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ANALYTICAL CHEMISTRY BRANCH ANNUAL REPORT
FISCAL YEAR 1969

SERVICE
EDUCATION
TECHNOLOGY

IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
IDAHO FALLS, IDAHO

U. S. ATOMIC ENERGY COMMISSION

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ANALYTICAL CHEMISTRY BRANCH ANNUAL REPORT
FISCAL YEAR 1969

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ANALYTICAL CHEMISTRY BRANCH ANNUAL REPORT FISCAL YEAR 1969

SUMMARY - J. M. Crawford

This report presents a general survey of special analytical services and of research to develop and to improve methods and equipment by the Analytical Chemistry Branch for FY 1969. The new and revised methods that have been established during the year are reported in detail in the appendix. Also presented is the analytical work in maintaining standards and quality control. This summary is a brief abstract of the year's work.

Analytical Development

Electroanalytical studies include a research program to investigate electrochemical field effects existing at solution-metal interface and to determine how these effects can be controlled. The data is needed to develop low energy methods of separating salt from water, to prevent scale formation, to prevent corrosion, and to devise electrochemical concentration transducers suitable for saline water conversion plants. Development work is continuing on the continuous monitoring system to control fissionable uranium and plutonium material in chemical processing plants. This is best accomplished by continuous monitoring of process points from dissolution through final product and waste streams.

Radiochemical studies include the evaluation of a specific separations technique for a radiochemical method. In this technique, a solid reagent in the pure form or mixed with an inert inorganic support is used. It is packed in an exchange column; the aqueous sample is passed through; the column is washed; and the desired product is either eluted from the column for counting, or the column is counted directly.

The Classical Methods Group, which mainly does development work, provided many analytical services; however, methods needed to be established before the services were performed. Two methods were established for separating niobium from fluoride solutions of zirconium-uranium fuels. Total nitrate concentration and acidity of electrolytic dissolver solutions of uranium-stainless steel were determined after correcting some difficulties. Analytical support is being rendered to analyze and to characterize the course of various reactions from samples originating from a fluidized bed process for manufacturing uranium aluminide. Irradiated hafnium metal and hafnium-aluminum alloy samples are being analyzed to determine the relative concentrations and isotopic distributions of the hafnium isotopes and the irradiation products Lu-175 and Ta-181. The work on the hafnium and lutetium is over 50% completed, and the work on tantalum has been deferred until satisfactory mass spectrometric procedures for analysis has been developed. The Advanced Test Reactor Mark VI fuel specifications lists specific amounts of U-235 and natural boron for various fuel plates. Two plates from a prospective fuel fabricator were analyzed successfully to determine total uranium, total boron, and to establish core loading and uniformity. Three Engineering Test Reactor fuel plates were analyzed for B-10, U-235, and Si. The analysis program for the ETR plates was similar to the program for the ATR plates. Nickel metal from a remelting process was analyzed spectrophotometrically for low concentrations of thorium.

As well as establishing methods with the services, many of the existing methods were revised and new methods were developed. These include the investigation of the method for determining free acidity of aqueous solutions containing hydrolyzable metal ions. Procedures were evaluated for the separation of Fe, Cr, Co, and Ni as a group for subsequent determination by atomic absorption and emission spectrography. The effects of diverse ions on the four analysis schemes in the spectrophotometric method for the determination of phosphorus were studied to establish applicability and limitations. A versatile spectrophotometric method for the determination of microgram amounts of silicon has been developed.

Several major improvement programs have been completed or are in process. These include completion of the Remote Analytical Facility (RAF) cave, procurement of five RAF replacement boxes and authorization for five more boxes, relocation of the glass shop from CPP-602 to CPP-637, conceptual design of an analytical chemistry building, and modification of heating and ventilating in CPP-627.

Spectroscopy

A method has been developed for the separation of cadmium from solutions of fission product, uranium, and plutonium. Good sensitivity for the cadmium as cadmium iodide has been repeatedly obtained with the Hitachi Crucible Source mass spectrometer.

A special analytical service was the laser probe analysis of 347 stainless steel by comparing elemental concentrations in metal grains and in the boundaries with a control.

A number of new and improved methods and techniques were established. A new technique for ashing Millipore filters for qualitative analysis by emission spectrography was developed. Because of the acceptable low detection limit for beryllium by an emission spectrographic procedure, Millipore filters now are being used instead of the Microsorban filters in air sampling equipment. The Olivetti Underwood Programma 101 was investigated and found inadequate for routine calculations of atomic absorption data. The standard spherical tip electrode used for spectrographic analysis by the vacuum cup technique was modified to a concave form tip to reduce spattering, increase precision, and improve detection limits. An atomic absorption method was developed to replace the emission spectrographic method previously used to determine nickel and chromium in potassium permanganate solutions. Studies are under way on laser sampling for analysis.

Chemical Analysis

The Radio and Special Analysis and the Remote and Service Groups perform special analysis work in addition to the routine work from the Chemical Processing Plant. The special services are for programs in Idaho Nuclear and outside contractors. Air from the TAN-609 battery room was analyzed for arsine and stibine. Air also is frequently analyzed for sulfur dioxide, and an improved colorimetric method was selected. Methods were evaluated for determining the quantity and size of particulates released from NRTS Boiler House stacks. Blood was analyzed for carbon monoxide. Coupon decrudding solutions were analyzed for Ni-63. Simulated Purex waste could not be analyzed by existing methods; therefore, other methods were developed to prepare the waste for subsequent analysis. The electrolytic dissolution of EBR-II fuel was analyzed for Fe, Mo, Na, Ru, Si, and U. Black liquor, the waste from paper pulp processing, was analyzed for density, pH, alkalinity, fluoride, phosphorus, undissolved solids, total solids, residue after combustion, total carbon, water, metallic impurities, and various sulfur species. Rover bed samples from the burn-leach process for the recovery of uranium from Rover fuel were analyzed for Al, Al_2O_3, and U. A zirconia-zircon ceramic cement was analyzed for B, Hf, Si, Y, and Zr. Cellulose acetate butyrate plastic strips impregnated with amorphous natural boron were analyzed for boron. Fiber-backed tapes were analyzed for sulfur.

The Chemical Analysis Section revised some existing methods and developed new ones—separation of americium from plutonium contaminated with curium; computer analysis of gamma-ray spectra obtained with lithium-drifted germanium detectors; determination of gross beta-gamma activity of reactor loop coolant, gross iodine activity, radiocesium, Kr-88 activity, Cs-139 activity, I-133 and I-131 activity, and dissolved oxygen; effect of nitrate on the colorimetric determination of cobalt; determination of molybdenum in EBR-II fuel; low-level sulfate; and calculations of radiochemical analysis using the Olivetti Programma 101.

Improvements in equipment include installation of a crystal-controlled clock in the Nuclear Data Analyzers to obtain a more stable and accurate time base, fabrication of a remote filtration and fusion apparatus, and fabrication of remotely operated apparatus for sealing glass sample ampoules.

Special Programs

The Quality Control Program is continuing, but significant changes were made in the program for analytical methods. The revised program provides the same data, if not more with less effort. A total of 45 methods currently is covered in the program. The range, unit, and precision of the methods are given in Table VII.

The Umpire Qualification Program is continuing, and the status of the following activities reported—participation of AEC, U. S. commercial, and foreign laboratories; preparation of test materials; distribution of test materials to U. S. commercial and foreign laboratories; statistical evaluation of data, preparation of program documents and qualification recommendations; inspection of U. S. commercial laboratories; nondestructive analysis of test materials for the determination of U-235 and Pu-235; and future plans.

The Burnup Determination of Nuclear Fuel Project has been completed, and a final report has been issued. Thermal fission yields were measured for 43 mass chains for U-233, U-235, Pu-239, and Pu-241. Fast reactor fission yields were measured for 45 mass chains for U-235 and Pu-239.

In the program for cleanup of reactor containment atmosphere, studies have been under way on specific inorganic adsorbers for the retention of airborne radioiodine. Current research has been devoted to evaluating the effects of various atmospheric pollutants upon the iodine adsorption characteristics of Linde Molecular Sieve 13X in the silver form.

The LOFT-ECCS (Loss of Fluid Test-Emergency Core Cooling System) Program is continuing. This Program is designed to provide information about loss of coolant accidents to pressurized, water-cooled power reactors. A summary of each task is given in Section X.

TABLE OF CONTENTS

FIGURES

TABLES

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[1] R. C. Shank and Staff, *Annual Report of ICPP Analytical Section for 1960*, IDO-14547 (April 1961).

[2] R. C. Shank and Staff, *Annual Report of ICPP Analytical Section for 1961*, IDO-14588 (May 1962).

[3] R. C. Shank and Staff, *Annual Report of Division Analytical Branch for 1962*, IDO-14605 (April 1963).

[4] R. C. Shank and Staff, *Annual Report of Division Analytical Branch for 1963*, IDO-14536 (June 1964).

[5] R. C. Shank and Staff, *Annual Report of Division Analytical Branch for 1964*, IDO-14655 (April 1965).

[6] R. C. Shank and Staff, *Annual Report of Division Analytical Branch for 1965*, IDO-14679 (June 1966).

[7] R. C. Shank and Staff, *Annual Report of Analytical Chemistry Branch for 1966*, IN-1063 (April 1967).

[8] R. C. Shank and Staff, *Annual Report for the Analytical Chemistry Branch for the Period Ending June 30, 1968*, IN-1203 (September 1968).

I. INTRODUCTION

This is the ninth annual report[1-8] of the Analytical Chemistry Branch. Previous to 1960, analytical progress was reported in the Idaho Chemical Processing Plant (ICPP) operations weekly and monthly reports and also was reported in the ICPP technical quarterly reports.

This annual report presents the work on projects of interest to analytical chemists, and the work that has been or will be published is only abstracted in this report thus allowing space for detailed information that will not be published elsewhere. New and improved methods are included in the appendixes.

The general goal of the Branch is to provide analytical support to various research programs by Idaho Nuclear Corporation, to perform research in analytical chemistry, to develop and improve methods, and to perform service analyses. The Branch hopes that this report will be of value to management, to those who submit samples, and to all analytical chemists.

This report has been organized according to the three Sections in the Branch except for the special programs - Umpire Qualification, Burnup Determination of Nuclear Fuels, Reactor Atmosphere Cleanup, and Loss of Fluid Test-Emergency Core Cooling System (LOFT-ECCS).

II. GENERAL INFORMATION

The organization of the Analytical Chemistry Branch as of May 31, 1969 is shown in Figure 1. The organization through May 31 is shown because during June, Idaho Nuclear Corporation was being reorganized which affected Analytical's organization. A maximum of 78 people were employed through May 31, 1969.

Table I shows the distribution of manpower for fiscal year 1969. The overhead was greater this year than usual because the work load was less than previous years. This reduction in work load was due mainly to the ICPP processing small amounts of fuel, the termination of the program for the Burnup Determination of Nuclear Fuels, and the cut back of LOFT-ECCS activities. As a result, the staff had been reduced to 69 by May 31. The time of the Branch Manager, three Section chiefs, administrative assistant, and two secretaries is not included in the table.

Table II shows the number of determinations and the sample source for fiscal year 1969.

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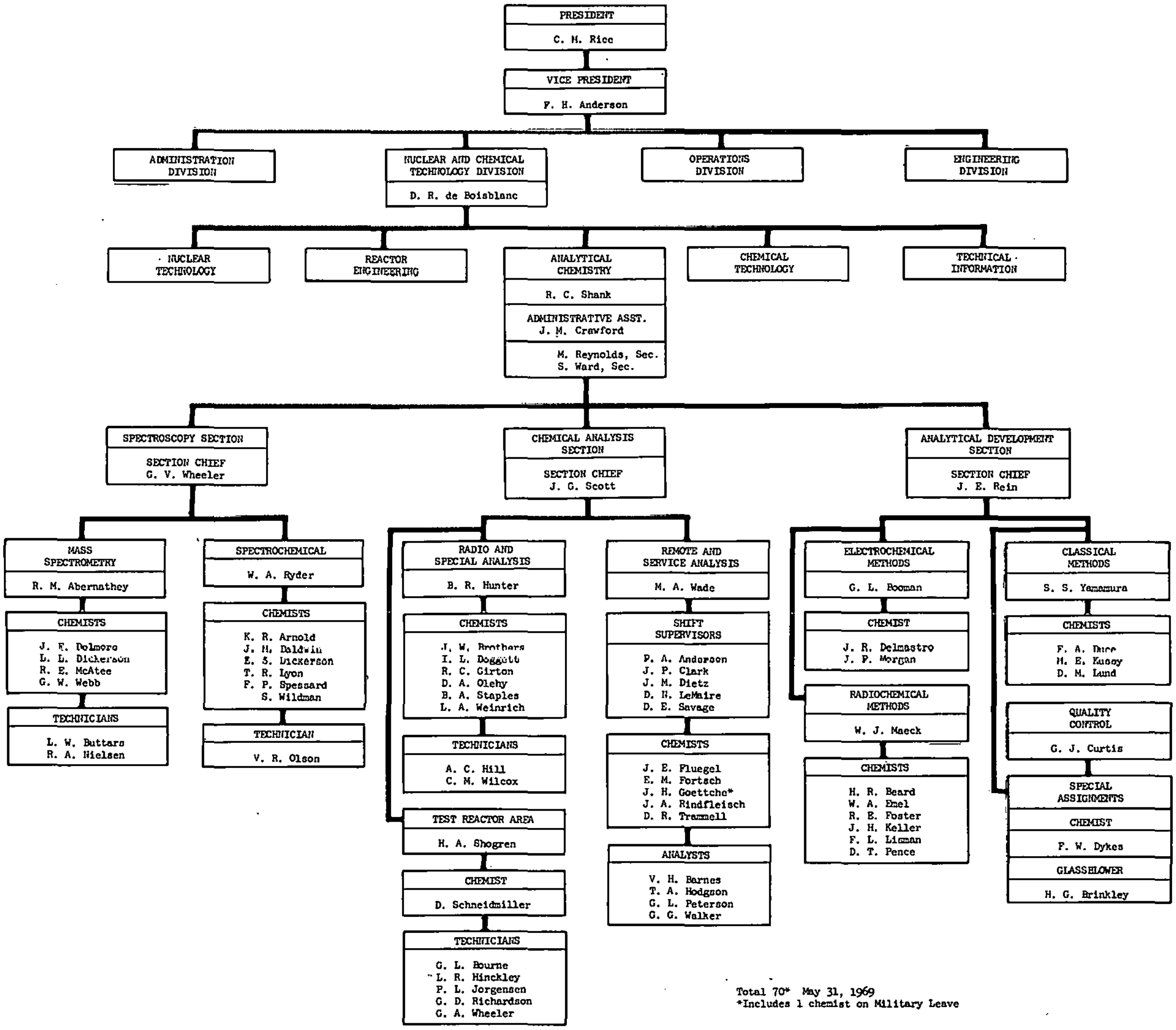

Total 70* May 31, 1969
*Includes 1 chemist on Military Leave

Fig. 1 Analytical chemistry branch within corporation organization.

TABLE I

DISTRIBUTION OF MANPOWER
(July 1, 1968 through June 30, 1969)

Section	CPP Operations	CPP Chem Tech	Plant Assistance	Analytical Development	Other INC	Outside INC[a]	Analytical[b]	Total
Spectroscopy	1469.0	689.0	1560.0	4359.5	3773.5	2368.0	18825.5	33044.5
Chemical Analysis								
Radio and Special Analysis	4768.0	212.0	1070.5	1501.5	15323.0	4099.0	9911.5	36885.5
Remote and Service Analysis	7048.0	2164.0	3445.5	1465.0	4102.0	1868.0	11502.5	31595.0
Analytical Development	745.5	107.0	311.5	13004.0	1498.5	6202.0	15325.5	37194.0
Analytical Branch	14030.5	3172.0	6387.5	20330.0	24697.0	14537.0	55565.0	138719.0
Analytical Percent	10.1	2.3	4.6	14.6	17.8	10.5	40.1	100.0

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[a] AEC Contractors other than Idaho Nuclear Corporation.

[b] Includes overhead such as housekeeping, vacations, training, and other items not charged directly to analytical service or existing projects.

TABLE II

DETERMINATIONS MADE BY THE ANALYTICAL CHEMISTRY BRANCH
(July 1, 1969 through June 30, 1969)

Section	CPP Operations	CPP Chem Tech	Plant Assistance	Analytical Development	Other INC	Outside INC[a]	Analytical	Total
Spectroscopy	545	322	1362	206	2382	3363	397	8577
Chemical Analysis								
Radio and Special Analysis	4552	278	701	95	32278	2620	565	41089
Remote and Service Analysis	7921	1675	3443	136	2929	1741	1124	18969
Analytical Development	122	5	22	138	207	109	0	603
Quality Control[b]							2542	2542
Analytical Branch	13140	2280	5528	575	37796	7833	2086	69238
Analytical Percent	19.0	3.3	8.0	0.8	54.6	11.3	3.0	100.0

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[a] AEC Contractors other than Idaho Nuclear Corporation.

[b] Reagents and controls prepared by this laboratory are not included in the total.

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III. ANALYTICAL DEVELOPMENT

1. ELECTROANALYTICAL STUDIES FOR THE OFFICE OF SALINE WATER

(G. L. Booman, J. R. Delmastro)

A fundamental research program in electrochemistry is being conducted for the United States Department of the Interior, Office of Saline Water, over a 3-yr period ending May 31, 1971. The purpose of this program is to investigate electrochemical field effects existing at solution-metal interfaces and to determine how these effects can be controlled, thus giving the basic data needed for developing low energy methods of separating salt from water, preventing scale formation, preventing corrosion, and for devising electrochemical concentration transducers suitable for saline water conversion plants.

Considerable work has been done on the theory of combined diffusion-kinetic processes under potential-step conditions. With these theoretical descriptions available, separation of surface charge phenomena from faradaic effects will be more readily accomplished and experimental data on the nature of water-metal ion bonding will be obtainable from electrochemical kinetic studies. Abstracts of the two papers published in the May, 1969 issue of Analytical Chemistry follow:

THEORY OF POLAROGRAPHIC KINETIC CURRENTS FOR SECOND-ORDER REGENERATION REACTIONS AT SPHERICAL ELECTRODES:
I. NUMERICAL SOLUTION OF FINITE-DIFFERENCE EQUATIONS

D. T. Pence, J. R. Delmastro and G. L. Booman

A numerical finite-difference method of solution, for the equations describing homogeneous reactions with kinetic complications as applied to stationary electrode polarography, is extended to include the effects of spherical diffusion at large values of time. The accuracy and speed of computation were improved by the application of the integral equation for the linear combination of concentrations which obeys the pure diffusion equation, and solution by a simultaneous equation, Newton-Raphson iteration method. The best data from both the finite-difference and steady-state integral equation methods of solution are tabulated. Measurements with spherical electrodes in the near steady-state region are shown to give a one electrode equivalent to a thin layer cell, and to permit the determination of rate constants in a nearly time-independent region by comparison with measurements at a planar electrode.

THEORY OF POLAROGRAPHIC KINETIC CURRENTS FOR SECOND-ORDER REGENERATION REACTIONS AT SPHERICAL ELECTRODES: II. NUMERICAL SOLUTION OF THE INTEGRAL EQUATION FOR STEADY-STATE BEHAVIOR

Joseph R. Delmastro

A numerical method is described for solving the non-linear, steady-state integral equation which arises in treating the second-order, one-half regeneration mechanism for large potential-step electrochemical experiments at stationary spherical electrodes. Computational procedures employed for efficiently obtaining results used in the preparation of working curves are discussed. These results demonstrate that for spherical diffusion the upper limit of the kinetic-to-diffusion current ratio is less than two and is highly dependent on the effective electrode sphericity. This numerical method is readily adaptable to first-order mechanisms which are difficult to solve analytically.

A third paper has been submitted to Analytical Chemistry for publication. The abstract follows:

POLAROGRAPHIC KINETIC CURRENTS FOR FIRST-ORDER PRECEDING AND REGENERATION REACTIONS AT SPHERICAL ELECTRODES

J. R. Delmastro and G. L. Booman

The linear integral equation which arises in treating the first-order preceding reaction mechanism in spherical geometry for large potential-step electrochemical experiments in the limiting current region is solved by a numerical method. The exact analogy between this mechanism and the first-order fractional regeneration mechanism is demonstrated. Numerically generated data are fitted to a Chebyshev polynomial for efficient tabulation of results. Tabulated Chebyshev coefficients and special forms of analytical solutions permit rapid generation of working curves for both the mechanisms considered, even on a small laboratory computer. The analytical solution for the first-order, one-half regeneration mechanism in spherical geometry is presented.

The Laplace transform solution of a specific kinetic case has been prepared for publication as an AEC Report, IN-1274. The abstract follows:

POLAROGRAPHIC KINETIC CURRENTS FOR THE FIRST-ORDER ONE-HALF REGENERATION MECHANISM AT SPHERICAL ELECTRODES

J. R. Delmastro and G. L. Booman

The analytical solution for the large potential-step electrode response at a stationary spherical electrode with the first-order, one-half regeneration mechanism is derived by a non-routine application of the Laplace transformation method. The form of the resulting solution depends on the value of the effective electrode sphericity.

With the completion of the above reported work, emphasis was placed on an electrochemical study of porous metallic membranes, proposed by this laboratory for application in electrodialysis and reverse osmosis separations for the production of desalinated water. The basic hypothesis underlaying this study is that some membrane separations are effected by the kind and density of charge distribution on the membrane pore surfaces. With a metallic membrane, this charge distribution would be controlled by an external electrical circuit, and not solely dependent on the chemical nature of membrane materials. Other projected advantages of metallic membranes include thermal stability, no compaction under pressure, electrical control of desorption and other cleaning cycles, and reliance on an established membrane preparation technology. Metallic membrane technology was developed on a large scale basis for the gaseous diffusion plants where uranium hexafluoride isotope enrichment is performed for the atomic energy program. The program required membranes with a high degree of pore size uniformity. Circuits to control the membrane potential in 4-electrode cells were constructed and successfully tested. Tests with membrane material having pore diameters of 0.2-μ and also theoretical calculations indicated that pore diameters of less than 200Å will be required, and that the metal layer should be as thin as feasible. Unfortunately, the proven technology developed for the gaseous diffusion plants is not available on an unclassified basis; hence, other methods of preparing membranes are being investigated. Etching of two-component alloys, thermal decomposition of organic gold compounds on a suitable porous substrate, vacuum evaporation, and chemical electro-less plating on the surface of a suitable nonconducting membrane material (eg cellulose acetate) are being considered.

2. IDAHO CHEMICAL PROCESSING PLANT FISSIONABLE ISOTOPE MONITOR BASED ON THE DELAYED NEUTRON TECHNIQUE FOR THE CONTINUOUS ANALYSIS OF CHEMICAL PROCESSING PLANT STREAMS

(G. L. Booman, J. P. Morgan, J. W. Brothers)

The control of fissionable uranium and plutonium material in a chemical processing plant is best attained by continuous monitoring of key process points covering steps from dissolution through intermediate process stages to the final product and waste streams. A test model of a monitor, for installation in the Idaho Chemical Processing Plant, operating on the delayed neutron technique, had previously been assembled and shown to have sensitivity to 0.1 mg/liter of U-235. This model consisted of a high flux Pu-238, beryllium neutron source, a pumped flow system, large water shielding tanks, a B-10 trifluoride detector, pulse amplifier, counting system, and a small on-line digital computer.

With special funding, design of interface circuits to permit input of stream flow and holding tank volume information to the on-line computer was completed and drawings were prepared. These additional inputs will improve the accuracy of fissionable material measurement and will permit criticality margin calculations as part of the computer program.

Also, minor hardware modifications were made to the interface control logic to reduce the deadtime of the source and sample counters during data transfers to the PDP-8/S on-line computer.

To facilitate system checkout and trouble shooting, an interface display panel was constructed. This display indicates the status of the input registers, interrupts, and the interface operating modes.

Minor modifications were made to the Teletype to allow the PDP-8/S computer to power the Teletype motor under program control, thus allowing the Teletype to be in a standby condition, except when actually needed for input or output.

Back plane wiring has been completed for the multiplexer and analog-to-digital converter interface. Operational checkout of this interface is under way.

Programming of the PDP-8/S computer was continued with emphasis on an evaluation of the operating characteristics of the system. A program was written to monitor the source and sample detectors and to type count rates and the time of day on the teletype at a preset time interval. The deadtime of the count registers caused by processing overflows is less than 0.01% of the count time.

Further program sections have been written and are being debugged. In these program sections, count data from the source detector are monitored. Count data from the sample detector are stored for later statistical tests. The precision at the 95% confidence level is calculated, based upon counting statistics, for the sample counts in an 8.5-sec count time as the basis for the detection of gross changes in the uranium concentration. Another statistical calculation is the t-test for nonzero slope using the slope and standard deviation of the least square line through data points representing equal consecutive count time intervals. Off-normal conditions are indicated on the Teletype.

Installation of this fissionable isotope monitor has been proposed for the CPP-IIIAR stream. Further development of this instrument is dependent on funding approval of the proposed installation.

3. RADIOCHEMICAL METHODS

3.1 Specific Separations (W. A. Emel, W. J. Maeck)

Previous studies in this laboratory have shown that many water-insoluble reagents used in liquid-liquid extraction systems for the selective separation of metal ions will function as well or better in the solid form in an exchange column. In this technique for a radiochemical method, the reagent either in the pure form or mixed with an inert inorganic support is packed into a column; the aqueous sample is passed through; the column is washed; and the desired product either is eluted from the column for counting or the column is counted directly. The advantages of this technique are (a) rapidity, (b) quantitative separation with no yield determination required, and (c) no introduction of a liquid organic phase.

This technique is being evaluated for separation of Mo-99 and Zr-95 from gross fission product solutions.

3.11 Molybdenum-99. Because Mo-99 is a widely used burnup monitor for short-term irradiated and short-cooled fissionable material, the above technique is being investigated to develop an improved Mo-99 radiochemical procedure. The present routine method used in our laboratory is a double liquid-liquid extraction with α-benzoinoxime followed by a gravimetric yield determination. Because this reagent is reasonably specific for molybdenum, its use in a column form is being investigated. Molybdenum-99 is quantitatively retained on a column (0.6-cm diam x 3.0-cm long) of solid α-benzoinoxime from a wide variety of mineral acids provided the amount of added molybdenum carrier per sample is in the range of 100 to 2500 μg. The retention of molybdenum was incomplete above and below this range. The retention of Mo-99 for various acids and acid concentration levels is given in Table III. The stability of α-benzoinoxime as a function of acidity also was investigated. The material is stable for 36 hr in 2N mineral acid and for 4 hr in 4N acid.

TABLE III

RETENTION OF Mo-99 ON A COLUMN OF SOLID α-BENZOINOXIME
FOR VARIOUS ACIDS AND ACID CONCENTRATION LEVELS

Acid	Normality	Mo-99 Retention, %
HCl	0.25 - 2.0	>99
HNO_3	0.25 - 2.0	>99
H_2SO_4	0.25 - 2.0	>99
HF in 0.5N HNO_3	0.001 -0.02	>99
HCl-Br_2	0.25 - 2.0	>99

The adsorption of molybdenum as a function of flow rate was studied over the range of 0.5 to 11.3 ml/min/cm^2. The retention was greater than 99% over the entire range, and the activity was adsorbed as a sharp band at the top of the column. Varying the aqueous sample size over the range of 1 to 20 ml gave no detectable effect.

Molybdenum can be eluted from the column with 1M NH_4OH. It is believed that the elution proceeds by dissolution of the Mo-α-benzoinoxime complex. Greater than 99% of the molybdenum can be recovered provided the elution step immediately follows the adsorption step.

The time for the procedure exclusive of pretreatment is 10 min compared to over 1 hr for the extraction procedure.

Interferences from a short-cooled fission product solution are iodine and niobium. Initial studies indicate that iodine can be preremoved by adding bromine, then heating to volatilize elemental iodine. Various complexing reagents are being investigated to eliminate the niobium interference.

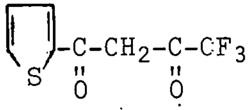
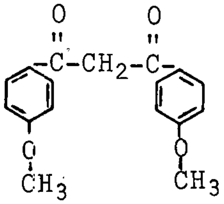
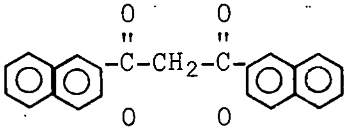
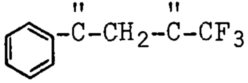
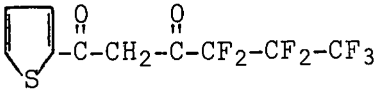
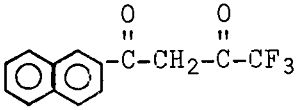
3.12 Zirconium-95. The β-diketone, thenoyltrifluoroacetone (TTA), is a widely used reagent for the selective extraction of zirconium. Its solubility, however, is too large to permit its use as a solid adsorbent for aqueous samples. Hence, a series of substituted β-diketones is being investigated for possible use.

In preliminary studies, the various solid β-diketones were packed into polyethylene columns (3-cm long x 6-mm ID) and preequilibrated with either 2M HCl or 2M HNO_3. Aliquots of 4-ml volume of 1-month cooled fission products and uranium dissolved in 2M HNO_3 were passed through the columns followed by several 1-ml rinses of 2M HCl or 2M HNO_3. The column effluent, the column, and the original solution were analyzed by gamma-ray spectrometry to determine the retention of Zr-95 and other fission products on the various β-diketones. The results are summarized in Table IV.

Additional studies pertaining to the acidity, flow rate, support composition, and the use of complexing agents are under way.

TABLE IV

RETENTION OF Zr-95 ON VARIOUS β-DIKETONES

B-Diketone		Properties	Zr-95 Retained, %	Remarks
Thenoyltrifluoroacetone		Slightly water soluble	90%	Retention varied with flow rate and temperature
1,3-Bis (p-methoxyphenyl-1, 3-propanedione) (BMP)		Less soluble in water than TTA. mp ∿110°C	< 1	Retained only I-131
1,3-Di(2-naphthyl)-1,3 propanedione (DNP)		Less soluble in water than TTA. mp 171°C	2%	14% I-131 retained
4,4,4-trifluoro-1 phenyl 1,3 butanedione (TPB)		Less soluble in water than TTA. mp 38°C	26%	3% I-131 retained
4,4,5,5,6,6,6-heptafluoro-1 (2-thienyl)-1,3 propanedione (HTP)		Coated on alumina substrate. mp ∿10°C	70%	40% Nb-95 retained[a]
4,4,4-trifluoro 1-(2-naphthyl)-1, 3 butanedione (TNB)			3%[b]	1% Nb-95 retained

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[a] Nb-95 was adsorbed on the alumina support.

[b] B-diketone not wetted by aqueous sample.

4. CLASSICAL METHODS

4.1 Analytical Services for Chemical Technology Branch

4.11 Separation of Niobium from Fluoride Solutions of Zirconium-Uranium Fuels (S. S. Yamamura, R. Fullerton). To determine small amounts of niobium in zirconium-uranium fuel and fuel recovery process streams by emission spectroscopy, it is first necessary to separate the niobium from the zirconium and the uranium which have extremely complex excitation spectra. The separation must be clean and essentially quantitative. Two suitable methods have been established for doing this. One is the extraction method based on N-benzoylphenylhydroxylamine discussed in Appendix B of this report. The second, also an extraction procedure, is a simplified version of a separation scheme reported by Milner et al[9]. In the latter, the niobium is extracted into hexone from a 10.5$\underline{M}$ HF-7.5±1.5$\underline{M}$ H_2SO_4-2.75±0.55$\underline{M}$ NH_4F medium. The niobium then is stripped from the hexone into 5% hydrogen peroxide. Finally, the hydrogen peroxide solution is evaporated, then diluted to a convenient volume with a 4$\underline{M}$ HF-4$\underline{M}$ HCl solution. The niobium recovery is 97% or more. Some Zr(IV), U(VI), and Cr(VI) coextract but do not interfere.

4.12 Determination of Total Nitrate Concentration and Acidity of Electrolytic Dissolver Solutions of Uranium-Stainless Steel Fuel (F. A. Duce, S. S. Yamamura). In one of the fuel recovery processes under study by the Chemical Technology Branch, uranium-stainless steel fuel is dissolved with nitric acid in an electrolytic dissolver. Samples of the dissolver solution are submitted for the determination of total nitrate concentration, acidity, undissolved solids, and other constituents. The determination of total nitrate and acidity was examined to explain the lack of agreement among replicate results. The difficulty was traced to the presence of volatile and unstable nitrogen oxide species which were partially lost in the filtration of the undissolved solids or which were slowly converted to nitrate by air oxidation. The problem was corrected by sampling the solution in a conventional 250- or 125-cc gas sampler and contacting the sample solution with oxygen at 5 psi for 20 min. This completely oxidized nitric oxide, nitrogen dioxide, and nitrite to nitrate to result in meaningful and reproducible nitrate and acidity results.

Macro amounts of nitrate are normally determined by reduction of nitrate to ammonia with Devarda's alloy and titration of the ammonia with standard acid. It has been shown that total nitrate in nitric acid solutions of Fe-Cr-Ni nitrate salts can be determined reliably and rapidly by passing an aliquot of the sample through an

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[9] Milner et al, "The Determination of Niobium or Tantalum in Uranium and Zirconium-Base Alloys", Analyst 80 (1955) p 380.

acid-form cation exchange column and measuring the acid in the column effluent with standard base. This is feasible in situations such as this where nitrate is the only anion present and the metal salts are normal, ie, of the form MXn rather than $M(OH)_aX_b$.

4.13 <u>Analytical Support for the Fluidized Bed Process for Manufacturing Uranium Aluminide</u> (S. S. Yamamura). The Development Engineering Section of the Chemical Technology Branch is investigating a proposed fluidized bed process[10] for the direct conversion of uranyl nitrate product solution to uranium aluminide, UAl_3. This process involves four steps:

(1) calcination of uranyl nitrate solution at 350°C in a bed of aluminum metal particles fluidized with argon

$$UO_2(NO_3)_2 \xrightarrow[350^\circ C]{Al^\circ} Al^\circ \cdot UO_3$$

(2) reduction of UO_3 to UO_2 with methanol under the same bed conditions

$$Al^\circ \cdot UO_3 \xrightarrow[350^\circ C]{MeOH} Al^\circ \cdot UO_2 + \text{off-gas}$$

(3) chlorination of the UO_2 to UCl_4 with carbon tetrachloride under the same bed conditions

$$Al^\circ \cdot UO_2 \xrightarrow[350^\circ C]{CCl_4} Al^\circ \cdot UCl_4 + \text{off-gas}$$

(4) conversion of $Al^\circ \cdot UCl_4$ to product UAl_3 by heating at elevated temperature

$$Al^\circ \cdot UCl_4 \xrightarrow[680^\circ C]{} UAl_3 + AlCl_3.$$

To form the desired product UAl_3 free of undesirable contaminants, all four steps must be controlled, especially the chlorination of the UO_2 per step 3. The Analytical Chemistry Branch was requested to analyze the various samples originating from the fluidized bed studies and to help characterize the course of the various reactions. Highest priority was assigned to the characterization of reactions 3 and 4 with special emphasis on the complete characterization of the UAl_3 product and the establishment of suitable means for signaling

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[10] E. S. Grimmett, R. K. Ballard, J. A. Buckham, "A New Process for Uranium Aluminide Manufacture Employing Fluidized Bed Technique," Chemical Engineering Symposium, Series 80, Vol <u>63</u> Nuclear Engineering, Part 18 (1967).

the completion of reactions 3 and 4. As of this report, some progress has been made in the characterization of the UAl_3 product. Little has been done with regard to the establishment of an indicator for reactions 3 and 4. A search of the literature produced little useful information.

(1) X-Ray Diffraction Detection Limits for Aluminum Metal, Alumina, and Uranium Oxides in UAl_3 (E. S. Dickerson, W. A. Ryder). Based on examination of binary mixtures, the detection limits for metallic aluminum (Al°), α-Al_2O_3, UO_2, and UO_3 in UAl_3 were found to be 2, 5, 0.5 and 5 wt%, respectively. These detection limits are for the case of one impurity in a UAl_3 matrix. When two or more impurities are present, the diffraction pattern becomes more complex and identification of individual components is difficult. The UO_3 cannot be determined with certainty because its pattern is isomorphous with that of U_3O_8. Of course, amorphous alumina is not determinable.

(2) Chemical Characterization of the UAl_3 Product (D. R. Trammell, I. L. Doggett, M. A. Wade, J. G. Scott). The impurities that could be present in the UAl_3 product are Al°, Al_2O_3, and UO_2 which are of prime importance and $AlCl_3$, UCl_x, UO_3, and $UO_2(NO_3)_2$ which are of lesser importance. At present, total Al, total U, total Cl^-, and Al_2O_3 can be determined chemically. The alumina determination entails selective dissolution of all components except alumina (the behavior of uranium oxides has not been established) with a solution of methanolic bromine. In the chloride determination, the sample is dissolved by a potassium pyrosulfate fusion procedure (a water leach is inadequate) wherein the off-gas from the fusion is scrubbed with a 0.05M NaOH solution. The fused melt is dissolved in water, then recombined with the 0.05M NaOH solution for the chloride determination. By considering the concentration of U, Cl^-, Al_2O_3, and the chemical material balance, it is possible to establish the level of chloride salts and to indicate the presence or absence of significant amounts of uranium oxides and $UO_2(NO_3)_2$. The status of Al° is not defined.

4.2 Analytical Services for Nuclear Technology Branch

4.21 Analysis of Irradiated Hafnium Metal and Hafnium-Aluminum Alloy Samples for Hafnium and its Irradiation Products Lu-175, Ta-181, and W-182 (S. S. Yamamura). The Reactor Experiments Section irradiated two hafnium metal rods and a series of hafnium-aluminum metal alloy sleeves to determine hafnium isotope cross sections. Lathe turnings of the two rod samples and the series of four pairs of sleeves were submitted for the determination of the relative concentrations and isotopic distributions of the hafnium isotopes and the irradiation products Lu-175, Ta-181, and W-182. The analytical approach selected for the analyses is chemical separation coupled with mass spectrometry.

As of this report, the work with hafnium and lutetium is over 50% completed. The two types of samples have been dissolved satisfactorily and tentative schemes have been developed for the isolation of hafnium and lutetium in a form compatible with the mass spectrometer. The standardization of the Hf-176 and Lu-176 spike solutions for the isotope dilution mass spectrometric measurement of hafnium and lutetium has been completed and the determination of hafnium is well under way. The analysis of tungsten has been cancelled and the analysis of tantalum has been deferred pending the development of satisfactory mass spectrometric procedures for isotopic distribution and concentration or spectrophotometric methods to determine concentration only. The project, in accordance with Murphy's familiar law, has had its fair share of problems, and it has been necessary "to go back to the drawing board" on several occasions. Because of the possible significance of the many developments, both positive and negative, to other researchers, this report will describe all pertinent phases of the project. For the sake of simplicity and clarity, a chronological order is maintained.

(1) Nature and Number of Samples. Four hafnium-aluminum alloy samples and 44 hafnium metal turnings samples were received, all quite radioactive. The four hafnium-aluminum alloy samples consisted of four pairs of 7.5-g sleeves containing 0, 1, 2.5, and 5.0 wt% hafnium. Although all four pairs were identified by an etched marking prior to irradiation, only one pair could be matched upon receipt. The remaining six sleeves subsequently were paired successfully by considering the pre- and post-irradiation sleeve weights, the observed gamma activities, and the make-up hafnium concentrations. The remaining 44 samples are turnings samples taken at successively increasing depths at two positions on each of two hafnium metal rods. Based on the irradiation history of the samples, the estimated Lu-175, Ta-181, and W-182 concentrations are 0.7%, 3%, and 0.3%, respectively, relative to hafnium.

(2) Dissolution of the Samples (J. A. Rindfleisch, M. A. Wade). The samples of hafnium metal turnings were weighed remotely, then dissolved with 15 ml of a 4:1:25 conc HF-conc HNO_3-water mixture in a tared, precalibrated 250-ml screw-cap polyethylene bottle. The dissolved sample was diluted to the calibration mark (the bottom of the bottommost ring at the neck) and weighed.

The dissolution of the sleeve samples was somewhat more involved. The following diagram describes the dissolution procedure.

