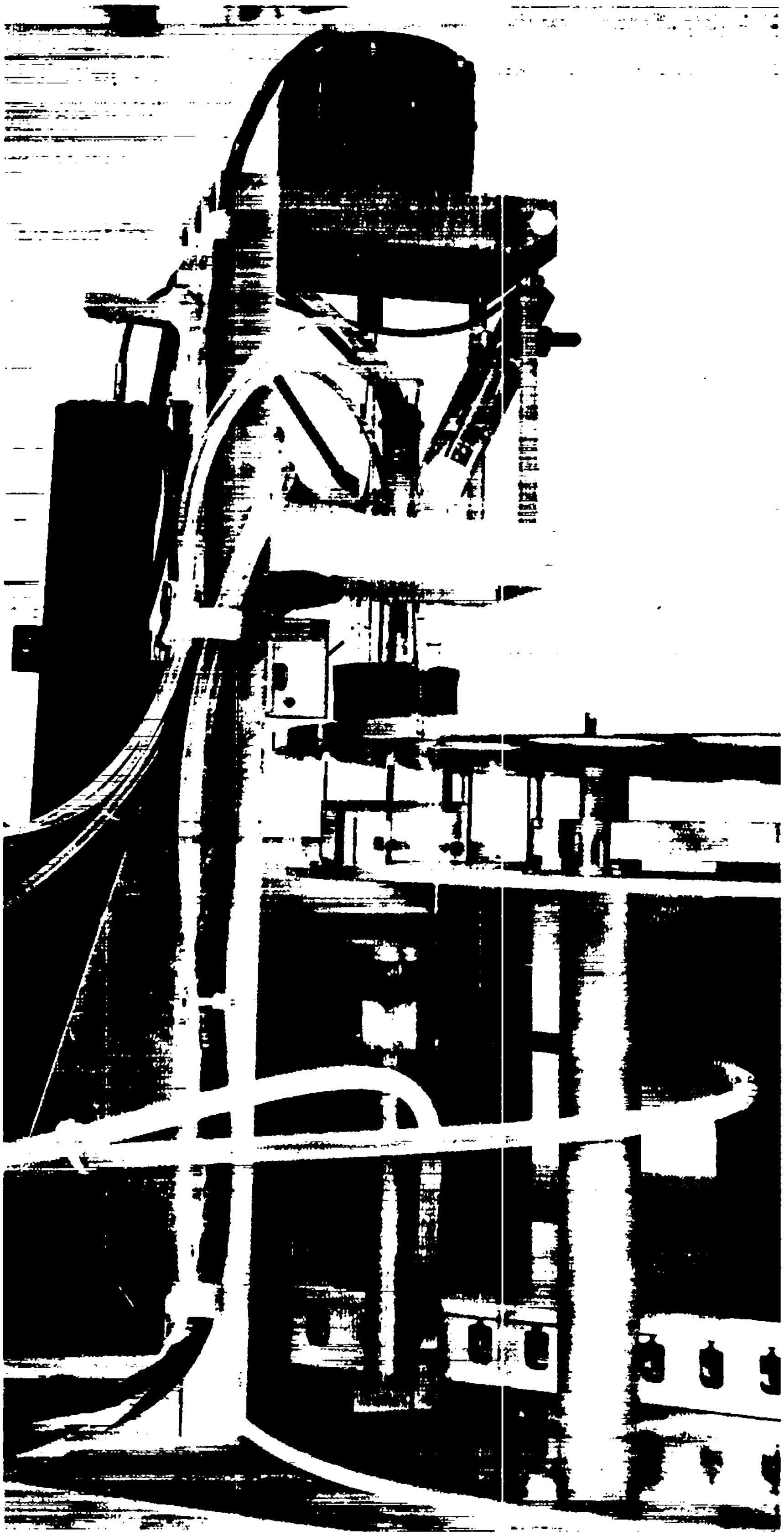

Fig. 4.
Cell-raising mechanism.

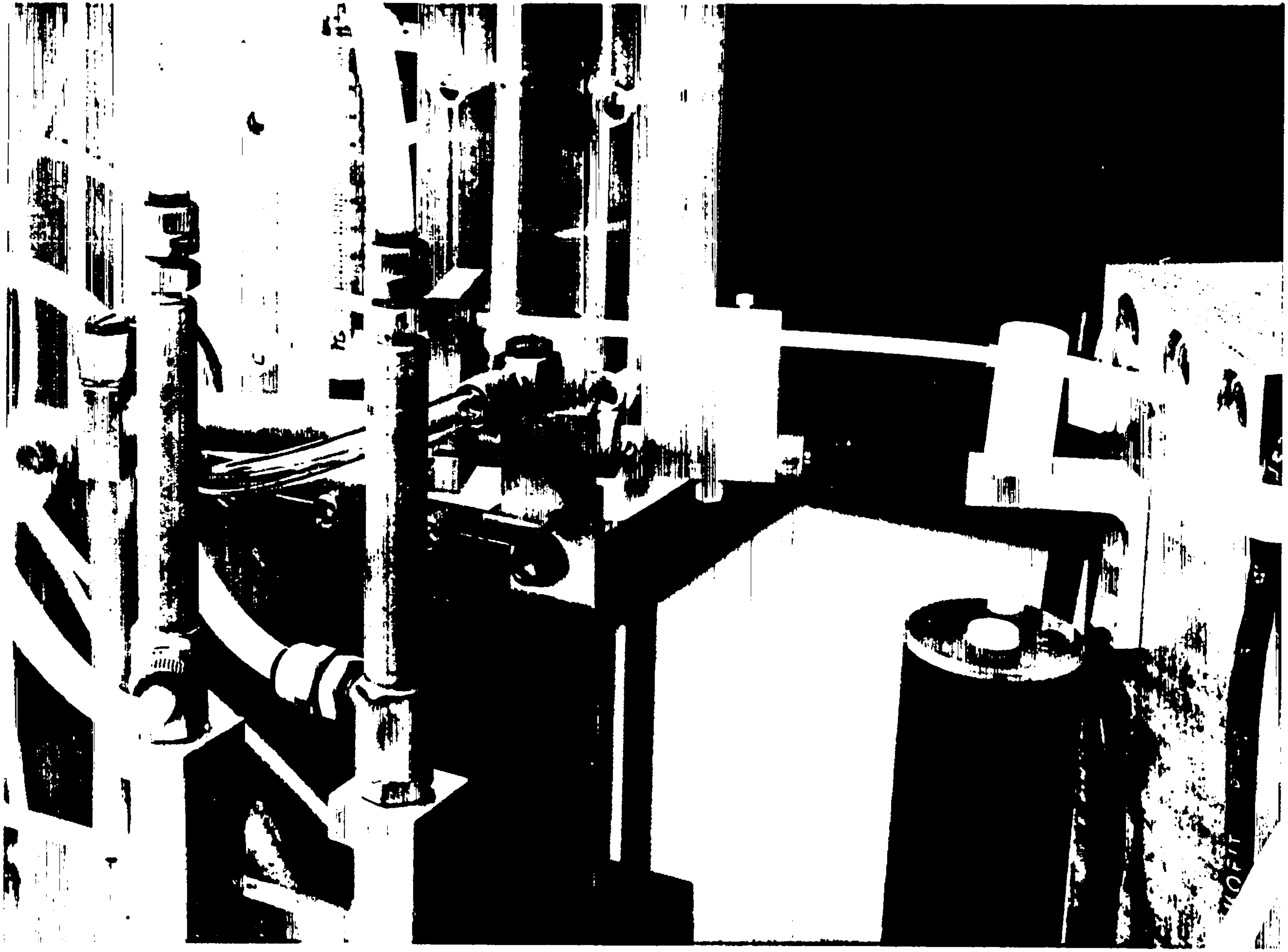

Fig. 5.
Rinsing mechanism.

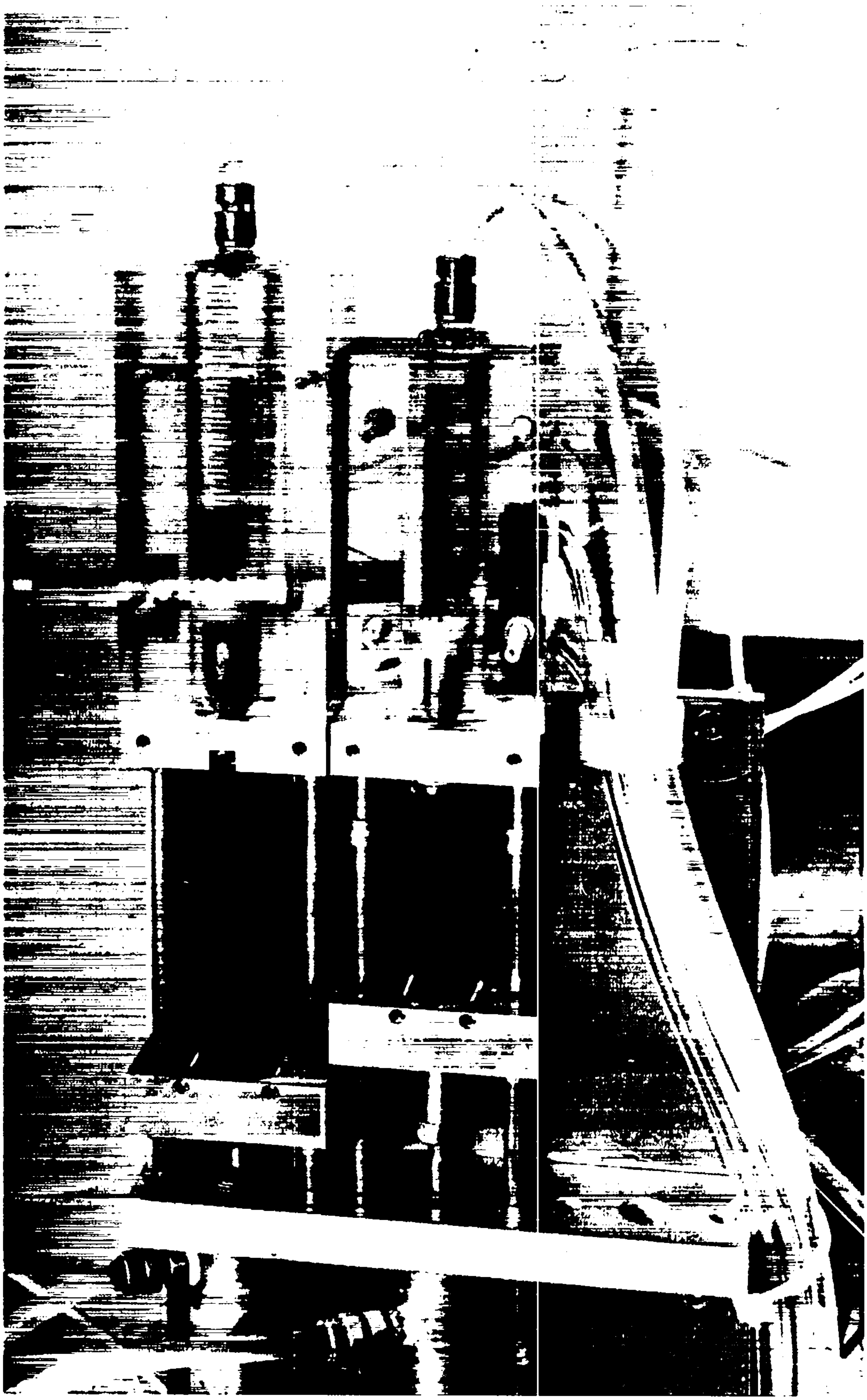

Fig. 6.
Reagent dispensing system.