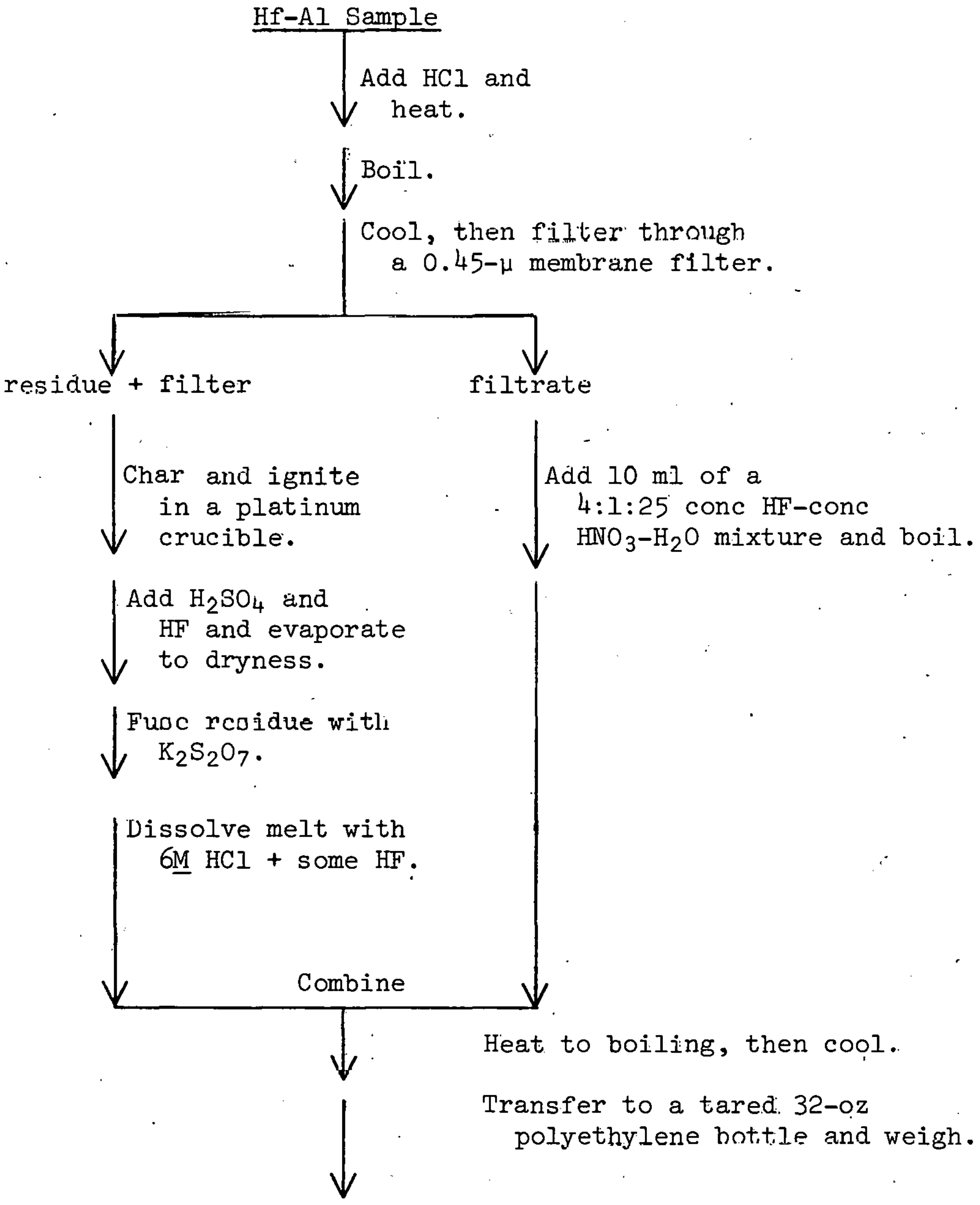

Fig. 2 Diagram of dissolution scheme for hafnium-aluminum sleeve samples.

(3) Preparation of Natural Standards and Spike Solutions of Hafnium, Lutetium, and Tantalum (S. S. Yamamura, R. Fullerton).

(a) Natural Standard Solutions. The hafnium and lutetium natural standards were prepared from freshly ignited hafnium oxide, (HfO_2) and lutetium oxide (Lu_2O_3) respectively. Both oxides were quoted by the supplier to be >99.9% pure. The HfO_2 was dissolved by fusion with potassium pyrosulfate in a quartz apparatus under total reflux and the melt was dissolved and diluted to volume with 6M HCl. The resulting solution was standardized gravimetrically by precipitation as the mandelate and ignition to the oxide. The lutetium solution was prepared by dissolving the oxide with ~6M HCl and diluting the resulting solution to volume with water. It was standardized by titration with EDTA. The EDTA was initially standardized against a solution of mercuric nitrate prepared from the triply distilled metal. These modes of preparation provided two independent measures of the concentration of the hafnium and lutetium solutions--one based on the original weight of the oxide, the other based on the chemical standardization. In both cases, there was less than 0.1% disagreement between the value based on the original oxide weight and the value obtained by analysis. Accurate dilutions of the standard solutions gave working solutions of the desired concentrations.

A standard tantalum solution was prepared by dissolving pure tantalum metal filament with a mixture of nitric and hydrofluoric acids. A working solution of the desired concentration was prepared by dilution with a $HF\text{-}HNO_3$ solution. Because of the presence of fluoride, all dilutions were made on a weight basis to facilitate precise delivery of small aliquots.

(b) Spike Solutions. The Hf-176 and Lu-176 spike solutions were prepared from Hf-176-enriched HfO_2 and Lu-176-enriched Lu_2O_3 obtained from ORNL. The HfO_2 was fused with potassium pyrosulfate and diluted with 6M HCl. The Lu_2O_3 was dissolved with hydrochloric acid and diluted with water. To eliminate the effect of evaporation on the concentration of the spike, aliquots of the solution were transferred immediately to 2-oz screw-cap polyethylene bottles.

Tantalum-180 is obtainable from ORNL in various enrichments. Although high enrichment simplifies the mass spectrometric measurement of tantalum, the very high cost of the highly enriched material dictates the use of one with a 4% Ta-180 content. Initial mass spectrometric experiments with a 0.3%-enriched Ta-180 spike showed that high background is encountered with the high temperature necessary for measurement of the small 180 mass peak.

(4) Mass Spectrometric Measurement of Hafnium, Lutetium and Tantalum (R. E. McAtee, G. D. Workman, R. M. Abernathey).

(a) Hafnium. Hafnium compounds are ionized only at high temperatures which lead to serious background enhancement. The use of a rhenium filament coated with carbon (sucrose carbonized on the filament), delivery of the hafnium as a chloride-sulfate solution, and application of a proper bakeout provide a satisfactory spectrum, free of interfering background at a hafnium level of 30 μg.

(b) Lutetium. The mass spectrometric measurement of lutetium is comparatively easy because the conditions for its ionization are less energetic than that for hafnium or tantalum. Only 3 μg of lutetium on the filament is adequate. The primary requirement is a clean sample. Organic residues from chemical separation schemes have been the most frequent source of problem in previous studies.

(c) Tantalum. Satisfactory conditions for the mass spectrometric analysis of tantalum have not been established. Tantalum, more so than hafnium, requires an extremely high temperature for ionization. This as noted above enhances the background. The background is particularly important in the case of tantalum because the Ta-180 content of natural tantalum is only 0.012%. It is possible that the background problem may be partially circumvented by increasing the quantity of tantalum on the filament. With this change and the use of a 4%-enriched Ta-180 spike, satisfactory measurement of the tantalum may be possible. Unfortunately, a few milligrams of the 4%-enriched oxide will cost about $1500. Under ideal conditions, 10 μg of tantalum on the filament is adequate. In actual practice, at least 30 μg of tantalum would be required to allow proper bakeout.

(5) Chemical Separation of Hafnium, Lutetium, Tantalum and Tungsten (M. E. Kussy, J. A. Rindfleisch, R. Fullerton, S. S. Yamamura, M. A. Wade). The development of separation procedures for hafnium, lutetium, tantalum, and tungsten was undertaken prior to the arrival of the samples to confirm the feasibility of the chemical separation-mass spectrometric measurement approach contemplated for the analyses. Considering the nature of the samples and the chemical nature of the four elements to be determined, a dissolution scheme involving hydrochloric, nitric, and hydrofluoric acids and potassium pyrosulfate was assumed. The initial development effort was limited to two weeks, so initial studies were directed to separation schemes based on extraction, precipitation, and simple ion exchange rather than on schemes involving more time-consuming ion exchange chromatography. Thereafter, new separation schemes were developed and many modifications were made to meet the requirements of the mass spectrometer and to circumvent unforseen problems such as that caused by the presence in the sample of gadolinium which has a 160-mass isotope that ionizes as a gadolinium monoxide species of mass 176.

(a) Hafnium. Initially, hafnium was separated by an extraction procedure involving: (a) extraction of hafnium cupferrate into 1:1 benzene-i-amyl alcohol, (b) evaporation of the solvents and destruction of cupferron with nitric and perchloric acids, (c) extraction of hafnium into xylene from a $2\underline{M}$ $HClO_4$ medium as the thenoyltrifluoroacetone (TTA) complex, (d) a $0.25\underline{M}$ HF-$0.25\underline{M}$ HNO_3 strip of the hafnium, (e) evaporation of the HF-HNO_3 strip with sulfuric acid, and (f) dissolution of the sulfate residue in hydrochloric acid. The purpose of the initial cupferron extraction was to separate the hafnium from fluoride and sulfate especially. Later, the procedure was simplified by fuming the sample aliquot initially with perchloric acid, then proceeding directly to the TTA extraction. Both schemes gave satisfactory recovery of hafnium in a clean form. Spectrographic analysis of the separated fraction showed only trace levels of Al, B, Mg, and trace to minor levels of zirconium. (The presence of zirconium is attributed to zirconium contamination in the natural hafnium used in the studies). The major deficiencies of these schemes were noticeable cross contamination and residual contaminants, presumably organic in nature, that precluded a successful scan.

The method subsequently developed and used for the analysis of actual samples involves: (a) precipitation of hafnium as the hydroxide, (b) dissolution of the hydroxide with conc HCl and adsorption of the hafnium on an anion exchange column from strong HCl medium, (c) elution of the hafnium with $1\underline{M}$ HCl, and (d) evaporation of the hafnium solution in a small plastic test tube. Commercially available one-unit polyethylene medicine droppers with the top of the squeeze bulb cut off are used as the ion exchange columns. Analysis of samples with this procedure revealed the presence of a contaminant that interfered to some extent at the 176 mass peak even after considerable high temperature bakeout. As yet, this contaminant has not been identified.

(b) Lutetium. The first procedure developed for the isolation of lutetium was based on an extraction procedure reported by Maeck et al[11]. The lutetium is precipitated as the hydroxide along with hafnium and perhaps tantalum with the aid of nickel carrier. The precipitate is dissolved with a minimum amount of nitric acid, then the lutetium is extracted selectively as a tetra-n-butylammonium nitrate complex into nitropropane from an aluminum nitrate-salted medium. The extracted lutetium is stripped from the nitropropane phase with water. Based on radiotracer studies, the lutetium recovery was adequate and spectrographic analysis of the isolated lutetium fraction showed only trace levels of aluminum and magnesium

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[11] W. J. Maeck, M. E. Kussy, J. E. Rein, "Spectrophotometric Determination of the Lanthanides as Extracted Nitrate Complexes," Anal. Chem. 37 (1965) p 103.

and minor to trace levels of iron; however, satisfactory mass spectrometric scans were not attainable because of residual organic matter. Evaporation of the final lutetium solution to dryness and ignition destroyed the organic matter, and a dilute hydrochloric acid leach of the ignited residue provided sufficient lutetium to give a satisfactory scan. On separation studies conducted on aliquots of the Lu-176 spike, the observed isotopic composition was identical with that of the original lutetium spike indicating that there was no introduction of natural lutetium in the process.

Subsequent analysis of samples with the above procedure revealed the presence in the samples of gadolinium which interferes in the measurement of the Lu-176 mass peak as noted earlier. A new separation procedure was developed to circumvent the gadolinium interference. The lutetium is separated from most of the fluoride and part of the hafnium by precipitation as the hydroxide from highly alkaline medium. The lutetium hydroxide and the accompanying nickel hydroxide carrier are then dissolved in conc HCl and passed through a small column of Dowex 1-X8, 100 to 200 mesh resin which retains the hafnium. The lutetium in the highly acidic column effluent is again precipitated as the hydroxide, then contacted as a dilute hydrochloric acid solution with a small amount of Dowex 50W-X8, 200 to 400 mesh resin in the ammonium form. The resin is placed at the head of a column of identical resin, and the adsorbed lutetium is chromatographically separated from gadolinium, the nickel carrier, and residual hafnium by preferential elution with an α-hydroxyisobutyrate solution at pH 3.4. Finally, the lutetium is separated from the organic elutriant by adsorbing it on a Dowex 50W acid form resin, then eluting it with hydrochloric acid. Evaporation of the hydrochloric acid solution in a plastic tube yields a clean sample suitable for the mass spectrometric measurement of lutetium. The critical phases of this separation scheme are the anion column removal of hafnium where the hydrochloric concentration ideally must be 11<u>M</u> or greater, the purity of the ammonium form cation resin (it is best to carry the resin through a thorough strong ammonium nitrate wash-water rinse cycle initially), and the final cation resin cleanup treatment where the removal of α-hydroxyisobutyrate must be complete. The chromatographic separation of lutetium from gadolinium is not as critical as might be expected. Under the conditions described, the lutetium emerges as a sharp band at 8±2 ml, whereas, the gadolinium does not appear until more than 15 ml of elutriant has been added.

Like in the case of hafnium, the separated lutetium fraction contains an unidentified contaminant that interferes at the 176 mass peak. This problem is very serious in the case of lutetium because lutetium is quite volatile and high temperature bakeout cannot be employed.

4.3 Analytical Service for Reactor Engineering Branch

4.31 Analysis of ATR Fuel Plate and Plate Punchings for Uranium and Boron (S. S. Yamamura, M. A. Wade). Specification IN-F-3-ATR for the Advanced Test Reactor Mark VI fuel lists specific amounts of U-235 and natural boron for the various plates. It further specifies that the uranium and boron loadings must be uniformly distributed within each plate. One prospective fuel fabricator reported an inability to determine whether these specifications were being met because of analytical method limitations. Two of the fabricator's plates, therefore, were submitted for determination of U-235 and boron. One of the plates was to be analyzed as a unit to establish the total amounts of uranium and boron in the plate. Small plate punchings were to be analyzed from the other plate to establish core loading and uniformity. Both the plate and plate punchings were analyzed successfully for uranium and boron without incident. One revised spectrophotometric procedure based on curcumin was developed for the determination of boron in the plate punchings. Details of this procedure and the analysis of the plate and the plate punchings for boron and uranium are described below.

(1) Description of ATR Fuel Plate and Plate Punchings. The ATR fuel element is composed of 19 curved fuel plates varying in size from 50 x 2 in. (plate 1) to 50 x 4 in. (plate 19). The uranium and boron loading per plate increases gradually with increasing plate size from 32 and 0.12 g to 71 and 0.28 g, respectively. The boron is present as boron carbide. Plate 1 has 350 g of aluminum and plate 19 has 880 g of aluminum. The aluminum content of the plates within these end plates varies from 220 g to 440 g. The two plates received for analysis were plates 2 and 10. Punchings were taken from plate 2; plate 10 was analyzed as a unit. The punchings are of two sizes: 0.08-in. diam for the uranium determination and 0.50-in. diam for the boron determination.

(2) Analysis of Plate Punchings

(a) Determination of Uranium (J. P. Clark). The samples are dissolved in nitric acid with mercury(II) nitrate and chloride "catalysis". A known amount of U-233 spike is added to the sample before dissolution. The uranium subsequently is isolated by an extraction-precipitation procedure (Appendix B) and determined by isotope dilution mass spectrometry. The precision of the analytical procedure including dissolution is known to be better than 0.5% relative standard deviation which is highly satisfactory. The specification states that the fuel concentration along the longitudinal scan shall not exceed the average (401 mg U-235/in.^{2}) by more than 8%. Assuming a confidence level of 95%, the required precision of the U-235 determination is about 3% relative standard deviation.

(b) Determination of Boron (S. S. Yamamura, J. E. Fluegel). The samples are dissolved by a two-step process including hydrochloric acid dissolution of the punchings and sodium carbonate fusion of the residue. Boron is determined on an aliquot of the dissolved sample by a simple spectrophotometric procedure based on curcumin. Details of the analysis procedure are described in Method B-Color-3 in Appendix B.

The precision of the analytical procedure has been established by analyzing a series of dissolved punchings in duplicate. Based on duplicate determinations of various prepared sample solutions, the standard deviation is 3.9 µg of boron per punching equivalent to a relative standard deviation of 1.1%. Based on the results for a series of 8 punchings from the sample plate, the standard deviation is 9.2 µg of boron per punching equivalent to a relative standard deviation of 2.6%. The first of these refers to the precision of the colormetric procedure, the second to the overall procedure including dissolution. The difference in precision between the two is attributed to differences between punchings and slight losses or gains (contamination) during the sample dissolution.

The ATR fuel specification states that the boron concentration along the plate shall not differ by more than 30% from specified levels so the required precision of the analytical procedure is about 10% for a confidence level of 95%. This is easily met by the established procedure.

(3) Analysis of Fuel Plate (D. R. Trammell, J. P. Clark, F. A. Duce, R. A. Nielsen, T. R. Lyon). The analysis of the fuel plate entails preliminary dissolution of the plate, then determination of the concentration and isotopic distribution of the boron and uranium by established methods. The fuel plate is dissolved by a process involving mercury(II) nitrate-catalyzed nitric acid decomposition of the plate, filtration-separation of undissolved residue, and sodium carbonate fusion-hydrochloric acid leach dissolution of the residue. This dissolution scheme yields two solutions. One is that of the residue phase which contains most of the insoluble boron carbide and small amounts of uranium. The other, high in uranium and low in boron, is the filtrate from the initial nitric acid dissolution. Boron is determined in the boron-rich and boron-lean solutions by acid-base titrimetry based on mannitol complexing and by emission spectrography, respectively. Its isotopic distribution is established mass spectrometrically on a small portion of boron isolated by methanolic distillation. Uranium is determined by fluorophotometry and isotope dilution mass spectrometry in the lean and rich solutions, respectively. Details of the analysis scheme

are presented in Appendix C.

The specifications for ATR fuel requires that the boron loading is within 8% of the specified level so the required precision (standard deviation) for the boron determination is about 3%. A precision of 0.6% relative standard deviation has been attained by the titrimetric procedure using one trained analyst. The precision of the spectrographic method is conservatively estimated at 4% relative standard deviation. Thus, even with an unfavorable boron distribution of 80% in the residue solution and 20% in the plate solution, the proposed analysis scheme provides the required precision.

The required uranium loading per plate is ±2% of specified levels. The isotope dilution mass spectrometric analysis procedure with an established precision of better than 0.5% easily meets the required precision of about 0.75% standard deviation. The precision of the fluorophotometric method for uranium is about 30%; however, this affects the overall precision insignificantly because the solution of the undissolved residue contains less than 0.5% of the total uranium.

4.32 <u>Analysis of ETR Fuel Plate and Plate Punchings for Boron, Uranium, and Silicon</u> (S. S. Yamamura, M. A. Wade, J. P. Clark, J. E. Fluegel, D. R. Trammell, R. A. Nielsen, T. R. Lyon). A complete fuel plate and punchings from two plates were analyzed for B-10, U-235, and Si to determine whether one fabricator's fuel fabrication process would produce fuel that meets present ETR fuel specifications. The ETR fuel plate has a "sandwich" construction as shown in Figure 3. With the exception of the silicon determinations which were requested on some of the plate punchings also analyzed for boron, the sampling and analysis program for the ETR fuel plate is similar to that for the ATR fuel discussed in Section 4.31. The silicon was determined both gravimetrically as SiO_2 and spectrophotometrically by the silicomolybdate molybdenum blue procedure (Appendix B). The analytical precision required for ETR fuel is identical to that for the ATR fuel. Despite increased difficulties in the fuel plate dissolution

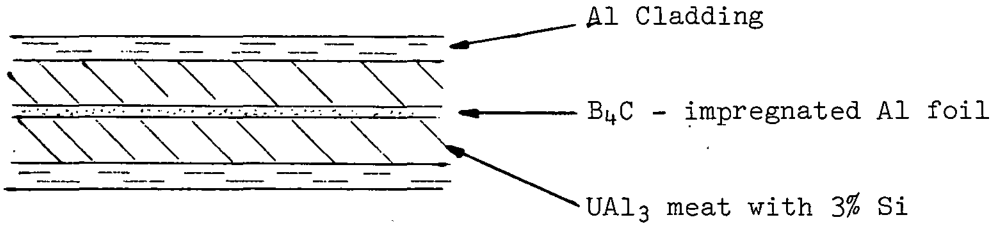

Fig. 3 Edge View of ETR Plate

caused by the increased silicon level, adequate analytical precision is obtained.

4.4 Analytical Services for USAEC

4.41 Determination of Low Concentrations of Thorium in Nickel Metal (S. S. Yamamura, M. E. Kussy). A large quantity of nickel metal-alloy containing about 5 wt% thoria was purified in six batches by a remelting process wherein the thoria separates to the slag to yield a nickel metal product with only a low concentration of thorium. Because thorium is an SS material, the recovered nickel came under the scrutiny of the USAEC Division of Materials Licensing. Mr. Don F. Harmon of the Source and Special Nuclear Materials Branch submitted one sample from each of the six batches of nickel metal for thorium assay. After consideration of several alternative approaches including emission spectroscopy, isotope dilution mass spectrometry, and absorption spectrophotometry, a spectrophotometric chemical procedure based on thorin was selected for the determination of thorium.

Chemical tests showed that the samples contained varying amounts of Fe, Nb, Si, and Ti. The method finally developed and used to determine the thorium in the nickel samples was as follows:

> A 0.600-g portion of sample turnings was dissolved in a minimum volume of conc HNO_3, diluted with water, then filtered to isolate insoluble residue. The residue, mainly silicon with small amounts of Fe, Nb, Th, and Ti was ignited, dissolved with a combination of HCl, HF, $HClO_4$, and H_2SO_4, and recombined with the original filtrate. The combined solution was heated to boiling and held at near boiling to precipitate niobium which subsequently was removed by filtration. Exactly half of the solution was taken for the final determination. The thorium was separated as the hydroxide at pH 5.5 with the aid of an aluminum hydroxide carrier, then the hydroxide precipitate was dissolved with hydrochloric and perchloric acids. Finally, the thorium-thorin-colored complex was developed in a $0.35 \pm 0.05\underline{M}$ $HClO_4$ medium containing hydroxylamine and measured at 545 mμ.

The analysis segment of the method was precise and bias-free when applied to prepared nickel-thorium mixtures; however, accurate measurement of the thorium content of the samples was not possible because the sample impurities, especially niobium, precluded the preparation of a sample solution compatible with the analysis scheme. Removal of niobium by precipitation resulted in losses of thorium by occlusion, and the addition of complexing agents to keep the niobium in solution hampered the separation and determination of thorium. Because only limited methods development effort was warranted, the samples were analyzed by a standard addition technique. This approach gave results with a relative standard deviation of about 35%.

It is possible that similar samples will be received for analysis in the future. If so, studies should be directed initially to the extraction removal of niobium (and possibly titanium from hydrochloric acid medium with a chloroform solution of benzoylphenylhydroxylamine (BPHA). This extraction procedure, described in Appendix B, will enable quantitative extraction of niobium despite the presence of fluoride in the sample solution.

4.5 Method Development

4.51 Investigation of the Method for Determining Acidity of Metal Salt Solutions (F. A. Duce, S. S. Yamamura). The established method[12] for the determination of free acidity of aqueous solutions containing hydrolyzable metal ions is applied to aluminum, stainless steel, and zirconium solutions; however, only bias controls with an aluminum matrix have been used up to now to establish bias and precision. Preparation of free acidity standards with aluminum, stainless steel, or zirconium matrices, and investigation of the various analytical procedures of the acidity method have been started. The purpose of the study is to determine the precision and bias for each frequently used procedure and to effect improvements where necessary.

To date, free acidity standards with stainless steel (Fe-Cr-Ni-nitrates in the mole ratio 7:2:1) and aluminum nitrate matrices have been prepared. Both series of standards were prepared by the same approach, i.e., the aluminum nitrate solution and the Fe-Cr-Ni nitrate solution first were analyzed to show that the salts were indeed normal salts, then spiked with a measured quantity of a standardized nitric acid solution. A normal salt is one that does not yield any H^+ or OH^- when the neutral salt is removed from solution. Within experimental error, the Al, Cr, Fe, and Ni nitrate salts are normal salts; so, it is possible to calculate a theoretical free acid normality on the basis of the acid added and the final volume of the solution.

In this method, the hydrolyzable metal ions are rendered inert by complexation with potassium oxalate. Oxalate complexes chromium very slowly at room temperature so a 2-hr wait is necessary after the addition of the sample to the oxalate. It has been found that the complexation time can be cut to about 10 min by heating the sample-oxalate mixture in a boiling water bath for 5 min. Volatilization losses of acid during the heating are prevented by confining the sample-oxalate mixture in a 2-oz screw-cap polyethylene bottle.

4.52 Evaluation of Procedures for the Separation of Iron, Chromium, Cobalt, and Nickel as a Group for Subsequent Determination by Atomic Absorption and Emission Spectroscopy (S. S. Yamamura, M. E. Kussy, T. R. Lyon, W. A. Ryder, R. Fullerton). One type of sample that is being received for analysis is a 2M HCl solution containing approximately 20 mg/ml of fused potassium pyrosulfate residue, 1 to 40 μg/ml of Fe, 0.05 to 15 μg/ml of Cr, 0.007 to 0.7 μg/ml of Co, and 0.05 to 5 μg/ml of Ni. Normally, 20-ml portions

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[12] Method Acidity-Vol-1, November 1968, INC Analytical Chemistry Manual.

of this type of solution are submitted for analysis to determine the concentrations of the Fe, Cr, Co, and Ni. The two analytical techniques used to analyze these samples are atomic absorption and emission spectroscopy. The latter is used only to determine cobalt at levels below the detection limit of the atomic absorption procedure. Both of these techniques require a prior separation-concentration of Fe, Cr, Co, and Ni from the hydrochloric acid-potassium pyrosulfate medium; so, the development and evaluation of various separation schemes have been undertaken. Two satisfactory procedures, one based on precipitation with N-benzoylphenylhydroxylamine (BPHA) and β-nitroso-α-naphthol, and another suggested by the customer on precipitation with sodium hydroxide, have been established. Of these two, the sodium hydroxide procedure is preferred because of its simplicity.

In the BPHA-nitrosonaphthol precipitation method, Fe, Cr, Co, and Ni are precipitated as a group at pH 5.5 to 6.0 with a mixture of BPHA and β-nitroso-α-naphthol. The nitrosonaphthol is present to precipitate cobalt. The precipitate is filtered on a membrane filter, then ignited in a platinum crucible to destroy the organic matter. The ignited oxide residue is dissolved in a measured 2- to 3-ml volume of 0.5$\underline{M}$ HCl. In the sodium hydroxide precipitation method, Fe, Cr, Co, and Ni are precipitated at pH 10- to 12; the precipitate is isolated on a membrane filter; the filter is destroyed with perchloric acid; and the residue is dissolved in a measured 2- to 3-ml volume of 0.5$\underline{M}$ HCl.

The reliability of both methods was tested by processing synthetic standards made up of 20 ml of 2$\underline{M}$ HCl, 0.4 g of potassium sulfate, and 0- to 2-ml portions of a mixture 100 μg/ml in Fe, 10 μg/ml in Ni, 5 μg/ml in Cr, and 1 μg/ml in Co. The results of these synthetic samples were compared to 0- to 2-ml portions of the standard ion mixture not carried through the separation processes. Satisfactory recoveries were obtained by both methods. The use of 200 μg of yttrium carrier in the sodium hydroxide method had no significant effect on the results at the ion levels studied. It may have a beneficial effect when the level of iron and the other constituents are very low.

4.53 Spectrophotometric Determination of Phosphorus (F. A. Duce, S. S. Yamamura). At this laboratory, the familiar molybdenum blue procedure is used alone in combination with a perchloric acid digestion treatment, and in combination with a cupferron-chloroform extraction to accommodate the wide diversity of analytical requests received for the determination of phosphorus. The effects of diverse ions on the four analysis schemes provided in the method were studied to establish their applicability and limitations. The results of this diverse ion study and details of the method are presented in Appendix B.

4.54 Spectrophotometric Determination of Silicon (F. A. Duce, S. S. Yamamura). A versatile spectrophotometric method for the determination of silicon has been developed to supplement the gravimetric and spectrographic methods currently in use at this laboratory. The following is the abstract of the paper, "Versatile Spectrophotometric Method for the Determination of Microgram Amounts of Silicon," that is to be presented at the 24th Annual Northwest Regional Meeting of the American Chemical Society, June 12 and 13, in Salt Lake City. Details of the method are presented in Appendix B.

> A versatile, spectrophotometric method for the determination of microgram levels of silicon as molybdenum blue is described. It combines the desirable features of existing spectrophotometic methods with three pretreatment procedures. The pretreatment procedures are: (a) the removal of cations with a cation resin in the acid form, (b) the conversion of all silicon species to the reactive monomer with an alkaline treatment, and (c) the decomposition of silicon fluoride with boric acid in the presence of cation resin. These procedures coupled with the color development provide five analysis schemes which are applicable to a wide variety of samples including natural and industrial waters and solutions of various nuclear reactor fuels and components. Provisions are included for the selective determination of the sum of the reactive monosilicic and disilicic acids and for the determination of total silicon.

4.55 Evaluation of Various β-Diketones for the Spectrophotometric Determination of Uranium (S. S. Yamamura, L. L. Braun*, R. Fullerton). A comparative study of 18 β-diketone reagents including three new compounds (Table V) has been made. The primary objective is the development of a chromogen sensitive enough to extend the lower determinable limit of the present spectrophotometric method based on the β-diketone chromogen dibenzoylmethane (DBM) and capable of forming a covalent complex compatible with the selective methyl isobutyl ketone extraction employed in the present method.

Six β-diketones have been found to be more sensitive than DBM (Table V). These six in decreasing order of sensitivity are: dithenoylmethane, curcumin, di-β-naphthoylmethane, 1,3-Bis(4-methoxylphenyl)-1,3-propanedione, thenoyltrifluoro-acetone (TTA), and 4,4,5,5,6,6,6-heptafluoro-(2-thienyl)-1,3-propanedione. The inclusion of diethenoylmethane is based on data reported by Purushottam and Atchaiah. The authors did not observe the reported high sensitivity in their studies with a synthesized dithenoylmethane reagent.

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* AWU Visiting Professor (Idaho State University.)

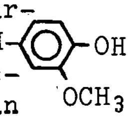
Critical examination of the chemical structure of the reagents studied provide an insight as to the direction for most fruitful future study. The desirable substituent groupings appear to be those that provide increased sensitivity through a long, conjugated double-bond structure, those that provide increased complex stability by increasing the acidity of the enolic hydrogen, and those that do not enhance the visual color of the uncomplexed reagent. Of these three, the conjugated double-bond structure appears to have the greatest effect. Substituent groups such as aminophenyl and nitrophenyl which increase the visual color of the uncomplexed reagent (shift the absorbance peak of the reagent and uranium-reagent complex to higher wavelengths), are undesirable almost without exception. The one exception is curcumin's -CH=CH- grouping which, because of its very large conjugated double-bond structure, gives a high molar absorptivity of 43,600 to the uranium-curcumin complex. On the basis of the foregoing, the desirable reagent appears to be one that has bulky, conjugated double-bond substituents with electron-withdrawing character. The preparation and evaluation of potentially useful new compounds of this type will be pursued at a future date. Because one of the authors (Professor Braun) has returned to his teaching position, continuation of studies involving synthesis has been postponed.

TABLE V

β-DIKETONES EVALUATED FOR THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

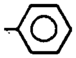
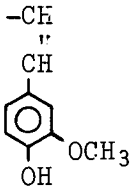
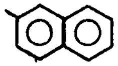
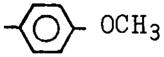
Reagent		Substituent Groups [a]	Molar Absorptivity and Absorbance Peak
1. 1,3-Diphenyl-1,3-propanedione [Dibenzoylmethane (DBM)]	R,R' =		18,100 @ 395 mμ
2. 1,3-Bis(2-thienyl)-1,3-propanedione (Dithenoylmethane)	R,R' =		~70,000 @ 420 mμ [b]
3. Curcumin	R,R' =		43,600 @ 483 mμ
4. 1,3-Bis(2-naphyl)-1,3-propanedione (Dinaphthoylmethane)	R,R' =		30,000 @ 413 mμ
5. 1,3-Bis(4-methoxyphenyl)-1,3-propanedione	R,R' =		25,500 @ 405 mμ

TABLE V (Continued)

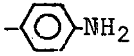
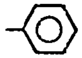
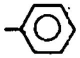
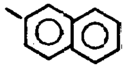
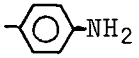
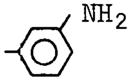
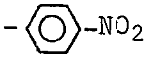
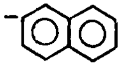
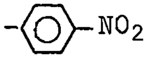
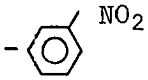
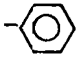
	Reagent	Substituent Groups [a]	Molar Absorptivity and Absorbance Peak
6.	4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione [Thenoyltrifluoroacetone (TTA)]	R' = $-CF_3$ R' = 	21,000 @ 382.5 mμ
7.	4,4,5,5,6,6,6-Heptafluoro-1(2-thienyl)-1,3-hexanedione	R = $-C_3F_7$ R' = 	21,000 @ 388 mμ
8.	1-(4-aminophenyl)-3-phenyl-1,3-propanedione[c]	R =  R' = 	16,000 @ 436 mμ
9.	4,4,4-Trifluoro-1-phenyl-1,3-butanedione	R = $-CF_3$ R' = 	12,900 @ 372.5 mμ
10.	1,1,1,5,5,5-Hexafluoro-2,4-pentanedione	R,R' = $-CF_3$	<500 @ 350 mμ
11.	1-(4-aminophenyl)-3-(2-naphthyl)-1,3-propanedione[d]	R =  R' = 	17,380 @ 446 mμ

TABLE V (Continued)

	Reagent	Substituent Groups[a]	Molar Absorptivity and Absorbance Peak
12.	1,3-Bis(4-aminophenyl)-1,3-propanedione[a]	R,R' = 	~15,300 @ 446 mμ
13.	1,3-Bis(3-aminophenyl)-1,3-propanedione[d]	R,R' = 	14,500 @ 410 mμ
14.	1-(4-nitrophenyl)-3-(2-naphthyl)-	R = 	–[e]
	1,3-propanedione[d]	R' = 	17,650 @ 420 mμ
15.	1,3-Bis(4-nitrophenyl)-1,3-propanedione	R,R' = 	–[e]
16.	1,3-Bis(3-nitrophenyl)-1,3-propanedione	R,R' = 	–[e]
17.	2,4-Pentanedione (Acetylacetone)	R,R' = $-CH_3$	2380 @ 350 mμ
18.	1-Phenyl-1,3-butanedione (Benzoylacetone)	R =  R' = $-CH_3$	7500 @ 375 mμ

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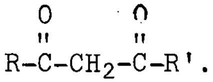
[a] β-Diketones have the general structure  $R-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-R'$.

[b] Based on the data of Purushottam and Atchaiah [f]. The high sensitivity observed by these investigators was not confirmed in experimental studies carried out with dithenoylmethane synthesized by a graduate student working with Professor Braun at Idaho State University.

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[c] In the second of three papers dealing with uranyl complexes of β-diketones[g], a molar absorptivity of 30,000 was reported for the uranium complex of this reagent.

[d] Newly synthesized reagents.

[e] A comparative study of these nitro compounds was not feasible because of their low solubility in alcohol. In both cases, they are less sensitive than DBM.

[f] D. Purshottam and M. Atchaiah, "Colorimetic Estimation of Uranium with β-diketones", Z. Ana. Chem., 196 (1963) p. 85.

[g] CA, 51 (1957) pp 11150-11151, Morizo Ishidate and Yasuhiro Yamane, "β-diketone-uranyl Chelate Compounds", Yokugaku Zasshi, 77 (1957) pp 386-400.

5. REMOTELY OPERATED FACILITIES

(F. W. Dykes, E. M. Fortsch)

5.1 RAF Cave

Construction of this facility began December 1968 and was scheduled for completion May 30, 1969, except the main viewing window. This window was broken by construction personnel and will require 3 to 6 months to repair. Consequently, the cave will not be available for use until at least July 15, 1969, more likely October 15, 1969.

5.2 Procurement of RAF Replacement Boxes

Authorization was obtained last year to replace five worn-out wood RAF boxes with stainless steel boxes. Design data were prepared, and the boxes were obtained through competitive bidding. Auxiliary items such as tong wrenches and exhaust connectors were fabricated locally. An additional five boxes have been authorized and design data are being revised to incorporate experience gained with the first group.

6. IMPROVEMENTS IN FACILITIES

6.1 Relocation of Glass Shop (F. W. Dykes, H. G. Brinkley).

AEC-ID authorized relocation of the glass shop from the potentially contaminated CPP-602 building to the CPP-637 building. The work started in January 1969 and was completed in May 1969.

6.2 Conceptual Design for Analytical Chemistry Building (F. W. Dykes, J. M. Crawford).

A conceptual design for a 4 module Analytical Chemistry Building was completed. The proposed location is adjacent to the CPP Area. Initial construction would include a modern hot cell complex, support facilities, and office space.

6.3 CPP-627 Heating and Ventilating Modifications (F. W. Dykes, M. A. Wade).

After several years of study, design is proceeding on modifications that will insure adequate ventilation in the CPP-627 building. The areas of concern for the Analytical Chemistry Branch are the RAF and Chemical Analysis Laboratory. Title I design has been reviewed, and the work is proceeding on Title II design. All hoods will meet Health and Safety requirements of 150 lfm, and air flow through the RAF will be doubled.

IV. SPECTROSCOPY

1. MASS SPECTROMETRY

1.1 Method Development

1.11 Determination of Cadmium with the Hitachi Crucible Source Mass Spectrometer (J. E. Delmore). A procedure has been developed for the separation of cadmium from solutions of fission product, uranium, and plutonium. Good sensitivity for the cadmium as cadmium iodide (CdI_2) has been repeatedly obtained with the Hitachi Crucible Source mass spectrometer. The separation procedure was adapted from standard radiochemical methods with greater emphasis for the absolute chemical purity than for the radiochemical purity.

Fission product cadmium was determined in four types of nuclear fuel. While making these determinations, it was found that 1 ng of an isotope could be accurately measured in a 2 μg sample. This demonstrates a carrier effect, because about 50 ng or more is required to obtain the same beam intensity from a single calutron-separated cadmium isotope. Also, zinc iodide (ZnI_2) was found to be closely enough matched physically to CdI_2 for the same carrier effect to be exhibited when microgram quantities of ZnI_2 are mixed with nanogram quantities of CdI_2.

Fission product cadmium now can be determined routinely in fission product mixtures when the sample contains at least 0.5 ng of the least isotope for which accurate measurements are required. This crucible source mass spectrometer had always shown a ZnI_2 spectrum when CdI_2 was present, and the reaction appeared to be $Zn^o + CdI_2 \rightarrow ZnI_2 + Cd^o$. Because zinc had never been introduced into the source, the ceramic spacers appeared to be the zinc source. This zinc memory was eliminated by replacing the ceramic with high purity quartz. After this modification was made, any zinc subsequently introduced was eliminated by heating the source to 450°C. Cadmium was eliminated by heating the source to 400°C. Mercury also is eliminated easily.

The crucible source mass spectrometer appears capable of memory-free isotope dilution determination of Cd, Zn, and Hg as iodides; although, cadmium is the only one for which a spike has been standardized and for which a reliable separation scheme completely tested.

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2. SPECTROCHEMICAL

2.1 Analytical Services

2.11 Battelle Memorial Institute

(1) Laser Probe Analysis of Irradiated Stainless Steel (J. M. Baldwin, W. A. Ryder). Laser probe analysis was requested on a sample of 347 stainless steel that had been subjected to irradiation exposure of 2.1 x 10^{22} nvt in the Engineering Test Reactor. Comparison of element concentrations in metal grains and in the grain boundaries with those in an unirradiated control sample was requested. The analysis was accomplished using normal laser probe techniques. Personnel shielding was accomplished by stacking lead bricks around the laser probe which was mounted in the usual position on the spectrograph optical bench. Contamination by the vaporized material did not present a serious problem due to the small amount of sample removed by the laser.

The results of the analysis are tabulated below.

TABLE VI

LASER PROBE ANALYSIS OF IRRADIATED STAINLESS STEEL

	Control		Irradiated Sample	
Element	Grain	Grain Boundary	Grain	Grain Boundary
Mn	M	L	ND	ND
Cr	M	L	M	L
Ni	M	L	M	L
Cu	=	=	ND	ND
Zn	ND	ND	ND	ND
V	ND	ND	ND	ND
Cr	M		L	
Ni	=		=	

[M] = More Concentrated
[L] = Less Concentrated
[=] = Equal Concentrations
[ND] = Not Detected

2.2 Improvements in Methods

2.21 New Technique for Ashing Millipore Filters for Qualitative Analysis by Emission Spectrography (T. R. Lyon). A simple ashing procedure for the recovery of solids collected on Millipore filters in a form acceptable for spectrographic presentation was developed. The filter is dampened with water, folded, placed on a graphite platrode electrode preheated to 400°C, and covered with an inverted beaker. This procedure ashes the filter gently and ensures that the ash can be removed from the platrode, weighed and placed in a cup electrode for excitation. Molded platrodes provide better recoveries and are preferred to extruded platrodes. Semi-quantitative procedures are possible for samples prepared in this manner because ashed blanks consistently weigh about 3 mg.

2.22 Modification of the Spectrographic Determination of Beryllium for Millipore Membrane Filter Sampling (T. R. Lyon). Millipore filters were selected to replace Microsorban filters used in air sampling equipment because of an acceptably low detection limit for beryllium by an emission spectrographic procedure. With this procedure, beryllium is determined in the filter ash on a silver platrode by sparking for 70 sec using established instrument conditions. To properly prepare the sample, the filter is dampened and ashed on a silver platrode preheated to 280 ± 10°C. This temperature which gives an even and tightly bonded ash must be carefully controlled to prevent the loss of the sample during either ashing or excitation. Carbon is used for the internal standard, and if the beryllium concentration is lower than 0.025 μg per filter, better precision is obtained if background corrections are made.

2.23 Atomic Absorption Calculations Using the Olivetti Underwood Programma 101 (T. R. Lyon, J. M. Baldwin). Programs were written to perform routine calculations on atomic absorption data using the Olivetti Underwood Programma 101. Fitted regression lines for percent absorption converted either to absorbance or natural logs were evaluated as calibration curves. An F-test was used to compare the "goodness of fit" of the regression lines to the standard data, and control sample data was used to compare the bias and precision obtained from these calculated calibration curves and from the visually fitted curves presently used. Neither regression method gave results with less bias or as precise as those by the present procedure; however, the results derived from the regression on the logarithmic data were better than those from the absorbance data. While linear representations of atomic absorption data are inadequate, more sophisticated techniques using a larger computer could provide acceptable results from calculated calibration curves.