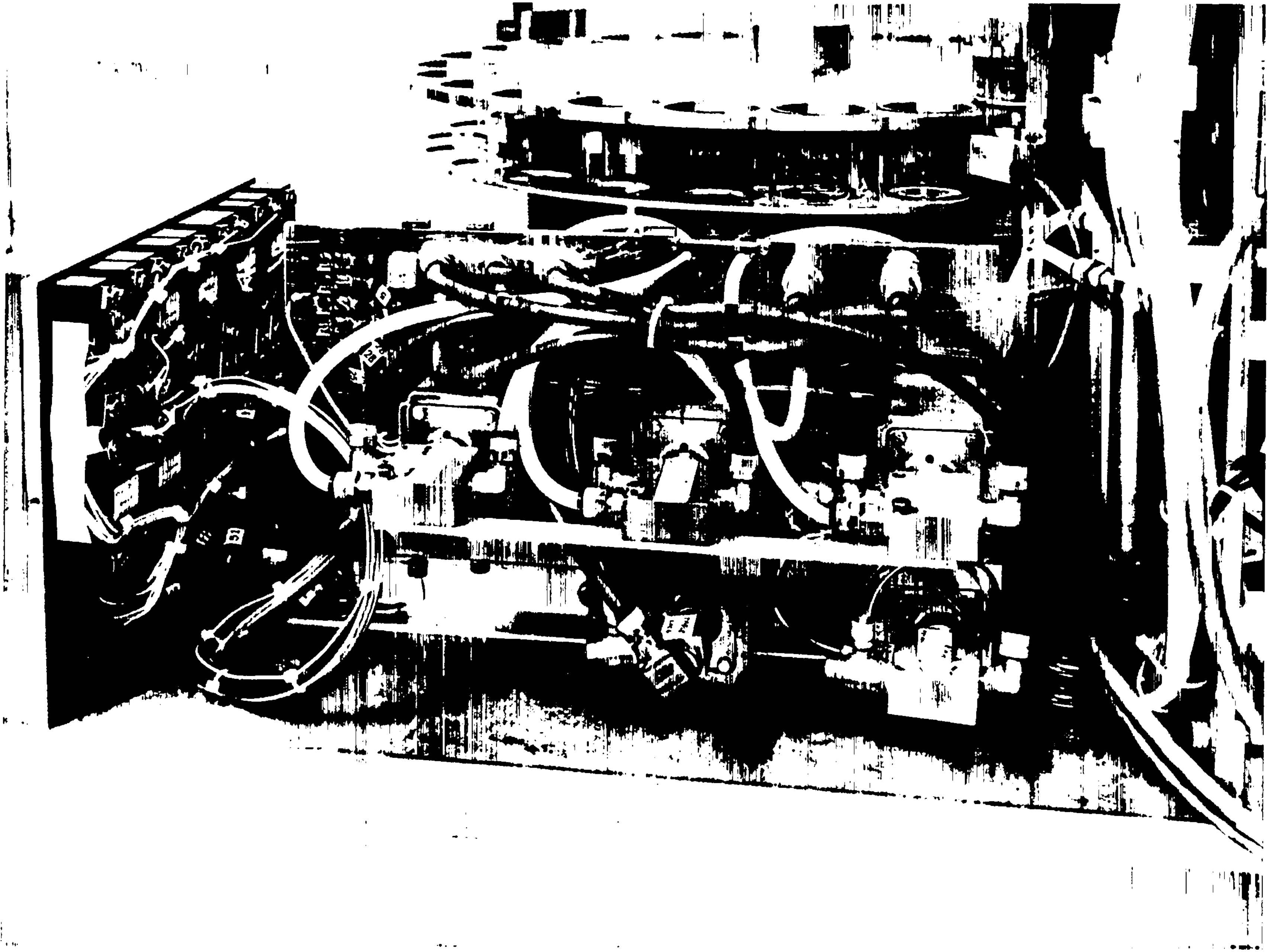

Fig. 7.
Control system for mechanical components.

U(IV). A more selective procedure, recommended for milligram levels of uranium,[7] is under investigation. It is based on titrating the intensely colored arsenazo I - U(VI) complex with dipicolinic acid (pyridine - 2, 6 - dicarboxylic acid), which forms a complex with U(VI). The recommended pH of 3.6 was attained with an acetate buffer. As this pH is below the optimum range of acetate buffering, other buffer systems over a wide pH range were investigated. Hexamethylenetetramine buffer at pH 4.9 increased the sensitivity threefold and sharpened the endpoint to provide titration of low-microgram uranium levels. Additional selectivity has been gained by use of the two masking agents cyclohexanediaminetetraacetic acid (CDTA) and diethylenetriaminepentaacetic acid (DTPA). One ml of a $3M$ hexamethylenetetramine - $0.11M$ CDTA - $0.05M$ DTPA - 0.025 wt% arsenazo I mixture is added to the sample, the solution is diluted to 25 ml with water, and the U(VI) is titrated with 1 mM dipicolinic acid.

The automated titration apparatus, consisting of low-cost commercial components, has been advanced by addition of a programmable calculator. Titrant is delivered by a motor-driven, micrometer, digital-output pipet. An absorbance measuring probe immersed in the solution is connected to a filter colorimeter by a fiber-optics light guide. White light transmitted through one-half of the light guide passes through a 2-cm path length of solution at the probe and back to the colorimeter through the other half of the light guide. Prior to the addition of the programmable calculator, the absorbance output of the colorimeter was produced on a stripchart recorder. Both the micrometer pipet and recorder are driven in synchronism by precision stepping motors from a preset index/controller to provide a plot of changing absorbance directly related to titrant volume. The inflection or endpoint was determined graphically.

A programmable (Hewlett Packard 9820A) calculator controls all mechanical operations, processes the titration data, and prints the endpoint results. A 0.01-ml titrant increment is added and a digitized voltage signal from the colorimeter detector, proportional to absorbance, is stored. A data-smoothing routine is sequentially applied to the last five stored values to give a smoothed value that is stored. This data treatment continues until the approximate endpoint, based on a preset slope change, is reached. A preset number of 0.01-ml titrant increments then is added to complete the titration. Values at preset intervals before and after the approximate endpoint are fitted to least squares lines. The endpoint is calculated as the intersect of these two lines and is printed in units of volume or millimoles of titrant.

Measurement precision for 30 to 180 μg of uranium is $< 0.4\%$ relative standard deviation. Analysis time is ≤ 20 min. A comprehensive study of diverse ion effects is under way. Preliminary results show high tolerance for iron, rare earths, thorium, and zirconium.

D. Microgram-Sensitive Spectrophotometric Determination of Plutonium (S. F. Marsh, N. M. Saponara, and J. E. Rein)

Development of an extraction-spectrophotometric method that can be used with the LASL-automated spectrophotometer has been initiated for determining microgram levels of plutonium. To be usable without major instrument modification, all operations must be done in a tube without any removal of solution. The desired system operations are additions of reagents and an organic solvent to the tube containing the sample, extraction of a plutonium complex into the organic solvent that disengages as a clear phase above the aqueous phase, and absorbance measurment without a reference tube comparison. Other objectives are: specificity to provide applicability to scrap materials containing high levels of diverse components relative to plutonium, sensitivity to determine low microgram amounts of plutonium, and $> 99\%$ extraction of plutonium, to provide a reliability of at least 5%. An extensive literature review failed to disclose a completely applicable method.

The choice seems limited to extraction of plutonium complexes in which the oxidation state of plutonium is either (IV) or (VI). The former has a likely disadvantage of interference from many metal impurities present in scrap materials such as the transition and periodic group IV metal ions. The latter probably will require a strong holding oxidant that may destroy the organic chromagen and also will be subject to uranium interference.

The first method investigated was the microgram-sensitive method used to determine uranium with the automated instrument (Sec. III. A.1). The U(VI) benzoyltrifluoroacetone (BTFA) complex is extracted into butyl propionate from an aqueous phase that is pH-buffered and contains Mg-cylohexanediaminetetraacetic acid (Mg-CDTA) as a masking agent to inhibit the extraction of other metal ions. Silver monoxide, silver-catalyzed persulfate, and bismuthate oxidants that are known to oxidize plutonium to Pu(VI) were tested. No extractable Pu(VI)-BTFA complex formed. Apparently, the strong formation constant of the Pu(IV)-CDTA complex shifted the potential of the Pu(IV) - Pu(VI) couple to the lower oxidation state.

It now appears unlikely that a method can be developed in which a Pu(VI) complex is selectively extracted into an organic phase. Emphasis, therefore, is being placed on extraction of an intensely colored and highly stable complex into an organic phase, preceded by a chemical separation of plutonium to attain selectivity. An advantage can be that chemical treatment is not necessary to adjust the oxidation state of plutonium to (IV). For example, Pu(III) is reported to convert quantitatively to Pu(IV) in the presence of the moderately strong complexant arsenazo I.[8]

The chromotropic acid - biazo type complexants, which form intensely colored and strong Pu(IV) complexes, are being considered first. Of these, the Pu(IV) - chlorophosphonazo III (CPA) complex appears to extract most completely. Yamamoto[9] reports that the CPA complex of U(IV), expected to be similar in chemical behavior to Pu(IV), extracts into 3-methyl-1-butanol from 1.5 to 3*M* HCl. Because a glove box containing a spectrophotometer was not available at the outset, Th(IV) was substituted for Pu(IV). Of five alcohol extractants evaluated, color intensity was higher and phase disengagement was better for pentanol, isopentanol, and hexanol than for cyclohexanol and p-methyl hexanol from 1 to 2*M* HCl.

Mixtures of plutonium initially in the (III), (IV), and (VI) oxidation states and CPA at HCl molarities of 1, 1.5, and 2 were mixed with equal volumes of the three selected alcohols for time periods of 2, 5, and 10 min in a 48-rpm inverstion rotator. The percentages of plutonium extracted (Table X) were measured by alpha counting the aqueous phases before and after extraction. Highest extraction, >99.5%, of the Pu(IV) - CPA complex was attained with n-pentanol at HCl molarities of 1.5 and 2. In the 10-min extraction time, conversion of Pu(III) to Pu(IV) was not sufficiently complete for analytical usefulness. An oxidation pretreatment using $NaNO_2$ was adopted to place all plutonium in the (IV) and (VI) oxidation states. A HCl molarity of 1.5*M* was adopted because extraction of the Pu-CPA complex was highest for plutonium initially present in the (VI) oxidation state.

TABLE X

PERCENT EXTRACTION OF THE Pu(IV) - CPA COMPLEX

Initial Plutonium Oxidation State	HCl *M*	Percent Plutonium Extracted								
		n-Pentanol			Isopentanol			n-Hexanol		
		2 min	5 min	10 min	2 min	5 min	10 min	2 min	5 min	10 min
(III)	1.0	80.6	98.0	98.6	87.9	97.1	97.9	76.5	90.7	93.6
(III)	1.5	72.4	97.1	98.0	93.8	98.9	97.3	84.5	96.1	95.7
(III)	2.0	65.9	98.3	96.1	95.2	98.8	98.3	84.6	96.2	94.5
(IV)	1.0	97.5	99.1	99.3	96.3	98.1	98.4	83.3	89.1	93.3
(IV)	1.5	99.1	99.5	99.6	99.1	99.2	---	95.5	97.0	98.0
(IV)	2.0	99.5	99.7	99.8	99.4	99.4	99.2	97.8	98.0	98.1
(VI)	1.0	97.7	97.9	99.0	95.5	96.7	98.2	86.2	97.0	93.1
(VI)	1.5	95.0	97.6	99.4	97.7	98.9	98.5	93.8	95.6	96.1
(VI)	2.0	75.0	97.1	97.7	83.7	98.9	98.4	84.6	95.5	94.5

A spectrophotometer was constructed and installed in a glove box. Absorbances of the disengaged n-pentanol phases containing the extracted Pu(IV) - CPA complex were measured in 1.6-cm-i.d. tubes fabricated from Trubore tubing. These tubes have variable wall thickness that causes error when only the peak absorbance at 673 mm is used as the measure of the plutonium concentration. (The design of the LASL-automated spectrophotometer precludes a cell blank measurement.) To correct for variable wall thickness of cells, the absorbance difference at two wavelengths is used, one near the peak and the other near an adjacent valley. Wavelengths of 680 and 710 mm were adopted for highest precision and least effect from diverse ions. The relative standard deviation, using this two-wavelength measurement and random positioning of tubes, is 2.5% for 2.5 to 10 μg of plutonium and 5% for 1 μg of plutonium

Development of a chemical separation to precede the spectrophotometric measurement is under way. Anion exchange of Pu(VI) in 12*M* HCl medium followed by elution of Pu(III) with a 12*M* HCl - 0.1*M* HI mixture is being evaluated first.

E. Determination of Trace Uranium in Plutonium (S. F. Marsh)

An important impurity in pure plutonium metal, including NBS SRM 949, is uranium, produced mainly as daughters of the 238, 239, 240, and 242 plutonium isotopes. An effective separation procedure has been developed that provides a pure uranium fraction suitable for analysis by various techniques. We have used it in conjunction with isotope-dilution mass spectrometry as described below. The basis of the separation scheme is a spin-off from one of our past investigations of ion exchange systems.[10]

Major steps in the procedure are the (1) dissolution of plutonium metal sample in 9*M* HBr with a ^{233}U spike aliquot present, (2) addition of a small quantity of Br_2 to oxidize uranium to U(VI), (3) passage of the solution through a column of anion exchange resin that has been equilibrated with 9*M* HBr on which U(VI) is sorbed strongly and Pu(III) is not sorbed, (4) elution of the Pu(III) with 9*M* HBr followed with a 0.1*M* HI-12*M* HCl mixture, (5) elution of the uranium, still as U(VI), with 0.1*M* HCl, and (6) mass-spectrometric measurement of the uranium sample quantity relative to the added ^{233}U spike.