2.24 Improved Electrode Shape for Spectrographic Analysis by the Vacuum Cup Technique (T. R. Lyon). Quantitative spectrographic analysis of radioactive solutions has been done only by the vacuum cup technique if remote handling is necessary. This method suffers from poor detection limits, from a tendency to spatter sample solutions onto optical surfaces, and from poor precision. A study, designed to reduce the spattering of sample solutions, resulted in the modification of the standard spherical tip electrode to a concave form which also increases precision and improves detection limits.

Microscopic examination of spherical tip and concave electrodes eroded by successive sparking periods showed similar electrode shapes, and electrode shape was indicated as an important variable in emission intensity. This conclusion was supported by the demonstration that the intensities of spectra produced with the eighth successive exposure of an electrode, regardless of its initial shape, were nearly equal for all of the elements studied except aluminum. Because spectral intensity is related to the shape of the electrode used in this technique, studying the concave electrode form could provide an understanding of the manner in which the solution enters the analytical gap and also provide an electrode design which would give the maximum intensity for remote analytical use.

2.25 Determination of Nickel and Chromium in Potassium Permanganate Solutions by Atomic Absorption (T. R. Lyon). An atomic absorption method was developed to replace the emission spectrographic method previously used to determine nickel and chromium in alkaline permanganate solutions. Excess hydrochloric acid is added to destroy the permanganate and to prevent the rapid formation of oxides which prohibit the presence of absorbing neutral atom species in the flame. The acid treatment also makes possible the recombination of the sample filtrate and acid-dissolved solids previously analyzed separately. This atomic absorption procedure is more simple, and the time required for the analysis is about one-half that required for the emission spectrographic method. Control data show that the bias and precision are comparable to any other nickel or chromium determination using atomic absorption.

2.26 Studies of Laser Sampling for Analysis (J. M. Baldwin). The capabilities of a Q-spoiled Nd-in-glass laser as a device for local and microscale sampling have been the topic of a continuing investigation. Improvements in mounting the Jarrell-Ash Mark II laser probe to the Bausch & Lomb 2-meter spectrograph and in the associated entrance optics have increased the sensitivity of the laser system when used as an emission source. The laser probe has been mounted on an auxiliary optical bench, allowing use of either the laser or the conventional source by simply repositioning one mirror.

The utility of a new technique, whereby the laser-generated vapor from a sample is collected on a thin film, and subsequently analyzed by one of a wide variety of methods, has been demonstrated.

A second laser, which will permit the application of this technique to highly radioactive samples, is being acquired. This approach permits the isolation of a few micrograms of the material with consequent improvement in safety and convenience of analysis.

A study of the composition change of metal alloys by laser sampling is under way. Composition changes in a series of brasses have been extensively studied and a new model for the evaporation process suggested. A paper describing this work has been submitted for journal publication. An abstract of the paper follows:

CHANGE OF COMPOSITION OF COPPER-ZINC ALLOYS DURING SAMPLING BY FOCUSED, Q-SPOILED LASER RADIATION

The differences in composition of the original target material and the vaporized material have been determined for the Q-spoiled laser sampling of a series of copper-zinc alloys. The vaporized material was found to contain a greater amount of zinc, relative to copper, than did the original target material. The vapor composition was independent of laser output energy and number of laser spikes per output pulse. The vapor composition depended on the zinc/copper ratio of the target, and could be predicted from the liquid-solid equilibrium diagram of the copper-zinc system. The importance of the melting process in the Q-spoiled laser sampling of the copper-zinc system was thereby demonstrated. A possible sequence of events in laser sampling of the copper-zinc system comprising equilibrium melting and a steady state ablation process was indicated.

V. CHEMICAL ANALYSIS

1. RADIO AND SPECIAL ANALYSIS

1.1 Analytical Services

1.11 Health and Safety Branch

(1) Determination of Arsine and Stibine in Air (I. L. Doggett). The Health and Safety Branch suspected hazardous amounts of arsine (AsH_3) in the TAN-609 battery room air. A measured volume of air from the battery room was bubbled through a standardized solution of silver diethyldithiocarbamate (AgDDC) in pyridine. Microgram quantities of arsine or stibine (SbH_3) react with AgDDC in pyridine by substitution giving AsDDC or SbDDC. Arsine DDC in pyridine is a dull red-colored solution with an absorption peak of 540 mμ, and SbDDC in pyridine is a light orange-colored solution with an absorption peak at 505 mμ[13]. The collected air sample taken from the TAN-609 battery room was a light orange-colored solution with an absorption peak at 505 mμ; therefore, the sample contained stibine, not arsine.

The antimony content of the sample was quantitatively determined. Using an adaptation of a published procedure[14], stibine was generated from standard antimony solutions spiked with a known trace of Sb-125. The stibine was reacted with AgDDC in pyridine to form SbDDC. The SbDDC-pyridine solutions were measured on a spectrophotometer at 505 mμ, and using standard tracer techniques, antimony in the absorbing solutions was calculated and plotted against absorbance. The absorbance of the SbDDC-pyridine sample, collected from the battery room air, was compared to standards to quantitatively determine antimony.

(2) Determination of Sulfur Dioxide in Air (I. L. Doggett). The procedure normally used for the determination of sulfur dioxide was a barium sulfate turbidimetric method[15]. As the frequency of analysis requests increased, mostly from the Health and Safety Branch, it became desirable to find a more accurate, sensitive, and selective method.

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[13] A. I. Vogel, Quantitative Inorganic Analysis, New York: Wiley, 1969, p 798.

[14] A. E. Greendale and D. L. Love, "Rapid Radiochemical Procedure for Antimony Arsenic," Anal. Chem., 35 (1960) p 632.

[15] R. E. Holeton and A. L. Linch, "Determination of Traces of Sulfur in Organic Compounds" Anal. Chem., 22 (1950) p 819.

A literature search indicated a colorimetric method, or adaptations of it, developed by West and Gaeke[16] would be ideally suited for our needs. The following methods were investigated in detail.

(1)	p-Rosanaline[16]	Sensitivity - 20 μg/abs unit
(2)	p-Aminoazobenzene[17]	Sensitivity - 48 μg/abs unit
(3)	p-Rosanaline (modified)[18]	Sensitivity - 37 μg/abs unit

The investigation revealed method No. 3 as the most adaptable because it is designed to eliminate the interferences of heavy metals and nitrogen dioxide. This method is being written for the Analytical Methods Manual and will be used on all future samples.

(3) Estimation of Stack Gas Particulates (I. L. Doggett). A study was made of methods available for determining the quantity and size of particulate material released to the atmosphere from various NRTS Boiler House stacks. Several methods investigated were:

(1) Glass Slide - One side of the microscope slide was coated with a thin coat of silicon grease. The slide then was held in the stack gas stream to obtain a sample of adhering particles. The particle size and count then was estimated under a microscope using incident lighting. Particle size ranges thus were determined, and the results were reported as % < 10 μ, % 10 to 45 μ, and % > 45 μ. This method gave no estimate of the weight of particulate material released to the atmosphere.

(2) Glass Fiber Filter - A known volume of stack gas was passed through a tared Type E Gelman glass fiber filter, and the filter then was reweighed. Manufacturers' specifications say the filters will retain a minimum of 99.7% of the particles larger than 0.3 μ as measured by the Dioctyl Phthalate Penetration Test. From the weight and measurement of the volume of the stack gas, the total weight of particulates released to the atmosphere was calculated. Particle size cannot be obtained because of the imbedding of the smaller particles in the filter material.

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[16] P. W. West and G. C. Gaeke, "Fixation of Sulfur Dioxide in Disulfitomercurate(II) and Subsequent Colorimetric Estimation", Anal. Chem., 28 (1956) p 1816.

[17] S. J. Kniseley and L. J. Throop, "p-Aminoazobenzene for the Spectrophotometric Determination of Sulfur Dioxide", Anal. Chem., 38 (1966) p 1270.

[18] F. P. Scaringelli, B. E. Saltzman, S. A. Frey, "Spectrophotometric Determination of Atomospheric Sulfur Dioxide", Anal. Chem., 39 p 1709.

(3) Electrostatic Sampler - Stack gas was passed through an electrostatic sampler. Particles in the gas were given a negative charge which caused them to be attracted to the positively charged collection cylinder. After sampling, the particles were removed from the collection cylinder with water and ether rinses onto a tared Millipore filter. The particles, after being dried and weighed, were sized under the microscope. Because of the agglomeration during removal from the cylinder, the sizing in this method was considered inaccurate.

(4) Anderson Sampler - The sampler consists of a stack of six pairs of alternately perforated and solid discs. The size of the perforations decreases in the direction of flow. The solid discs were greased to trap the particles which are separated into six aero-dynamic sizes. The particles were removed from the solid discs with water and ether rinses onto a tared Millipore filter for weighing and sizing. Because of the agglomeration in the washing and filtering step, faulty sizing was obtained.

(5) Metal Membrane Filter - A known volume of stack gas was passed through a tared silver metal membrane filter. The collection technique used was similar to that described for the glass fiber filter, differing only in that a reduced stack gas flow rate was used to prevent the filter from fracturing. Because of the small amount of particles collected due to the reduced gas flow, only sizing could be determined with this technique. The light-colored particles are difficult to see on the silver membrane, and the silver particles in the filter make sizing difficult below 10 μ.

(6) Impacter - The impacter is a device equipped with two greased microscope slides to collect particles and a series of baffles to properly channel the particle-laden gas stream. Stack gas passing through deposits particles of decreasing size on each of two sections of each slide. The slides are removed, and the particles sized under a microscope. Successive water and ether rinses were used to wash the particles onto a tared filter for weighing. This method proved to be unsatisfactory because of particle losses in handling.

After investigation of the six methods, the decision was that a combination of methods would be best for obtaining particle size and weight. Consequently, the glass fiber filter method was selected for particle quantity, and the glass slide or the silver metal membrane methods were selected for particle sizing.

(4) Determination of Carbon Monoxide in Blood (I. L. Doggett, B. R. Hunter). Samples of blood were submitted for the determination of carbon monoxide (CO). The technique, suggested by the Health and Safety Branch, was that of Williams, Linn and Zak[19]. The blood is treated with sulfuric acid in a Conway diffusion cell to release CO, and the released gas reacts with a standard palladium chloride solution to reduce the palladium. The palladium chloride is transferred from the Conway cell, diluted with hydrochloric acid, and measured by absorption spectrometry.

Difficulty was encountered with the suggested technique, and consistent absorption values could not be attained. A CO-saturated blood solution was prepared by passing a stream of CO (5 cc/min) through 10 cc of blood for 30 min. The blood became a cherry red color indicative of the presence of CO; however, repeated analysis of this blood failed to give reproducible results. This failure to obtain consistent results is probably due to losses of CO from the Conway cell during CO release, diffusion, and absorption. Four different blood samples were analyzed: nonsmoker, subject, smoker, and saturated; while quantitative results were not obtained, the samples did exhibit a reproducible trend.

Blood Source	Results
nonsmoker	negative
subject	positive
smoker	more positive
saturated	strongly positive

1.12 General Electric Company (KAPL)

(1) Determination of Ni-63 in Coupon Decrudding Solutions (B. A. Staples, B. R. Hunter). Four types of solutions prepared by the S5G Group from decrudding treatments were received for Ni-63 determination. The first type was made from filter papers used to wipe coupons. The filter papers were ashed, fused, and the melt was dissolved in water. The second type was ethylenedinitrilotetraacetic acid (EDTA) coupon decrudding solutions. The third type was filtered alkaline permanganate coupon decrudding solutions. The fourth type was manganese dioxide samples filtered from the potassium permanganate decrudding solutions. The manganese dioxide samples were then dissolved in hydrochloric acid for Ni-63 determinations.

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[19] L. A. Williams, et al, "Ultraviolet Absorptiometry for Determination of Carbon Monoxide Hemoglobin", American Journal of Clinical Pathology, 34, No. 4 (October 1960) pp 334-337.

The EDTA solutions were pretreated prior to Ni-63 determination by evaporating the solutions to dryness with a perchloric acid-nitric acid-hydrogen peroxide mixture to break down any metal complexes present. The residues from the evaporation of these solutions were dissolved in conc HCl. The other types of solutions were diluted with conc HCl. An ion exchange separation was used to separate nickel from Fe, Co, Cr, and Mn. Dowex 1-X10, 200-400 mesh, chloride form resin was used in the ion exchange columns. Nickel was eluted from the columns with conc HCl, further purified by using dimethylglyoxime separation procedure[20], and then determined by liquid scintillation counting.

1.2 Improvements in Methods

1.21 Separation of Americium and Curium (R. C. Girton, J. G. Scott). Plutonium fuel samples contaminated with curium were analyzed for Am-241. The di(2-ethylhexyl) phosphoric acid extraction method (Am-1)[6] was not satisfactory because the curium interferes.

A calcium fluoride column was used to separate curium from americium after oxidation of americium to Am(VI). The basic steps in the method involve precipitation of the actinides with a lanthanum hydroxide precipitation step to separate them from other fission products. The precipitate is dissolved in nitric acid and the americium oxidized to Am(VI) with silver-activated ammonium persulfate. The solution then is passed through a calcium fluoride column. Vacuum is applied to the column to adjust the flow rate to 4 drops/min. The column effluent contains the americium and plutonium. After another lanthanum hydroxide precipitation, the reduced americium is separated from the plutonium by the di(2-ethylhexyl) phosphoric acid extraction method. An aliquot of the aqueous phase is plated and gross alpha-counted for americium. A purity check of the americium separation can be obtained by alpha pulse height analysis.

The method gives complete separation of americium from curium. The samples contained approximately 100 times as much curium as americium, and it is assumed that the method will tolerate even higher concentrations of curium.

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[20] D. Olson (ed.), Manual of Radiochemical Methods, IDO-14613 (January 1964).

1.22 Computer Analysis of Gamma-Ray Spectra Obtained with Lithium-Ion Drifted Germanium Detectors (J. W. Brothers). The Analytical Chemistry Branch is responsible for counting many differing types of gamma emitting samples, and existing computer programs for NaI(Tl) detection systems[21] have not proven satisfactory for high resolution gamma-ray spectrometry using Ge(Li) detection systems. The FORTRAN program SLAVE was written to process Ge(Li) spectra written on magnetic tape or cards. The full-energy gamma photopeaks are computer resolved by constructing a base line through the spectral data points, integrating the peaks above the base line, and separating overlapping peaks. An estimate of the precision at the 95% C. I. is calculated for each peak area. The peak areas are converted to gammas and peak positions are converted to gamma-ray energies in MeV. The experimental peaks are identified; then, disintegration rates are calculated using a table of nuclides, including half-lives, gamma energies, and associated branching ratios for 98 nuclides.

Computer output consists of the following: a list and Cal-Comp plot of the raw spectral data, counts per channel above the base line, peak areas versus gamma energies, numbers of gammas versus gamma energies, and disintegration rates for all nuclides identified, with intermediate results included. Decay corrections and correction factors may be included. The calculation time per 2048-channel spectrum is approximately 1.6 min on the CDC-1604 computer. The program was written taking into account the present equipment and techniques at this site and will be updated as the state of the art advances.

1.3 Improvement In Equipment

1.31 Improved Time Base for Nuclear Data Analyzers (J. P. Morgan). The ND-130 and ND-180 Nuclear Data Analyzers used by the Special Analysis personnel exhibited count time variations of several percent due to drift of the RC-type internal clocks.

To obtain a more stable and accurate time base for the analyzers, a crystal-controlled clock was substituted for the individual RC-clocks. A Raytheon (Model MCGI) 1-MHZ crystal-controlled clock with ±0.02% stability at 25°C provides the time base. Four integrated circuit decade dividers (SN 7490N) reduce the 1 MHZ to 100 HZ before the time base is supplied to the analyzer's live time clock circuits. Only minor modifications to the ND-130 were necessary to provide an external clock input.

Live time counting periods are now in the more desirable units of seconds rather than minutes due to the 100-HZ clock frequency.

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[21] R. Helmer, R. Heath, L. Schmittroth, G. Jayne, and L. Wagner, "Analysis of Gamma-Ray Spectra from NaI(Tl) and Ge(Li) Spectrometers". Computer Programs. Nuclear Instruments and Methods, 47 (1967) pp 317-319.

2. TEST REACTOR AREA

(H. A. Shogren, D. Schneidmiller)

The Analytical Chemistry Branch operates three laboratories at the Test Reactor Area (TRA). Two laboratories are located in the MTR building and one in the ATR building. These laboratories are staffed to provide 24-hr chemical coverage 7 days a week. The primary responsibility of the TRA chemistry group is to analyze and control experimental loop coolants to make sure they are within limits specified by the experiment sponsors. Currently, samples are received from 17 loops, four at MTR, seven at ETR, and six at ATR.

The loop clearance procedures, analytical methods, and special corrective actions must either be approved or submitted by loop sponsors. To improve precision and accuracy, several revisions and new procedures have been added to the TRA Loop Chemistry Manual.

2.1 Determination of Gross Beta-Gamma Activity of Reactor Loop Coolant.

The counting planchet was changed from a dish type metal planchet to a microscope cover glass. This gives a more even distribution after sample evaporation and also provides a more reproducible counting geometry. The transparent tape, used to cover the counting planchets, was replaced with commercial grade Handiwrap which permits improved counting efficiency for low energy beta samples.

2.2 Determination of Gross Iodine Activity.

Toluene was substituted for trichloroethane as the organic extraction solution. This eliminates several sample transfers, and therefore, shortens the analysis time and reduces the possibility of cross contamination. In the sequence of steps for the precipitation of iodine as silver iodide, the sample is acidified and boiled before silver nitrate is added. This prevents the occlusion of sulfates that resulted in erroneous yields.

2.3 Determination of Radioactive Cesium.

Three separate cesium methods were combined into one procedure, and the method of counting samples was changed from gross beta to counting with a NaI(Tl) detector and multichannel gamma-ray spectrometer. This provides the identification and quantitative determination of each cesium isotope present.

2.4 Determination of Krypton-88 Activity

The Kr-88 concentration in a sample is determined by waiting until the transient equilibrium state between Kr-88 and its daughter product Rb-88 is reached. The krypton is removed by boiling the sample, and the rubidium is separated from other nuclides and precipitated as rubidium chloroplatinate. The 1.86-MeV photon of Rb-88 is measured by gamma-ray spectrometry, and equilibrium and decay corrections are applied to obtain the Kr-88 value at sampling time.

2.5 Determination of Cesium-139 Activity.

Cesium-139 is determined by analysis of the Ba-139 daughter. Cesium-139 decays with a half-life of 9.5 min to the 82.9 min daughter product Ba-139. This is a case of no equilibrium; therefore, cesium must be calculated from the time it takes Ba-139 to grow to its maximum activity from an initially pure Cs-139 fraction. The time for maximum activity of this parent-daughter pair has been established at 33 min. The sample is treated with Ba, Sr, and Fe carriers, and these are precipitated by hydroxide and carbonate precipitation steps. This removes the Ba-139 and leaves a pure Cs-139 parent solution. A known amount of barium carrier is added; and after a 33-min period for Ba-139 maximum activity to be obtained, the barium is separated by a series of precipitations--carbonate, chromate, and sulfate. The Ba-139 then is measured by gamma-ray spectrometry and calculated back to the activity level at time of maximum activity.

2.6 Determination of Iodine-133 and Iodine-131 Activity in Reactor Loop Coolants.

After separation of iodine from the sample solution, the iodine is counted several times over a period of ten days. This allows decay of short half-life isotopes and permits calculation of the desired isotopes. Results obtained by sequential counting with NaI(Tl) detection systems were compared to results obtained with the same sample using a Ge(Li) detection system. Using the two counting techniques, results agreed within 3% of each other.

2.7 Determination of Dissolved Oxygen.

The indigo carmine method for determination of dissolved oxygen in concentrations less than 50 ppb was adopted for use in the loop sampling staions. Dissolved oxygen reacts under alkaline conditions with the indigo carmine solution to produce a progressive color change from yellow-green through red to blue. The concentration of oxygen is determined by comparing the sample color with color standards. The indigo carmine is introduced into the sample without removing the sample from the loop sampling station. A hypodermic syringe is used to introduce the indigo carmine solution. This prevents contamination of the sample by eliminating sources of oxygen that could cause high results.

3. REMOTE AND SERVICE ANALYSIS

3.1 Analytical Services

3.11 Chemical Technology Branch

(1) Analysis of Samples from Calcination of Purex Waste (M. A. Wade). The recent in-bed combustion calcination of simulated Purex waste produced samples that were not amenable to analyses by existing laboratory methods. The waste contained 0.1M Al(III), 0.5M Fe(II, III), 0.6M Na(I), 1M SO_4^{-2}, and .01M PO_4^{-3}. The high iron interfered in the aluminum method, and the presence of phosphate and sulfate in the product made dissolution difficult for subsequent Al(III), PO_4^{-3}, and SO_4^{-2} analyses.

(a) Dissolution of Product and Fines (J. P. Clark). Several dissolution schemes using hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, perchloric acid, and combinations of these acids were tried without satisfactory results. The fines were dissolved using a 4M $HCl-H_2O_2-HF-HNO_3$ treatment. Repeated additions and fumings were necessary to effect complete dissolution of the fines. This technique, however, did not completely dissolve the product. Pyrosulfate fusion readily dissolved both the fines and the product, but this technique did not permit a subsequent sulfate analysis.

(b) Determination of Aluminum (J. A. Rindfleisch). Because of the high iron content (5:1 mole ratio to aluminum), it was necessary to separate the aluminum prior to analysis by Method Aluminum-Vol-1 (Appendix B). Two procedures were used for the separation: (a) Electrolytic deposition of the iron in mercury using an Eberbach Dyna-Cath. The nitrate content of the sample was so high, however, that good separation was not obtained. Efforts to remove the nitrate by fuming with sulfuric acid were not successful because the high salt content caused the sample to spatter. (b) The iron was precipitated at pH 12.75; the aluminum remained in solution as the AlO_2^- ion at this pH. After separation of the iron, the aluminum was precipitated at pH 6.5, separated by centrifuging, dissolved in perchloric acid, and analyzed by Method Aluminum-Vol-1.

(2) Analysis of EBR-II Fuel Containing Fission Oxide (D. R. Trammell). Samples from the electrolytic dissolution of EBR-II fuel containing fissium oxide (oxides of Ru, Mo, Rh, Pd, and Zr) were filtered, and the residue and filtrate were analyzed separately. The solids, composed primarily of fissium oxide and stainless steel components, were dissolved by a 10-min fusion with a 1:1 mixture of sodium peroxide and sodium carbonate in a zirconium crucible. The melt was partially dissolved by heating in the presence of water and by agitation on a magnetic stirrer. The slurry was transferred to a Teflon beaker, acidified by slowly adding hydrochloric

acid and heated to complete the dissolution. Some samples required a second fusion for complete dissolution.

The dissolved solids were analyzed for Fe, Mo, Ru, Si, and U. The filtrate was analyzed for acid, Fe, Mo, Ru, Na, and U. Standard laboratory methods (INC Analytical Chemistry Manual) were used for all analyses except sodium and molybdenum. Sodium was determined by flame photometry, and molybdenum was determined colorimetrically by a method described in Section 3.22 (page 54).

(3) Analysis of "Black Liquor" from Paper Pulp Processing (J. P. Clark, B. A. Staples, M. A. Wade). The Chemical Technology Branch is applying fluidized bed calcination technology to the control of air pollution produced by paper pulp mills. Paper pulp is produced from the cellulose in wood. The cellulose is separated from lignin and other wood constituents by a sulfate digestion process. The waste from this process is called black liquor and is processed to recover valuable sulfur and sodium. In this recovery process, the black liquor is concentrated to about 50% w/v and then sprayed into large furnaces where it is burned at 980°C in an oxygen-deficient atmosphere. The organic material is converted to carbon and carbon monoxide, and the sulfate is reduced to sulfide. This process is the primary source of the air pollution and is the process that Chemical Technology is studying.

Because of the lack of information on composition, the black liquor was submitted to the Analytical Chemistry Branch for analysis. It was analyzed for density, pH, alkalinity, fluoride, phosphorus, undissolved solids, total solids, residue after combustion, total carbon, water, metallic impurities, and various sulfur species. The density was determined by weight on a 100-ml sample. The 100-ml sample aliquot then was evaporated to dryness at 100°C to determine total solids. A portion of the solids was ignited in a furnace to determine residue after combustion. Undissolved solids were determined by filtering a known sample aliquot and weighing the residue; a 4 to 1 dilution was necessary before the sample could be filtered. Alkalinity, fluoride, phosphorus, and carbon were determined by existing methods, and water was determined by a Karl Fischer titration. Metallic impurities were determined by emission spectroscopy.

The sulfur species were separated and analyzed for sulfide, sulfate, organic sulfur, and total sulfur. An aliquot of the black liquor was acidified, and nitrogen was bubbled through to separate volatile sulfides. The sulfides (as H_2S) were carried by the nitrogen stream to a silver nitrate trap where silver sulfide precipitated. The precipitate was separated and weighed. The acidified black liquor sample was centrifuged, and the two fractions were separated. Inorganic sulfate was determined in the aqueous supernatant solution by precipitation as barium sulfate. Organic bound sulfur was determined in the residue fraction by conversion to sulfate in a Parr peroxide bomb and precipitation as barium sulfate. Total sulfur was determined on the original sample by the latter technique.

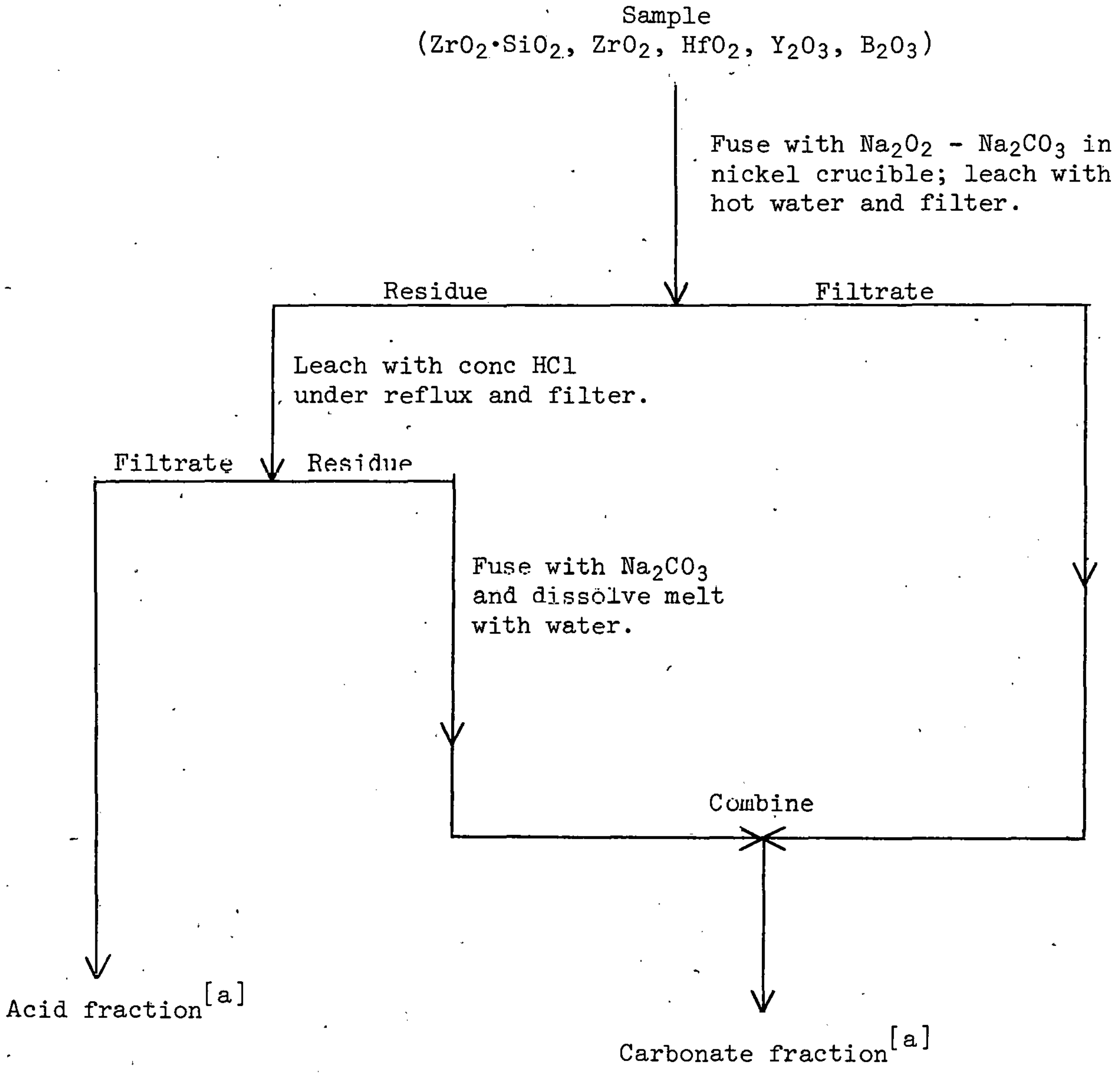
A modified Karl Fischer titration method was used to determine water content. The sample was known to contain mercaptans and thiosalts which stoichiometrically oxidize the iodine present in the Karl Fischer reagent. The method was modified to eliminate these interferences by oxidation of the sample in the presence of an acetic acid catalyst with boron trifluoride gas dissolved in ethyl ether. Pyridine was substituted for methanol as the titration matrix because boron trifluoride esterifies methanol.

(4) Analysis of Rover Bed Samples for Aluminum, Alumina, and Uranium (D. R. Trammell). The Chemical Technology Branch is developing a burn-leach process for the recovery of uranium from Rover fuel. The graphite in the fuel is removed by burning in a fluidized bed, and the uranium which is carried over in the air stream is leached with nitric acid. Aluminum metal was added to an experimental fuel before processing to simulate an aluminum containing fuel, and bed samples were analyzed for Al metal, Al_2O_3, and U. The aluminum metal was dissolved with methanolic bromine, and the aluminum oxide residue was dissolved by two fusions with potassium pyrosulfate followed by a hydrochloric acid dissolution of the melt. Uranium partially dissolved in the methanolic bromine, and the remainder dissolved in the pyrosulfate fusion. Both fractions were analyzed for uranium and aluminum by existing procedures. A residue, composed of sand used as a starting bed in the fluidized bed process, remained undissolved.

3.12 Phillips Petroleum Company

(1) Dissolution and Analysis of a Zirconia-Zircon Ceramic Cement (D. R. Trammell). A ceramic cement was dissolved and analyzed for B, Hf, Si, Y, and Zr. The ceramic cement consisted of 60% zircon ($ZrO_2 \cdot SiO_2$), 37% zirconia (ZrO_2), 1% yttrium oxide, and 1% hafnium oxide. The yttrium oxide was added to the zirconia to stabilize the face-centered cubic structure, and the hafnium oxide was present as an impurity. The cement is used during destruct tests to coat a stainless steel screen that surrounds the fuel rod. During the test the fuel rod becomes supercritical, explodes, and molten temperatures as high as 3000°C are reached. The destruct test is carried out in an expensive steel capsule, and without the ceramic coating, the molten fuel rod would burn through the capsule thus destroying it.

The cement was dissolved according to the dissolution scheme illustrated in Figure 4. The sample was fused with a 1:1 mixture of sodium peroxide and sodium carbonate for 30 min in a nickel crucible. The melt was leached with boiling water in a Teflon beaker and then filtered with a Teflon Millipore apparatus into a Teflon beaker. The residue was leached with concentrated hydrochloric acid under reflux in a quartz still. Hydrogen peroxide was added



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[a] Equal volumes from each solution were combined for analysis.

Fig. 4 Scheme for dissolving zirconia-zircon cement.

to the still to help destroy the Millipore filter. The solution was filtered, and the residue was fused with sodium carbonate. The fusion melt was dissolved in water and combined with the filtrate from the first water leach. Both the carbonate fraction and the acid fraction were diluted to the same volume in volumetric flasks and then stored in polyethylene bottles.

Analysis aliquots were prepared by combining equal volumes from the two solutions. Silicon was determined gravimetrically by perchloric acid dehydration and ignition to silicon dioxide. Zirconium plus hafnium were determined by amperometric titration with cupferron, and Hf, Y, and B were determined by spectrographic methods.

3.13 Reactor Engineering Branch

(1) Determination of Boron in Plastic (J. A. Rindfleisch, M. A. Wade, J. P. Clark). Thirty-six cellulose acetate butyrate plastic strips impregnated with amorphous natural boron were analyzed for boron to determine if fabrication specifications had been achieved. The plastic was destroyed by ashing in a muffle furnace starting at 100°C and raising the temperature 75°C every 10 min until 650°C was reached. The sample was left at this temperature until all the organic material was destroyed (usually 20 min). The residue was fused with 2.5 g of sodium carbonate in a muffle furnace by raising the temperature from 200°C to 900°C in not less than 1 hr and maintaining this temperature for 40 min. The melt was dissolved in 3M HCl, and the boron was determined by Method B-Vol-1.

Controls, prepared by adding a known amount of boron to boron-free plastic, were analyzed with a precision of 0.3% relative standard deviation. The boron and the plastic used for the controls were from the same source as that used to prepare the impregnated plastic strips. The determination of known amounts of boron without any plastic indicated no loss of boron during the ashing procedure.

3.14 Special Services

(1) Analysis of Tape for Sulfur (D. E. Savage). Fiber-backed tapes used for marking and identification purposes were analyzed for sulfur. The tapes were first oxidized by one of two methods: (a) oxidation with a Leco induction furnace using a 3% hydrogen peroxide solution to trap the sulfur dioxide, or (b) oxidation in a Parr oxygen bomb under 30 atm of oxygen; a 3% hydrogen peroxide solution was used to absorb the sulfur dioxide. The resulting sulfate was determined by a photometric titration procedure described in Section 3.23, (page 55).

3.2 Improvements in Methods

3.21 Effect of Nitrate on the Colorimetric Determination of Cobalt (D. E. Savage).

Cobalt is determined colorimetrically by reacting the cobalt with α-nitroso-β-naphthol, extracting the complex from a 6M HCl media into xylene-carbon tetrachloride, scrubbing the excess reagent from the organic phase with sodium hydroxide, and measuring the absorbance of the pink cobalt-α-nitroso-β-naphthol complex. Recent calibration and bench standards produced a yellowish, sometimes cloudy solution that gave erroneous results. The problem was traced to the use of nitric acid in the preparation of these standards. Apparently the nitrate reacts with the α-nitroso-β-naphthol in the strong hydrochloric acid extraction medium to form degradation products that extract into the xylene-carbon tetrachloride. The formation of the interferences seems to be a function of time of contact, temperature of the solutions, and nitrate concentrations. Additional sodium hydroxide scrubs would, in some samples, remove the interferences. Fuming the standards with sulfuric acid prior to use removed the nitrate and eliminated the problem. New standards were prepared using sulfuric acid.

3.22 Determination of Molybdenum in EBR-II Fuel (D. R. Trammell).

Molybdenum was determined in dissolved EBR-II fuel containing fissium oxide (oxides of Ru, Mo, Rh, Pd and Zr) by a modification of the colorimetric procedure of Sarma, et al, [22]. In this method, molybdenum is complexed with thiosulfate, extracted into a butanol-benzene mixture, and the absorbance is measured at 470 mμ. The 1-butanol extracts the Mo(V) complex, and the benzene is added to decrease the solubility of butanol in the aqueous phase. In the published method, the Mo(V)-thiosulfate complex is extracted into a 2:3, 1-butanol-benzene mixture from a 2M HCl 0.1M sodium thiosulfate solution. Using these conditions, it was observed that the Mo(V)-thiosulfate complex precipitated from the butanol-benzene causing a steady rise in absorbancy for 1 hr after extraction. The absorbancy then would drop rapidly due to complete precipitation and settling of the complex.

The precipitation of the Mo(V)-thiosulfate complex was avoided by increasing the ratio of 1-butanol to benzene in the extractant. Ratios of 1-butanol to benzene of 1:1, 3:2, 2:1, 3:1, and 4:1 were studied. Only the 3:1 and 4:1 mixtures gave clear solutions that were stable for 1 hr. The 4:1 mixture of 1-butanol to benzene was chosen for the analysis of samples.

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[22] B. V. S. Sarma, D. Satyanarayana, V. Pandu Ranga Rao, "Photometric Determination of Molybdenum Employing Thiosulfate," Chemist-Analyst, 56 (1967) pp 76-79.

The range of the modified method is 50 to 900 μg of molybdenum in a sample aliquot of 20 ml or less. The sample must contain not more than 40 meq of acid. The range may be expanded to analyze samples in the 0- to 50-μg range by reducing the volume of extractant from 20 to 10 ml and by measuring the sample absorbance in 5-cm cells rather than in 1-cm cells.

3.23 Determination of Low Level Sulfate (D. E. Savage, M. A. Wade). An improved method for the determination of small quantities of sulfate has been developed. This method is based on the method of Fritz and Yamamura[23]. In their method, sulfate in an 80% ethanol medium is titrated with barium perchlorate to a thorin [2(2-hydroxy-3, 6-disulfo-1-naphthylazo) benzenearsonic acid] end point. The yellow orange color transition at the end point is very difficult to observe, especially under artificial light. The end point detection was improved by titrating photometrically at 520 mμ. The titration is performed in a pyridine-buffered media at a pH of 5 to 6. A simple photometric-titration cell was designed for use with a Bausch and Lomb Spectronic 20 spectrometer, and the sample is titrated directly in the cell. The method was applied to the analysis of samples containing phosphate and sulfite.

3.24 Programma 101 Calculations for Radiochemical Analyses (J. M. Dietz, B. R. Hunter, M. A. Wade). The application of a desk top computer, the Programma 101, to routine analytical chemistry calculations[24] has been extended to radiochemical calculations. Programs to calculate the disintegration rate in disintegrations per unit time and volume were written for Co-60, Co-58, Fe-59, and Mn-54. A special work sheet containing the program operating instructions was designed and is used for all four isotopes. These programs contain all constants including the half-life and photons per disintegration of the isotope being calculated. The relationship $e^{-\lambda t}$ also is incorporated in the program so that results are calculated back to a designated zero time. A general program has been written that can be used for any radioisotope; in this case, however, all constants must be entered by the analyst. As previously demonstrated[24], this method of calculating results will reduce both calculation time and calculation errors.

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[23] J. S. Fritz and S. S. Yamamura "Rapid Microtitration of Sulfate," Anal. Chem., 27 (1955) pp 1461-1464.

[24] See Reference 8, p 50.

3.3 Improvement in Equipment

3.31 Remote Filtration and Fusion Apparatus (E. M. Fortsch). A remote filtration and fusion apparatus was designed to process 1-liter descaling samples in the X-cell cave. Equipment was provided for filtration, filter-ashing, fusion of solids, and mixing of solutions. The fused residue was dissolved in the filtrate, and aliquots of the solution were sent to various laboratories for subsequent analysis. More than 100 samples, measuring to 55 R/hr, were processed with this equipment.

The filtration apparatus (Figure 5) is capable of filtering large volumes of solution remotely. Provisions are available for (a) remote assembly and disassembly of each unit, (b) storage of filtrate, (c) washing of residue, (d) removal of any residue which might adhere to the walls of the filtering vessel, (e) transferring of wash solutions directly to the cell drain, (f) installation and removal of the filter, and (g) cleaning of the system between samples.

The filtering process is as follows: The filter holder is attached to a vacuum line via a Nalgene "quick disconnect" and inverted into a beaker containing a filter. The vacuum draws the filter onto the filter holder. The filter holder and filter are clamped to the receiver vessel with a standard Millipore filter clamp. The vacuum line is removed, and the filter holder is attached to a line which leads to the filtrate vessel. Valve A is opened and valves B, C, and D are closed. Vacuum is applied to the system and the sample is poured into the receiver vessel. When the sample has passed through the filter and the filtrate has collected in the filtrate vessel, valve A is closed and valve B is opened. The sample bottle is washed with distilled water, and the washings are transferred to the receiver vessel. The sides of the receiver vessel are washed with distilled water to rinse any adhering solids onto the filter. The wash solutions are collected in the wash vessel.

The vacuum is released, and the line is removed from the filter holder. An air line is attached to the filter holder. The filter holder is removed from the receiver vessel and inverted over a quartz beaker. The air valve is opened, and the filter and residue are transferred to the beaker. Solids remaining on the base of the receiver vessel are washed into the beaker with a minimum amount of distilled water. In most cases, dri-filming of the receiver vessel prevents hangup of residue. Valve D is opened to allow the wash solutions to be transferred to the drain.