F. New Reagent for Plutonium Separation (S. F. Marsh and M. R. Betts)

J. S. Fritz of the Ames Laboratory synthesizes a wide variety of organic reagents that he applies to inorganic analysis. Because the Ames Laboratory has no plutonium facility, Fritz is providing us with selected reagents to evaluate their usefulness for plutonium analysis.

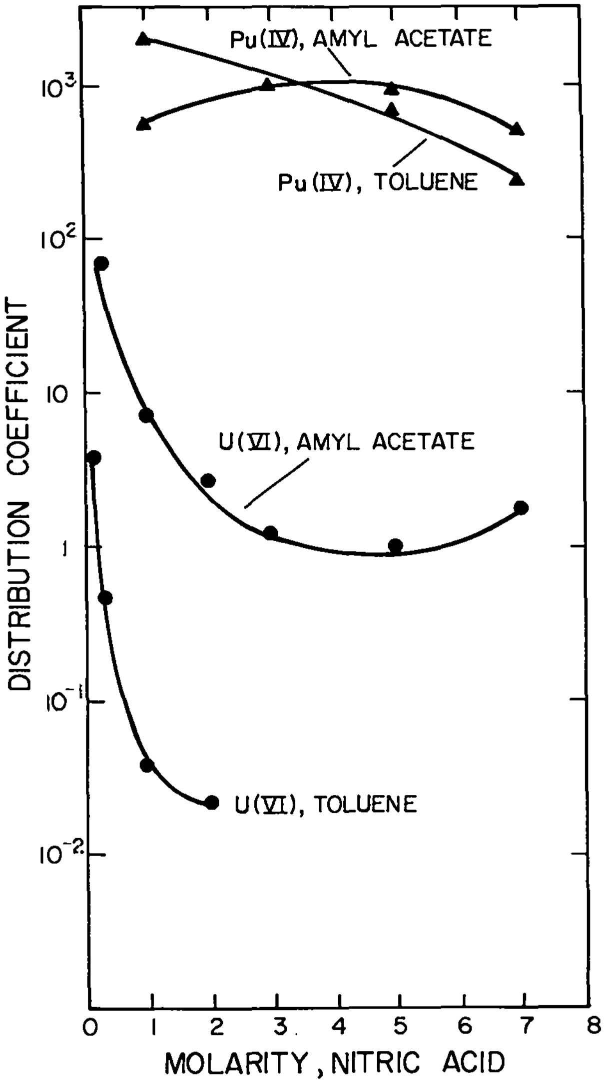

Fig. 8.
Extraction of U(VI) and PU(IV) into 0.1M PMBP diluent from nitric acid.

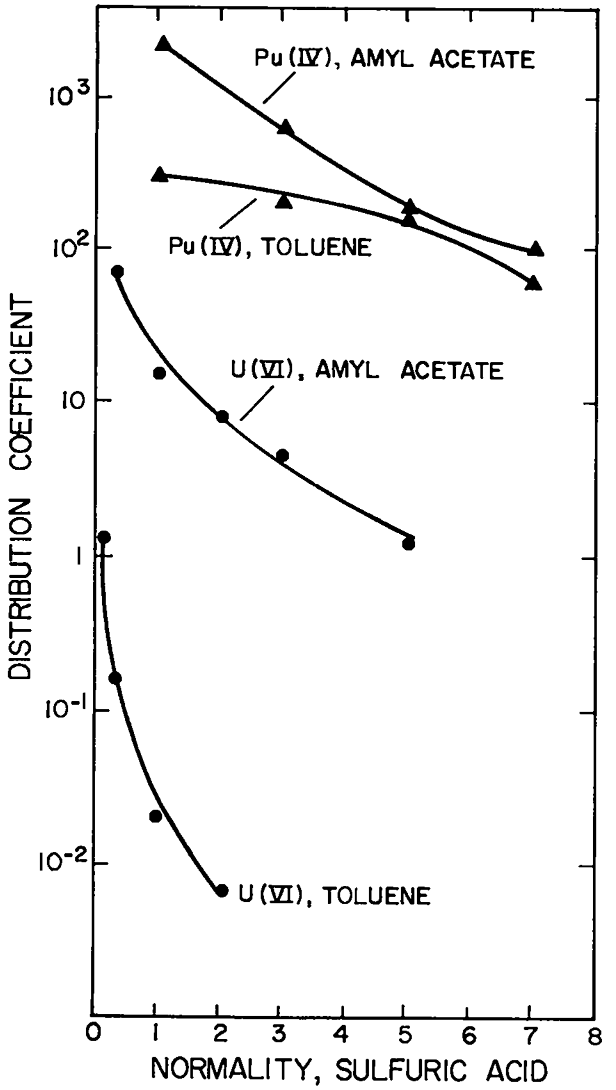

Fig. 9.
Extraction of U(VI) and Pu(IV) into 0.1M PMBP diluent from sulfuric acid.

The first reagent provided, 1-phenyl-3-methyl-4 benzylpyralazone (PMBP), is promising for the separation of plutonium and uranium. Distributions were measured for 0.1M PMBP in toluene and in amyl acetate from 0.1 to 7*M* HNO_3 and from 0.1 to 7*N* H_2SO_4 (Fig. 8 and 9). Distribution coefficients for plutonium were $> 10^4$ those of uranium for many conditions, with highest separations obtained with toluene as the solvent.

Fritz has supplied a chelating resin with PMBP incorporated as a functional group to evaluate column separations.

G. Titration of Thorium (P. Kiefer, S. F. Marsh, and J. E. Rein)

The objective of this task is to develop highly reliable titrimetric methods for determining microgram to milligram amounts of thorium that are applicable to fuel cycle materials. Because many materials contain a wide variety of elements, highly selective methods are desired. Another factor considered is method applicability to the automated titration apparatus described for the microcomplexometric titration of uranium (Sec. III. C).

The initial method developed was a microcomplexometric titration of the Th(IV) - xylenol orange complex with DTPA in 0.05*M* HBr medium.[2] Although the endpoint is sharp to provide better than 1% relative standard deviation at the 100-μg thorium level, the method is not selective. To attain selectivity, modifications of this method as well as other complexometric titrations are being investigated. Because evidence is mounting that a highly selective titration method for thorium may not be attained, development of a selective chemical separation of thorium followed by its complexometric titration is under way.