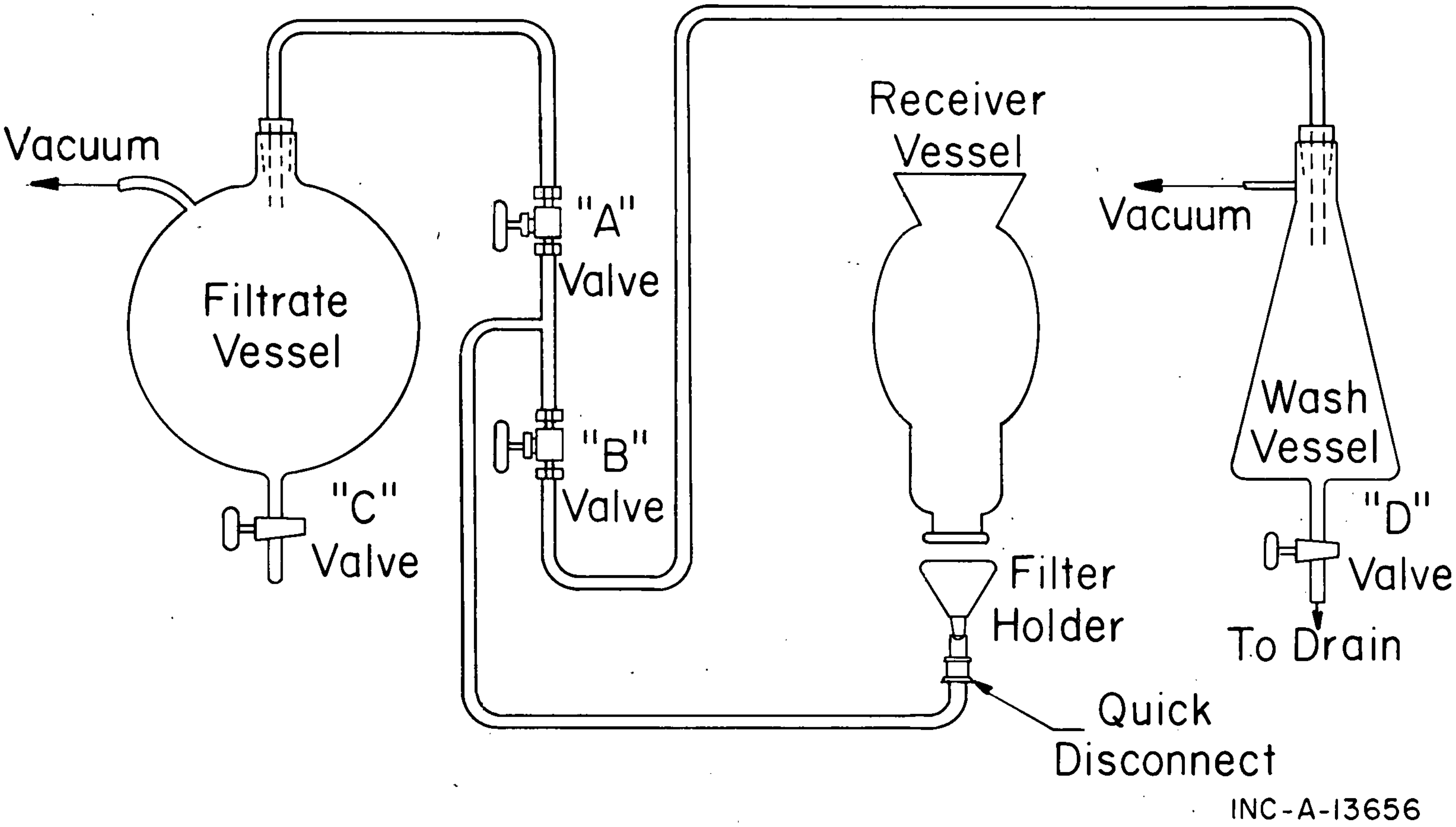

Fig. 5 Filtration apparatus.

The beaker containing the filter and solids is placed on a small hot plate; the excess water is evaporated; the filter is charred by applying heat from a heat lamp and low heat from the heater. When charring is complete, the heat is increased to ash the filter. Sodium bisulfate is added, and the sample is heated until the residue dissolves.

When fusion is complete, the beaker is removed from the heater. A Teflon stirring bar and about 50 ml of filtrate solution are added to the beaker. The solution is stirred with a magnetic stirrer until the melt is dissolved. The solution and stirring bar are poured into the original sample bottle with rinsings from the filtrate vessel. The remaining filtrate also is returned to the bottle. EDTA containing descale solutions often precipitate when the filtrate is added to the flux. The addition of solid sodium hydroxide pellets to these solutions solubilizes the precipitate. The sample is stirred for 1 hr to ensure homogeniety.

The filtration apparatus is cleaned between samples by reassembling the apparatus minus a filter and then running water through the system. Additional rinsing of the filtrate vessel is done by removing the stopper on top of the vessel and rinsing with water. The rinsing solutions are poured into the drain.

The use of Nalgene "quick disconnects" simplifies many remote manipulations. The apparatus is versatile and can be adapted for use in a large variety of remote filtering problems.

3.4 Studies for Safeguards of Nuclear Materials

3.41 Remotely Operated Apparatus for Sealing Glass Ampoules (D. R. Trammell, E. M. Fortsch, H. G. Brinkley). The Analytical Chemistry Branch is frequently required to store input measurement samples from dissolved fuel. Presently these solutions, which are highly radioactive, are stored in glass ampoules which are flame sealed with an oxygen-propane torch. A lead barricade is used to provide shielding while filling and sealing the ampoules. Under these conditions, the radiation exposure to personnel is high, and the ampoules are difficult to seal.

A working model of an apparatus, essentially a vertical lathe, to seal ampoules remotely has been constructed[25]. It consists of one chuck to hold the top of the ampoule and one to hold the bottom, both chucks are rotated at the same speed. An oxygen-hydrogen flame is used to melt the neck of the ampoule. When the glass softens, the top chuck is raised with another remotely operated motor, and the melted glass pulls in to form a seal.

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[25] D. R. Trammell, M. A. Wade, E. M. Fortsch, H. G. Brinkley, G. A. Huff, Equipment and Techniques for Sealing Ampoules containing Irradiated U-235 Solution, IN-1275 (1969).

A Henes Water Welder is used for a sealing flame for the ampoules. This apparatus produces oxygen and hydrogen by electrolysis of water. The gases then are burned in a methanol-saturated atmosphere to give a 3300°F flame.

VI. QUALITY CONTROL

(G. J. Curtis, F. A. Duce, S. S. Yamamura)

The primary functions of the Quality Control Laboratory are (a) establishment of the precision and bias and surveillance of analytical methods by a methods quality control program, (b) training and testing of new analysts, (c) preparation of standards and reagents for the Analytical Chemistry Branch and other on-site groups, and (d) calibration of miscellaneous analytical equipment. During the past year, the activities of the Quality Control Group mainly were directed to functions (a) and (c). Because of low turnover in personnel, little training and testing of new analysts was conducted. Of particular significance is the change made during the year in the quality control program for analytical methods. A detailed description of the revised system follows.

1. QUALITY CONTROL PROGRAM FOR ANALYTICAL METHODS

In the system heretofore used for establishing the precision and bias of the various methods and for monitoring method status, standard "unknowns" were analyzed at regular intervals whether samples were being analyzed or not. In addition, "known" bench standards were analyzed when samples were being analyzed. The results for the unknowns were reported to the Quality Control Laboratory uncorrected for bias, and the results for the bench standards were plotted on a control chart with acceptable limits of ±2 standard deviations. A serious drawback of this program was that it consumed considerable analyst time.

The revised quality control program suggested by G. A. Huff* provides the same amount, if not more data, with considerably less effort. The principal features of the new program are:

(1) Bench standards with values stated to within ±2 standard deviations are used to test bias and precision.

(2) The bench standards are analyzed only when samples are analyzed.

(3) The actual results uncorrected for bias are recorded and used for precision and bias calculations. All results corrected for bias are plotted on a chart to enable rapid recognition of method status. The method is deemed suitable for use on samples only when the result is within specified limits.

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* Former supervisor of the Chemical Analysis Section, now with Allied Chemical Company in Morristown, New Jersey.

(4). The specified limits for the result on the control is about ±3 standard deviations. In practice, the control chart consists of two lines 5 standard deviations apart. The control is prepared to have a value within about a 2 standard deviations range at the middle of the 5 standard deviation chart. Periodically, the value of the control is altered to fall at the top, the middle or the bottom of the 2 standard deviations range. Two control chart forms are used (Figures 6 and 7). That for colorimetric methods (Figure 6) has a 6-chart capacity that accommodates calibration data and the data from four controls. The other (Figure 7) with a capacity for up to five controls is used for all nonspectrophotometric methods. Figure 8 is an example of a partially filled form with typical data for a spectrophotometric uranium method.

The revised quality control program has several advantages. Foremost, it costs considerably less than the previous program. One of the features of the revised program is the analysis of controls only when samples are being analyzed. This automatically drops a method from the quality control program when it is not in use. Conversely, this same feature provides more data and more current data for active methods than heretofore obtained. The main disadvantage of the revised program is that the analyst knows the true value to within about 2 standard deviations. In actual operation, however, it has been observed that the analysts are extremely honest in the reporting of their results. This disadvantage, therefore, is of only slight significance compared to the advantages cited above.

2. METHODS CURRENTLY IN THE QUALITY CONTROL PROGRAM

A total of 45 methods is currently covered in the quality control program. Tables of bias correction and precision data obtained from regression equation computer calculations of control results are supplied at 1- to 3-month intervals. These tables are used by the analysts so that all results are corrected for bias and are reported with 1-standard deviation uncertainty limits. Table VII summarizes the ranges and precisions of the 45 procedures.

TABLE VII

PRECISION OF ANALYTICAL METHODS

Procedure	Range and Unit[a]	Precision[b]
Acid; phenolphthalein indicator titrimetric	0.5 to 4.5 meq	0.01 to 0.04 meq
Acid; oxalate complexing pH titrimetric, nonremote	0.5 meq acid-deficiency to 1.2 meq acid	0.02 to 0.01 meq
Acid; oxalate complexing pH titrimetric, remote	0.5 meq acid-deficiency to 1.2 meq acid	0.02 to 0.06 meq
Ammonia; Nessler spectrophotometric (high range)	3 to 25 µg	0.3 to 2.7 µg
Ammonia; Nessler spectrophotometric (low range)	0.09 to 0.20 µg	0.04 to 0.03 µg
Aluminum; fluoride complexing, pH titrimetric	5 to 11 mg	0.10 to 0.12 mg
Barium; ō-cresolphthalein spectrophotometric	20 to 100 µg	2.6 to 3.4 µg
Beta Activity; gross	45 to 475 d/m	5 to 58 d/m
Boron, mannitol complexing, titrimetric (ion exchange)	0.20 to 5.0 mg	0.10 mg, constant
Boron; mannitol complexing, titrimetric (direct)	0.20 to 5.0 mg	0.01 to 0.26 mg
Cs-137; perchlorate	$5x10^4$ to $1x10^6$ d/m	$7x10^3$ to $3.7x10^4$ d/m
Chromium; redox titrimetric	1.6 to 15.6 mg	0.08 to 0.33 mg
Chromium (total); Ce(IV oxidation, diphenylcarbazide spectrophotometric	5 to 50 µg	0.3 to 4.0 µg
Chromium(VI); diphenylcarbazide spectrophotometric	1 to 49 µg	0.1 to 0.6 µg

TABLE VII (Continued)

Procedure	Range and Unit[a]	Precision[b]
Chloride; Hg-diphenylcarbazone spectrophotometric	75 to 200 ppb	95 to 48 ppb
Ce-144; oxalate precipitation	3×10^5 to 3×10^6 d/m	4.4×10^4 to 6.1×10^5 d/m
Fluoride; pyrolysis, Ce(III) titrimetric	6 to 40 mg	1.1 to 2.7 mg
Hydrogen; Cambridge Analyzer	1 to 8.5 cc	0.44 to 0.58 cc
Nickel; dimethylgyloxime precipitation, EDTA titrimetric	2 to 28 mg	0.1 to 0.8 mg
Nitrate; Devarda reduction, distillation, titrimetric	0.2 to 4.5 mmole	0.01 to 0.15 mmole
Nitrite; azo dye spectrophotometric	0.25 to 10 μg	0.04 to 0.45 μg
Oxygen, Winkler (modified)	0.05 to 2.0 ppm	0.08 to 0.18 ppm
pH; Beckman Model G pH meter	8.10 to 10.50	0.02 to 0.04
Phosphate; molybdenum blue, spectrophotometric	1 to 100 μg	1.2 to 3.1 μg
Reducing normality; dichromate titrimetric	0.1 to 0.9 meq Fe(II)	0.01 meq, constant
Iron; column octanone extraction, EDTA titrimetric	2 to 25 mg	0.09 to 0.59 mg
Iron; o-phenanthroline spectrophotometric	2 to 98 μg	0.7 to 5.3 μg
Iron; column octanone extraction, o-phenthroline spectrophotometric	4 to 100 μg	2.2 to 6.8 μg

TABLE VII (Continued)

Procedure	Range and Units[a]	Precision[b]
Mercury; EDTA titrimetric	17 to 152 mg	0.35 to 0.57 mg
Mercury; dithizone spectrophotometric	1 to 35 µg	0.9 to 1.7 µg
Nickel; dimethylglyoxime spectrophotometric	0.01 to 0.10 mg	0.001 to 0.002 mg
Specific gravity; Westphal balance	0.790 to 1.590 specific gravity units	0.003 specific gravity unit, constant
Specific gravity; falling drop, remote	1.050 to 1.350 specific gravity units	0.001 to 0.005 specific gravity unit
Tin; pyrocatechol violet spectrophotometric	15 to 150 µg	7.4 to 9.7 µg
Tributylphosphate; acid extraction, bromthymol blue indicator, titrimetric	1.5 to 12% TBP	0.1%, constant
Uranium; mass isotopic distribution, hand pipetted	1.014% U-234 93.133% U-235 0.181% U-236 5.672% U-238	0.009% 0.056% 0.008% 0.024%
Uranium; mass isotopic distribution, remote pipetted	1.011% U-234 93.124% U-235 0.181% U-236 5.686% U-238	0.008% 0.062% 0.008% 0.038%
Uranium; concentration, isotopic dilution mass spectrometric, hand pipetted	1.00 mg	0.008 mg
Uranium; concentration, isotopic dilution mass spectrometric, remote pipetted	1.00 mg	0.015 mg

TABLE VII(Continued)

Procedure	Range and Units[a]	Precision[b]
Uranium; hexone extraction, tetrapropylammonium uranyl trinitrate spectrophotometric	0.5 to 35 mg	0.04 to 0.87 mg
Uranium; hexone extraction dibenzoylmethane spectrophotometric	0.005 to 0.075 mg	0.001 to 0.002 mg
Uranium; hexone extraction, pellet fluorophotometric, A instrument	5×10^{-5} to 0.1 mg/ml	2.3×10^{-5} to 2.7×10^{-2} mg/ml
Uranium; hexone extraction, pellet fluorophotometric B instrument	5×10^{-5} to 0.1 mg/ml	1.5×10^{-5} to 5×10^{-2} mg/ml
Uranium; ignition to U_3O_8, spectrographic impurity correction	220.0 to 230.0 mg	0.18 mg
Zirconium; cupferron amperometric	0.01 to 0.1 mmole	0.001 to 0.003 mmole

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[a] Amount in aliquot of control taken for analysis.

[b] In terms of standard deviation for a single determination over range of method.

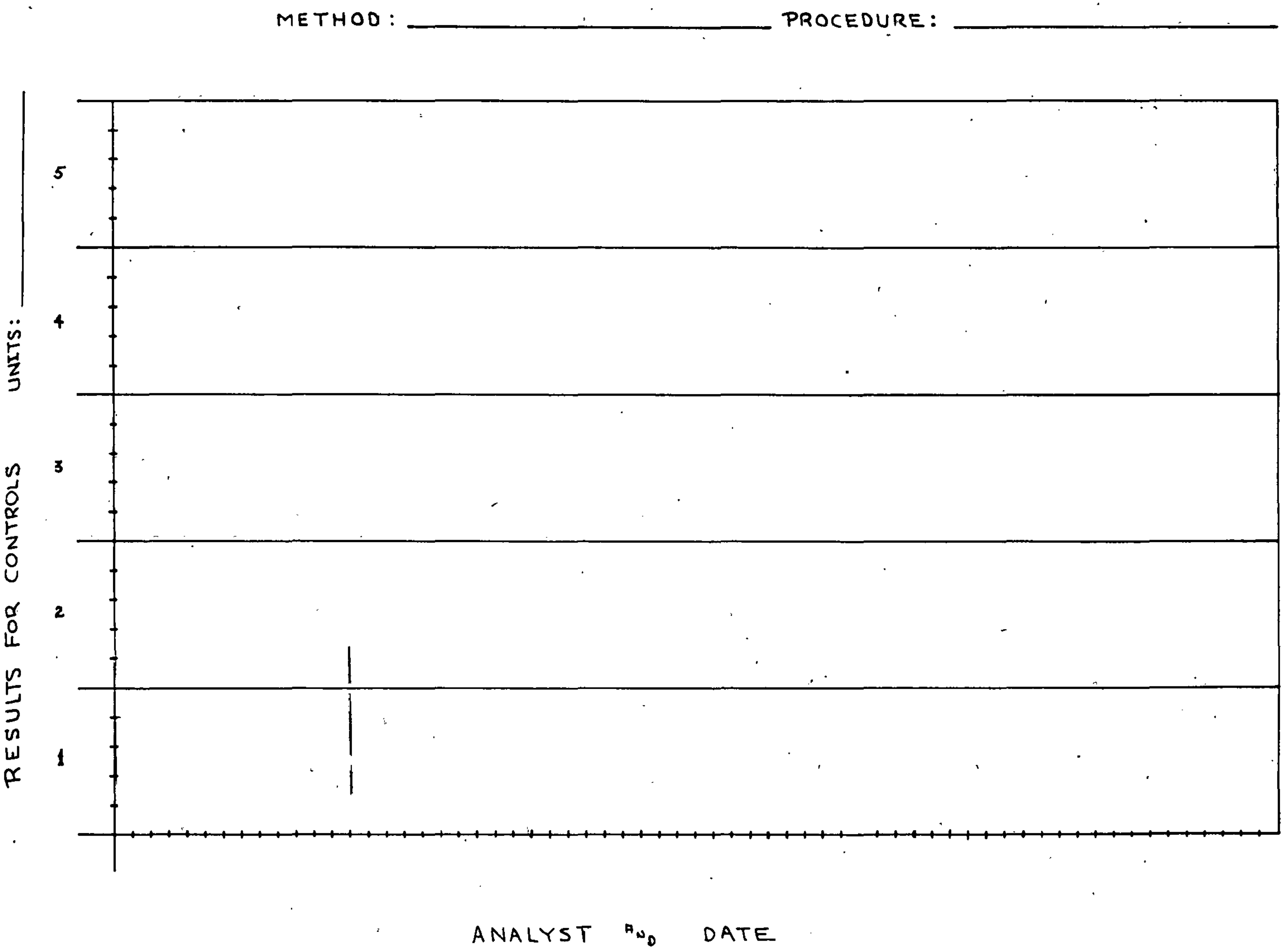

Fig. 6 Control chart form for spectrophotometric methods.

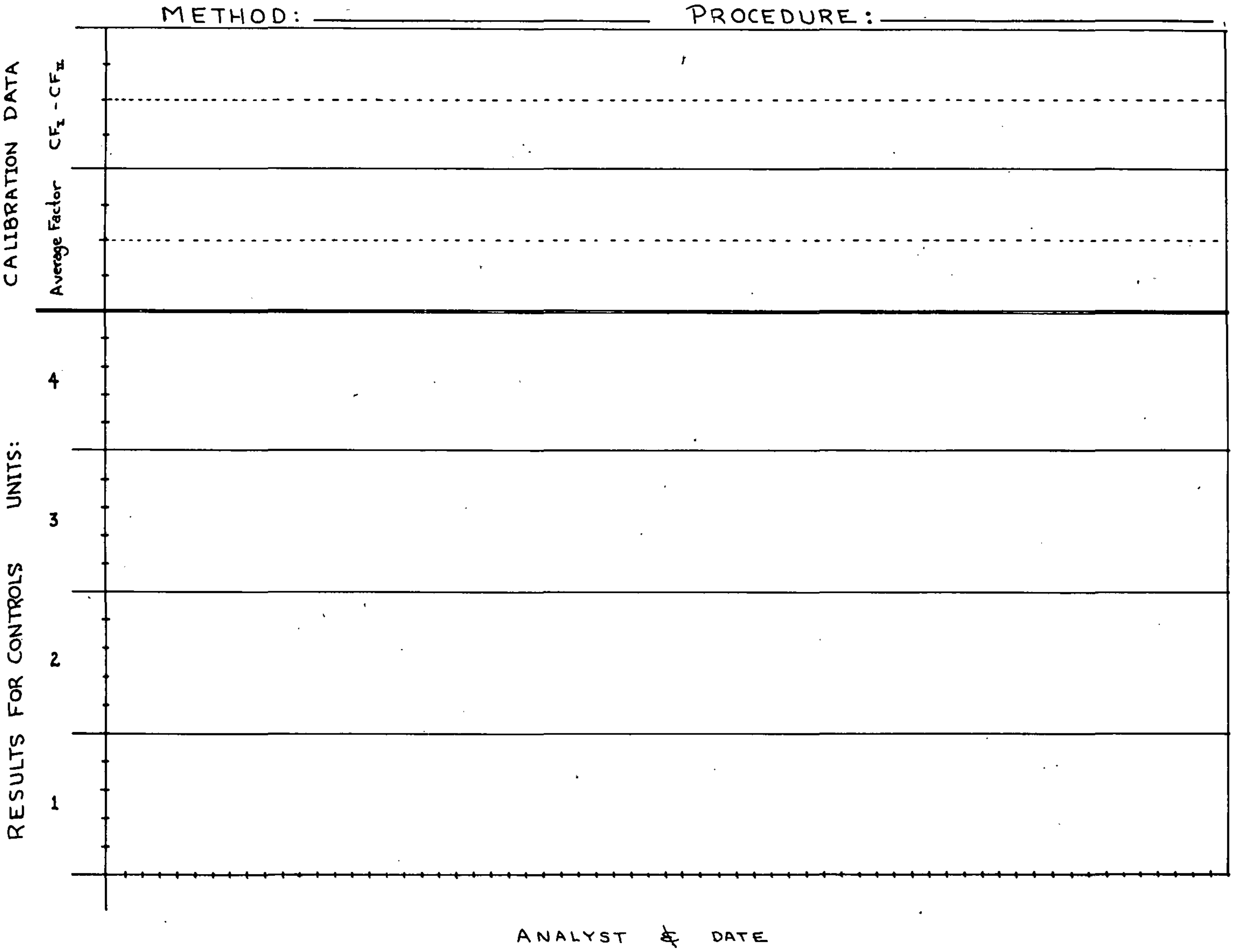

Fig. 7. Control chart form for nonspectrophotometric methods.

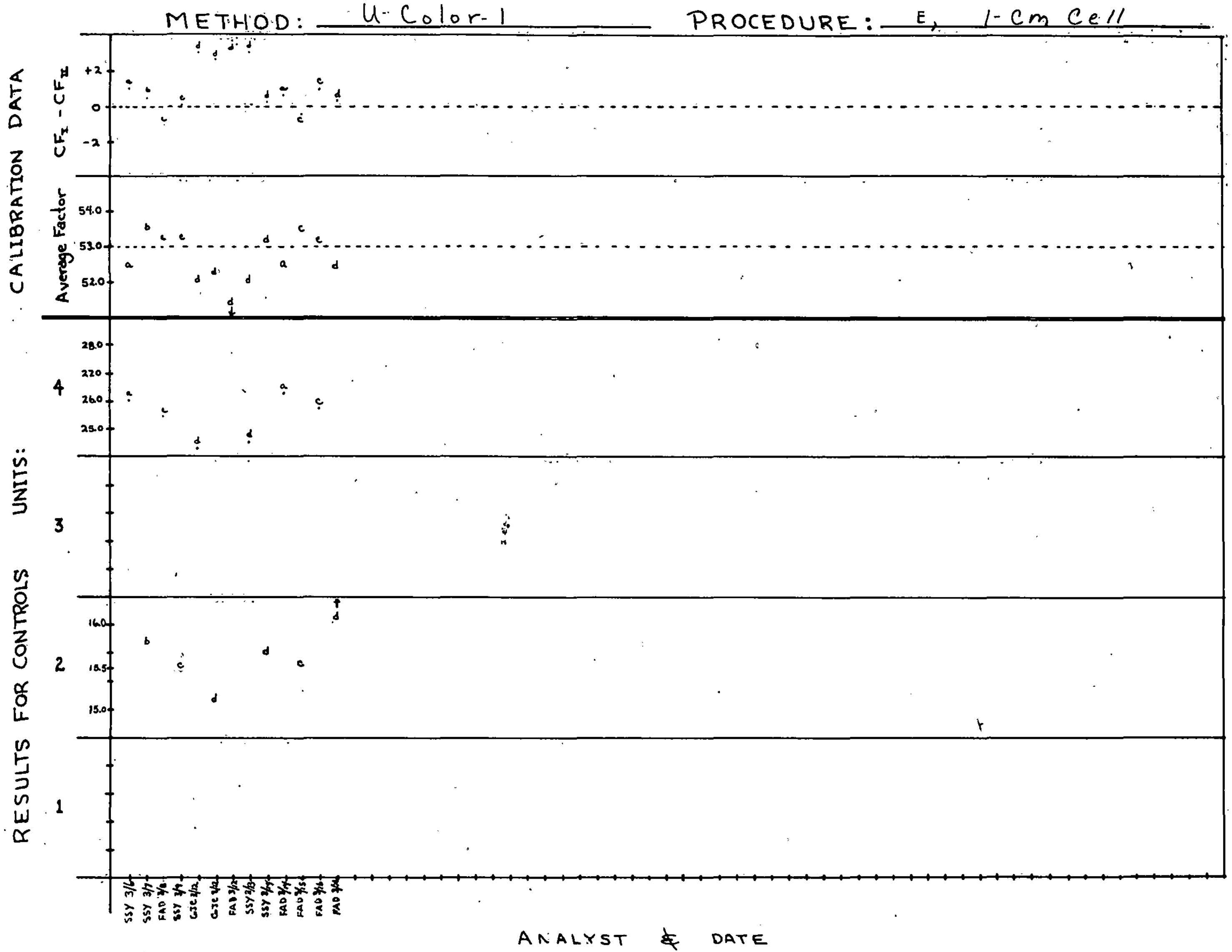

Fig. 8 Partially filled control chart form for spectrophotometric uranium method.

VII. UMPIRE QUALIFICATION PROGRAM

(D. M. Lund, S. S. Yamamura, J. E. Rein)

The Umpire Qualification Program was started in April, 1965 under the direction of the Division of Nuclear Materials Management of the AEC, now reorganized as the Office of Safeguards and Materials Management (OSMM). The objective of the Program is to qualify U. S. Commercial and foreign laboratories to act as umpires in resolving shipper-receiver differences resulting from the transfer of uranium and plutonium materials between the AEC and other parties.

The primary basis for the recommended qualification of a participating laboratory is a demonstrated ability to accurately and precisely analyze uranium and plutonium materials that are prepared and analyzed in AEC laboratories. Other considerations are competency of personnel, adequacy of facilities and equipment, and the maintenance of a satisfactory quality control program. These are evaluated by a questionnaire and a personal visit to the laboratory. Qualification is for a two-year period after which requalification is required.

1. PARTICIPATION OF AEC, U. S. COMMERCIAL, AND FOREIGN LABORATORIES.

Eight AEC and AEC-Contractor laboratories, eight U. S. Commercial laboratories, and six foreign laboratories are participating in various segments of the Program. This information is summarized in Table VIII.

2. PREPARATION OF TEST MATERIALS

Laboratories that wish to qualify as umpires for the analysis of a given material are tested on their technical ability to analyze samples of that material. Seven types of test materials are being used. Table IX summarizes the preparation and analysis of the test materials by the AEC and AEC-Contractor laboratories.

3. DISTRIBUTION OF TEST MATERIALS TO U. S. COMMERCIAL AND FOREIGN LABORATORIES

Appropriate samples of the uranium and plutonium test materials have been sent to the 14 participating Commercial and foreign laboratories (Table VIII). With the distribution of the uranium oxide test material during the past year, all seven test materials have been distributed.

TABLE VIII

AEC, U.S. COMMERCIAL, AND FOREIGN LABORATORY PARTICIPATION

	Material Type													
	UF_6		UN		UO		U-233 UN		PuN		PuO		Pu	
Laboratory[a]	Prep	Anal	Prep	Anal	Prep	Anal	Prep	Anal	Prep	Anal	Prep	Anal	Prep	Anal
AEC														
ORGDP	X	X		X		X		X						
NBL		X		X		X		X		X		X		X
GAT		X		X		X		X						
INC (CPP)			X	X	X	X	X	X						
RF									X	X	X	X		X
ARHCO										X		X	X	X
LASL										X		X		X
U.S. Commercial														
Avco		X		X		X		X		X		X		X
Eberline				X										
Ge-Val		X		X		X		X		X		X		X
Isotopes		X		X		X		X						
Nat'l Lead				X		X								
NFS				X		X		X		X		X		X
NUMEC				X		X		X		X		X		X
Tracerlab		X		X		X				X		X		X
Westinghouse				X		X		X		X		X		X

TABLE VIII (Continued)

Laboratory[a]	Material Type UF_6		UN		UO		U-233 UN		PuN		PuO		Pu	
	Prep	Anal	Prep	Anal	Prep	Anal	Prep	Anal	Prep	Anal	Prep	Anal	Prep	Anal
Foreign														
ALKEM				X		X				X		X		X
CBNM		X		X		X		X		X		X		X
CEA				X		X				X		X		X
CEN-BN		X		X		X				X		X		X
MH		X		X		X								
NUKEM		X		X		X								

[a] ORGDP = Oak Ridge Gaseous Diffusion Plant
NBL = New Brunswick Laboratory
GAT = Goodyear Atomic Corporation
PAD = Paducah Gaseous Diffusion Plant
INC (CPP) = Idaho Nuclear Corporation Chemical Processing Plant
RF = Dow Chemical Company (Rocky Flats Div.)
ARHCO = Atlantic Richfield Hanford Company
LASL = Los Alamos Scientific Laboratory
Avco = Avco Instruments (Tulsa, Oklahoma)
Ge-Val = General Electric Company
Eberline = Eberline Instruments (Santa Fe, New Mexico)
Ge-Val = General Electric Company Vallecitos Atomic Laboratory (Pleasanton, California)
Isotopes = Isotopes Incorporated (Westwood, New Jersey)
Nat'l Lead = National Lead Co., (Albany, New York)
NFS = Nuclear Fuel Services (West Valley, New York)
NUMEC = Nuclear Materials and Equipment Corp., (Apollo, Pennsylvania)
Tracerlab = Tracerlab (Richmond, California)
Westinghouse = Westinghouse Electric Corporation (Madison, Pennsylvania)
ALKEM = Alpha-Chemie und -Metallurgie (Postfach, West Germany)
CBNM = Bureau Central de Mesures, Nucleaires (Geel, Belgium)
CEA = Commissariat a L'Energie Atomique (Grenoble, France)
CEN-BN = Central de Nucleaires-Belgonucleaire (Mol, Belgium)
MH = Metallurgie Hoboken (Hoboken, Antwerp, Belgium)
NUKEM = Nuclear-Chemie und -Metallurgie [Hanou (Main), West Germany]

TABLE IX

STATUS OF THE PREPARATION AND ANALYSIS OF URANIUM AND PLUTONIUM TEST MATERIALS

Test Material and Description of Work	Number of Test Materials	Laboratory Assigned	Status of Work
Uranyl Nitrate	2		
Preparation		CPP	2 Prepared
Analysis		CPP	2 Analyzed
		GAT	2 Analyzed
		K-25	2 Analyzed
		NBL	2 Analyzed
Uranium Hexafluoride	1		
Preparation		K-25	1 Prepared
Analysis		GAT	1 Analyzed
		K-25	1 Analyzed
		NBL	1 Analyzed
		PAD	1 Analyzed
Uranyl Nitrate (U-233 enriched)	2		
Preparation		CPP	2 Prepared
Analysis		CPP	2 Analyzed
		GAT	2 Analyzed
		K-25	2 Analyzed
		NBL	2 Analyzed
Uranium Oxide (U_3O_8)	2		
Preparation		CPP	2 Prepared
Analysis		CPP	2 Being Analyzed
		GAT	2 Analyzed
		K-25	2 Being Analyzed
		NBL	2 Being Analyzed

TABLE IX (Continued)

Test Material and Description of Work	Number of Test Materials	Laboratory Assigned	Status of Work
Plutonium Nitrate	2[a]		
Preparation		RF	1 Prepared
Analysis		ARHCO	1 Analyzed
		LASL	1 Analyzed
		NBL	1 Analyzed[b]
		RF	1 Analyzed
Plutonium Oxide	2[c]		
Preparation		RF	2 Prepared
Analysis		ARHCO	1 Analyzed
		LASL	1 Analyzed
		NBL	2 Analyzed[b]
		RF	2 Analyzed
Plutonium Metal	2[c]		
Preparation		ARHCO	2 Prepared
Analysis		ARHCO	1 Analyzed
		LASL	1 Analyzed
		NBL	2 Analyzed[b]
		RF	1 Analyzed

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[a] Preparation and analysis of the second plutonium nitrate test material is scheduled for FY-1971.

[b] Because of an extremely heavy work load NBL is performing concentration and isotopic distribution analyses only on the plutonium test materials.

[c] Complete analysis by the AEC laboratories of the second plutonium oxide and plutonium metal test materials is scheduled for FY-1970.

4. STATISTICAL EVALUATION OF DATA, PREPARATION OF PROGRAM DOCUMENTS, AND QUALIFICATION RECOMMENDATIONS

The results for the uranyl nitrate, uranium hexafluoride, and plutonium nitrate test materials have been statistically evaluated. A series of documents entitled "Qualification of Umpire Laboratories for the Analysis of Uranium and Plutonium Materials Specifications" is being prepared. Four of these documents have been issued: (a) Report I. Basic Program, (b) Report II. First Report on Uranyl Nitrate, (c) Report III. First Report on Uranium Hexafluoride, and (d) Report IV. First Report on Plutonium Nitrate. The first document (Report I) defines the objectives and explains the implementation of the Program. The subsequent documents (Reports II to IV and others to follow) list the specifications and describe the preparation and analysis of the various test materials by the AEC laboratories. Also included in these reports are the statistical evaluation of the analytical data and recommendations regarding qualification for the U. S. commercial and foreign laboratories who have analyzed the test materials. Reports II, III, and IV recommend fourteen laboratories for qualification as umpires for specific analyses of uranyl nitrate, six for uranium hexafluoride, and five for plutonium nitrate, respectively.

5. INSPECTION OF U. S. COMMERCIAL LABORATORIES

Eberline Instrument Corporation of Santa Fe, New Mexico and Westinghouse Electric Corporation of Madison, Pennsylvania were visited to ensure their performance capabilities. Eberline Instrument Corporation was judged incapable of performing the type of work required in the Program because their primary workload is low level bioassay and environmental radiological analyses. This judgement is shared by Eberline Instrument Corporation's Management and supervisory personnel. Eberline indicated that if the required capability is attained in the future, qualification would be requested. Westinghouse Electric Corporation of Madison is deemed capable of performing all analyses for which it is seeking qualification. During the Madison Laboratory visit, it was learned that a second Westinghouse Laboratory, now under construction at Cheswick, Pennsylvania, is interested in the entire plutonium segment of the Program. The Cheswick laboratory will request plutonium samples when facilities are completed.

6. NONDESTRUCTIVE ANALYSIS OF TEST MATERIALS FOR THE DETERMINATION OF U-235 AND Pu-239

Gulf General Atomic (GGA) of San Diego, California and Los Alamos Scientific Laboratory (LASL) of Los Alamos, New Mexico are developing methods for the nondestructive analysis of uranium and plutonium materials. To aid the evaluation of these methods, OSMM requested that we provide GGA and LASL with samples of the uranium and plutonium test materials used in the Umpire Qualification Program. Empty test sample containers for calibration purposes have been sent to both laboratories at their request. Also, uranyl nitrate, uranium hexafluoride, and uranium oxide samples have been shipped to GGA. Other samples of the various test materials will be shipped to the two laboratories as they are requested. Results have not been reported by either laboratory as of April 1, 1969.

7. FUTURE PLANS

With reference to the foregoing, the following activities are planned for the next 1-year period: (a) distribute the second round plutonium oxide and plutonium metal test materials to the AEC laboratories for analysis (b) continue the statistical evaluation of the analytical data resulting from the analysis of all uranium and plutonium materials, (c) prepare first round documents for plutonium oxide, plutonium metal, uranium oxide, and U-233 enriched uranyl nitrate, (d) prepare supplemental reports to cover additional data submitted on all uranium and plutonium test materials, and (e) recommend qualification of successful laboratories by material type, type of analysis, and if variation between analysts is a significant component of error in the statistical evaluation, by analyst.

VIII. BURNUP DETERMINATION OF NUCLEAR FUELS

F. L. Lisman, W. J. Maeck, J. E. Rein, R. E. Foster
R. M. Abernathey, J. E. Delmore, W. A. Emel,
M. E. Kussy, R. E. McAtee, G. D. Workman

The objective of this project has been the development of methods for the accurate determination of burnup of nuclear fuels. The emphasis has been on power reactor fuels having long residence time and high burnup rather than on short term, experimental irradiations. The principal measurement technique studied has been chemical analysis for fission products. The use of long-lived, radiochemically determined fission products is not applicable because the errors of the in-pile decay corrections are magnified with long term irradiations, the nuclear constants are not known with sufficient accuracy, and the few available nuclides, Cs-137 and Sr-90, are volatile. The use of stable fission product nuclides, determined by isotope dilution mass spectrometry, was therefore selected. The degree of reliability of a burnup determination based on stable fission product analysis depends on three factors: the accuracy of the values used for the fission yields, the linearity between the number of fissions and the number of fission product atoms present at the end of the irradiations, and the reliability of the analysis methods.

The project has been completed, and the final report has been issued[26]. Thermal fission yields were measured for 43 mass chains for U-233, U-235, Pu-239, and Pu-241. Fast reactor fission yields were measured for 45 mass chains for U-235 and Pu-239. Based on these fission yield values, fission product monitors are recommended for the determination of total fissions and for the relative fissions in sources of more than one fissioning isotope that typify existing and future reactor fuels.

1. SUMMARY OF THE THERMAL FISSION YIELDS OF 43 MASS CHAINS FOR U-233, U-235, Pu-239, AND Pu-241

The thermal fission yields measured in this program for 43 mass chains are listed in Table X. The specially prepared fission yield samples had been irradiated in the Materials Testing Reactor at a position where the cadmium ratio for cobalt was 15±1.5. The error associated with each value is in terms of the standard deviation and was calculated by error propagation techniques. Except where noted, the measurement technique for the atoms of the fission products was isotope dilution mass spectrometry.

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[26] F. L. Lisman, et al, Burnup Determination of Nuclear Fuels; Project Report for the Quarter April 1 - June 30, 1968 and Final Report, IN-1277, March, 1969.

TABLE X

SUMMARY OF THERMAL CHAIN YIELDS FOR U-233, U-235, Pu-239, AND Pu-241

Mass Number	Fission Yield, %			
	U-233	U-235	Pu-239	Pu-241
83[a]	1.03±0.01	0.497±0.009	0.301±0.006	0.200±0.006
84[a]	1.73±0.02	0.930±0.015	0.487±0.010	0.353±0.010
85[a]	2.22±0.02	1.30±0.01	0.574±0.011	0.387±0.010
86[a]	2.90±0.03	1.81±0.03	0.770±0.016	0.601±0.018
87	4.06±0.03	2.54±0.01	1.00±0.02	0.741±0.020
88	5.57±0.04	3.61±0.02	1.35±0.03	0.954±0.025
90	6.96±0.06	5.90±0.04	2.09±0.04	1.53±0.04
91	6.60±0.05	5.90±0.03	2.52±0.04	1.82±0.05
92	6.69±0.05	5.95±0.03	3.02±0.05	2.23±0.06
93	7.09±0.06	6.34±0.04	3.95±0.07	2.90±0.08
94	6.91±0.05	6.41±0.04	4.50±0.08	3.33±0.09
95	6.40±0.05	6.45±0.03	4.86±0.11[b]	3.92±0.09[b]
96	5.84±0.05	6.23±0.04	5.12±0.09	4.33±0.12
97	5.52±0.05	5.86±0.03	5.64±0.16[b]	4.76±0.14[b]
98	5.22±0.04	5.77±0.03	NM[c]	NM[c]
99	5.16±0.07	6.14±0.10	6.59±0.18[b]	6.17±0.16[b]
100	4.46±0.04	6.24±0.03	NM[c]	NM[c]
101	3.27±0.02	5.03±0.04	6.50±0.28[b]	5.94±0.26[b]
102	2.48±0.02	4.19±0.04	6.65±0.29[b]	6.32±0.28[b]
103	NM[d]	NM[d]	NM[d]	NM[d]
104	1.04±0.01	1.82±0.01	6.61±0.29[b]	6.80±0.30[b]
106	0.262±0.002	0.389±0.004	4.55±0.19[b]	6.08±0.25[b]
111	[e]	[e]	[e]	[e]
112	[e]	[e]	[e]	[e]
113	[e]	[e]	[e]	[e]
114	[e]	[e]	[e]	[e]
116	[e]	[e]	[e]	[e]
125	0.116±0.013[b]	0.0291±0.0033[b]	0.116±0.014[b]	0.0416±0.0050[b]
131	3.51±0.04	2.79±0.04	3.60±0.09	3.15±0.09
132	4.88±0.06	4.16±0.06	5.09±0.12	4.64±0.13
133	6.06±0.05	6.73±0.04	7.18±0.15	6.71±0.18
134	6.13±0.07	7.51±0.11	7.20±0.17	8.06±0.22
135	[f]	[f]	[f]	[f]
136	[f]	[f]	[f]	[f]
137	6.93±0.06	6.28±0.03	6.74±0.14	6.60±0.17
138	5.97±0.05	6.80±0.03	5.40±0.11	6.37±0.17
140	6.53±0.05	6.31±0.03	5.61±0.12	5.86±0.16
141	[g]	5.50±0.34[b]	[g]	[g]
142	6.71±0.05	5.88±0.03	5.04±0.11	4.80±0.13
143	5.85±0.05	5.90±0.03	4.48±0.10	4.48±0.12
144	4.67±0.04	5.42±0.02	3.78±0.08	4.13±0.11
145	3.37±0.03	3.86±0.02	3.03±0.06	3.19±0.08
146	2.53±0.02	2.95±0.01	2.49±0.05	2.68±0.07

TABLE X (Continued)

Mass Number	Fission Yield, %			
	U-233	U-235	Pu-239	Pu-241
147	1.78±0.04	2.12±0.04	2.15±0.08	2.22±0.06
148	1.30±0.01	1.69±0.01	1.70±0.03	1.89±0.05
149	0.773±0.007	1.00±0.01	1.24±0.03	1.43±0.04
150	0.500±0.004	0.638±0.004	0.965±0.020	1.16±0.03
151	0.365±0.011	0.408±0.012	0.811±0.044	[h]
152	0.186±0.004	0.212±0.006	0.581±0.031	0.725±0.034
154	0.0458±0.0006	0.0563±0.0009	0.270±0.006	0.370±0.010

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[a] Krypton and xenon were quantitatively recovered from the off-gas during dissolution of the samples and the atoms of each isotope were determined by a combination of vapor phase chromatography and gas mass spectrometry.

[b] The measurement technique for these mass chains was gamma-ray spectrometry with either a Ge(Li) or NaI(Tl) detector-pulse height analyzer system.

[c] Not measured, end members of chains are Mo-98 and Mo-100 and molybdenum plated out during dissolution.

[d] Not measured due to the short half-life of Ru-103.

[e] Not measured, end member of chain is a cadmium isotope and a mass spectrometer suitable for the measurement was not available earlier in the program when the samples were analyzed.

[f] Not measured, thermal cross section of Xe-135 is greater than 10^6 barns.

[g] Not measured, experimental phase of program was terminated before the measurements could be completed.

[h] Not reported, unexplained disagreement in experimental results of the two irradiated capsules.

2. SUMMARY OF THE FAST FISSION YIELDS OF 45 MASS CHAINS FOR U-235 AND Pu-239

The fission yields measured in this program for 45 mass chains for the EBR-I U-235 and Pu-239 irradiated fuel rods are listed in Table XI . The error associated with each value is in terms of the standard deviation and was calculated by error propagation techniques. Except for the 125 mass chain, the measurement technique for the atoms of the fission products was isotope dilution mass spectrometry.

TABLE XI

SUMMARY OF FAST FISSION CHAIN YIELDS FOR U-235 AND Pu-239

	Fission Yield, %			Fission Yield, %	
Mass No.	U-235	Pu-239	Mass No.	U-235	Pu-239
83	0.615±0.18	0.366±0.008	125	0.073±0.009	0.19±0.02
84	1.07±0.01	0.559±0.013	131	3.15±0.08	4.06±0.08
85	1.49±0.03	0.672±0.012	132	4.45±0.12	5.42±0.11
86	1.93±0.05	0.882±0.020	133	6.69±0.13	6.91±0.12
87	2.66±0.06	1.16±0.02	134	7.09±0.19	7.35±0.15
88	3.63±0.08	1.44±0.03	135	6.54±0.13	7.54±0.13
90	5.48±0.16	2.24±0.05	136	5.93±0.16	6.92±0.14
91	[a]	2.58±0.05	137	6.20±0.16	6.58±0.11
92	[a]	3.13±0.06	138	6.60±0.12	4.97±0.09
93	[a]	3.91±0.07	140	6.21±0.11	5.59±0.10
94	[a]	4.39±0.08	141	[d]	[d]
95	6.47±0.13	4.78±0.09	142	5.82±0.11	4.95±0.09
96	[a]	5.11±0.10	143	5.80±0.12	4.30±0.08
97	6.13±0.12	5.47±0.10	144	5.26±0.11	3.68±0.07
98	6.04±0.12	5.81±0.11	145	3.85±0.08	3.04±0.05
99	[b]	[b]	146	3.00±0.06	2.52±0.04
100	6.35±0.13	6.76±0.13	147	[e]	[e]
101	5.46±0.11	6.88±0.13	148	1.75±0.03	1.73±0.03
102	4.65±0.10	6.97±0.13	149	1.09±0.02	1.36±0.02
103	[c]	[c]	150	0.832±0.030	1.06±0.02
104	2.35±0.05	6.77±0.12	151	0.438±0.009	0.839±0.015
111	0.0456±0.0009	0.376±0.007	152	0.309±0.006	0.683±0.012
112	0.0391±0.0008	0.207±0.004	154	0.098±0.003	0.324±0.006
113	0.0342±0.0007	0.133±0.002			
114	0.0342±0.0007	0.099±0.002			
116	0.0359±0.0007	0.064±0.001			

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[a] Not measured, end member of chain is a zirconium isotope and the fuel was clad in Zircaloy-2.

[b] Not measured, end member of chain is Tc-99 which is suspected to have plated out during dissolution.

[c] Not measured, the member of chain is Rh-103 and rhodium was not determined in the program.

[d] Not measured, end member of chain is Pr-141 and praseodymium isotopes were not determined in the program.

[e] Not measured, intermediate member of chain is 2.5-yr Pm-147. The long and intermittent irradiation exposure causes large uncertainties in the decay correction calculation for this chain.

3. FISSION PRODUCTS RECOMMENDED AS MONITORS

Table XII summarizes those fission products which are most potentially useful as burnup monitors for U-235, Pu-239, and mixed U-235, Pu-239 fuels. The symbol X indicates usefulness. Caution must be exercised if an X does not appear in the "unknown" neutron energy column because the fission yield of the particular fission product varies with neutron energy.

The only fission product which has general applicability as a monitor of total fissions in mixed U-235, Pu-239 fuels is Nd-148. However, its fission yield increases with neutron energy, being 4% higher for a metal U-235 fuel in liquid NaK (EBR-I) than a light-water enriched-uranium fuel (MTR), and 2% higher for Pu-239 for comparable reactor conditions.

For the thorium breeder reactor in which U-235 and U-233 will be the fissioning isotopes, the only two apparently useful monitors of total fissions are Mo-95 and Ce-140. Both these isotopes are centrally located in the peaks of the fission yield curve, hence, should not be very sensitive to neutron energy changes.

Also reported in the final report[26] for this project is the use of the ratio of two isotopes of the same element as monitors of total fissions and of relative fissions from duofissionable sources. The ratios Kr-84/Kr-83 and Xe-132/Xe-131 are acceptable monitors of total fissions for a thermally fissioned U-235 or Pu-239 fuel. The three pairs Nd-148/Nd-150, Nd-146/Nd-148, and Ru-101/Ru-104 will provide measures of the relative fissions from U-235 and Pu-239 in a mixed U-235, Pu-239 source provided that the neutron spectrum is known.

TABLE XII

USEFUL NUCLEAR FUEL BURNUP MONITORS OF TOTAL FISSION

	U-235			Pu-239			U-235 + Pu-239			
	Neutron Energy			Neutron Energy			Neutron Energy			
Fission Product	Thermal	Fast	Unknown	Thermal	Fast	Unknown	Thermal	Fast	Unknown	Comments[a]
Sr-88	X	X	X	X	X					Easily determined by ID[b,27]. Natural Sr contamination[c] is a serious problem. Migration in fuel can be a problem.
Sr-90	X	X		X	X					As for Sr-88. Corrections required for in-pile and out-of-pile decays which adversely affect reliability.
Zr-92	X			X	X					Determined by ID[28,29] with some difficulty. Large amounts of natural contamination cause decreased reliability[c].
Zr-93	X			X	X	X				As for Zr-92.
Zr-94	X			X	X	X				As for Zr-92.
Zr-96	X			X	X	X				As for Zr-92.
Mo-95	X	X	X	X	X	X				Determination by ID is difficult[26]. MoO_3 is volatile causing migration in UO_2 and PuO_2 fuels. Natural contamination either of Mo or Zr seriously affects reliability.

TABLE XII (Continued)

Fission	U-235 Neutron Energy			Pu-239 Neutron Energy			U-235 + Pu-239 Neutron Energy			
Product	Thermal	Fast	Unknown	Thermal	Fast	Unknown	Thermal	Fast	Unknown	Comments[a]
Mo-97	X	X		X	X	X				As for Mo-95.
Mo-98	X	X								As for Mo-95
Mc-100	X	X	X							As for Mo-95
Ru-101 -102 -104	X	X								Easily determined by ID[30].
Cs-133	X	X	X	X	X			X		Easily determined by ID[29]. Natural contamination seriously affects reliability[c]. High volatility causes migration in fuels.
Cs-137	X	X		X	X					Easily determined both by ID[29] and by radiochemistry[31]. High volatility causes migration in fuels. Corrections required for in-pile and out-of-pile decays which adversely affect reliability
Ce-140	X	X	X	X	X	X				Easily determined by ID[28,31].
Ce-142	X	X	X	X	X	X				As for Ce-140.

TABLE XII (Continued)

Fission Product	U-235 Neutron Energy			U-239 Neutron Energy			U-235 + Pu-239 Neutron Energy			Comments[a]
	Thermal	Fast	Unknown	Thermal	Fast	Unknown	Thermal	Fast	Unknown	
Nd-148	X	X	(X)?	X	X	X	X	X	X	Easily determined by ID[28,31]. The fission yield values vary 4% between the U-235 thermal and EBR-I fast fission yield values.

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[a] References 27 through 31 are listed on page 84.

[b] ID denotes determination by the technique of isotope dilution mass spectrometry, usually after a chemical separation.

[c] All sources of natural contamination must be considered including the fuel, dissolution reagents and apparatus, chemical separation procedure, and the filaments used in mass spectrometry.

[27] F. L. Lisman et al, Burnup Determination of Nuclear Fuels: Project Report for the Quarter January 1 - March 1, 1967, IN-1157 Rev. (1968).

[28] F. L. Lisman et al, Burnup Determination of Nuclear Fuels: Project Report for the Quarter July 1 - September 30, 1967, IN-1189 (1968).

[29] F. L. Lisman et al, Burnup Determination of Nuclear Fuels: Project Report for the Quarter October 1 - December 31, 1966, IN-1113, (1967).

[30] W. J. Maeck et al, Burnup Determination of Nuclear Fuels: Project Report for the Quarter October 1 - December 31, 1965, IDO-14676 (1966).

[31] W. J. Maeck et al, Burnup Determination of Nuclear Fuels: 1964 Annual Report, IDO-14656 (1965).

IX. IODINE ADSORBERS-REACTOR ATMOSPHERE CLEANUP

1. DEVELOPMENT OF SPECIFIC INORGANIC ADSORBERS FOR THE RETENTION OF AIRBORNE RADIOIODINE

(W. J. Maeck, D. T. Pence, J. H. Keller)

In the reactor safety program, the cleanup of reactor containment atmospheres for fission products, especially the volatile iodine species, is of major importance. Charcoal (potassium iodide impregnated) currently is the material commonly used for the cleanup systems; however, it has disadvantages of iodine desorption at relatively low temperatures, flammability, and unsatisfactory performance with steam atmospheres.

A more promising approach is the use of inorganic adsorbents in which the reaction mechanism involves the formation of a stable iodine compound. With selected inorganic materials the preferred properties of nonflammability, high temperature operability, rapid reaction rates with various iodine species, and a high tolerance to steam atmospheres can be obtained.

Both organic and inorganic materials, with the latter emphasized, were investigated for the uptake of I-131 tagged elemental iodine and methyl iodide from water-saturated air at room temperature and steam-air mixtures.

Of the materials that adsorbed both iodine species, Linde Molecular Sieve 13X converted to the silver form has the best overall properties. It is inorganic, easily and reproducibly prepared, stable up to high temperatures with no desorption of iodine, and stable to moisture with no loss of silver. It has high capacity, and a rapid rate of reaction with both elemental iodine and methyl iodide such that the adsorbed species is tightly bound at the entrance of the bed. Significant features of the material are its high surface area-to-volume ratio and the incorporation of the silver in a reactive state throughout the crystal lattice. The results of this study have been published in an AEC report[32] and presented at the 10th USAEC Air Cleaning Conference[32].

Because of the unusual properties of this material, current research has been devoted to evaluating the effects of various atmospheric pollutants upon the iodine adsorption characteristics of LMS-13X-Ag. The purpose of these experiments is to evaluate applications of the material including: off-gas systems in reactor fuel processing plants, scrubbers of natural gas released by plow-share explosions, face masks and air filtration units for the military, air filtration units for civil defense fallout shelters, Health-Safety air sampling and monitoring devices, and iodine cleanup systems for sodium-cooled fast reactors.

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[32] W. J. Maeck, D. T. Pence, J. H. Keller: A Highly Efficient Inorganic Adsorber for Airborne Iodine Species (Silver Zeolite Development Studies), IN-1224 (October 1968). Also, Proceedings of the Tenth AEC Air Cleaning Conference, New York, New York (August 1968) USAEC Report, Conf-680821, December 1968.

1.1 Gaseous Pollutant Studies.

The effects of various gases upon the iodine adsorption properties of LMS-13X-Ag have been examined to determine possible poisoning of the adsorbent. None of the gases studied and listed in Table XIII had any degrading effect upon the iodine adsorption characteristics of LMS-13X-Ag except when the beds became very wet.

To study the effects of the various gases, a simple glass dissolver and water condenser were fabricated, and a 1-in. diam x 1-in. long LMS-13X-Ag adsorbent bed was placed at the gas exit of the condenser. Two types of experiments were conducted. The first involved passing the gas through the dissolver, condenser, and LMS-13X-Ag adsorbent bed followed iodine carrier and I-131 tracers, then sweeping the generated elemental iodine through the bed with air. This procedure resulted in the LMS-13X-Ag bed becoming very wet. The effects of NO_2, CO_2, and O_2 were determined in this manner as well as the effects of the mixed oxides of nitrogen generated during the dissolution.

To reduce the moisture problem on the bed in a second series of experiments, the gases were bubbled through $0.1\underline{M}$ H_2SO_4 in the dissolver flask; iodine carrier and I-131 tracer were added; elemental iodine was generated by adding a solution of sodium nitrite which then was swept through the bed with air. The LMS-13X-Ag remained dry using this procedure. The effects of CO_2, O_2, SO_2, H_2S, and propane were evaluated in this manner. Hexone was distilled through the bed prior to the addition of the sulfuric acid. The test bed was wet with condensed hexone during the iodine release.

Of particular interest was the effect of hydrogen sulfide. In the test, 70 liters of an 8% H_2S-air mixture were passed through a LMS-13X-Ag bed. The bed rapidly adsorbed the hydrogen sulfide forming Ag_2S. Despite the high sulfide loading, the iodine adsorption remained greater than 99.9%.

TABLE XIII

EFFECT OF VARIOUS GASES ON IODINE ADSORPTION CHARACTERISTICS OF LMS-13X-Ag

Gas	Amount of Gas (Total Flow Time)	Dissolver Contents	I_2 Retention	Remarks
NO_2	55 liters (4 hr)	$Al-HNO_3$	99.7	Wet Bed
CO_2	50 liters (7 hr)	$Al-HNO_3$	94.2	Very Wet Bed
	600 liters (1.3 hr)	$Al-HNO_3$	99.2	Wet Bed
	430 liters (1.5 hr)	$H_2SO_4-NaNO_2$	>99.9	Dry Bed
O_2	630 liters (1.2 hr)	$Al-HNO_3$	98.4	Wet Bed
	1200 liters (2 hr)	$H_2SO_4-NaNO_2$	>99.9	Dry Bed
SO_2	500 liters (10% SO_2) (1.5 hr)	$H_2SO_4-NaNO_2$	>99.9	Dry Bed
H_2S	70 liters (8% H_2S) (2 hr)	$H_2SO_4-NaNO_2$	>99.9	Dry Bed
Propane	560 liters (1.2 hr)	$H_2SO_4-NaNO_2$	>99.9	Dry Bed
Hexone	200 ml distilled through bed	$H_2SO_4-NaNO_2$	>99.9	Wet with Hexone

1.2 Application to LMFBR Program.

The LMS-13X-Ag material was investigated for the removal of iodine from a sodium-cooled reactor containment atmosphere in which the atmosphere contained freshly generated particles of sodium oxide (Na_2O) that were produced by ignition of sodium metal. The retention of iodine was greater than 99.9% on the first two components of a three-component adsorber unit. The three major components, in order of flow, were a glass fiber filter for particulates, a bed of LMS-13X-Ag, and a bed of Barneby-Cheney 151 charcoal.

Three tests were conducted. The components of the adsorber units for each test are described in Table XIV, and the test results are summarized in Table XV.

The general experimental procedure was as follows. A weighed amount of sodium metal was placed in a quartz boat on a layer of sand in a glass flask which was then connected to the adsorber unit.

The flask was purged with oxygen and the sodium was ignited by heating the flask. Elemental iodine with I-131 tracer was flowed into the flask with helium, and the vapor phase mixture of Na_2O smoke, I_2, O_2, and He flowed into the adsorber unit. The unit was scanned for I-131 activity distribution along the axis of flow. The unit then was disassembled and the individual components were counted for I-131 activity to establish the relative distribution. The components were reassembled as the original adsorber unit and were purged with air. The unit again was scanned along the flow axis, disassembled, and the individual components were counted.

In tests 1 and 3, the constituents of the adsorber unit were the same. In test 1, the elemental iodine was flowed into the flask after the ignition of the sodium had ended, whereas in test 3, the iodine was introduced within 3 sec after the initiation of ignition. In both tests, less than 0.1% of the iodine penetrated through to the charcoal bed. As expected, the amount of iodine associated with sodium oxide particles was greater for test 3 as evidenced by the larger percentage of iodine on the glass fiber filter. The iodine was adsorbed on the LMS-13X-Ag bed in a narrow band at the entrance. Air purges of 18 hr produced no detectable movement of the iodine on the LMS-13X-Ag bed.

In test 2, a course mesh Teflon screen was substituted for the initial glass fiber filter. This increased the penetration of iodine through the LMS-13X-Ag bed to almost 5%, of which almost all was retained on the glass fiber filter located immediately downstream of the LMS-13X-Ag bed. This indicates that very small particles of sodium oxide containing adsorbed iodine penetrated the LMS-13X-Ag bed, and that the penetrated iodine species was not volatile.

TABLE XIV

COMPOSITION OF ADSORBER UNITS

Test	First Filter for Particulates	LMS-13X-Ag Bed	Charcoal Bed
1 and 3	Flanders 700 HEPA Glass Fiber filter	1.0-in. diam x 1.25-in. bed of LMS-13X-Ag, 10-20 mesh followed by Flanders 700.	1.0-in. diam x 1.25-in. bed of Barneby-Cheney 151, 20-40 mesh, preceded and followed by Flanders 700 filters.
2	Teflon screen, 30 mesh	1.0-in. diam x 1.25-in. bed of LMS-13X-Ag, 10-20 mesh followed by Flanders 700.	1.0-in. diam x 1.25-in. bed of Barneby-Cheney 151, 20-40 mesh, preceded by and followed by Flanders 700 filters.

TABLE XV

DISTRIBUTION OF IODINE ON ADSORBED UNITS

Test	Amount of Na Ignited, g	Ignition Temp, °C	Duration of Combustion, sec	O_2 Flow, cc/min	Distribution[a] of Iodine on Components, Relative %						
					First Filter[b]	LMS-13X-Ag Bed	Flanders 700	Sub Total	Flanders 700	Charcoal Bed	Sub Total
1	0.5	310	10	300	25.5	74.0	0.5	100	ND	ND	ND
2	0.6	305	7	300	5.9	89.4	4.3	99.6	0.1	0.3	0.4
3	1.0	280	15	300	88.6	11.3	ND	99.9	<0.1	<0.1	0.1

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[a] Computed on data obtained after the air purge of the reassembled units.

[b] See Table XIV.

X. LOFT-ECCS SUPPORT PROGRAM

The LOFT-ECCS (Loss of Fluid Test-Emergency Core Cooling System) Program, part of the AEC Nuclear Safety Program, is designed to provide information concerning loss-of-coolant accidents to pressurized, water-cooled power reactors. The LOFT facility will consist of a 50-MW pressurized-water reactor in a 3x10^5-ft^3 containment vessel. A series of tests is scheduled in which the main coolant line will be ruptured with the reactor at power. In the initial tests, the reactor vessel will be flooded or sprayed and the containment vessel will be sprayed to evaluate these industry-installed safety systems. The tests will progress to unperturbed accident conditions. In this planned sequence, the levels of released fission products will progressively increase.

To provide information for the evaluation of fission product behavior, a large variety of samples from the reactor vessel, the containment vessel, and the environs will be analyzed as a function of time and space position. This report presents the objectives, major accomplishments, and status of those tasks in support of the LOFT-ECCS program that are the prime responsibility of the Analytical Chemistry Branch. The Chemical Technology Branch and the Physics Section in the Nuclear Technology Branch also are assigned tasks; information concerning these is reported in their respective annual reports[33, 34]. All these support tasks are performed cooperatively by the three organizational units.

SUMMARY

The following is a summary of each task assigned to the Analytical Chemistry Branch.

1. SAMPLE PROCESSING AND PACKAGING

The objective of this task is to develop and proof test techniques and equipment for the disassembly of samplers and the packaging and storage of the various samples.

The criteria for a suitable sample container are: complete containment of fission products during handling, storage, and analysis; capability of being decontaminated to a smear-clean surface and to a radiation activity level that is biologically tolerable; capability to withstand handling and decontamination operations with no migration of fission products within the container which would change the counting geometry; and use of material which does not distort gamma-ray spectra.

[33] J. R. Bower (ed.) Chemical Technology Branch Annual Report Fiscal Year 1969, IN-1314.

[34] R. M. Brugger et al, Nuclear Technology Branch Annual Report, IN-1317.

A 2-in. diam by 2-in. tall aluminum can-aluminum lid combination meets these criteria and is recommended for use in the LOFT-ECCS test series.

Redirection of the LOFT-ECCS test program toward greater stress on an evaluation of the core flooding and containment vessel spray systems should reduce the levels of airborne fission products. As a result, a less expensive sample processing system is under review. This system is based on the use of laboratory hoods rather than gloveboxes.

2. BEHAVIOR OF LOW-LEVEL AIRBORNE IODINE: DISCUSSION OF HYPOIODOUS ACID

Hypoiodous acid was first postulated by this laboratory to exist as an airborne iodine species based on CDE and laboratory experiments. Initial experiments indicate that hypoiodous acid constitutes a significant fraction of the total iodine remaining in the containment atmosphere after the initial washout of elemental iodine. It, therefore, is important from the standpoints of the final removal rate of iodine and the design of gas cleaning systems.

Two types of experiments are reported that show that hypoiodous acid volatilizes from aqueous media as a stable airborne species. In the first type, hypoiodous acid was identified directly by a specific chemical reaction. In the second type, hypoiodous was inferred from reactions of airborne iodine on various adsorbent materials.

Based on a consideration of the equilibria involved with the hydrolysis of iodine at 25 and 100°C, an expression has been derived for the fraction hypoiodous acid/total initial iodine as a function of hydrogen ion concentration and initial total iodine. Hypoiodous acid is a dominant species at low iodine concentration levels, and the relative amount increase with decreasing total iodine concentration, decreasing hydrogen ion concentration, and increasing temperature.

The conditions that should prevail upon the accident of a water-cooled power reactor seem ideal for the formation of hypoiodous acid and for its stable existence in the vapor state. Such conditions are the contacting of the released fission products with a heated water solution at a pH of 7 to 10 and subsequent transport to a steam-air atmosphere.

3. PARTICULATE-IODINE SAMPLING SYSTEM

The Particulate-Iodine sampler is one of the principal atmosphere sampling devices being developed for the LOFT-ECCS tests. Its purpose is to measure the concentrations of airborne fission products, other than noble gases, differentiated into at least the following fractions: noniodine particulate matter, total inorganic iodine species, and organic iodides. Most previous samplers included some type of a silver surface component on which all inorganic iodine species were to be adsorbed. At low levels of iodine, silver surfaces do not effectively adsorb inorganic iodines.

A sampler currently being evaluated contains five components: (a) a series of three Flanders F-700 glass fiber HEPA filters to retain particulate activity, (b) hydrous zirconium oxide in the iodide (HZO-I) form to retain elemental iodine and pass hypoiodous acid and organic iodides, (c) a hypoiodous acid (HOI) adsorbent, (d) Linde Molecular Sieve 13X in the silver form (LMS-13X-Ag) to retain organic iodides and other species not adsorbed on the upstream components, and (e) KI-I_2 impregnated charcoal (Barnebey-Cheney 151) as a backup adsorbent.

4. WALL CONDENSATE SAMPLING SYSTEM

The CDE wall condensate sampler furnishes time-dependent samples of steam condensate from a large isolated surface with known heat transfer characteristics. The time-dependent distribution of radionuclide activity between the containment vessel atmosphere and the steam condensate on the walls is useful for understanding the airborne iodine behavior.

Currently, the six materials being tested for the separation of iodine from liquid streams are Linde Molecular Sieve 13X, Dowex-50-12X, Vermiculite, and Ultramarine Blue all in the silver form, Dowex-1-10X in the chloride form, and Amberlite XAD-2.

5. RADIOMETRIC SURFACE SCANNER

The radiometric surface scanner is designed to establish the distribution of fission products on various surfaces. An improved scanner is being developed with a slide mechanism for vertical and horizontal positioning of the samples. Continuous movement of the slide is provided from one end of its travel to the other, and by using preselect switches, a reduced scan length can be obtained.

6. SEPARATION OF KRYPTON AND XENON FOR RAW GAS MONITOR

A Raw Gas Monitor will be installed in the LOFT-ECCS containment vessel near the blowdown nozzle to follow the airborne concentrations of krypton and xenon on a time-dependent basis. The measurement technique will be by gamma-ray spectrometry, but prior to measurement, airborne iodine activity will be separated to improve the reliability of the analysis.

7. SAMPLING AND ANALYSIS OF AQUEOUS SOLUTIONS FOR METHYL IODIDE

Two analytical procedures were investigated for the determination of methyl iodide in aqueous solutions. Both procedures gave excellent results of >95% recovery for pure methyl iodide solutions when the recovery calculations were based on the relative activities in the separated fractions.

Precautions must be observed to obtain valid analytical results for iodine species in aqueous samples. Procedures for methyl iodide based on extraction into an organic solvent are subject to high bias caused by coextraction of other iodine species. The effect of hypoiodous acid is especially significant. Methyl iodide volatilizes from aqueous solution and is extremely difficult to retain in sample containers. Elemental iodine plates out on container walls.

8. GAS CHROMATOGRAPHY STUDIES AND APPLICATIONS

Gas chromatography is used extensively in the development program for LOFT-ECCS samplers and for the analysis of atmosphere samples from CDE tests. It provides an unambiguous quantitative measurement of methyl iodide, krypton, and xenon, and a detection of organic iodides with molecular weights higher than methyl iodide.

A series of dilutions of a standard gas mixture containing natural krypton and xenon was analyzed on the gas chromatograph. The linearity of the measured areas plotted as a function of the dilution factors was within 10% over the range from 3.5 to 3700 ng of xenon and within 10% from 9.5 to 495 ng of krypton.

The Raw Gas Sampler in the CDE provides an unperturbed atmosphere sample for organic iodides by gas chromatography. This measurement serves as the basis to evaluate the performance of the CSM and P-I samplers for organic iodides.

9. IODINE SPECIES PREPARATIONS

The development of adsorbent materials for the P-I Sampler requires gaseous mixtures that contain essentially one iodine species. The iodine species used in this program are prepared from a commercial solution containing approximately 20 atom percent of I-131 and 80 atom percent stable iodine in 0.1M NaOH.

Methyl iodide is prepared by adding an aliquot of the I-131 solution to a reaction flask containing calcium carbonate and dimethyl sulfate. Helium is flowed through the system and the generated methyl iodide is retained in a Porapak Q collection trap.

Two methods have been used to prepare elemental iodine: the reaction of molten potassium dichromate with the evaporated caustic residue of the commercial I-131 solution, and the dropwise addition of the I-131 solution into an acidified solution of potassium iodate.

Another method, based on the oxidation of iodide to elemental iodine by nitrite in an acid solution, was evaluated.

10. IODINE DECONTAMINATION OF SAMPLERS AND COMPONENTS

Decontamination of samplers and components are needed because the various equipment is expensive and must be reused. Various commercial agents were evaluated on various items of equipment and no one agent satisfactorily decontaminated all items without corrosive damage. However, various agents were satisfactory for specific materials. The agents tested were chlorox; Kern 85D; L+A Formula 50 and 52; Radiacwash; sodium carbonate; Turco-4306, 4502, and 4521; and oxalic acid.

1. SAMPLE PROCESSING AND PACKAGING

(F. W. Dykes, F. O. Cartan)

The objective of this task is the development and proof testing of the techniques and equipment for the disassembly of samplers and the packaging and storage of the various samples. A large proportion of the samples will be relatively small components, such as plate-out coupons and adsorbent filters, from the samplers. Most of these will be analyzed for fission products by direct gamma-ray spectrometry. An aluminum container suitable for this purpose has been successfully tested. Detailed design was continued during the early part of the year on a glove box system for the processing and packaging of samples. In January, at the request of the LOFT-ECCS organization, this design work was suspended, and a review of the needs was initiated with the objective of a simpler and less expensive system based on laboratory hoods. This review was instigated because of a change in the LOFT-ECCS test program which results in an expected decrease in the fission product levels of the samples.

1.1 Sample Container Development (F. A. Duce, J. H. Keller)

The criteria for a suitable sample container are: complete containment of fission products during handling, storage, and analysis; capability of being decontaminated to a level where the surface is smear-clean and the surface activity is negligible; capability to withstand the handling and decontamination operations with no migration of fission products within the container which would change the counting geometry; and use of material which does not distort gamma-ray spectra. Studies last year indicated that aluminum containers would meet these criteria, but the selection of the best lid was delayed pending further study.

The proposed sample container is a commercially available 2-in. diam by 2-in. tall aluminum can with either an aluminum or a tin-plated steel lid. A small, motor-operated can sealer crimp-seals the lid to the can. Both types of lids have gasket compounds around their peripheries, but of different compositions. The machine-applied gasket on the steel lids is more uniform than the manually applied gasket on the aluminum lids. Cans sealed with both types of lids have been leak tested with helium. The cans with the steel lids had lower leakages and withstood mechanical abuse better[8].

The helium leak test is very severe, and the results are difficult to extrapolate to fission products. As an alternate test, leakages of methyl iodide tagged with I-131 have been measured. Methyl iodide, a nonreactive, volatile form of iodine, is expected to be a persistent airborne iodine species in the LOFT-ECCS containment, and therefore, is ideal for this purpose.

The methyl iodide test begins with the generation of methyl iodide tagged with approximately 5 mCi of I-131 in each can. The method used is that of Hartman [35], wherein potassium iodide, calcium carbonate, methyl sulfate, and the I-131 tracer (as potassium iodide) are placed in a 5-ml beaker in the open can. The can is quickly sealed, then is swirled to mix the ingredients to produce the methyl iodide. Each can is sealed in a jar containing a bed of activated charcoal which retains any methyl iodide leaking from the can. After one month, the jars and charcoal are counted with and without the cans. The leakage is calculated from the amount of I-131 trapped in the charcoal.

Table XVI summarizes the results for 12 cans with tin-plated steel lids and 12 cans with aluminum lids.

TABLE XVI

METHYL IODIDE LEAKAGES FROM ALUMINUM CANS

	Tin-Plated Steel Lids	Aluminum Lids
Average percent leakage in one month	1.9	0.06
Range	1.3 to 3.8	0.006 to 0.52

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[35] A. H. Blatt (ed.), Organic Synthesis, Collective Volume II, New York: John Wiley and Sons, Inc. 1943 (p 404).

Contrary to expectation from the previous helium leak tests, the average leakage of the cans sealed with the steel lids was greater, by a factor of over 30, than that of the cans sealed with the aluminum lids. This is attributed to a difference in the gasket materials of the two types of lids. Apparently the diffusion of methyl iodide is greater for the gasket material of the steel lids.

Based on the above data and the results of last year's decontamination and handling tests, the aluminum can and aluminum lid combination is recommended for use in the LOFT-ECCS test series.

1.2 Sample Processing Equipment (B. R. Hunter)

The glove box system proposed for processing LOFT-ECCS samples must be integrated with sampler storage and processing units. Because this requires extensive modification of "standard" glove boxes, it appears less expensive to use custom-fabricated units, designed for each particular operation. A sketch of a basic glove box was prepared which is readily adaptable to the required configurations, including shielded units for sampler disassembly. Further work on this system was suspended by LOFT-ECCS in January. Changes made in the test program are in the direction of lower fission product releases. The feasibility of a less expensive system based on laboratory hoods is under review.

Design Engineering completed a conceptual design of the sample transfer device to be installed between the disassembly and the canning glove boxes in the sample processing line. This device inserts the sample into the can during the transfer operation between the boxes. The design has considerable merit and should facilitate the canning operation.

2. BEHAVIOR OF LOW LEVEL AIRBORNE IODINE: DISCUSSION OF HYPOIODOUS ACID

(J. H. Keller, D. T. Pence, H. R. Beard, F. O. Cartan, W. J. Maeck)

Hypoiodous acid was first postulated by this laboratory[36] to exist as an airborne iodine species based on the Contamination-Decontamination Experiment (CDE) and laboratory experiments. In these experiments, adsorber data and gas chromatographic analyses showed the presence of a volatile iodine species with an airborne half-time of at least half a day that was neither elemental iodine nor an organic iodide.

The existence of an inorganic iodine species that forms under Pressurized Water Reactor (PWR)-accident conditions and remains airborne for days is of great concern to the reactor safety program. If such a species were to constitute a significant fraction of the total iodine remaining in the containment atmosphere after the initial washout of the elemental iodine, it, rather than methyl iodide, could govern both the final removal rates of iodine and the design of gas cleaning systems. Information concerning it would be vitally important in extrapolating the models for fission product release, transport, and diffusion in LOFT-ECCS to full-scale PWR systems. This species could well be the "unidentified iodine species," reported by various investigators, that penetrates various adsorbents including silver metal surfaces. Its property of penetrating adsorbents is similar to that of the organic iodide species and thus may explain the abnormally high organic iodide fractions reported by various investigators who did not measure organic iodides by direct techniques such as gas chromatography. A species like this also is important to the spray technology program because its washout rate should be different than that of elemental iodine and methyl iodide.

Since our initial reporting of this species, the reaction of investigators in other laboratories concerned with fission product iodine release and its measurement has been varied. Many agree that hypoiodous acid can exist in aqueous solution but doubt that it is sufficiently volatile to exist in the gaseous state.

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[36] F. O. Cartan, H. R. Beard, F. A. Duce, J. H. Keller, "Evidence for the Existence of Hypoiodous Acid as a Volatile Iodine Species Produced in Water-Air Mixtures," Proceedings of the Tenth AEC Air Cleaning Conference, New York, New York (August 1968) USAEC Report, Conf-680821, December, 1968.

Experiments are described in this report which demonstrate that hypoiodous acid is volatilized from aqueous solutions and has airborne stability. The significance of this is discussed in light of the various equilibria involved in iodine hydrolysis reactions, especially as it relates to the often quoted paper of Eggleton[37].

From these equilibria, relationships have been developed that give the ratio of hypoiodous acid to total iodine in solution as a function of total iodine concentration, pH, and temperature.

2.1 Identification of Hypoiodous Acid in the Vapor State.

Two experiments have been conducted that show that hypoiodous acid is volatilized from aqueous media as a stable airborne species. In the first, hypoiodous acid was identified directly by a specific chemical reaction. In the second, it was implied from reactions observed on various adsorbent materials.

In the first experiment, hypoiodous acid was generated in solution by the well known reaction of elemental iodine with excess mercuric oxide[38].

$$2HgO + 2I_2 + H_2O \rightarrow 2HOI + HgO \cdot HgI_2.$$

The solution was filtered to remove the mixed mercuric iodide-mercuric oxide residue, and the clear filtrate was placed in a distillation flask except for a small portion that was set aside for an analysis for hypoiodous acid. A slow air purge of approximately 100 cc/min was passed through the filtrate as it was heated to boiling. The vapor was passed through a water trap maintained just above freezing until droplets of water were observed in the distillate. Then a second trap was substituted which collected 5 cc of the distillate. Aliquots from each trap and the small portion of the initial clear filtrate that had been set aside previously were tested for elemental iodine and for hypoiodous acid.

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[37] A. E. G. Eggleton, A Theoretical Examination of Iodine-Water Partition Coefficients, AERE-R-4887, 1967.

[38] J. R. Partington, Textbook of Inorganic Chemistry, 6th ed., New York: McMillan, p 333, 1957.

Thiodene, which forms a highly sensitive colored product in the presence of elemental iodine, was added and no elemental iodine was present in any of the three solutions. The test for hypoiodous acid was based on the generation of elemental iodine and its reaction with Thiodene after iodide and dilute sulfuric acid were added to the sample under two conditions (a) with phenol added prior to the addition of the iodide and sulfuric acid and (b) with no phenol added. With no phenol present, any positively charged iodine species oxidizes iodide to iodine. With phenol present, only iodine species with oxidation states higher than hypoiodous acid oxidize iodide to iodine. This is because hypoiodous acid is the sole iodine species that iodinates phenols[39]. In all three test solutions, no iodine was produced when the phenol was present, only when it was absent. This confirms that the hypoiodous acid that had been generated by the reaction of elemental iodine and mercuric oxide was volatilized as a relatively stable species on heating an aqueous solution.

The second type of experiment, the reaction of airborne iodine species with various adsorbent materials, provides indirect evidence for the existence of hypoiodous acid as a stable airborne species. We first postulated that airborne hypoiodous acid can be formed when air is passed through a heated solution of elemental iodine in water. This postulation was based on experimental evidence that a significant fraction of the airborne iodine was neither elemental iodine nor methyl iodide. This fraction penetrated adsorbents that retain elemental iodine, including various silver metal surfaces and hydrous zirconium oxide in the iodide form. Gas chromatographic analyses showed that it was not methyl iodide.

Since the original postulation, many laboratory experiments have been performed with the hydrous zirconium oxide-iodide adsorbent to ensure that the observed effect was not caused by some property of the adsorbent itself. One possibility considered was the incomplete retention of elemental iodine when the flow rates through the adsorbent are unrealistically high or when water condenses on the adsorbent. Many experiments were performed in which air at a slow flow rate was passed through a heated aqueous solution of elemental iodine tagged with I-131, then through the adsorbent bed maintained at a temperature higher than the stream temperature so that condensation did not occur. Longitudinal scanning of the test bed with a scintillation counter showed that the adsorbed activity was concentrated in a sharp band at the entrance of the adsorbent bed. However, a significant fraction of the I-131 activity passed through the bed that was not methyl iodide based on gas chromatographic analysis. The conclusion is that the sharp band was adsorbed elemental iodine and that another inorganic

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[39] V. Colman, The Active Substance in the Iodination of Phenols, J. Chem. Soc., 115 (1049-9), 1919.

iodine species, namely hypoiodous acid, passed through the adsorbent bed.

2.2 Discussion of the Equilibria Involved with the Hydrolysis of Iodine

The major equilibria controlling the hydrolysis of iodine in solution are:

		25°C	100°C
(1)	$I_2 + I^- \rightleftarrows I_3^-$	768	305
(2)	$I_2 + H_2O \rightleftarrows H^+ + I^- + HOI$	5.4×10^{-13}	1.6×10^{-10}
(3)	$I_2 + H_2O \rightleftarrows H_2OI^+ + I^-$	1.2×10^{-11}	3.9×10^{-11}
(4)	$3I_2 + 3H_2O \rightleftarrows IO_3^- + 5I^- + 6H^+$	4×10^{-48}	not reported

Only the first three reactions are known to attain equilibrium rapidly and will be discussed independently of Reaction 4. Using these three equilibria and a mass balance relationship for iodine, algebraic expressions were derived for the equilibrium concentration of the five iodine species I_2, I^-, I_3^-, HOI, and H_2OI^+. Over the acidity range of 10^{-1} to 10^{-10}N and an initial elemental iodine range of 10^{-4} to 10^{-8}M, Equilibrium 2 is governing and accounts for over 98% of the hydrolysis both at 25 and 100°C. The fraction of hypoiodous acid, expressed as the mole ratio with respect to total initial iodine, as a function of hydrogen ion concentration and initial total iodine is shown in Figure 9 for 25°C and Figure 10 for 100°C. It is evident that hypoiodous acid is a dominant species at these low iodine concentration levels, and that the relative amount increases with decreasing total iodine concentration, decreasing hydrogen ion concentration, and increasing temperature. Care must be emphasized when extrapolating data or conclusions beyond the range limits of the variables. This especially applies to highly alkaline solutions where other reactions become important. Equilibrium 4 will now be considered for its effect on the existence of hypoiodous acid in solution. At equilibrium, calculations show that the formation of iodate becomes essentially complete at pH $\geq$ 7 and at elemental iodine concentrations $\leq 10^{-6}$ molar. Because our experiments show that hypoiodous acid is volatilized from solutions with pH values as high as 10, the kinetics of equilibrium must be considered.