The addition of cetyltrimethylammonium bromide was incorporated in a recently published spectrophotometric method based on measurement of the absorbance of the Th(IV) - xylenol orange complex.[11] It provides color development. at lower pH where fewer diverse metal ions interfere. Its addition in titrimetric systems with DTPA and other complexants prevents formation of a discernible endpoint. It is believed that the Th(IV) - xylenol orange - cetyltrimethylammonium bromide complex is sufficiently stable to not be displaced by the titrant.

Semi-xylenol orange, an impurity in the commercial xylenol orange reagent, is claimed to provide more sensitive and selective complexometric titrations of thorium.[12,13] However, there no longer appears to be a commercial source. If not found, the need to synthesize it makes its application unfeasible.

A claimed selective method for thorium is titration of the bromophenol blue or bromochlorophenol blue complex with aspartic acid.[14] Using the recommended procedure, we were not able to obtain satisfactory endpoints with the bromophenol blue complex. Bromochlorophenol blue has been ordered.

A review of chemical separation systems indicate that extraction into a thenoyltrifluoracetone - organic diluent will separate thorium from diverse ions most effectively. Separation of thorium from all would-be interfering ions in the Th(IV) - xylenol orange - DTPA titration appears obtainable by controlling the acid levels of the extraction of thorium into an organic phase and its stripping into an aqueous phase.[15] An experimental evaluation is under way.

IV. EVALUATION OF THE CHEMISTRY PRECEDING THE MASS-SPECTROMETRIC, ION-EXCHANGE-BEAD TECHNIQUE (S. F. Marsh, M. R. Betts, R. M. Abernathey, and J. E. Rein)

The mass-spectrometric, ion-exchange-bead technique, developed at the Oak Ridge National Laboratory (ORNL)[18] is being evaluated by ORNL and the International Atomic Energy Agency (IAEA) Safeguards Laboratory for determining uranium and plutonium in reprocessing plant input samples. Our preliminary investigations showed that the sorption of plutonium onto Dowex-1 x 2, 50-100 mesh beads from 8*M* HNO_3 was slow, being 30% complete in 15 min and 75% complete in 4 days.[2] In the intended application of the technique, a plutonium spike isotope of ^{242}Pu or ^{244}Pu and a uranium spike isotope of ^{233}U are to be added to the sample aliquot to provide isotope dilution analysis of the plutonium and uranium quantities. Attainment of accuracy requires that equal fractions of the sample and spike isotopes are sorbed on the ion beads. This necessitates their chemical identity, because the total sorption of uranium and plutonium are considerably below 100%. The attainment of chemical identity for uranium isotopes can be expected because only the stable U(VI) ion should be present. Plutonium in HNO_3 media, however, exists in at least the (IV), (V), and (VI) oxidation states, each of which has a different distribution coefficient for the ion exchange resin. We are investigating chemical treatments that will ensure chemical identity and equal sorption of plutonium isotopes.

Four reduction-oxidation systems were evaluated initially. The three reductants were: 0.25*M* Fe(II) in 1*M* sulfamic acid, 1*M* hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), and 1*M* sodium sulfite (Na_2SO_3) followed by oxidation with 1*M* sodium nitrite ($NaNO_2$). The fourth system was 30% hydrogen peroxide (H_2O_2) reduction followed by addition of Fe(III) as a catalytic oxidant. One-ml solutions containing 15 μg of Pu(VI) and 1.5 mg of U(VI), simulating a typical dissolved PWR fuel having a uranium-to-plutonium ratio of 100, were reacted with 0.1 ml of the various reductants for 20 min at 60°C, then with 0.3 ml of 1*M* $NaNO_2$ for 10 min at 60°C, or with added trace Fe(III) for the H_2O_2 reaction. Each of the four treatments was done at HNO_3 levels of 1, 2, 3, and 4*M*. The percentage of Pu(IV) produced was measured by the quantity of plutonium extracted into 0.5*M* thenoyltrifluoroacetone (TTA)-xylene, which extracts only Pu(IV) from acidic media. When adjusted for the decrease in extraction efficiency at the higher acidity levels, the results showed that only the Fe(II) in sulfamic acid reduction-$NaNO_2$ oxidation gave > 99% formation of Pu(IV) over the 1 to 4*M* HNO_3 range. The Pu(IV) formations with the $NH_2OH \cdot HCl$-$NaNO_2$ and Na_2SO_3 - $NaNO_2$ systems were less than 50% from 1 to 4*M* HNO_3. The Pu(IV) formation with the H_2O_2 - Fe catalyst system was less than 50% at the lower HNO_3 levels with a trend of increasing formations with increasing acidity.

In a second set of experiments, the solutions resulting from various reduction-oxidation treatments were contacted with resin beads, and the liquid phases before and after contact were assayed for plutonium content by liquid scintillation alpha counting as the measure of plutonium sorption. The experimental conditions were similar to those used in the initial experiments except that the 15 μg of plutonium consisted of 7.5 μg of ^{239}Pu in the (III) oxidation state and 7.5 μg of ^{242}Pu in the (VI) oxidation state. Although the $NH_2OH \cdot HCl$ - $NaNO_2$ system gave < 50% formation of Pu(IV) in the initial experiment, its evaluation was continued because it is commonly used in radiochemical procedures to produce Pu(IV). Evaluation of the Na_2SO_3 - $NaNO_2$ system was not continued. The acid levels of the reactions were extended to 6 and 8*M* HNO_3; and the H_2O_2 - Fe catalyst system, indicated to form Pu(IV) effectively at higher acidity based on the initial experiment, was evaluated only at the 4, 6, and 8*M* HNO_3 levels. After the reduction-oxidation reactions, the solutions were adjusted to 8*M* HNO_3 and shaken with 100 mg of macroporous, 50-100 mesh, nitrate-converted anion-exchange resin for 30-min and 20-h periods. The results are given in Table XI.