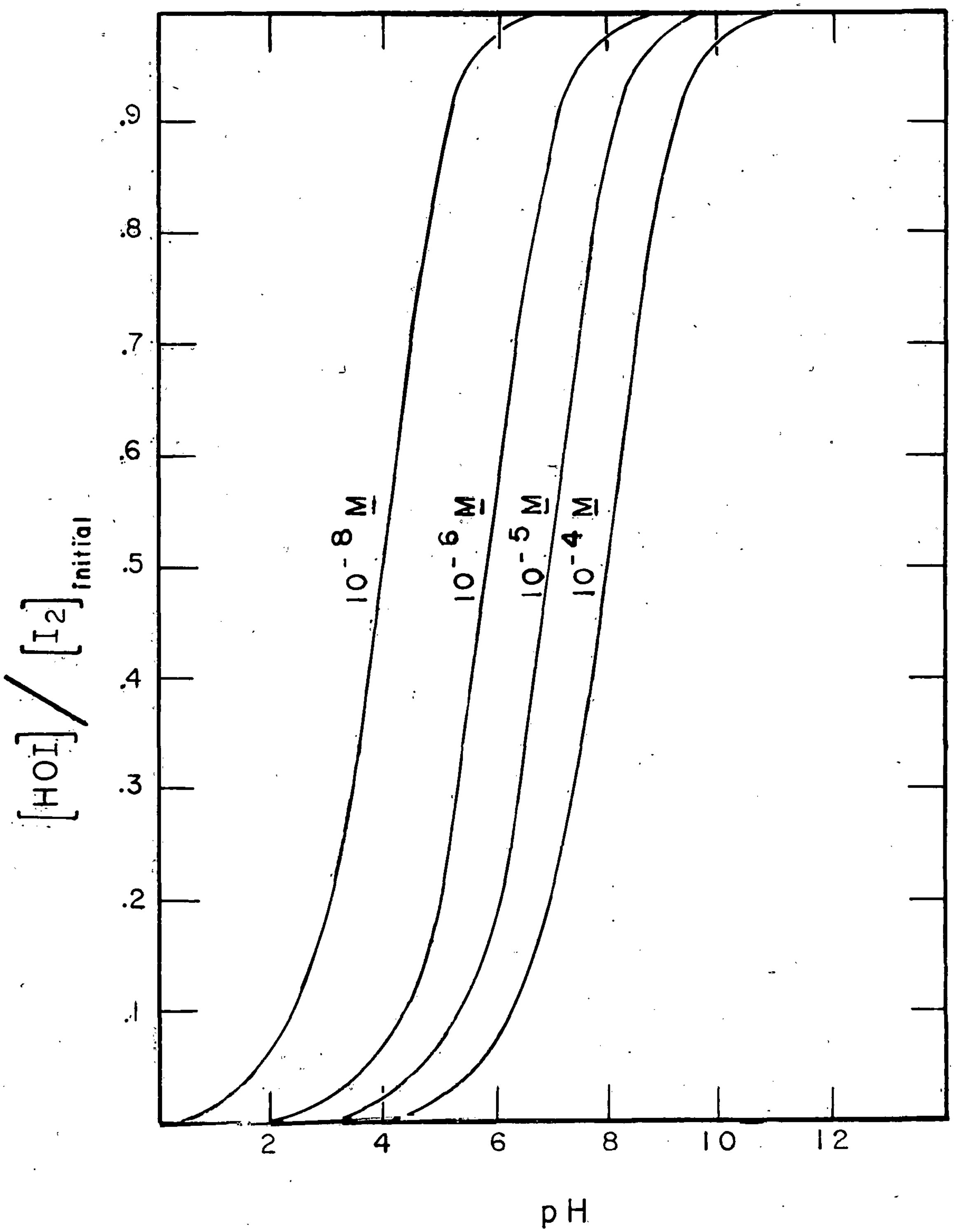

Fig. 9 Mole ratio of $[HOI]/[I_2]_{initial}$ as a function of pH and initial molarity of elemental iodine at 25°C.

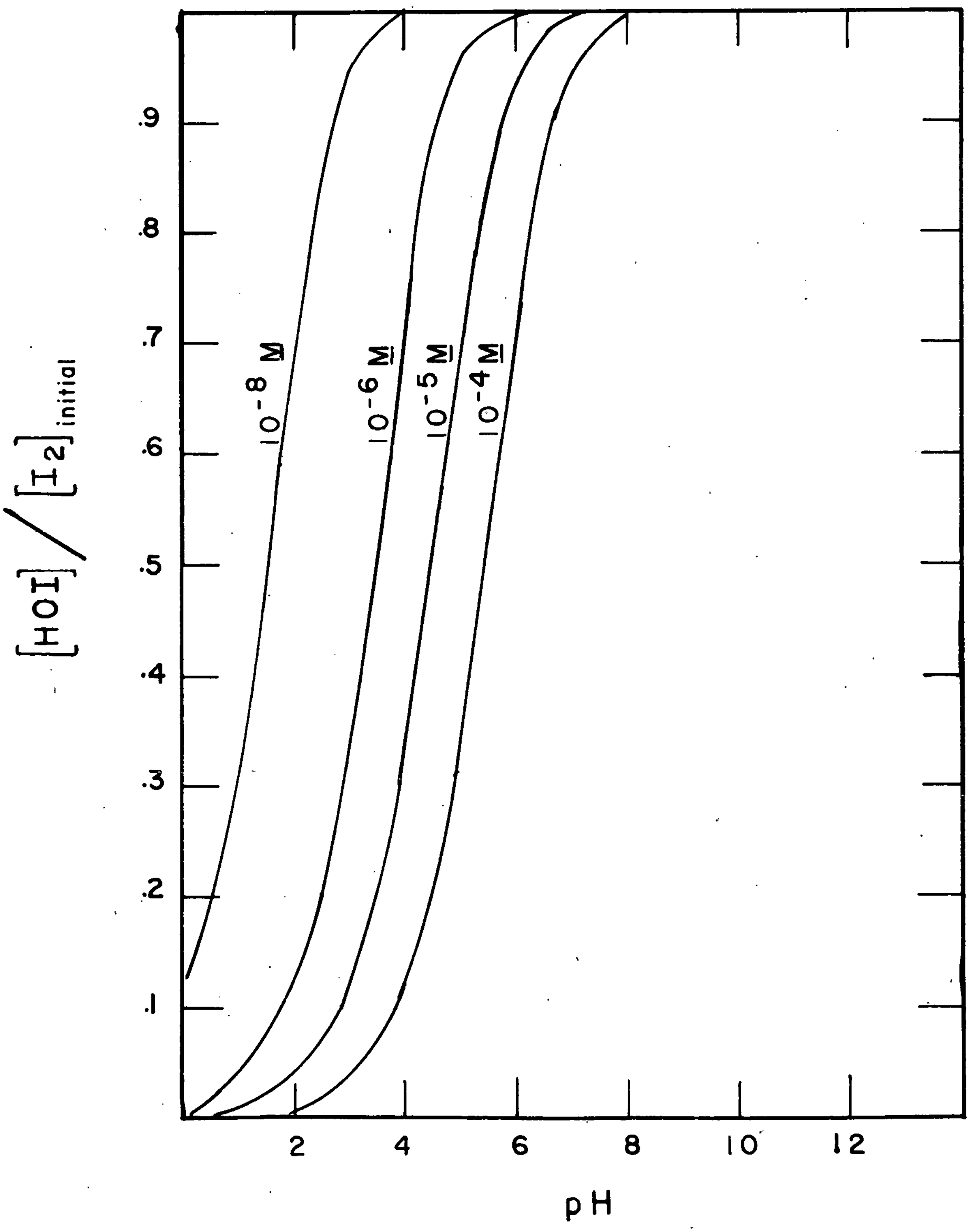

Fig. 10 Mole ratio of $[HOI]/[I_2]_{initial}$ as a function of pH and initial molarity of elemental iodine at 100°C.

The reaction rate that apparently governs the disappearance of iodate in Equilibrium 4 at low concentrations of total iodine has been given[40] as:

$$(5) \quad - \frac{d[IO_3^-]}{dt} = k\,[IO_3^-][I^-][H^+]^2 \text{ mole } \ell^{-1} \text{ min}^{-1}.$$

The experimental data for this rate were obtained with acidic solutions. Eggleton and investigators before him assumed that the rate constant for the reverse direction, the hydrolysis of elemental iodine to form iodate and iodide, was the same value. This seems highly unlikely for such a complicated reaction which involves a series of intermediate reactions with multiple electron transfers. From the standpoint of considering the competitive effect of this hydrolysis reaction with the hydrolysis reaction that produces hypoiodous acid, a more pertinent consideration is that the rate of hydrolysis Reaction 4 is different for strongly alkaline solution than it is for acidic media[41]. Therefore, in the intermediate pH range of about 4 to 10 where the rate for the hydrolysis reaction is not known, one cannot calculate the relative amounts of hypoiodous acid, iodate, and other hydrolysis products at nonequilibrium conditions.

2.3 Implications of the Existence of Hypoiodous Acid to the Reactor Safety Program.

In a water-cooled power reactor, the accident-released fission products will contact a heated water solution at a pH of 7 to 10 and transport to a steam-air atmosphere. These conditions seem ideal for the formation of hypoiodous acid and its stable existence in the vapor state. Presently, our experiments indicate that approximately 5% of the iodine in a solution of 10^{-6} to 10^{-8} M initial iodine, pH 10, and 90°C is transported to the vapor phase by an air purge. The ratio of hypoiodous acid to elemental iodine in this vapor phase is about 20 to 1. We also find that hypoiodous acid at an initial level of approximately 1 $\mu g/m^3$ remains airborne in a water-saturated atmosphere for several days, even when the temperature becomes ambient.

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[40] E. Abel and K. Helferding, Z. Physikal. Chem., 136 (1928) p 186.

[41] O. Haimovich and A. Treinin, J. Phys. Chem., 71, (1967) p 1941.

3. PARTICULATE-IODINE SAMPLING SYSTEM

(J. H. Keller, H. R. Beard, R. E. Foster, W. J. Maeck)

The Particulate-Iodine (P-I) sampler is one of the principal atmosphere sampling devices being developed for the LOFT-ECCS tests. Its purpose is to measure the concentrations of airborne fission products, other than noble gases, differentiated into at least the following fractions: noniodine particulate matter, total inorganic iodine species, and organic iodides. At the low airborne iodine concentrations and at the environmental conditions of a saturated steam-air mixture and basic condensate anticipated in the LOFT-ECCS containment vessel,hypoiodous acid is expected to be a major airborne species (see subsection 2), especially, after the initial washout of elemental iodine.

Most previous samplers of airborne iodine in steam-air atmospheres included some type of a silver surface component on which all inorganic iodine species were to be adsorbed. This premise is essentially valid when the incident amount of inorganic iodine are relatively large. However, at the low levels of iodine anticipated in the LOFT-ECCS containment vessel, our previous experiments[42] show that all silver surfaces do not effectively adsorb inorganic iodines. Because of this unsatisfactory low retention, the classical Maypack concept has been dropped in favor of a sampler with a series of inorganic materials that selectively retain the individual iodine species under LOFT-ECCS conditions. The evaluation of these materials is being conducted on a laboratory scale and in the CDE Facility. The latter consists of a 86-ft^3 containment vessel and equipment to introduce fission products under various atmosphere conditions.

The laboratory apparatus (Figure 11) consists basically of a glass steam-air generator and a 22-liter glass containment vessel with sampling and instrumentation ports. This system provides the capabilities for: (a) varying the ratio of steam to air in the containment atmosphere, (b) injecting various iodine species, (c) introducing atmospheric contaminants, (d) continuously monitoring the pressure and temperature of the containment vessel, (e) measuring the sample flow through the samplers, and (f) collecting condensate samples. The laboratory samplers are glass tubes 6 in. long and 0.5 in. in diam. The sides of the tubing are indented at 1-in. intervals to separate the test components. Samples of the vessel atmosphere are pulled through the samplers at a flow rate of 2000 cc/min for 2 to 4 min. After sampling, the samplers are gamma scanned with a surface scanner, disassembled, and each component is counted for iodine activity. In the CDE tests, samplers similar to those proposed for LOFT-ECCS are used.

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[42] J. H. Keller, F. A. Duce, F. O. Cartan, Retention of Iodine on Selected Particulate Filters and a Porous Silver Membrane Being Considered for the LOFT Maypack, USAEC Rept. IN-1078 (May 1967).

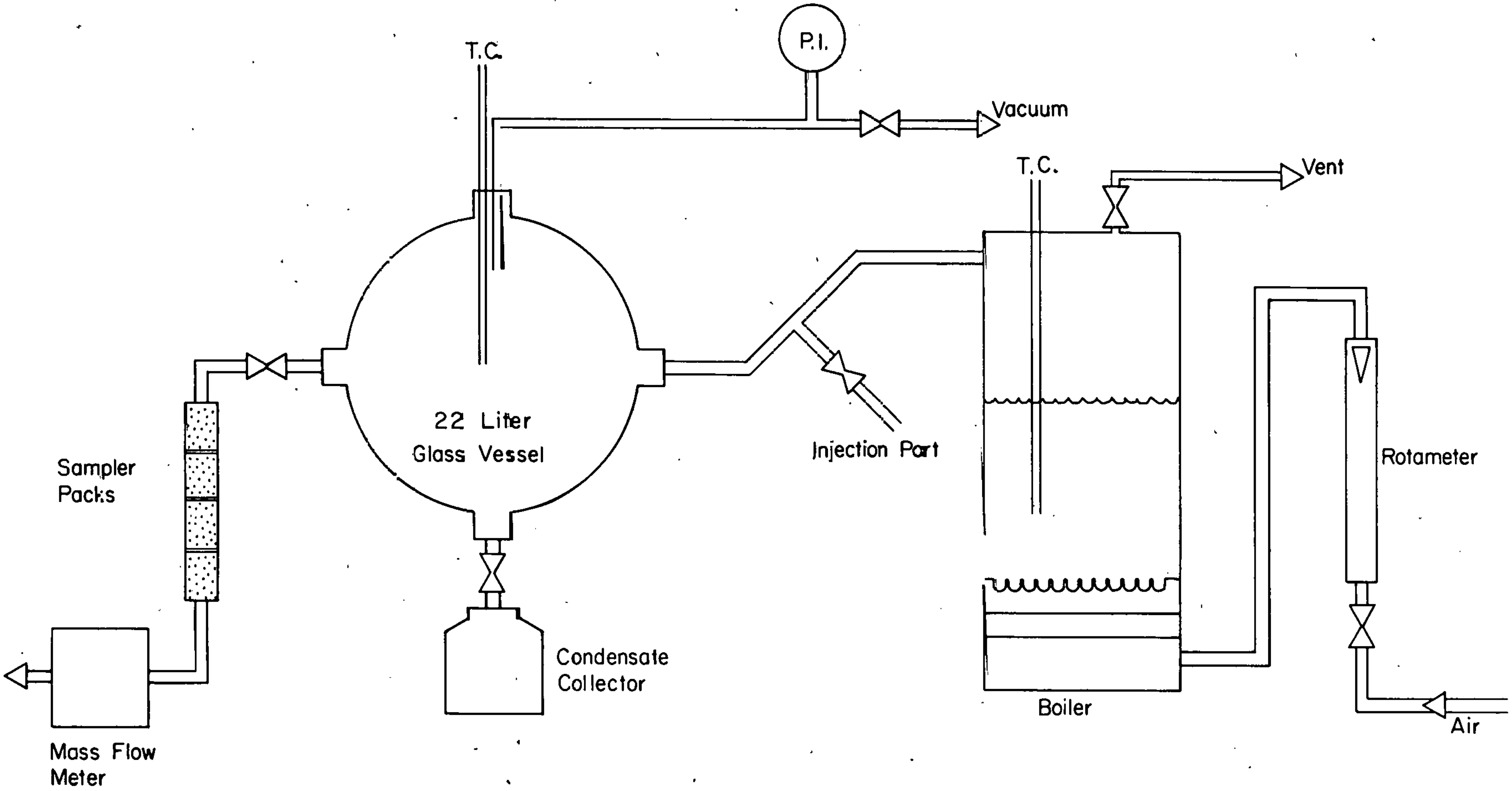

Fig. 11 Laboratory P-I sampler test apparatus.

The sampler currently being evaluated contains five components. The components and desired functions are:

(1) Particulate filter (three Flanders F-700 glass fiber HEPA filters)--retain particulate activity.

(2) Hydrous zirconium oxide in the iodide (HZO-I) form--retain elemental iodine (and presumably any hydrogen iodide) and pass hypoiodous acid and organic iodides.

(3) Hypoiodous acid (HOI) adsorbent - various materials are being evaluated.

(4) Linde Molecular Sieve 13X in the silver form (LMS-13X-Ag)--retain organic iodides and other species that penetrate the upstream components.

(5) KI-I_2 impregnated charcoal (Barnebey Cheney 151)--backup adsorbent.

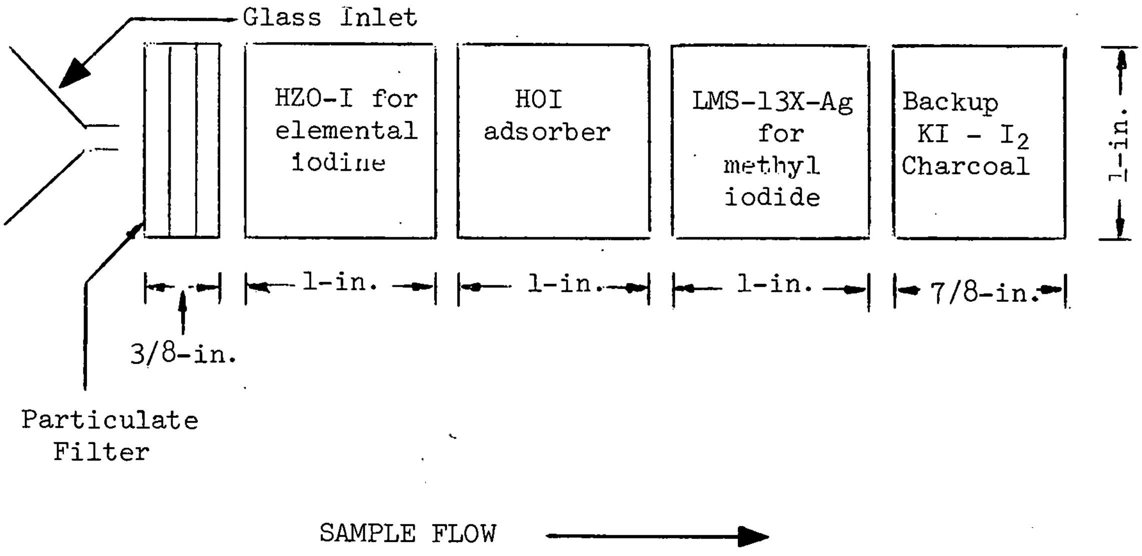

Fig. 12 P-I sampler currently under evaluation.

The laboratory studies have shown that hydrous zirconium oxide in the iodide form (HZO-I) efficiently adsorbs elemental iodine. However, this material also adsorbs methyl iodide at high temperatures and low flow rates, apparently by a heterogeneous exchange reaction. Experiments were conducted to establish the effects of flow rate and temperature on the retention of methyl iodide and hypoiodous acid on HZO-I. The retention of methyl iodide on HZO-I is satisfactorily low at 75°C and a face velocity of 50 ft/min. Because this face velocity is the design value for the P-I Sampler in LOFT-ECCS, the discrimination of elemental iodine and methyl iodide appears satisfactory. This will be evaluated further in future CDE tests.

Preliminary experiments with steam-air mixtures containing hypoiodous acid indicate that the effects of face velocity and bed temperature on the retention of this species on HZO-I are similar to those for methyl iodide with a generally higher retention of hypoiodous acid than for methyl iodide. Other materials being tested are metals, metal iodides, and metal sulfides supported on 60-80 mesh Chromosorb-P, a commercial silicaceous material used for gas chromatographic separations.

The material selected for the adsorption of methyl iodide is Linde Molecular Sieve 13X in the silver form.

4. WALL CONDENSATE SAMPLING SYSTEM

(D. T. Pence, W. J. Maeck)

The CDE wall condensate sampler furnishes time-dependent samples of steam condensate from a large isolated surface with known heat transfer characteristics. The time-dependent distribution of radionuclide activity between the containment vessel atmosphere and the steam condensate on the walls is useful for understanding the airborne iodine behavior. With the low iodine activity levels expected in the LOFT-ECCS tests, large samples of condensate will be required to provide sufficient activity for reliable counting; however, large sample volumes are undesirable because of low gamma counting efficiencies. A second deficiency associated with collecting large aqueous volumes is the loss of volatile iodine species which invalidates the data.

Adsorbents that provide total retention of iodine, as well as differentiation of species from a flowing stream, offer a solution to the problem. These adsorbents would concentrate the activity in the sample, minimize the loss of volatile iodine species, and increase the gamma counting efficiency and analysis reliability, especially at the low activity levels predicted for the ECCS tests.

Currently, several materials are being investigated for use as adsorbents for the Wall Condensate Sampler, both in the laboratory and in the CDE. Linde Molecular Sieve 13X in the silver form and Dowex-1 anion exchanger in the chloride form have been tested in the

CDE. Six materials have been tested in the laboratory. Solutions of five iodine species, elemental iodine, iodide, iodate, methyl iodide, and hypoiodous acid, were used to test the adsorbents.

For testing, the adsorbents were loaded into a 9-mm ID column to a bed depth of 8 to 10 cm. About 10-ml volumes of the test solutions, each containing about 60 μg/ml of total iodine and 1 to 2 μCi/ml of I-131, were flowed through the test bed at a rate of 1 to 2 ml/min, depending on the particle size of the test material. The percent retention was determined from the ratio of activity measured on the test bed to the total activity. Table XVII summarizes the test results and Figure 13 shows the distribution of the I-131 activity on the bed as determined by the radiometric surface scanner.

None of the materials adsorbed iodine species preferentially; however, several showed promise as total iodine adsorbents. Further experiments are planned with the more promising materials.

TABLE XVII

RETENTION OF IODINE SPECIES FROM A FLOWING AQUEOUS STREAM ON VARIOUS ADSORBENT MATERIALS

	Percent Retention				
Adsorbent Material	Iodide	Elemental Iodine	Iodate	Methyl Iodide[a]	Elemental Iodine-Hypoiodous Acid[a]
Linde Molecular Sieve 13X-Ag Form	59	45	19	99+	---
Dowex 1-10X-Cl$^-$ Form	99	95	97	---	96, 99
Amberlite XAD-2	93	8	60	---	---
Dowex 50-12X-Ag Form	95	84	73	99+	---
Vermiculite-Ag Form	88	41	93	93	---
Ultramarine Blue-Ag Form	99	99	99	92	99+, 99

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[a] Data from laboratory experiments concerned with the P-I Sampler development program.

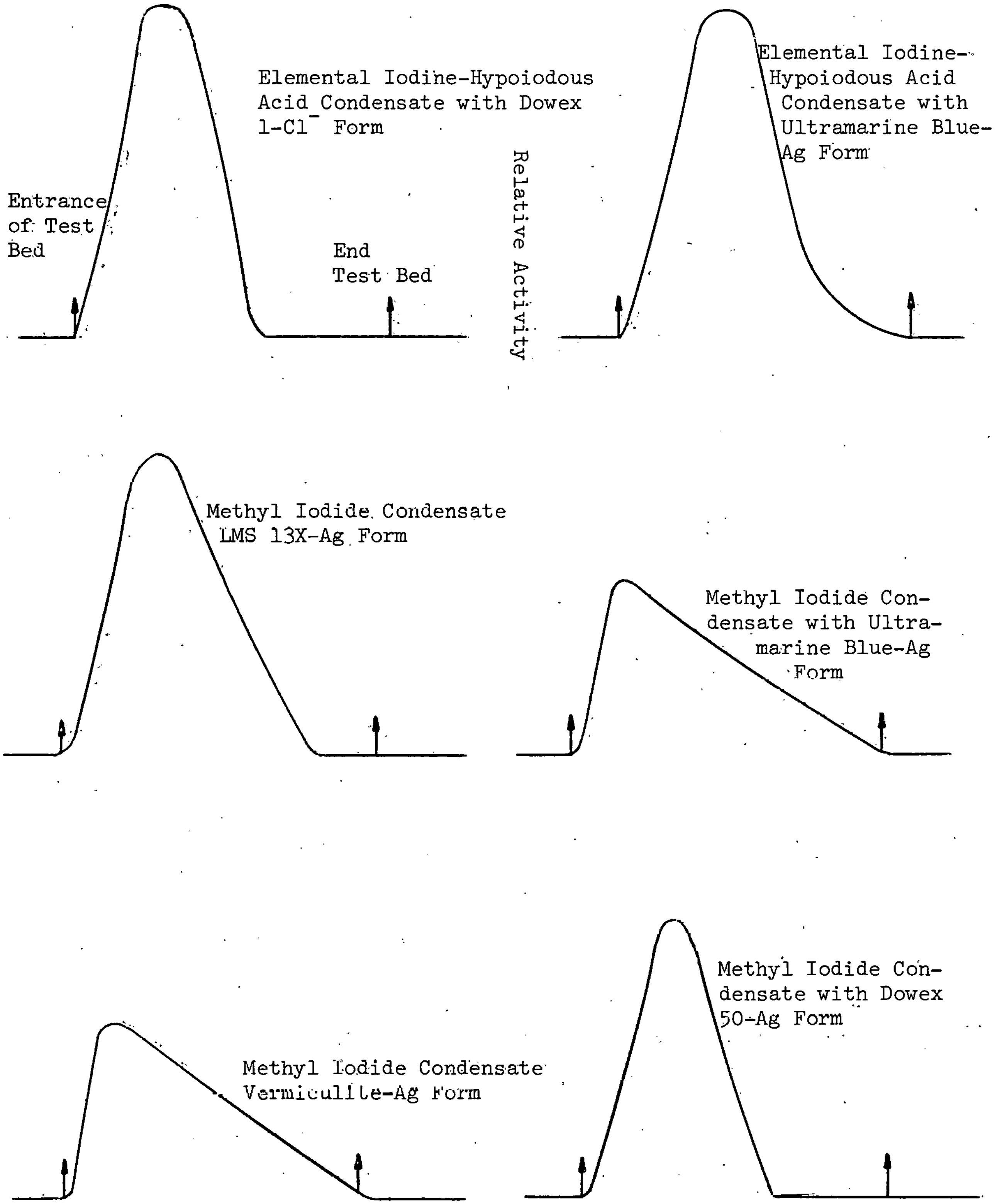

Fig. 13 Profiles of adsorbed iodine species on various adsorbent materials being evaluated for the wall condensate sampler.

5. RADIOMETRIC SURFACE SCANNER

(J. P. Morgan, W. J. Maeck)

Certain samplers in the LOFT-ECCS test program are designed to establish the distribution of fission products on various surfaces. This is best accomplished by a radiometric surface scanner. Based on the successful operation of a prototype scanner[43], an improved model is being developed.

This new model consists of a Setco Industries slide mechanism for vertical and horizontal positioning of the sample relative to the collimated aperture in the detection device. Horizontal travel of the slide is 28 in., and the vertical travel is 14 in. Horizontal slide motion is provided by a Slo-Syn stepping motor (X1000-1002) driving the slide lead screw, with 1-in. of slide travel equal to 2000 motor steps. A Slo-Syn Model ST1800B Translator provides the motor drive power. Motor direction and stepping rate are controlled by a Digital Logic System constructed of Raytheon M Series Logic Boards. The motor direction and step signals are applied to a 5-digit up-down counter; thus, the slide position is equivalent to the number of counts in the 5-digit counter. Mechanical backlash is effectively removed by circuitry within the Digital Logic System. Decade preselect switches are used to terminate or reverse the direction of the slide at any position of its travel.

Continuous movement of the slide is provided from one end of its travel to the other with the direction reversed by automatic switching of the motor. By using this continuous scanning mode and the preselect switches, a reduced scan length can be obtained. A single scan mode of operation stops the slide at a preselected position, allowing time for the vertical position to be manually set to a new position before the rescan is started.

An incremental mode of operation is provided which moves the slide a preselected distance, stops the slide (for counting of the activity at that location), and then upon an external command (printing of accumulated data) again advances the slide a preselected distance. This mode of operation will incorporate the use of a teletype and Digital Ratemeter to obtain a punch paper tape output that is computer compatible. Currently the radiometric profile of the sample (counts/second as a function of slide position) is obtained on a strip-chart recorder.

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[43] See Reference 8, p 75.

6. SEPARATION OF KRYPTON AND XENON FOR RAW GAS MONITOR

(R. E. Foster, Jr., W. J. Maeck)

A Raw Gas Monitor will be installed in the LOFT-ECCS containment vessel near the blowdown nozzle to follow the airborne concentrations of krypton and xenon on a time-dependent basis. The measurement technique will be gamma-ray spectrometry. To obtain improved reliability in the analysis, airborne iodine activity will be separated on an adsorbent prior to the measurement. Because Linde Molecular Sieve 13X in the silver form (LMS-13X-Ag) efficiently adsorbs all iodine species, this material was tested for the retention of krypton and xenon.

The retentions of krypton (Kr-85) and xenon (Xe-131) on LMS-13X-Ag were measured for a flow of water-saturated air at 25°C in the apparatus shown in Figure 14. The amount of LMS-13X-Ag was 5 g. The retentions of both gases were less than 0.2%. All the krypton and xenon adsorbed on the first Linde Molecular Sieve 5A (LMS-5A) trap which was immersed in an isopentane-liquid nitrogen bath at -154°C. No krypton nor xenon migrated off this trap with a continued air flow of 100 cc/min for 15 min. The technique, therefore, provides the means to obtain an integrated flow sample of krypton and xenon free of iodine activity.

The krypton and xenon were desorbed completely from the LMS-5A trap by heating to slightly above room temperature for 3 min. Because the noble gases can be purged easily from the trap, the krypton and xenon can be collected separately and analyzed, or the trap can be analyzed for the rubidium and cesium daughter decay products.

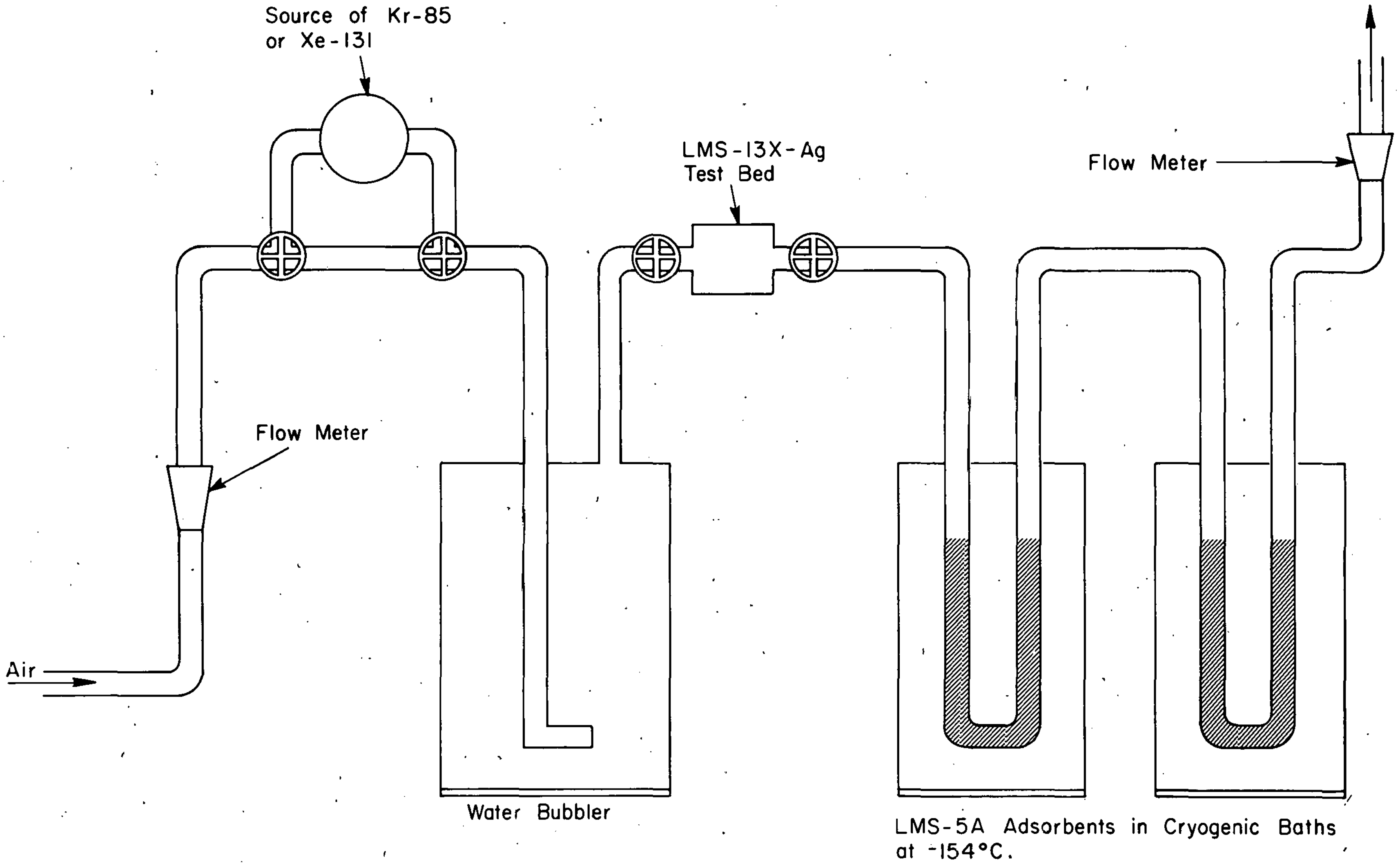

Fig. 14 Apparatus used to measure the retention of Kr and Xe on LMS-13X-Ag.

7. SAMPLING AND ANALYSIS OF AQUEOUS SOLUTIONS FOR METHYL IODIDE

(F. O. Cartan, J. H. Keller, B. A. Staples, G. W. Webb)

Two analytical procedures, one from the Brookhaven National Laboratory[44] and the other from the Oak Ridge National Laboratory[45] were investigated for the determination of methyl iodide in aqueous solutions. These procedures are outlined in Figures 15 and 16.

Both procedures gave excellent results of >95% recovery for pure methyl iodide solutions when the recovery calculation was based on the relative activities in the separated fractions. As discussed below, relatively large amounts of methyl iodide volatilize from solution to invalidate recovery calculations that are based on the amount of methyl iodide added in the sample aliquot. When applied to solutions of initially elemental iodine with no methyl iodide added, the BNL procedure indicated 45% methyl iodide and the ORNL procedure 10% methyl iodide. The extracted species was suspected to be hypoiodous acid which is not highly dissociated, and therefore, should distribute significantly to the organic, carbon tetrachloride, phase. A solution was prepared under conditions that favored the hydrolysis equilibrium of elemental iodine to hypoiodous acid (see Section X, 2.2). This solution was analyzed for methyl iodide by both procedures and by vapor phase chromatography. The indicated methyl iodide results were 74% for the BNL procedure and 37% for the ORNL procedure contrasted to 2.5% for vapor phase chromatography.

As stated above, methyl iodide volatilizes from solution to invalidate results. To assess this effect, solutions of methyl iodide tagged with I-131 were placed in 17-ml screw-cap glass bottles with Teflon-disc cap liners. For comparison purposes, solutions of elemental iodine also tagged with I-131 were placed in identical bottles. The bottles were gamma-ray counted over a 3-day period. The activities of the methyl iodide containing bottles decreased with a half time of 7 to 10 hr. The activities of the elemental iodine containing bottles remained constant. The methyl iodide volatilized and diffused through or around the Teflon cap liner and the plastic cap of the bottle.

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[44] A. W. Castleman, Jr., I. N. Tang, H. R. Munkelwitz, J. Inorg. Nucl. Chem., 30, (1968) pp 5-13.

[45] G. W. Parker, private communication to F. O. Cartan (June 1968).

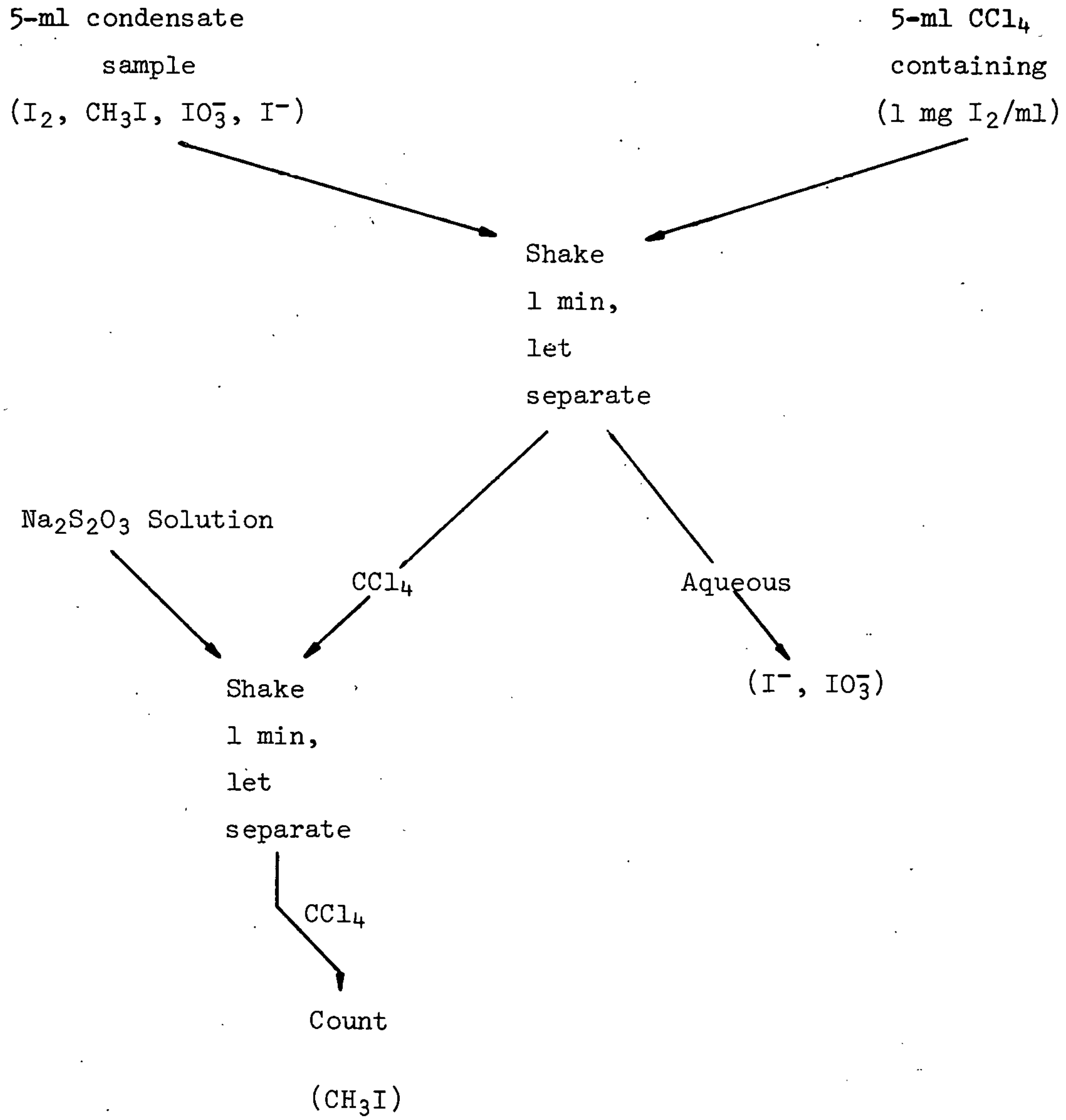

Fig. 15 BNL procedure for extraction of methyl iodide.

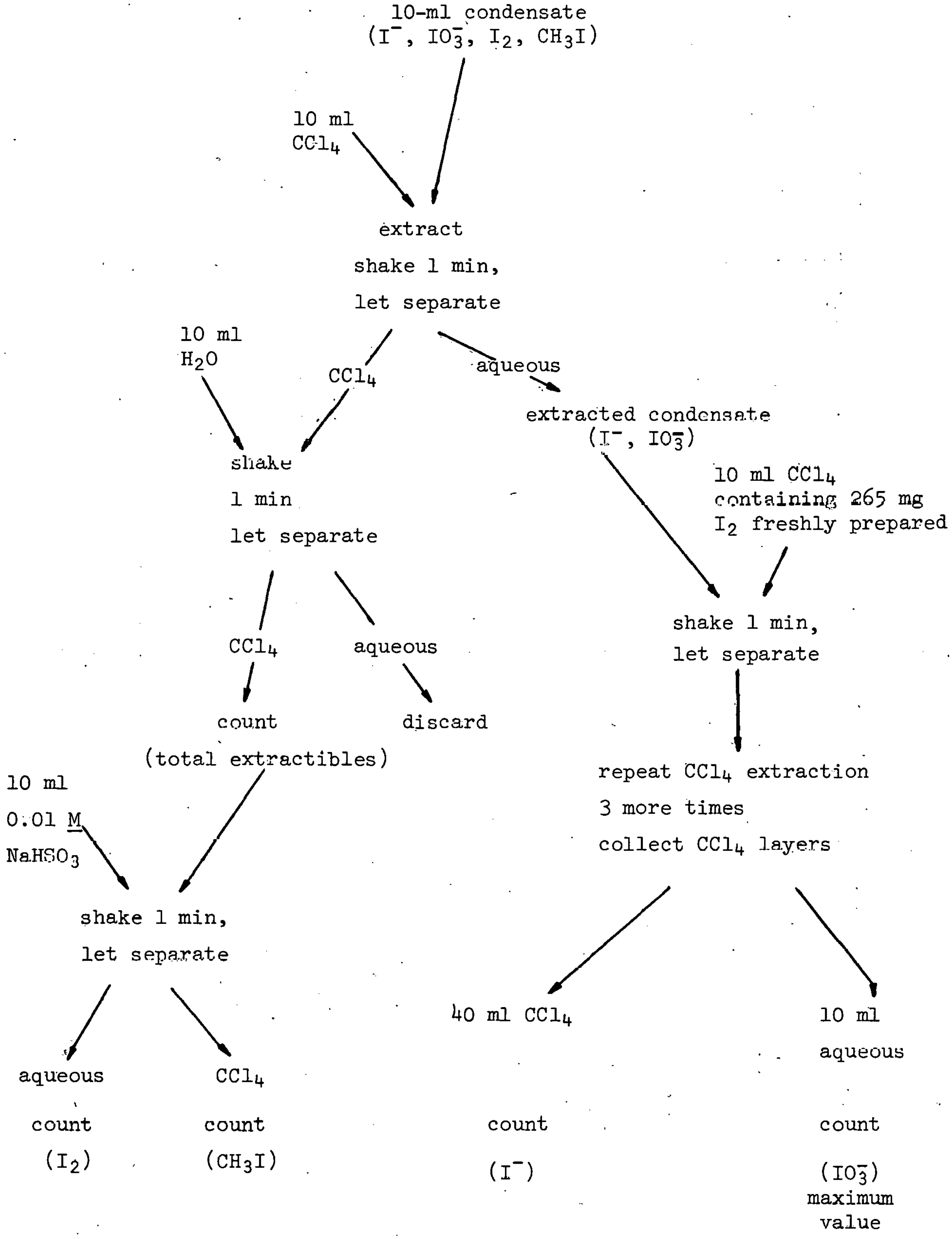

Fig. 16 ORNL procedure for extraction of methyl iodide.

These experiments show that precautions must be observed to obtain valid analytical results for iodine species in aqueous samples.