TABLE XI

SORPTION OF PLUTONIUM ONTO MACROPOROUS, 50-100 MESH, NITRATE-CONVERTED, ANION-EXCHANGE RESIN AFTER VARIOUS REDUCTION-OXIDATION REACTIONS AT ACID LEVELS FROM 1 TO 8*M* HNO_3

	α Activity Ratio, Plutonium on Resin/Plutonium in Liquid Phase					
	Fe(II) in Sulfamic Acid - $NaNO_2$ System		$NH_2OH \cdot HCl - NaNO_2$ System		H_2O_2 - Fe System	
HNO_3 Molarity	30-min Reaction	20-h Reaction	30-min Reaction	20-h Reaction	30-min Reaction	20-h Reaction
1	1500	4000	---	---	---	---
2	2000	4500	200	200	---	---
3	2000	5000	100	100	---	---
4	2000	4000	100	100	30	1000
6	2000	6000	100	100	600	3000
8	2000	8000	100	100	900	2000

A difficulty in interpreting the results of this experiment is the conversion of the measured α activity ratios to percentages of plutonium sorbed and unsorbed on the resin. Equal weights of the ^{239}Pu isotope as Pu(III) and ^{242}Pu as Pu(VI) were used. The specific activity ratio of $^{242}Pu/^{239}Pu$ is 16. Thus, measured α activity ratios of 100, 1000, and 8000 could, in the extreme case, represent complete sorption of the initial ^{239}Pu(III), and leave 17, 1.7, and 0.2%, respectively, of the initial ^{242}Pu(VI) unsorbed.

The results generally agree with the initial experiment results. The Fe(II) in sulfamic acid - $NaNO_2$ system at all acid levels and the H_2O_2 - Fe catalyst system at high acidity are effective treatments, especially for 20-h reactions. The effectiveness of the $NH_2OH \cdot HCl - NaNO_2$ system is questionable.

A more definitive experiment is under way. Experimental conditions are those used for the second experiment with only 3*M* and 8*M* HNO_3 levels and the incorporation of isotope-dilution mass spectrometry to establish the individual sorptions of the initial ^{239}Pu(III) and initial ^{242}Pu(VI). Following the ion exchange reactions, ^{244}Pu is added to aliquots of the aqueous phase and the unsorbed quantities of ^{239}Pu and ^{242}Pu are determined. To more closely simulate the operating conditions expected to be used for irradiated fuel samples, the quantity of ion-exchange resin in each experiment is 100 beads. This corresponds to uptake of 0.15 μg of plutonium per bead at 100% sorption.

V. ISOTOPE CORRELATION TECHNIQUES (J. E. Rein and G. R. Waterbury)

A meeting dedicated to a consideration of isotope correlation techniques to verify plutonium input to a reprocessing plant was attended at the Brookhaven National Laboratory, June 18-19, 1979. Our personal conclusions are quite consistent with the concensus of the attendees. Isotope correlation techniques, which relate the plutonium-to-uranium ratio in a fuel assembly to some function of uranium and plutonium isotopic values, have 95% confidence limit uncertainties of 5 to 10% and require a large data base. Further, the relationships are not universally applicable. They appear unique for each reactor and are affected by geometric location as well as initial uranium enrichment in the fuel. Because of the large uncertainty, isotope correlation techniques will not serve for IAEA verification of the reprocessing plant's measurement of the plutonium quantity input over a designated campaign. This appears attainable only by independent chemical assay analysis of replicate samples from the accountability tank combined with a verification of the tank content.

The state-of-the-art assay technique for accountability tank samples is isotope-dilution mass spectrometry. None of various proposed alternate measurement techniques seemed capable of providing plutonium and uranium assays as accurate as are obtained by isotope-dilution mass spectrometry and considerably less accurate uranium and plutonium isotopic distribution measurements. Measurement techniques considered were x-ray fluorescence and absorption-edge densitometry, atomic fluorescence, ion-cyclotron resonance, neutron-resonance transmission, and lead slowing-down time spectrometry. Further, several require large and complex installations that seem beyond practical use by inspectors in the field.

A practical use of isotope correlation techniques is to indicate outliers in plutonium assay measurements during a reprocessing plant campaign. Here, the data base is restricted to a specific reactor fuel to be more reliable.

VI. PREPARATION OF PLUTONIUM-CONTAINING MATERIALS FOR THE NBS (S. F. Marsh, J. W. Dahlby, J. E. Rein, G. R. Waterbury, and staff)

Packaging of a ^{244}Pu material has been completed and its characterization for assay and isotopic distribution values is in progress. The packaging operation and background information, including its applicability to isotope-dilution mass-spectrometric analysis, was presented last year.[2] Over 900 aliquots of a ^{244}Pu solution were distributed by weight into Teflon bottles. The aliquots contain 1 mg of ^{244}Pu except for 19 that contain 5 mg that serve as the samples for assay characterization at NBL and our laboratory using controlled-potential coulometry. During the packaging operation, NBS chemists selected seven of the 1-mg portions for assay characterization by isotope-dilution mass spectrometry. The remaining 1-mg portions have been evaporated and the bottles sealed with Teflon caps. A recommended procedure for dissolving the evaporated residue and for preparing a standard solution was sent to NBS for incorporation in the certificate.

We are using two different controlled-potential coulometric methods for the plutonium assay with an objective reliability of at least 0.1%. The analysis by the method using a HCl-sulfamic acid electrolyte, described in Sec. III. B, has been completed. The method using a H_2SO_4 electrolyte[17] is subject to a 4.4-fold interference from iron, present at about 0.03% based on semi-quantitative emission spectrographic and atomic absorption analyses. The sensitivity of the method, which is a spectrophotometric determination of the Fe(II)-orthophenanthroline complex that is normally used to obtain an iron correction, is so low as to require a quantity of ^{244}Pu that exceeds that available for the purpose.

To obtain an accurate correction, a more sensitive spectrophotometric method using Ferrozine [3-(2-pyridyl)-5, 6-bis (4-phenylsulfamic acid) - 1, 2, 4-triazine] is being developed.

Another lot of ^{239}Pu metal, which contains less than 3% ^{240}Pu, was purified and prepared for cutting into small pieces for packaging as a plutonium metal chemical standard (SRM 949) for dispensing by NBS. The metal was purified by electro-refining, cast in a thin sheet, and cleaned by machining the surfaces. A nibbler was obtained recently for breaking the metal into small pieces weighing 0.2 to 0.3 g in an inert atmosphere. Approximately 0.5-g portions will be weighed accurately and then heat-sealed in all-glass ampoules during the first quarter of FY 1980. After a comprehensive chemical characterization of the metal, evaluation of each sealed sample appearance will be made as a final check on the integrity of the containment. Samples passing the purity and appearance tests will be available to NBS.