(1) Procedures for methyl iodide based on extraction into an organic solvent are subject to high bias caused by coextraction of other iodine species. Evidence indicates that the effect of hypoiodous acid is especially significant.

(2) Methyl iodide volatilizes from aqueous solution and is extremely difficult to retain in sample containers.

(3) Elemental iodine plates out on container walls.

8. GAS CHROMATOGRAPHY STUDIES AND APPLICATIONS

(J. H. Keller, G. W. Webb)

Gas chromatography has been used extensively in the development program for LOFT-ECCS samplers and for the analysis of atmosphere samples from CDE tests. It has provided an unambiguous quantitative measurement of methyl iodide, krypton, and xenon, and a detection of organic iodides with molecular weights higher than methyl iodide.

8.1 Determination of Krypton and Xenon

With a helium ionization detector, the Beckman GC-5 Gas Chromatograph used in this program is a highly sensitive instrument. Further sensitivity for krypton and xenon in fission product release studies is obtained by using the instrument to separate these two gases onto charcoal traps at -78°C followed by gamma-ray counting of the traps. The detection limits were established for the instrument-detector system and for the separation-gamma ray counting system.

A gas mixture containing natural krypton and xenon in an air matrix was prepared and its composition was established by mass spectrometry. A series of dilutions of this standard was prepared and analyzed on the gas chromatograph. For these measurements, the volume of the sample loop was 3 cc and the pressure of the sample was a minimum of 50 mm Hg. The areas of the krypton and xenon peaks were measured with a planimeter and plotted as a function of the dilution factors. The linearity was within 10% over the range from 3.5 to 3700 ng of xenon and within 10% from 9.5 to 495 ng of krypton. The concentration sensitivity limits can be improved by the use of (a) a larger volume sample loop, (b) a higher sample pressure, and (c) helium carrier gas of greater purity.

8.2 Determination of Organic Iodides

The Raw Gas Sampler in the CDE provides an unperturbed atmosphere sample for the analysis of organic iodides by gas chromatography. This measurement serves as the basis to evaluate the performance of the CSM and P-I samplers for organic iodides.

The column used in the GC-5 chromatograph to separate methyl iodide and ethyl iodide was a 4-ft long by 0.25-in. diam glass tube packed with 100-120 mesh Porapak Q[a]. To eliminate inorganic iodides, which might react with the Porapak Q to produce organic iodides, a 1-cm long bed of silica gel was placed ahead of the Porapak Q. At 150°C, inorganic iodides are retained on the silica gel and organic iodides pass. The retention times for methyl iodide and ethyl iodide are 3 min and 6 min, respectively, at a column temperature of 150°C and a helium carrier gas flow of 100 cc/min.

The concentrations of methyl and ethyl iodides in many of the samples were below the detection limit of the helium ionization detector. Therefore, to determine the total organic iodide concentrations, the effluent from the chromatograph flowed by a radiation monitor into a potassium iodide impregnated charcoal bed which retained all the organic iodides. The traps then were removed, and the I-131 activity collected on the charcoal was determined by gamma-ray counting. Normally, the column was flushed for 10 min after the time of injection, but in several instances, the column was flushed for longer periods to determine whether organic iodides other than methyl and ethyl iodides were present; however, no other species were detected by either the ionization detector or the radiation monitor.

The quantitative measurement of airborne organic iodide concentrations by gas chromatography depends only on the sample pressure in the chromatograph sample loop, the temperature of the chromatograph sample loop, and the volume of the chromatograph sample loop. Therefore, this method is independent of any measurements of variables made in the CDE. When applied to samples from the CSM gas stream, the method also is independent of measurements associated with the CSM.

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[a] Porapak Q is a porous polymer bead manufactured by Waters Associates, Inc., Fountain Street, Framingham, Mass.

The chromatograph has proven useful for the detection of organic materials other than iodides. For example, chromatograms of raw gas samples from an elemental iodine tracer test in the CDE showed that several nonradioactive organic contaminants were present. Subsequent mass spectrometry analysis identified the two major contaminants as Freon-113 and 1,1,1-trichloroethane. Minor contaminants were xylene and acetone.

9. IODINE SPECIES PREPARATIONS

(J. H. Keller, H. R. Beard)

The development of adsorbent materials for the P-I Sampler requires gaseous mixtures that contain essentially one iodine species. The production of a gaseous mixture with only one iodine species is particularly difficult at the low concentration levels that are predicted for the LOFT-ECCS containment atmosphere and which, therefore, must be used for this development program.

The iodine species used in this program are prepared from a commercial solution containing approximately 20 atom percent I-131--80 atom percent stable iodine in 0.1M NaOH at time of shipment. Dilutions, if necessary, are made with distilled water.

Methyl iodide is prepared by a scaled-down method based on that of Hartman[46]. The apparatus (Figure 17) is fabricated of glass and Teflon. To the reaction flask containing 0.5 g of calcium carbonate and 1 ml of dimethyl sulfate, an aliquot of the I-131 solution containing less than 1 μg of total iodine is added. The helium flow is adjusted to 15±5 cc/min for 5 min to purge air from the system, the liquid nitrogen bath is raised into position around the second U-tube, and the reaction flask is heated to generate the methyl iodide. (The progress of the reaction can be followed by monitoring the location of the I-131 gamma activity in the system). Water vapor and unreacted dimethyl sulfate are retained in the U-tube that is immersed in the ice bath. Trace amounts of elemental iodine that may be produced in the system are retained on the Porapak Q cleanup trap along with a small fraction of the methyl iodide. The reaction usually is complete within 5 to 10 min with a yield greater than 90%. Upon completion of the reaction, the helium flow through the reaction flask is stopped and the Teflon stopcock, just ahead of the U-tube immersed in the liquid nitrogen bath, is turned to the closed position. The liquid nitrogen bath is removed and the U-tube is allowed to warm to room temperature. During this warming period, most of the methyl iodide

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[46] A. H. Blatt (ed.), Organic Synthesis, 18 (1938) p 88.

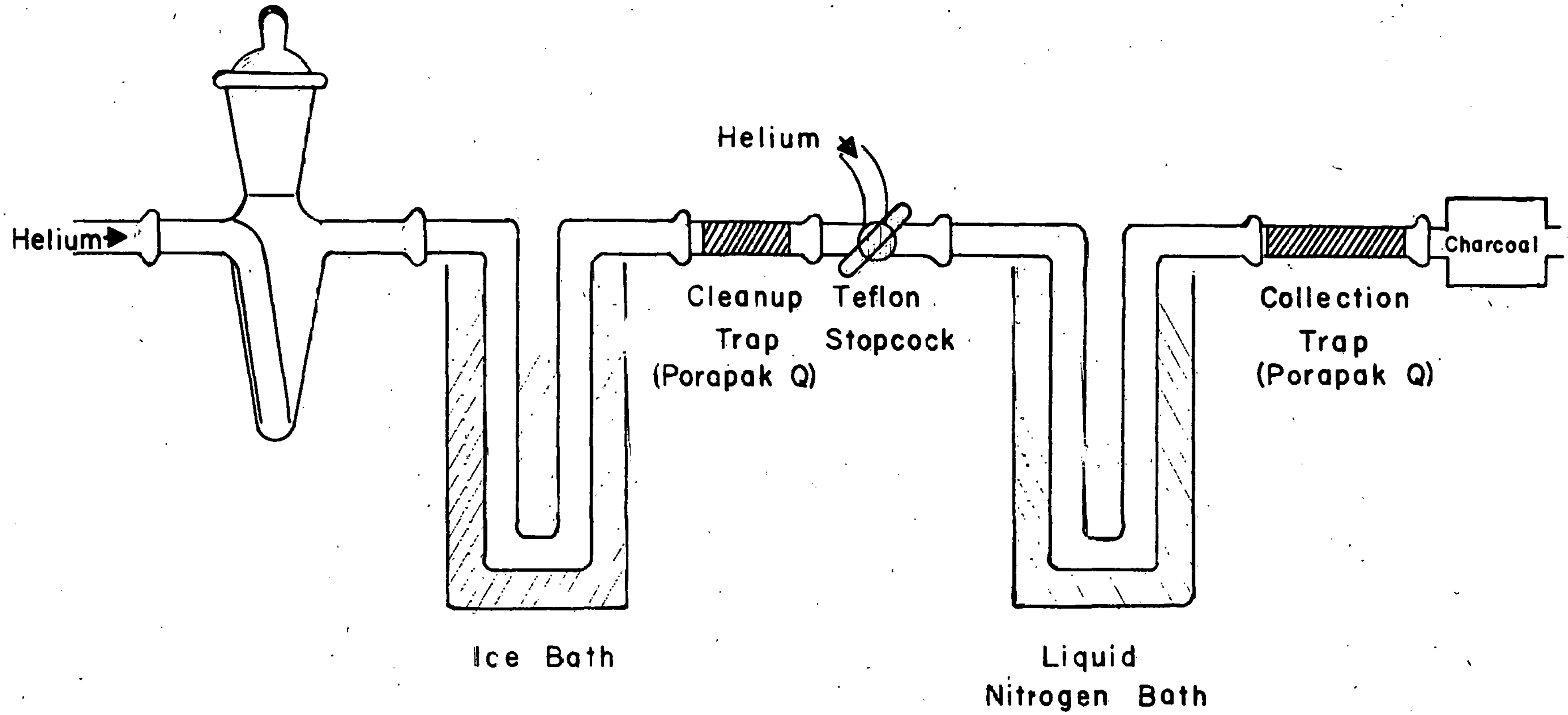

Fig. 17 Diagram of apparatus for the preparation of methyl iodide.

diffuses from the U-tube to the Porapak Q collection trap. The residual methyl iodide in the U-tube is transported to the collection trap by a helium purge of 10 cc/min for 5 min. This purge also diffuses the methyl iodide evenly throughout the Porapak Q trap which provides a more even release of methyl iodide when the trap is used as the iodine source in an experiment. The U-tube must not be purged at a high flow rate nor for a prolonged period of time because the methyl iodide will pass through the collection trap. When used as the iodine source, a more rapid release of methyl iodide can be obtained by purging the Porapak Q trap in the direction reversed from that of loading. The trap can be used until it is depleted of methyl iodide because any elemental iodine produced by decomposition of methyl iodide remains adsorbed on the trap. Based on gas chromatographic analysis, no volatile organic species other than methyl iodide have been observed in the trap effluent. Based on adsorption data obtained with various adsorbent materials, the inorganic iodide species content is less than the detection limit of 0.1%.

Two methods have been used to prepare elemental iodine: (a) the reaction of molten potassium dichromate with the evaporated, caustic residue of the commercial I-131 solution, and (b) the dropwise addition of the I-131 solution into an acidified solution of potassium iodate.

In the first method, the desired quantity of the I-131 solution is placed in a glass reaction tube (with carrier potassium iodide, if desired). The solution is slowly evaporated with an infrared lamp aided by a helium purge, an excess of potassium dichromate is added, and the mixture is heated with a flame. Elemental iodine, which forms when the mixture becomes molten, is transported by helium to a cold trap maintained at 0°C. Heating for approximately 5 min produces yields of 35 to 50%; longer heating does not increase the yield appreciably. The elemental iodine generated by this method contains about 1% methyl iodide as indicated by gas chromatographic analyses and no volatile chromium species based on tests using Cr-51 tagged potassium dichromate. Little of this methyl iodide condenses in the trap when it is at 0°C. If the trap is immersed in a liquid nitrogen bath, all generated iodine species condense in the trap. Then, when the trap is used as an iodine source in experiments, the methyl iodide is released immediately upon warming and purging. Thus, the initial test stream contains high proportions of methyl iodide and this proportion is further enhanced in the test atmosphere by rapid non-reversible plate-out of the elemental iodine.

The potassium dichromate method with the trap maintained at 0°C is most useful for the preparation of large elemental iodine sources. Such sources are generally used in experiments requiring "puff" releases.

The iodide-iodate preparation method is better suited for experiments in which elemental iodine releases over extended time periods are required. The I-131 solution is added dropwise to a solution of potassium iodate in sulfuric acid, and the generated elemental iodine is purged from the flask with air. The rate of release is a function of the purge air flow rate, the volume of solution, the temperature of the system, and the amount of I-131. Based on gas chromatographic analysis, the amount of methyl iodide produced by this method is insignificant.

Another method, based on the oxidation of iodide to elemental iodine by nitrite in an acid solution, was evaluated. This method produced elemental iodine with no detectable amounts of methyl iodide, but had the disadvantage of producing oxides of nitrogen.

Two preparation methods have been used to prepare atmospheres with significant concentrations of hypoiodous acid. Water solutions of low concentrations, approximately 10^{-6} <u>M</u>, of elemental iodide are heated and purged with air. In the second method, low levels of elemental iodine are purged into a vessel which contains an air-steam atmosphere.

10. IODINE DECONTAMINATION OF SAMPLERS AND COMPONENTS

(F. A. Duce, J. H. Keller, F. O. Cartan)

In a program to evaluate sampling devices for LOFT-ECCS, effective decontamination procedures are required for radioactive iodine-contaminated experimental sampling apparatus, aluminum cans which will be used to package sampler components for gamma-ray spectrometry, and other test apparatus that have been contaminated with radioactive iodine. Such procedures are needed because the various equipment is expensive and must be reused. Various agents, mostly commercial decontaminating and cleaning solutions, were evaluated for this purpose on such items as aluminum sample cans, aluminum Maypack cups, carbon steel snap rings, stainless steel screens, brass fittings, Teflon gaskets, rubber O-rings, and laboratory glassware. No one agent satisfactorily decontaminated all the items without corrosive damage. Various agents were satisfactory for specific materials.

Many of the commercial agents evaluated in this study are not sold for the purpose of iodine decontamination and no such claim is made by the manufacturers. Thus, the reported findings that some agents are superior or inferior for this purpose does not imply any general superiority or inferiority of the agents for their intended purposes. Further, the experimental data apply only to the specific test conditions.

The agents tested in this study are listed in Table XVIII along with available descriptive information. The procedures used for the preparation of the various agent solutions are summarized in Table XIX.

The aluminum cans, glassware, and aluminum Maypacks including various components were contaminated with iodine under various conditions.

The aluminum cans were contaminated with elemental iodine tagged with I-131 generated in a laboratory-scale apparatus. A mixture of high specific activity I-131 (as sodium iodide) and potassium iodide was reacted with potassium dichromate in a helium atmosphere. The iodine vapor, mainly elemental iodine, was captured in a glass U-tube submerged in an ice bath. The U-tube was heated and the iodine was swept over the cans in a helium stream at room temperature.

The glassware was contaminated with elemental iodine vapor, generated as described above, except that the sweep gas was a water-saturated air-helium mixture at temperatures ranging from room temperature to 100°C.

The aluminum Maypack and various components, aluminum cups, steel rings and screens, brass fittings, Teflon gaskets, and rubber O-rings, were contaminated with elemental iodine in a steam atmosphere in the 86-ft^3 containment vessel of the CDE.

Two systems of decontamination were used, immersion in a solution of the agent in a sonic bath at 40 to 45°C for 10 to 20 min and immersion in a boiling solution of the agent for about 30 min with no sonic agitation.

The iodine activities on the items were measured before and after decontamination with a 3- x 3-in. NaI(Tl) detector connected to a multichannel spectrometer. Decontamination factors were calculated simply as the ratio of the activities before and after the decontamination.

Table XX summarizes the effectiveness of the tested agents for the various materials.

Of the reagents tested on aluminum cans in the sonic bath, 1M sodium carbonate gave the best decontamination. However, the cans become coated with a black residue which is removable with 3 to 6M HNO_3. Turco 4521 was almost as effective as sodium carbonate. For an all-purpose decontaminating and cleaning agent for aluminum, Kern 85D at pH 2 is recommended. Although it is the most expensive, it will decontaminate, clean, and degrease in one operation. The corrosion rate is insignificant.

All reagents tested corrode brass and none gave excellent decontamination. Of three agents, Kern 85D, L+A-52, and Radiacwash, that gave fair decontamination, Radiacwash is the least expensive.

Kern 85D at pH 2 and a two-cycle Turco 4502-oxalic acid procedure are excellent for decontaminating glass. The latter is less expensive.

None of the agents tested decontaminated rubber.

All four agents tested for steel gave only fair decontamination. The Turco 4502-oxalic acid procedure gave slightly better decontamination and is comparable in price to the other three agents.

For Teflon, Radiacwash and Turco 4502-oxalic acid procedure gave fair decontamination. There is little to choose between the two.

TABLE XVIII

AGENTS AND THEIR DESCRIPTION

Agent	Description[a]	Supplier	Cost/Liter[d]
Chlorox[b]	Sodium hypochlorite	Chlorox Co., (widely distributed)	$ 0.20
Kern 85D[c]	Alkaline solution	Kern Chemical Corp., 854 S. Robertson Ave. Los Angeles, Calif.	1.20
L+A Formula 50[b]		L+A Products, Inc., West County Road 132 St. Paul, Minn.	0.10
L+A Formula 52[b]		As above,	0.36
Radiacwash[c]		Atomic Products Corp., Center Moriches Long Island, N. Y.	0.16
Sodium Carbonate	Common chemical		0.29
Turco-4306D[c]	Mildly acidic powder inhibited. Contains no fluorides or chlorides.	Turco Products Purex Corp., 24500 S. Main St. Wilmington, Calif.	0.05
Turco-4502[c]	Alkaline permanganate	As above	0.29
Oxalic Acid	Technical grade	As above	0.11
Turco-4521[c]	Inhibited acidic powder containing oxalate, citrate, and ammonium ions, surfactant and foam suppressant.	As above	0.12

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[a] Descriptions are sketchy because compositions are proprietary information.

[b] Recommended by the supplier as a cleaning agent rather than as a decontaminating agent.

[c] Recommended by the supplier as a decontaminating agent.

[d] Cost per liter of the solution used in the test calculated from the manufacturers' price, winter of 1968.

TABLE XIX

PREPARATION PROCEDURES FOR THE VARIOUS AGENT SOLUTIONS

Chlorox Undiluted commercial product	
Kern 85D Dilute 200 ml of the stock solution to 1 liter with water and adjust to pH 2.0 with conc HNO_3.	Kern states there is no hazard in acidifying the diluted solution with nitric acid. However, the solutions should not be boiled dry.
L+A Formula 50 Dilute 100 ml of the stock solution to 1 liter with water.	
L+A Formula 52 Dilute 330 ml of the stock solution to 1 liter with water.	
Radiacwash Dilute 100 ml of the stock solution to 1 liter with water.	
Sodium Carbonate 1M. Dissolve 106 g of sodium carbonate in 0.5M. Dissolve 53 g of sodium carbonate in 1 liter of water.	
Turco 4502 Dissolve 45 g of Turco 4502 in 1 liter of water.	This is an alkaline permanganate agent and must be added slowly with stirring to prevent accumulation of heat and localized boiling or eruption during dissolution. Avoid contact with skin, eyes, and clothing.
Oxalic Acid Dissolve 45 g of technical grade oxalic acid in 1 liter of water.	
Turco 4521 Dissolve 60 g of Turco 4521 in 1 liter of water.	
Turco 4306D Dissolve 45 g of Turco 4306D in 1 liter of water.	

TABLE XX

EFFECTIVENESS OF DECONTAMINATING SOLUTIONS FOR SURFACES CONTAMINATED WITH IODINE

	Chlorox	Kern 85D	L+A 50	L+A 52	Radiac-wash	Na_2CO_3 1M	Na_2CO_3 0.5M	Turco 4306D	Turco 4502[a]	Turco 4521
Aluminum	F	E	F	F	F	E	E	F	NT	E
Brass	NT	F	NT	F	F	NT	NT	NT	P	NT
Glass	NT	E	NT	NT	P	NT	NT	NT	E	NT
Rubber	NT	P	NT	NT	P	NT	NT	NT	P	NT
Steel	NT	F	F	NT	F	NT	NT	NT	F	NT
Teflon	NT	P	NT	NT	F	NT	NT	NT	F	NT

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[a] A two-cycle decontamination method.

E(Excellent); greater than 200 decontamination factor (DF).

F (Fair); 50 to 200 DF.

P (Poor); less than 50 DF.

NT (not tested).

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APPENDIX A

PUBLICATIONS AND OTHER ACTIVITIES

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PUBLICATIONS AND PAPERS

1. U. S. Atomic Energy Commission Reports

IN-1203	R. C. Shank and Staff	Annual Report for the Analytical Chemistry Branch for Period Ending June 30, 1968
IN-1207	F. L. Lisman W. J. Maeck J. E. Rein	Burnup Determination of Nuclear Fuels, Project Report for the Quarter October 1 - December 31, 1967
IN-1211	G. L. Booman J. P. Morgan W. J. Maeck H. R. Beard F. L. Lisman J. E. Rein	ICPP Fissionable Isotope Monitor, Status Report
IN-1215	F. L. Lisman W. J. Maeck J. E. Rein	Burnup Determination of Nuclear Fuels, Project Report for the Quarter January 1 - March 31, 1968
IN-1219	J. M. Baldwin	Bibliography of Laser Publications of Interest to Emission Spectroscopists
IN-1223	R. C. Girton J. G. Scott G. A. Huff	A Laboratory Dissolution and Radio-Chemical Analysis of a Uranium, Calcium, and Zirconium Oxide Nuclear Fuel
IN-1224	W. J. Maeck D. T. Pence J. H. Keller	A Highly Efficient Inorganic Adsorber for Airborne Iodine Species (Silver Zeolite Development Studies)
IN-1257	D. R. Trammell M. A. Wade E. M. Fortsch H. G. Brinkley G. A. Huff	Equipment and Techniques for Sealing Ampoules Containing Irradiated U-235 Solutions
IN-1262	J. M. Baldwin	Bibliography of Laser Publications of Interest to Emission Spectroscopists: II
IN-1275	J. E. Fluegel M. A. Wade E. M. Fortsch	Analysis of Irradiated Zirconium-Clad Thorium Tubes

IN-1277	F. L. Lisman et al.	Burnup Determination of Nuclear Fuels, Project Report for the Quarter April 1 - June 30, 1968 and Final Report

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E. R. Brown, D. E. Smith, G. L. Booman, "A Study of Operational Amplifier Potentiostats Employing Positive Feedback for IR Compensation: I. Theoretical Analysis of Stability and Bandpass Characteristics" (Work done in cooperation with Northwestern University), Anal. Chem., 40 (August 1968)pp 1411-1423.

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S. S. Yamamura, "Use of Sodium Cerium EDTA for Titrimetric Determination of Metallic Elements with EDTA," Anal. Chem., 40 (October 1968) pp 1898-1901.

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J. R. Delmastro, "Theory of Polarographic Kinetic Currents for Second-Order Regeneration Reactions at Spherical Electrodes. II. Numerical Solution of the Integral Equation for Steady-State Behavior," Anal. Chem., 41 (May 1969).

3. Papers

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W. J. Maeck*, D. T. Pence, J. H. Keller, "A Highly Efficient Inorganic Adsorber for Airborne Iodine Species (Silver Zeolite Development Studies), Tenth Annual Air Cleaning Conference, New York, New York, August 1968.

F. O. Cartan*, H. R. Beard, F. A. Duce, J. H. Keller, "Evidence for the Existence of Hypoiodous Acid as a Volatile Iodine Species Produced in Water Air Mixtures," Tenth Annual Air Cleaning Conference, New York, New York, August 1968.

R. C. Shank, "Activities of ASTM: E-10 Subcommittee I on Nuclear Fuel Burnup" 156th National ACS Meeting, Atlantic City, New Jersey, September 1968.

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* Presented Paper.

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G. J. Curtis*, F. O. Cartan, "A New, Rapid Method for Average Particle Size Measurements," 24th Northwest Regional ACS Meeting, Salt Lake City, Utah, June 1969.

F. A. Duce*, S. S. Yamamura, "Versatile Spectrophotometric Method for the Determination of Silicon," 24th Northwest Regional ACS Meeting, Salt Lake City, Utah, June 1969.

D. E. Savage*, M. A. Wade, "Improved Procedure for the Determination of Low Sulfate," 24th Northwest Regional ACS Meeting, Salt Lake City, Utah, June 1969.

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* Presented paper.

APPENDIX B

METHODS ADDED TO THE ANALYTICAL MANUAL

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VOLUMETRIC DETERMINATION OF ALUMINUM

ABSTRACT

Aluminum is determined indirectly by titrating the hydroxyl ions released when aluminum, in the basic aluminate form, is complexed with an excess of fluoride. The end point of the titration is determined potentiometrically. Various interferences are eliminated by an initial perchloric acid fuming and by oxalate complexing.

APPLICABILITY

This adaptation of Hay's method [1] is fairly selective and applicable to a variety of samples. These samples include solutions from the processing of both aluminum-clad and zirconium-clad uranium fuels and could contain some or all of the ions: BO_2^-, Ca(II), Cr(III), F^-, NO_3^-, Sn(IV), U(VI) and Zr(IV).

Potential interferences are: (a) anions such as citrate, EDTA, fluoride, phosphate, and tartrate that complex aluminum; (b) large concentrations of common anions such as chloride and nitrate that adversely affect reliability; and (c) metal ions that form insoluble hydroxides, especially those metal ions that also are complexed by fluoride.

The interference of anions except phosphate is avoided by fuming the sample with perchloric acid. The fuming also effectively breaks up hydroxy complexes of aluminum and eliminates Cr(III) interference by oxidizing it to noninterfering Cr(VI).[3].

Phosphate buffers the titration medium and decreases both the precision and accuracy of the determination [2]. At a phosphate to aluminum molar ratio less than 5:1, the phosphate effect can be minimized by standardizing the titrant against aluminum standards containing phosphate in amounts similar to that of the sample. At higher ratios, aluminum must be determined by other techniques such as spectrophotometry or emission spectrography.

Most metal ions are potential interferences. They may, like aluminum, convert to a hydroxide or an oxy anion, then react with fluoride to release hydroxide. Others may precipitate under the analysis conditions and coprecipitate aluminum. Therefore, metal ions must be removed by actual physical separation, or rendered inactive by in-situ masking. This method employs oxalate for masking which effectively prevents the interference of Ca(II) at a 4:1 molar ratio, Hg(II) at 15:1, Pb(II) at 3:1, and the metal ions: Bi(III), Ce(III, IV), Cu(II), La(III), Mo(VI), U(VI), V(V), and Zr(IV) at 1:1 (Table B-I).

Oxalate masking is inadequate for 1:1 ratios of Fe(III) and Ni(II) which precipitate as the hydroxide and carry down aluminum even in the presence of oxalate. Oxalate masking also is inadequate for Cr(III);

however, as discussed previously, the initial perchloric acid fuming oxidizes Cr(III) to noninterfering Cr(VI). One gram of iron, for example, carries 30 mg of aluminum. Table B-I lists the known tolerance levels for these ions. Cadmium(II), Co(II), and Zn(II) also interfere at the 1:1 metal to aluminum molar ratio. Tolerance ratios for these ions have not been established. Thorium(IV) which behaves like aluminum interferes at 1:1, but its interference can be avoided by filtering off thorium oxalate at pH 2. In the filtration, the pH must be held at about 2. At higher pH, aluminum partially hydrolyzes to filterable aluminum hydroxide and results will be low.

TABLE B-I

TOLERANCE RATIOS OF DIVERSE METAL IONS

Ion	Permissible Metal to Aluminum Molar Ratio
Bi(III), Ce(III, IV), Cu(II), La(III), Mo(VI), U(VI), V(V), Zr(IV)	At least 1 for each ion individually.
BO_2^-	0.2[a]
Ca(II)	4
Cr(III)[b]	0.5
Cr(VI)	10[a]
Fe(III)	0.3
Hg(II)	15
Ni(II)	0.05
Pb(II)	3[a]
Sn(IV)	0.02[a]

---

[a] Highest ratio studied. Aluminum level was held at 8 mg (0.3 mmole) in the study of diverse ion effects.

[b] This is the interference level without the initial perchloric acid fuming. See text.

Ions, such as acetate, ammonium, carbonate, and dichromate, that buffer at a low pH will have little effect at the high pH (10.5) used in this procedure.

Occasionally, stainless steel and other very complex samples with high diverse ion concentrations may be involved. Mercury cathode electrolysis is recommended for the removal of metal ions from these samples. This technique efficiently removes Ag, Au, Bi, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, In, Ir, Mo, Ni, Pd, Po, Pt, Re, Rh, Sn, Tl, and Zn. It also converts As, Os, Pb, Se, and Te into forms removable by filtration.

The range of the titration procedure is 1.5 to 25 mg of aluminum. From a practical standpoint, the largest sample aliquot is 50 ml. This permits the analysis of solutions as low as 0.03 mg/ml in aluminum. When the diverse metal ion content is low, the aluminum present in large sample volumes may be concentrated by evaporation. The upper range of the method is fixed by the 0.4M strength of the titrant and the 10-ml capacity of the buret. However, by refilling the buret during a titration, up to at least 40 mg of aluminum can be determined in the absence of metal ions.

DISCUSSION

Aluminum ions are converted to aluminate at a high pH(>12.5), then reacted with potassium fluoride to release hydroxyl ions by the reaction:

$$NaAlO_2 + 6KF + 2H_2O \longrightarrow \underline{K_2NaAlF_6} + 4KOH$$

Titration of the hydroxyl ions with a standard acid provides a measure of the aluminum present. Theoretically 4 moles of hydroxyl ions are released per mole of aluminum. In practice, however, the reaction is not stoichiometric and only about 3.9 moles of hydroxide are released per mole of aluminum. To correct for this nonstoichiometry, an aluminum standard is titrated with the acid titrant and an aluminum titer or conversion factor is assigned to the titrant. The factor with the units, mg Al/ml, must be determined for each new batch of titrant.

The principal steps of this procedure are:

(1) evaporation of the sample with perchloric acid

(2) addition of oxalate

(3) conversion of Al(III) to aluminate at pH 12.75 ± 0.25

(4) readjustment of the pH to 10.55 ± 0.05

(5) addition of potassium fluoride

(6) titration of the hydroxyl ions released with standard hydrochloric acid to the preadjusted pH of 10.55 ± 0.05.

Each step is critical and should be carried out as prescribed.

As noted under APPLICABILITY, the perchloric acid fuming removes anionic interferences, breaks up hydroxy complexes of aluminum, and oxidizes Cr(III) to Cr(VI). This is a critical step because results will be low if the aluminum is converted to insoluble species by excessive heating. Of course, if the sample contains organic matter, there must be nitric acid present at the start of the digestion to prevent an explosion.

Oxalate in acid medium reduces noninterfering Cr(VI) to Cr(III) which cannot be tolerated except in small amounts (Table B-I). It is important, therefore, to adjust the pH to 12.75±0.25 immediately after the addition of oxalate. In basic medium, Cr(VI) is not reduced by oxalate.

Aluminum is converted to aluminate when the pH is raised to 12.75±0.25. If the pH goes above 13, the results tend to be low and the sensitivity decreases. As noted under APPLICABILITY, high concentrations of common anions decrease precision and accuracy; hence, a large excess of base should be avoided. In some samples such as those containing high amounts of uranium the pH may not rise above 12.5. If the pH does not rise after the addition of 2 to 3 drops of 50%(w/w)NaOH, discontinue the addition and continue with the procedure.

The readjustment of the pH to 10.55±.05 must be done slowly as the pH approaches 12. If the pH is lowered too rapidly, the tendency is to drop below 10.5 where some aluminate reverts to aluminum hydroxide. This aluminum hydroxide does not always convert to the aluminate form on reajustment to pH 10.55±0.05 and the results may be low.

The volume of potassium fluoride reagent added must be closely controlled especially if there is an appreciable titration blank. Though prepared identically, different potassium fluoride solutions yield blanks ranging from 0.03 ml to 0.25 ml. A fresh solution must be prepared and a blank determination must be performed each shift.

The final titration must be performed at room temperature with efficient stirring. High temperatures cause high results while inadequate stirring leads to low results, especially when copious amounts of precipitate are present.

SAFETY PRECAUTIONS

Extreme care should be taken in the fuming of samples with perchloric acid to make sure there are no organics present. Fuming should be done in a special perchloric acid hood. Dilute all acid solutions carefully, especially after fuming. Concentrated sodium hydroxide and conc $HClO_4$ can cause serious burns. Wash contacted areas with copious amounts of water.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, Griffin, low-form, 50-ml with 10-ml graduations.

2. Buret, 10-ml, graduated in 0.02-ml increments.

3. Electrode, combination calomel-glass, high pH range (to pH 13). The Thomas electrode has proved satisfactory.

4. Hot plate.

5. Magnetic stirrer with plastic-coated magnetic stirring bars.

6. pH meter.

7. Pipet, volumetric, macro and micro; assorted sizes with control syringe and suction bulb.

8. Ring stand with buret clamp.

9. Watch glass, 3-in., Speedyvap.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water throughout.

1. Aluminum calibration standard, 13.00 mg Al/ml. Dissolve 13.00 g of pure aluminum metal in HNO_3 and dilute to 1 liter. Catalyze the dissolution with $Hg(NO_3)_2$. About 3 drops of a 1<u>M</u> solution is usually sufficient.

2. Aluminum bench and control standards. Prepare standards by dissolving aluminum metal in nitric acid as described for reagent 1.

3. Buffer solution, pH 10.

4. Hydrochloric acid, 6M.

5. Hydrochloric acid titrant, 0.4M.

6. Diverse ion matrix, 0.4M Zr, 0.008M Cr, 2.4M HF and 1.3M Ca. Place 19 g of Zircaloy II and 25 ml of water in a 500-ml Teflon beaker. Add slowly 42 ml of conc HF. After the Zircaloy has dissolved, add 72.1 g of $CaCl_2$ and 1.24 g of $Cr(NO_3)_3 \cdot 9H_2O$. Dilute to 500 ml with water. Filter the solution and store the filtrate in a polyethylene bottle.

7. Perchloric acid, conc.

8. Potassium fluoride solution. Using a Teflon beaker, dissolve 30 g of $KF \cdot 2H_2O$ in 20 ml of water. Bring the solution to room

temperature and adjust the pH to 11.25 ± 0.15 with silica-free 1M KOH. Prepare a fresh solution each shift and store it in a screw-cap polyethylene bottle.

9. Potassium hydroxide, 1M, silica-free.

10. Potassium oxalate solution, 2M. Dissolve 368.5 g potassium oxalate, monohydrate, in 500 ml of water and dilute to 1 liter in a volumetric flask.

11. Sodium hydroxide solution 50%(w/w).

PROCEDURE

A. Blank

A blank determination is required each time a fresh solution of potassium fluoride is made. Process the blank per Procedure D beginning at step 2. If the pH drops when the potassium fluoride is added, record the blank as zero. Add 0.5 ml of matrix to the blank if it is also added to the bench and control standard.

B. Standardization of 0.4M HCl Titrant

Each new batch of 0.4M HCl must be standardized against the 13.00 mg/ml aluminum standard. To standardize a new titrant, each crew is to analyze two 1.00-ml aliquots of the 13.00 mg/ml aluminum standard per Procedure D. Report the data to the Quality Control Laboratory for calculation of the conversion factor.

C. Analysis of Bench and Control Standard

Process a bench standard according to Procedure D with each series of samples. If the samples contain metal ions, add 0.50 ml of the diverse ion matrix to the bench standard. The result for the bench standard must fall within limits specified by the Quality Control Laboratory. If not, process another bench standard. Contact your supervisor if troubles persist.

D. Analysis of Samples

1.	Pipet a sample aliquot containing 1.5 to 25 mg of aluminum into a 50-ml beaker graduated in 10-ml increments.	Steps 2 through 6 may be omitted if the sample is known to be free of fluoride, Cr(III), high concentrations of acids, and hydroxy aluminum species.
2.	Add 1 ml of conc $HClO_4$.	
3.	Cover with a Speedyvap watch glass and evaporate to near dryness on a hot plate set at low heat. Do not bake the sample.	The ideal time for terminating the fuming is when liquid $HClO_4$ is not visible but the residue is still moist and perchloric fumes are still being evolved.

4.	Remove the beaker from the hot plate and allow it to cool.	
5.	Add 5 drops of conc $HClO_4$ and about 1 ml of water.	
6.	Dissolve the residue by warming the solution on a hot plate set at low heat. Swirl the contents occasionally and heat until water vapor just starts to evolve.	If the residue does not dissolve, add 1 or 2 drops of conc HCl.
7.	Cool the sample and dilute to 15 ml with water. Let the diluted sample cool to room temperature.	Best results are obtained if the final volume at the end of the titration is less than 40 ml; therefore, the volume at this stage must not exceed 15 ml. The sample must be cooled to room temperature or the results will be high.
8.	Standardize the pH meter with pH 10 buffer.	
9.	Add a plastic-coated magnetic stirring bar to the beaker, place the beaker on the stirrer, and adjust the stirrer speed to give satisfactory mixing.	Thorough stirring is necessary to obtain good results.
10.	Insert the tip of the electrode into the solution.	
11.	Add 5 ml of the 2<u>M</u> potassium oxalate solution and immediately adjust the pH to 12.75±0.25 with 50% (w/w) NaOH.	In acidic medium, oxalate reduces Cr(VI) to Cr(III) so the sodium hydroxide must be added without delay. Do not exceed pH 13 because high salt concentrations cause low erratic results. If the pH rises above 13, discard the sample and process a new one.

12.	Immerse the buret tip into the solution. To adjust the pH to 10.55±0.05, add 6M HCl dropwise until the pH approaches 12, then add the 0.4M HCl titrant from the buret until the pH is within the range 10.55±0.05. Record the exact pH to the nearest 0.01 pH unit.	The pH should not drop below 10.5. If it does, results will likely be low so discard the sample and process a new one.
13.	Pipet 2.0 ml of the potassium fluoride solution into the sample.	
14.	Fill the buret with the 0.4M HCl titrant and titrate the solution to the exact pH recorded in step 12.	Some titrations are characterized by drifting pH near the end point. Wait 30 sec between increments of titrant and continue the titration until the drifting stops.
15.	Record the data and calculate the results as shown on the example work sheet. Report all results to 3 significant figures.	

REFERENCES

1. S. A. Hays, "The Acidimetric Determination of Aluminum with Fluoride at pH 10-11", HW-18178, Richland, Washington (1950).

2. M. A. Wade, Personal Communication.

3. D. R. Trammell, Personal Communication.

January, 1969

J. A. Rindfleisch
S. S. Yamamura

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME ____________

LOG NUMBER ____________

ACTIVITY (mR/hr) ____________

DETERMINATION Aluminum

CHARGE NUMBER ____________

PROCEDURE Al-Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Volume 0.4 M HCl used, ml	Blank, ml	Acid Factor mg Al/ml	mg Al	mg Al corrected for Bias	mg Al/ml		RESULT M
# 1	0.500 ml	3.41	0.03	2.64	8.92	8.80±0.15	17.6±0.3		0.65±0.01

ANALYZED BY ____________ DATE ____________

CALCULATIONS:

$$D = (A-B)(C) = (3.41-0.03)(2.64) = 8.92 \text{ mg Al}$$

$$F = \frac{E}{0.500} = \frac{8.80 \pm 0.15}{0.500} = 17.6 \pm 0.3 \text{ mg Al/ml}$$

$$\text{Result} = \frac{F}{26.98} = \frac{17.6 \pm 0.3}{26.98} = 0.65 \pm 0.01 \underline{M}$$

APPROVED BY ____________

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DETERMINATION OF BORON IN ATR FUEL PLATE PUNCHINGS

ABSTRACT

The fuel plate punching is decomposed with concentrated hydrochloric acid under reflux in a fused quartz apparatus. The residue is filtered, dissolved by a sodium carbonate fusion-hydrochloric acid dissolution process, then recombined with the original filtrate. Boron is determined by a simplified curcumin procedure based on a method developed by Hayes and Metcalf[1,2]. A 300-μl aliquot of the prepared sample is reacted with curcumin in an acetic acid-sulfuric medium and the absorbance of the red boron-curcumin complex is measured in an ethanol-acetic acid-sulfuric acid medium at 555 mμ.

APPLICABILITY

This procedure is designed specifically for the determination of low concentrations of boron in ATR fuel plate punchings; however, it also is applicable to uranium-stainless steel and uranium-zircaloy samples[2]. Aluminum at 4 mg or less, Cr, Fe, Ni, U, and Zr and trace levels of metallic constituents normally present in aluminum, stainless steel, and zirconium alloys do not interfere. Principal interferences are fluoride which complexes boron and oxidants such as nitrate and perchlorate that react with the curcumin reagent. These should not be present even in small amounts. Oxidizing metal ions like cerium(IV), chromium(VI), and manganese (VII) cannot be tolerated and must be reduced prior to color development.

The range of the colorimetric procedure is 0.25 to 3.5 μg of boron. The maximum aliquot is 300 μl so the lowest determinable boron concentration is about 0.8 μg/ml in the prepared solution. In terms of the solid plate punching, the lowest determinable boron concentration is 80 μg/g. This assumes a dilution of 1 g to 100 ml. If greater sensitivity is desirable, refer to Method B-Color-2[2].

DISCUSSION

The critical facets of this method are: the dissolution of the plate punchings, the introduction of boron contamination through reagents and apparatus, and the variables (water level, reaction time, and reagents) affecting formation and measurement of the boron-curcumin complex. The 0.5-in. diam punchings contain less than 1 mg of boron as boron carbide so extreme care should be exercised to recover all the boron carbide from the dissolution flask and to dissolve it completely without boron losses. The curcumin and acetic acid-sulfuric acid reagents should be prepared and stored in fused quartz flasks previously cleansed with boiling hydrochloric acid and water rinses. Though low in boron, fused quartz ware still introduces boron into the reagents so weekly preparations are recommended. Under the prescribed conditions, quantitative color development will be obtained in the interval 15 to 60 min after the addition of the acetic acid-sulfuric acid reagent. After dilution with 95% ethanol, the boron-curcumin complex is stable for 4 hr.