VII. PLUTONIUM ISOTOPE HALF-LIFE MEASUREMENTS

The Half-Life Evaluation Committee (HLEC), consisting of representatives of the Argonne National Laboratory (ANL), LASL, Lawrence Livermore Laboratory (LLL), Mound Laboratory (ML), NBS, and the Rockwell International Rocky Flats Plant (RI-RFP), is guiding an effort to measure accurately the half-lives of longer-lived plutonium isotopes. In this effort, LASL is (1) preparing, characterizing, and distributing batches of high-purity plutonium from specially provided, enriched isotope materials, and (2) determining the half-lives using techniques of mass spectrometry and alpha particle counting. Our characterization measurements include assay, isotopic distribution, metal impurities including other transuranics, and nonmetal impurities.

Measurement of the ^{239}Pu half-life has been completed and published.[18] The recommended value is 24,119 ± 26 yr. Characterization of a batch of about 99.3% enriched $^{240}PuO_2$, to be used for interlaboratory half-life measurements, is in progress. We started the half-life measurement using the technique of isotope-dilution mass spectrometry to determine ^{236}U daughter growth. We completed a half-life measurement of ^{241}Pu based on mass-spectrometric measurement of the decrease of ^{241}Pu relative to long-lived ^{242}Pu as a function of time. The measured value is 14.38 y. An error analysis in progress indicates the uncertainty will be about 0.05 yr. The HLEC proposed a ^{238}Pu half-life value of 87.74 yr, which is the average of a recent alpha-particle-activity measurement of 87.71 ± 0.03 yr[19] and a calorimetric measurement of 87.77 ± 0.03 yr.[20]

A. Plutonium-240 (S. F. Marsh, R. M. Abernathey, J. W. Dahlby, J. E. Rein, G. R. Waterbury, and staff)

A recent ANL measurement[21] of the ^{240}Pu half-life of 6569 yr, determined by alpha-particle counting, is considerably higher than the American National Standard Institute recommended value of 6537 yr.[22] The HLEC, therefore, recommended a measurement by participating laboratories.

At LASL, a 28-g quantity of 99.3% enriched $^{240}PuO_2$ was dissolved and purified by an anion exchange separation in nitric acid medium.The plutonium fraction was calcined at 1250°C to stable PuO_2, which was blended. Recalcination at 900°C in steam further purified the PuO_2 from trace halogens and other nonmetal impurities. Final impurity content was about 200 ppm, mainly iron, plus ^{241}Am and ^{236}U, which grow-in from decay of ^{241}Pu and ^{240}Pu.

Weight portions of the purified and calcined $^{240}PuO_2$ were distributed into various containers, including three designed for calorimetric half-life measurements. These containers, plus those having portions intended for other half-life measurements and for plutonium assay measurements, were sent to ML where the relative portion weights were verified by calorimetry. Except for portions retained by ML for half-life measurements and plutonium assays, the others were returned to us. We dissolved them in hydrochloric acid using the sealed-tube technique, packaged weight aliquots, and sent them to laboratories participating in the characterization and half-life measurements.

Our half-life determination, using isotope-dilution mass-spectrometric measurement of grown-in ^{233}U, is in progress. The technique consists of adding a known number of ^{233}U atoms to a stated number of ^{240}Pu atoms, then after 1 yr determining the number of ^{233}U atoms by mass-spectrometric measurement of the $^{236}U/^{233}U$ ratio. Using the relationship $-dn/dt = \lambda N$ and the fact that each ^{240}Pu decay produces one ^{236}U atom, the half-life calculation is

$$HL = \frac{(\ln 2)(\Delta t)}{(^{233}U/^{240}Pu)\Delta(^{236}U/^{233}U)} \quad .$$

Duplicate weight aliquots of each of three dissolved $^{240}PuO_2$ portions are being used to provide an objective overall uncertainty of < 0.2% in the half-life measurement. After the initial ^{236}U in each portion was removed by an ion-exchange separation, weighed portions of a calibrated ^{233}U solution were added in an amount that will give a $^{233}U/^{233}U$ ratio of unity in a 1-yr grow-in period to maximize accuracy of the mass-spectrometric measurement. The ^{233}U concentration was calibrated by isotope-dilution mass spectrometry relative to NBS SRM 960 natural uranium metal and a highly pure enriched ^{233}U metal prepared at LASL. The uncertainty of the ^{233}U concentration is < 0.1%. The number of initial atoms of ^{240}Pu in each of the six solutions will be computed from the weights of $^{240}PuO_2$ dissolved, the solution portion weights, and the concensus values for the assays and isotopic abundances obtained by the laboratories doing the characterizations.

The initially measured $^{236}U/^{233}U$ ratios were essentially zero, verifying effective ion-exchange separations. This provides excellent zero-time values. Losses of ^{240}Pu in the separation, measured by assaying all fractions including the resin, were very low.

Our characterization of the $^{240}PuO_2$ was completed for (1) plutonium content by one of two assay methods, (2) isotopic distribution by mass spectrometry, (3) metal impurities by emission spectrography, (4) nonmetal impurities by chemical methods, (5) ^{238}Pu, ^{237}Np, and ^{241}Am by alpha-particle counting, and (6) trace uranium by isotope-dilution, mass-spectrometric analysis.

B. Plutonium-241 (S. F. Marsh, R. M. Abernathey, and J. E. Rein)

The ^{241}Pu/^{242}Pu ratio has been measured at 6-month intervals, following chemical separation of ^{241}Am, on a prepared < 3-yr-old mixture of highly enriched isotopes of ^{241}Pu and ^{242}Pu originally at a 1.27 ratio. About two years ago, portions of the mixture were distributed to LLL, ML, NBS, and RI-RFP as participants in the half-life measurement. We have been notified that none of these laboratories plans to continue the measurements. Our measurements over a 3.6-yr period yield a half-life value of 14.38 yr with an expected uncertainty at the 95% confidence level of about 0.05 yr based on an error propagation now in progress.

VIII. PREPARATION AND ANALYSES OF SALE MATERIALS (G. R. Waterbury and staff)

Consultations have continued concerning preparations of plutonium materials for distribution by NBL to SALE participants. LASL is obtaining three plutonium oxide lots having slightly different isotopic compositions. Packaging of these materials and possible other plutonium materials will be discussed at the next SALE Steering Committee Meeting during November 1979.

Participation in the analyses of SALE uranium materials for uranium content and isotopic compositions has continued on a bimonthly basis throughout the year. The summary reports of SALE results, prepared by NBL, have enabled us to use this program for internal quality control.

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