SAFETY PRECAUTIONS

Use caution in the handling of the acetic acid-sulfuric acid reagent.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, 100-ml, fused quartz or Teflon.
2. Bottles, polyethylene, 2-oz capacity, with screw-caps. Before use, clean thoroughly by rinsing successively with 2 to 4*M* HCl and water. Those bottles that are used to dilute the dissolved sample should be calibrated.
3. Condenser, fused quartz, straight water-jacketed type approximately 15-in in length with ₮ joint to fit the 100-ml flasks.
4. Cover glasses, plastic.
5. Cuvettes (optical cells), 1-cm
6. Filter paper, Whatman 42, 11-cm diam.
7. Flasks, round bottom, fused quartz, 100-ml, with female ₮ joint.
8. Flasks, round bottom or Erlenmeyer, 500-ml.
9. Flasks, volumetric, fused quartz, 250- or 500-ml.
10. Funnels, plastic.
11. Funnel rack.

12. Hot Plate
13. Medicine droppers, polyethylene.
14. Meker burner.
15. Muffle furnace.
16. Pipets, micro, assorted sizes, with syringe.
17. Pipets, volumetric or Mohr type of fused quartz or plastic, suitable for delivery of constant 3-ml aliquots of reagents.
18. Platinum crucible, 15-ml.
19. Ringstand.
20. Spectrophotometer, Beckman Models DU or DK or Cary Model 14.
21. Tongs, platinum-tipped.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for all reagents.

1. ATR fuel matrix solution. Dissolve 1.5 g of NBS U_3O_8 in a quartz beaker or flask with 5 ml of conc HCl plus 10 drops of conc HNO_3. Heat gently to hasten dissolution. If complete dissolution of the U_3O_8 is not obtained, add another 5 ml of conc HCl and 5 drops of conc HNO_3 and continue heating. When dissolution is complete, evaporate to dryness. Add 5 ml of conc HCl and evaporate to dryness, repeat the evaporation to dryness with 3 ml of conc HCl, and dissolve the residue in 500 ml of water. Meanwhile, using a 1-liter polyethylene bottle, dissolve 16.7 ± 0.5 g Na_2CO_3 in about 500 ml of water and cautiously with intermittent mixing, add 110 ml of conc HCl. Dissolve 62.7 ± 1 g $AlCl_3 \cdot 6H_2O$ in this solution, add the uranium solution, and dilute the mixture to 1 liter with water.

2. Boron stock standard, 1.000 mg B/ml. Prepare an aqueous solution 1.000 mg/ml in boron and store the solution in a screw-cap polyethylene bottle. For 100% assay boric acid, use 2.8589 ± 0.0005 g per 500 ml of solution.

3. Boron calibration standard I, 4.00 µg B/ml. Dilute 400 µl of the 1.000 mg B/ml stock standard to 100 ml with the ATR fuel matrix solution. Transfer to a 4-oz polyethylene screw-cap bottle.

4. Boron calibration standard II, 8.00 μg B/ml. Dilute 800 μl of the 1.000 mg B/ml stock standard to 100 ml with the ATR fuel matrix solution. Transfer to a 4-oz polyethylene bottle.

5. Curcumin reagent, 0.125 ($^{w}/v$)%. Dissolve 0.3125 ± 0.0010 g of curcumin in 250 ml of glacial acetic acid. Prepare and store the reagent in a fused quartz flask.

6. Ethyl alcohol, 95% or absolute.

7. Hydrochloric acid, conc.

8. Sodium carbonate, anhydrous powder.

9. Sulfuric acid-acetic acid solution, 1:1 mixture. Mix, with appropriate ice-bath chilling and swirling, equal volumes of glacial acetic acid and conc H_2SO_4. Prepare and store the acid mixture in a fused quartz flask.

PROCEDURE

A. Blank

Process a 300-μl aliquot of the ATR fuel matrix solution per Procedure D beginning at step 2 with each series of standards and samples.

B. Calibrations and Bench Standards

Process two calibration standards with each series of samples. Use 300 μl of calibration standards I and II and follow procedure D beginning at step 2. Divide the micrograms of boron in the standard by its respective absorbance to obtain the conversion factor. The difference between the two should be within limits set by the Quality Control Laboratory. Also, the average of the two factors should agree with the theoretical factor within established limits. For the boron-curcumin complex, the molar absorptivity is about 170,000; hence, the calibration factor should be 4.01 μg B per unit absorbance for this method. If both or either specification is not met, discard the samples and reprocess another pair of standards. Notify your supervisor if difficulties continue.

C. Dissolution of Plate Punchings

1. Weigh the sample to ± 0.1 mg.

2. Transfer the sample to a 100-ml quartz round bottom flask, connect the water-cooled condenser, and add 7.5 ml of conc HCl through the top of the condenser.

3. When decomposition of the sample is complete, rinse the condenser with 5 ml of water, and disconnect it.

4. Swirl the flask to mix its contents and filter the sample through a Whatman-42 filter paper supported in a plastic funnel. Transfer the undissolved residue quantitatively to the filter, then wash the filter with small water rinses. Collect the filtrate in a 100-ml fused quartz or Teflon beaker.

   The total volume of filtrate plus washings should not exceed 40 ml.

5. Fold the filter paper and place it in a 15-ml platinum crucible. Place the crucible in an oven or on a hot plate to dry the filter

6. Ash the filter and residue as follows: With the crucible inclined at 45°, char the filter paper over a low blue flame of a Meker burner until flames no longer are observed. Carefully, continue the ashing at the mouth of a 950°C muffle furnace. Complete the ashing by placing the crucible in

   Steps _6_ and _7_ are extremely critical for the ashing and fusion must be done without any loss of the minute 0.3-mg B_4C residue. In the ashing process, step _6_, avoid drafts that tend to carry particles of residue from the crucible. In the fusion, step _7_, place a lid over the crucible to prevent spatter losses. The Na_2CO_3 melt does not dissolve the furnace for 30 min.

the residue completely. The fusion shuld be continued until all lumps break down and black particles disappear.

7. Let the crucible cool and add 1 g of anhydrous Na_2CO_3. With a small platinum wire, intimately mix the Na_2CO_3 with the ashed residue. Place a lid on the crucible and fuse the sample in a 950°C muffle furnace for 20 min. Let the melt cool and examine the fused sample. It should be free of black matter. If not, continue the heating until the black coloration disappears.

8. Let the crucible cool to room temperature, then lay it in the 100-ml beaker containing the original filtrate. Add 3-ml of conc HCl.

9. When the Na_2CO_3 cake disintegrates completely, heat the beaker on a hot plate without boiling the solution until the solution clears, then chill the sample to room temperature.

10. Transfer the dissolved sample with water rinses to a precalibrated 2-oz polyethylene screw-cap bottle. Dilute to volume with water and mix well.

Use the bottom of the first ring as the reference point.. The capacity of the 2-oz polyethylene bottles is sufficiently uniform ($\overline{X}_6$ = 61.73 ml; s.d. = 0.84 ml) so calibration is not necessary when a relative precision of 4 to 10% is satisfactory.

11. Record the sampling data on the work sheet and continue with the determination per Procedure D.

D. Determination of Boron in the Dissolved Sample

1. Pipet 300 µl of the dissolved sample to a precalibrated, clean, dry 2-oz polyethylene screw-cap bottle.	A borosilicate pipet is satisfactory for delivering the sample. When a precision of 4 to 10% is satisfactory, precalibration of the polyethylene bottles is unnecessary.
2. Pipet 3.00 ml of the 0.125 ($^w/v$)% curcumin reagent.	Use plastic or quartz pipets to dispense the curcumin and sulfuric acid-acetic acid reagents.
3. Pipet 3.00 ml of the 1:1 sulfuric acid-acetic acid mixture.	
4. Mix additives 1, 2, and 3 thoroughly by swirling the bottle.	
5. Let stand for 25 min.	
6. Dilute to volume with 95% ethanol and mix thoroughly.	Use any reference point, such as the bottom of the first ring, but dilute all standards and samples identically.
7. Measure the absorbance of the sample in a 1-cm cell at 555 mµ against 95% ethanol within 4 hr.	
8. Record the data and calculate the results as shown on the attached work sheet. Report all results to 3 significant figures.	

REFERENCES

1. M. R. Hayes and J. Metcalf, "The Boron-Curcumin Complex in the Determination of Trace amounts of Boron", Analyst, 87 (1960), p. 956.

2. S. S. Yamamura, Method B-Color-2 of this manual.

S. S. Yamamura
August 1968

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME ______

LOG NUMBER ______

ACTIVITY (mR/hr) ______

DETERMINATION Boron

CHARGE NUMBER ______

PROCEDURE B- Color - 3

SPECIAL INSTRUCTIONS: The requestor may ask for results in terms of total micrograms boron per plate punching. If so, disregard the sample weight in the calculation of the final result.

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Sample weight, g	Absorbance Vs ETOH	Net Absorbance	Conv Factor µg B/abs	µg B in Sample Aliquot	µg B Corrected for Bias		RESULT µg B/g
Blank			0.065						
Std I, 1.2 µg B			0.368	0.303	3.960				
Std II, 2.4 µg B			0.658	0.593	4.047				
				$\bar{X}$ =	4.004				
Punching B-1	0.5050g/61.7ml/300λ	0.5050	0.385	0.320	4.004	1.28	1.28 ± 0.04		522 ± 17

ANALYZED BY ______ DATE ______

CALCULATIONS:

$$\text{Conv. Factor} = \frac{1.2}{0.303} = 3.960$$

$$= \frac{2.4}{0.593} = 4.047$$

$$\bar{X} = 0.5(3.960 + 4.047) = 4.004 \ \mu g B/\text{abs unit}$$

Sample

$$\mu g \ B \text{ in Sample Aliquot} = CD = 0.320\,(4.004) = 1.28 \ \mu g \ B$$

$$\text{Result} = \frac{F\ (\text{Dilution volume})}{(\text{wt. of punching})(\text{Size of Aliquot})} = \frac{(1.28 \pm 0.04)(61.7)}{(0.5050)(0.30)} = 522 \pm 17 \ \mu g B/g$$

APPROVED BY ______

GASOMETRIC DETERMINATION OF CARBON

ABSTRACT

In this gasometric method for the determination of carbon in materials of relatively low-level carbon content, the sample is ignited in a LECO induction furnace under an oxygen atmosphere. The carbon dioxide and excess oxygen are collected in a measuring buret, then exposed to a potassium hydroxide absorber for removal of the carbon dioxide. The final gas volume is measured and the decrease in volume calculated as percent carbon.

APPLICABILITY

This method uses an induction furnace to melt the samples and to oxidize the carbon to carbon dioxide. It is, therefore, designed primarily for the analysis of conducting metals such as steel. Nonconducting samples such as metal oxides and miscellaneous deposits are analyzable by adding a conducting accelerator.

The range of the method is 0.3 to 15 mg of carbon. Best results are obtained in the 2- to 15-mg range. The maximum sample size is 1 g giving a lower limit of 0.03% carbon. The upper limit of 15 mg is set by the volume (28 ml) of the measuring buret.

DISCUSSION

The LECO gasometric carbon analyzer [1] is schematically illustrated in Figure B-1. Its individual components are shown in detail in Figures B-2 through 5. Oxygen is purified by passing it through the purification train which contains (a) conc H_2SO_4 to remove moisture, (b) Ascarite to remove acid gases, and (c) anhydrous magnesium perchlorate (Anhydrone) to protect the Ascarite from moisture when the apparatus is idle. The oxygen then flows through the rotameter at a controlled rate of 2 cu ft/hr over the heated sample in the induction furnace where combustion takes place. The gaseous combustion products, carbon monoxide, carbon dioxide, sulfur dioxide, and water are carried by the oxygen stream over the manganese dioxide in the sulfur dioxide absorber, and then to the catalytic furnace where carbon monoxide is oxidized to carbon dioxide. The gas enters the carbon analyzer (Figure B-5 through the buret valve shown in detail in Figure B-6. The gas is collected and its volume is measured in the buret bulb at atmospheric pressure and room temperature. The gas then is transferred via the buret valve to the caustic absorption vessel where the carbon dioxide is removed as potassium carbonate. The gas is returned to the buret bulb and the volume is measured. The decrease in volume is corrected to standard temperature and pressure and converted to percent carbon.

Leaks in the train constitute a very serious source of error. A leak test should be made prior to each series of analyses.

SAFETY PRECAUTIONS

Handle the ignited crucibles with tongs and always set hot crucibles in the crucible holder. Do not touch the crucibles after ignition.

APPARATUS AND REAGENTS

A. Apparatus

1. Barometer.
2. Carbon Analyzer Apparatus, LECO (Figure B-1), including crucible holder, induction furnace, catalytic furnace, and oxygen purification train.
3. Crucibles, as obtained from LECO, Cat. No. 528-25.
4. Forceps, 12-in., steel.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Ascarite.
2. Caustic solution. Dissolve 900 g of KOH in 1800 ml of water with appropriate chilling.
3. Iron accelerator, as obtained from LECO, Cat. No. 160.
4. Leveling solution. Add 40 ml of conc H_2SO_4, 10 drops of methyl orange indicator, and 2 ml of LECONAL wetting agent to 500 ml of water, and mix.
5. Magnesium perchlorate, anhydrous, such as Anhydrone.
6. Manganese dioxide, specially prepared for SO_2 absorption, as obtained from Fisher Scientific Company, Cat. No. M-103.
7. Sulfuric acid, conc.

8. Tin accelerator, as obtained from LECO, Cat. No. 155.

9. Wetting agent, LECONAL, as obtained from LECO, Cat. No. 501-79.

PROCEDURE

A. Test for Leaks

1.	Turn on the oxygen.	Avoid excess oxygen pressure from the line by opening the rubber diaphragm valve (Figure B-5) one full turn and adjusting the oxygen flow to 2 cu ft/hr as indicated by the rotameter.
2.	Turn the buret valve to the furnace position and the pressure valve to the empty position.	See Figure B-6 for the valve operating positions.
3.	Close the raising mechanism of the furnace and open the rubber diaphragm valve to allow oxygen into the system.	See Figure B-3 for the raising mechanism. See Figure B-5 for the location of the rubber diaphragm valve.
4.	Close the rubber diaphragm valve when the top of the leveling solution is in the calibrated stem of the buret. If the solution level remains steady indicating the system is leak-free, continue with Procedure <u>B</u>. If the solution level continues to fall, continue with step <u>5</u>.	See Figure B-5 for the location of the buret.
5.	Progressively pinch off sections of the line from the carbon analyzer to the oxygen supply to locate the leak.	When the level of the solution remains steady, the leak is in the last section pinched off.

6. Repair the leak and again test the apparatus for leaks.	A leak between the buret and the absorption vessel (Figure B-5) will be detected in Procedure B and repaired at that point.

B. Zero the Apparatus

This procedure (a) removes any residual CO_2 from the system, (b) insures the cleanliness of the measuring buret, and (c) tests the buret and absorption vessel portion of the apparatus for leaks. This operation must be done before beginning an analysis. Proceed according to Procedure E, steps 3 through 13. Repeat these steps a minimum of three times or until a zero reading is obtained on the calibrated buret stem (Figure B-5). If a zero reading is not obtained after three attempts, test the tubing connectors between the buret and the absorption vessel and replace the tubing, if necessary. Also test the buret valve and apply a high vacuum stopcock grease, if necessary. Repeat the procedure to obtain a zero reading on the buret. If further trouble is encountered, contact your supervisor.

C. Blank

1. Process a blank prior to each series of samples. Use the same amount and type of accelerator that is used for the sample and proceed with steps 3 through 13 of Procedure E.	See note Procedure E, step 1.
2. Record the buret reading as the blank.	

D. Bench Standards

Process an NBS bench standard according to Procedure E. Choose a bench standard that has approximately the same carbon content as the sample.

E. Analysis of Samples

1.	Weigh a sample to ± 1 mg into a tared (to ± 1 mg) crucible, add accelerator, and place the crucible on the raising mechanism of the furnace. The sample should contain 0.3 to 15 mg of carbon.	If less than 0.75 g of sample is used, add 1 scoop each of the iron and tin accelerators. If greater than 0.75 g of sample is used, add only the tin accelerator. If the sample is a nonconductor, both iron and tin accelerators are required, regardless of the sample weight.
2.	Turn on the filament switch and then the high voltage switch.	
3.	Turn the buret valve to the exhaust position and the pressure valve to the empty position and allow the leveling solution to drain to zero.	Note the level of the leveling solution. If it is not at zero on the calibrated stem, add leveling solution to the reservoir.
4.	Turn the pressure valve to the fill position and allow the leveling liquid to fill the buret.	When the buret is full, the float valve will seat. This valve must be observed to insure that H_2SO_4 solution does not flow into the KOH solution. If the H_2SO_4 does flow into the absorption vessel, the absorption vessel must be emptied, washed thoroughly with water, and a new KOH solution prepared and added. If this occurs, begin again with Procedure <u>B</u>.
5.	Turn the pressure valve to the lock position and turn the buret valve clockwise to the furnace position.	
6.	Open the rubber diaphragm valve until the rotameter reads 2 cu ft/hr. Then simultaneously close the raising mechanism of the furnace and turn the pressure valve to the empty position.	Gas will displace the leveling solution in the buret.

7.	When the leveling solution is 2/3 of the way down the calibrated stem of the buret, immediately close the rubber diaphragm valve and open the raising mechanism.	
8.	Turn the buret valve counter-clockwise to the exhaust position and let the leveling solution settle to the zero point on the buret.	The buret should drain for 20 sec. This drain time must be consistent to obtain reproducible results.
9.	Note the level of the caustic around the float valve in the absorption vessel.	The caustic level must be closely observed so that the same level may be reached in step <u>11</u>.
10.	Turn the buret valve to the caustic position and the pressure valve to the fill position. Allow the leveling solution to force the trapped gas into the absorption vessel until the float valve in the buret seats.	
11.	Turn the pressure valve to the empty position and the gas will return to the buret until the float valve seats.	The level of the caustic around the float valve must be the same as that noted in step <u>9</u>.
12.	Turn the buret valve to the lock position and let the leveling solution drain for 20 sec. Adjust the level in both columns of the buret to the same level by turning the pressure valve to either empty or fill position, whichever is necessary.	The pressure valve is turned to the fill position if the right column is the higher and to the empty position if the left column is the higher. Turn the valve cautiously and approach the level position slowly.
13.	Read the percent carbon directly from the left hand side of the buret.	This reading must be made 20 sec after the buret valve was turned to the lock position in step <u>12</u>.

CALCULATIONS

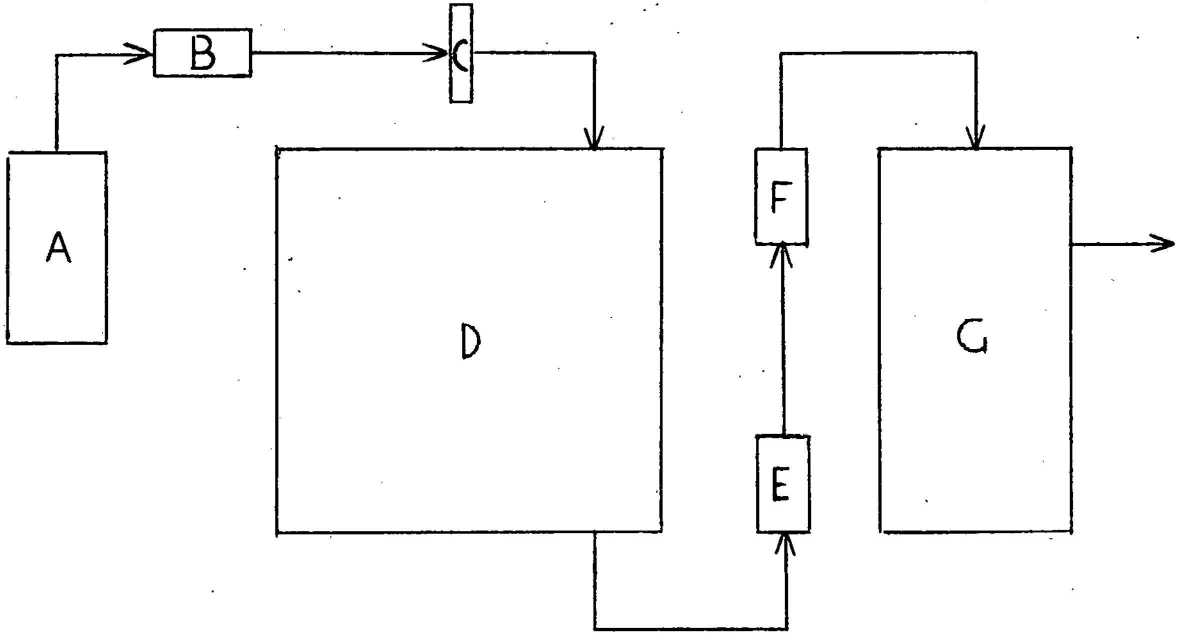
The buret is graduated in percent carbon based on a 1-g sample. The buret reading must be divided by the sample weight when other than 1-g samples are analyzed. A gas volume is being measured in the buret; therefore, the results must be converted to standard temperature and pressure.

The value 0.359 shown in the calculations on the example worksheet is the ratio 273/760 that corrects the gas volume to standard conditions.

REFERENCES

1. Instruction Manual for Operation of LECO Carbon Determinators, Laboratory Equipment Corporation, St. Joseph, Michigan, November, 1953.

March 1969
D. E. Savage



A. oxygen supply
B. purification train
C. rotameter
D. induction furnace
E. sulfur dioxide absorber
F. catalytic furnace
G. carbon analyzer

Fig. B-1 Schematic of LECO carbon analysis.

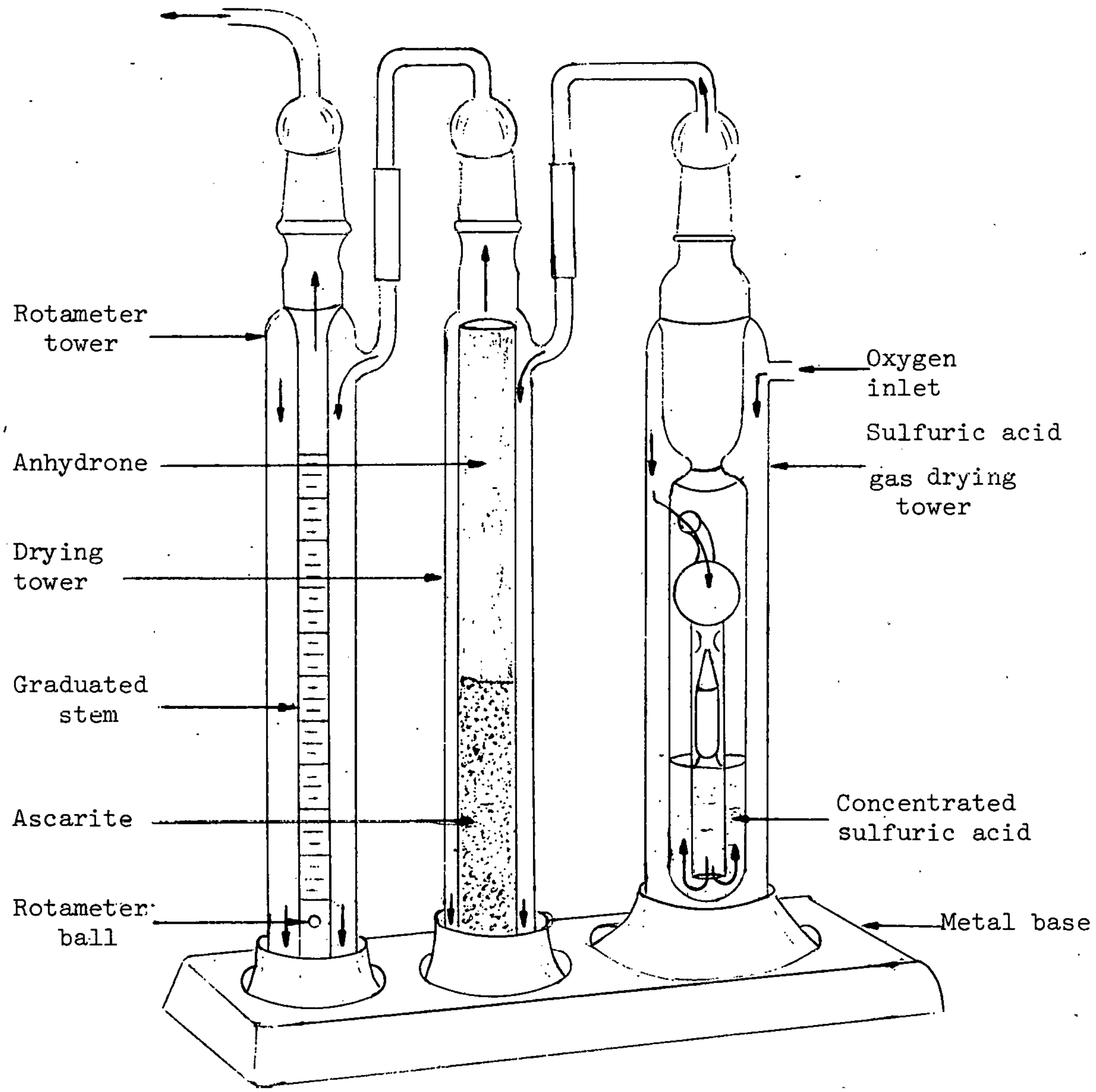
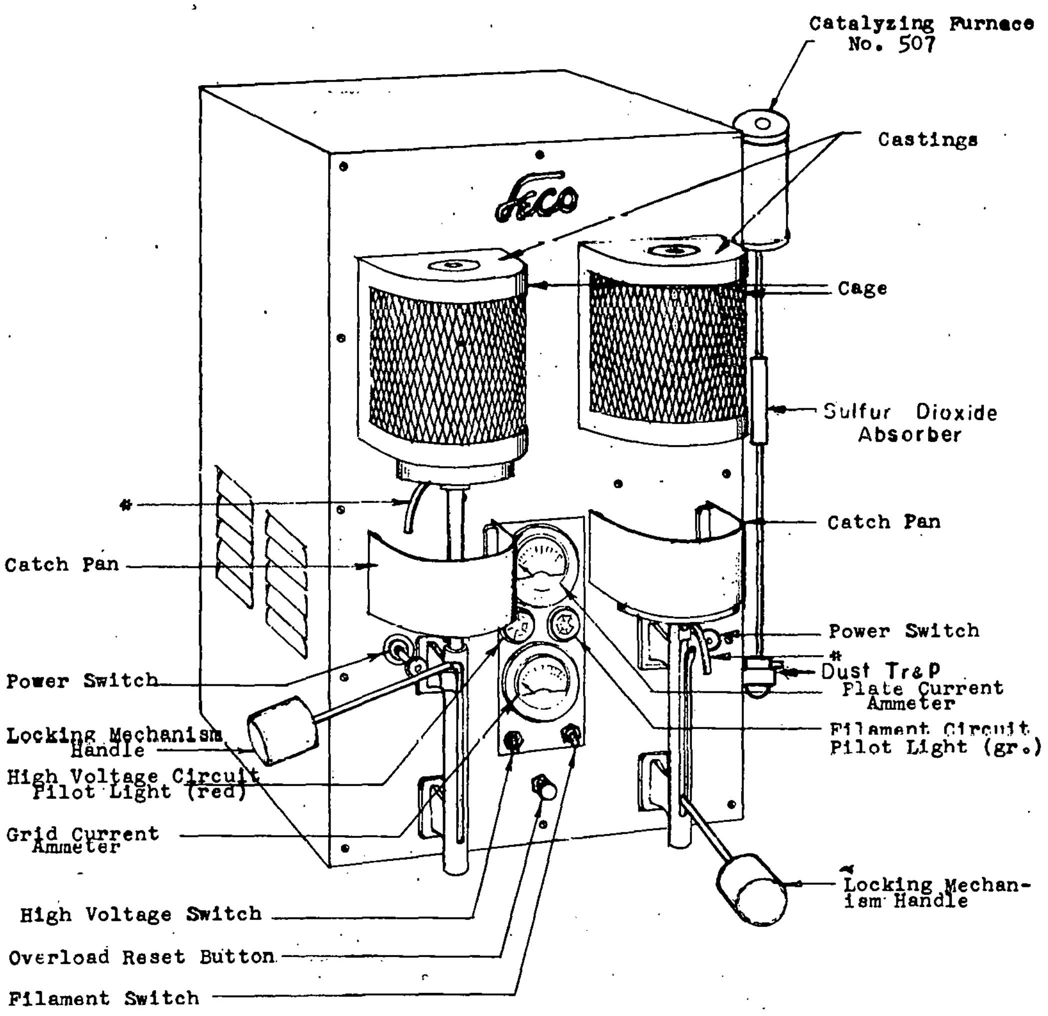


Fig. B-2 LECO oxygen purification train.



* Combustion Gas Outlet for Analyzing Carbon and the Oxygen Inlet when Analyzing Sulfur

Fig. B-3 LECO induction furnace.

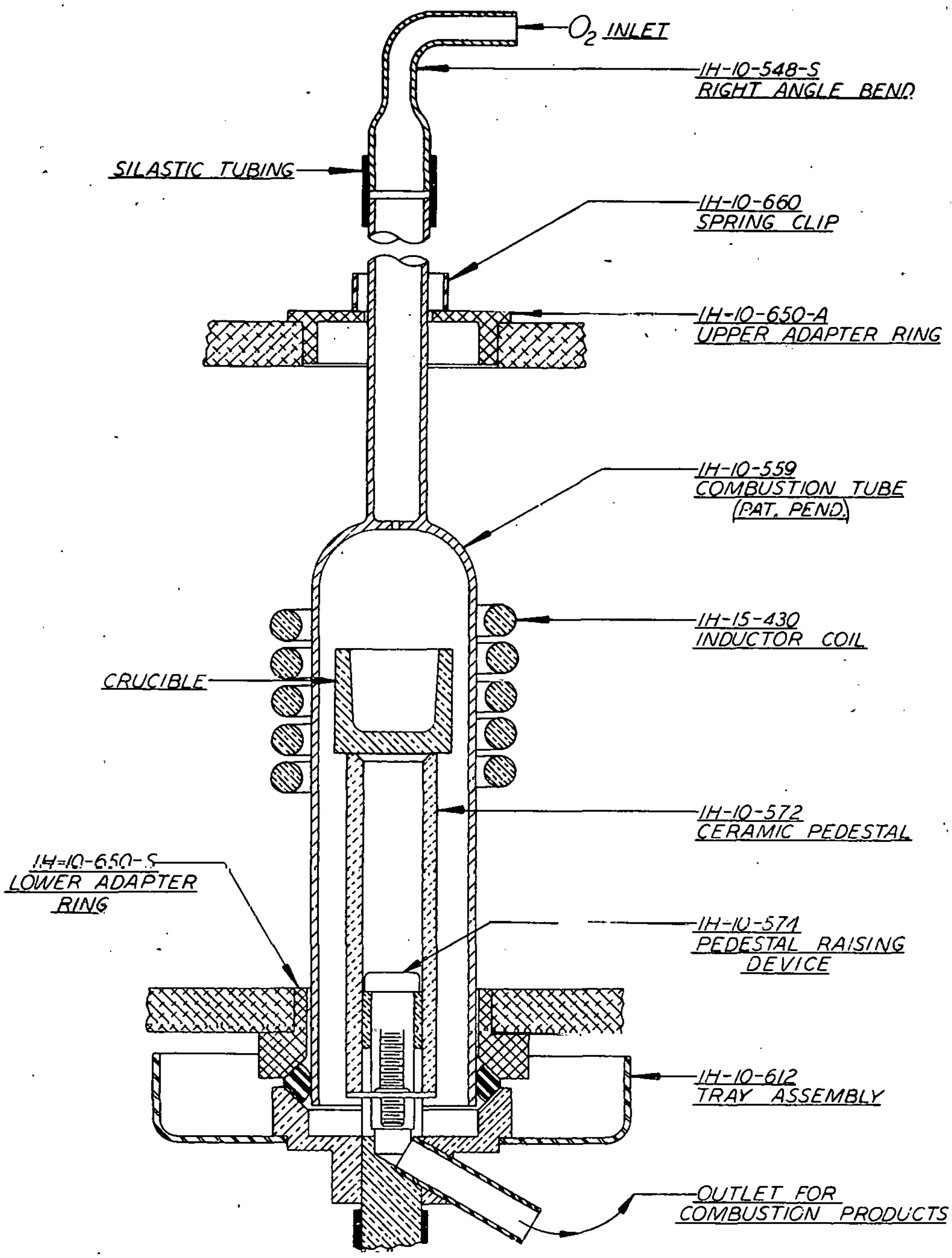


Fig. B-4 Combustion tube.

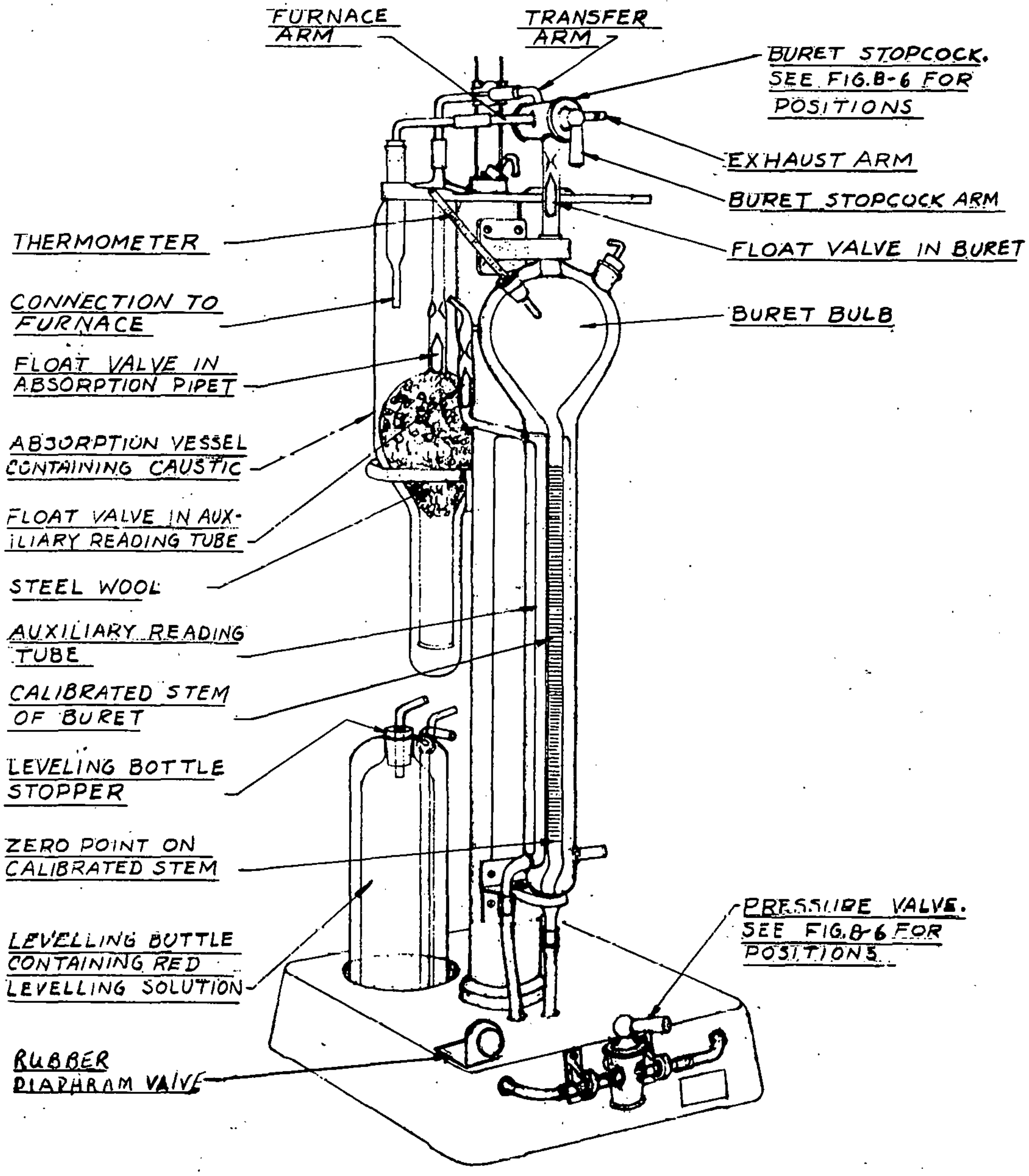


Fig. B-5 LECO carbon analyzer.

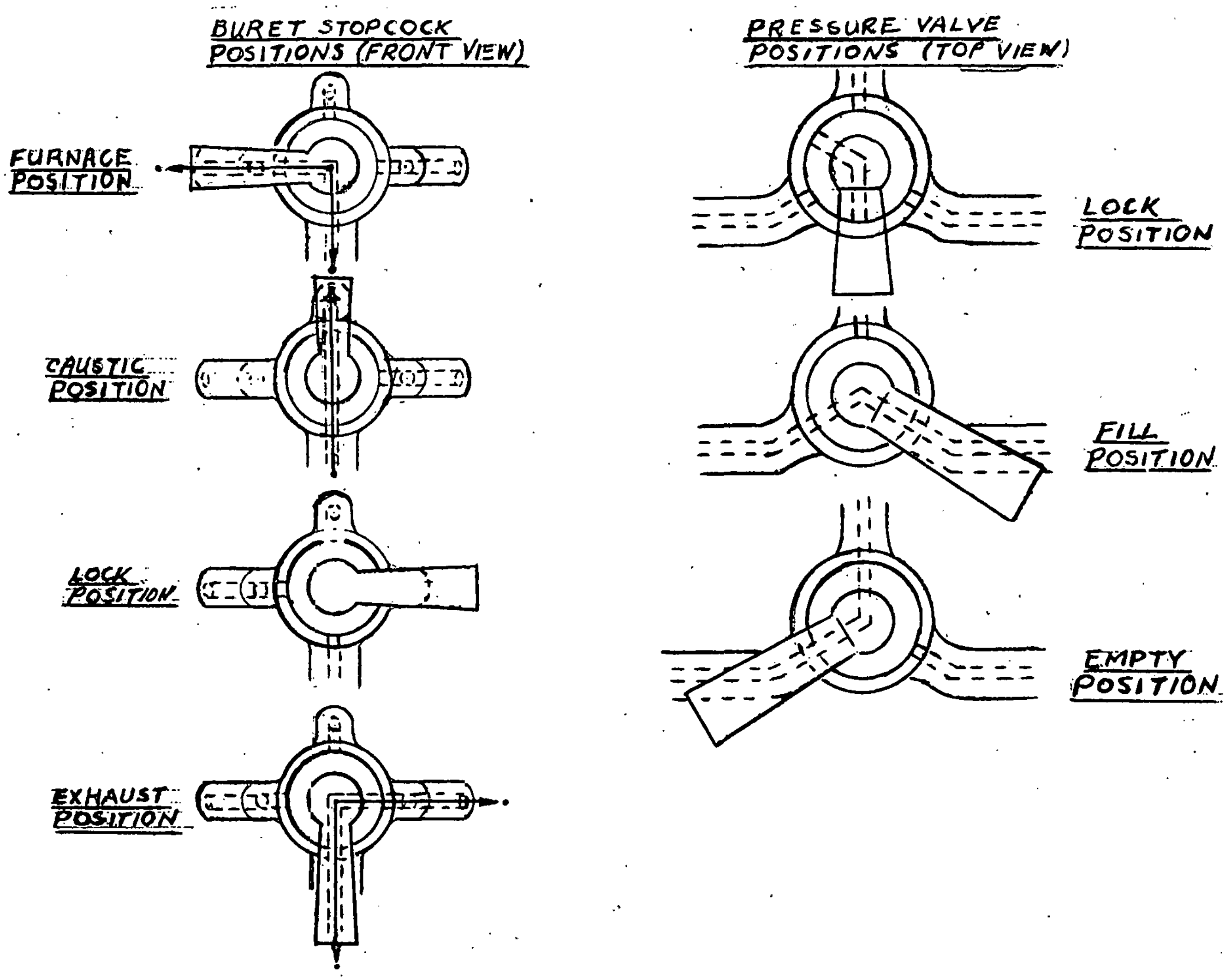


Fig. B-6 Buret valve and pressure valve.

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME ____________________

ACTIVITY (mR/hr) ____________________

CHARGE NUMBER ____________________

LOG NUMBER ____________________

DETERMINATION Carbon

PROCEDURE C- Gas-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$ Sample wt	Buret Reading	Blank	Net Buret Reading	Pressure in mm of Hg	T, °K	STP Factor		RESULT wt% C
# 1	0. 997	0.090	0. 015	0.075	645	297	0.781		0. 059
	1. 014	0.095		0. 080					0. 062
# 2	1.035	0.180		0.165					0.129
	1.006	0.170		0.155					0.120

ANALYZED BY ____________________ DATE ____________________

CALCULATIONS:

$$\text{STP Factor} = (0.359)\left(\frac{D}{E}\right) = (0.359)\left(\frac{645}{297}\right) = 0.781$$

$$\#1)\quad \text{Result} = \frac{(A-B)F}{\text{Sample wt}} = \frac{(0.090-0.015)\ 0.781}{0.997} = 0.059\ \text{wt\%}$$

APPROVED BY ____________________

INC Analytical Chemistry Manual
Method F-Vol-1; May, 1969

PYROLYSIS SEPARATION-INDIRECT COMPLEXOMETRIC DETERMINATION OF FLUORIDE

ABSTRACT

Milligram amounts of fluoride are separated by pyrolysis and quantitatively precipitated as cerium trifluoride with an excess of standard cerium(III). The excess cerium is titrated with ethylenediaminetetraacetic acid (EDTA) to a xylenol orange end point in a pyridine-buffered medium.

APPLICABILITY

This method is based on work at this laboratory[2] and is designed for the analysis of milligram amounts of fluoride in liquids and solids containing such fluoride-complexing ions as Al, B, Ca, and Zr.

Most metal ions, with the exception of the alkali metals, interfere in the titration procedure by reacting with either fluoride or EDTA. When such ions are present, the samples must be pyrolyzed. CPP process streams containing Al, B, Ca, Hg, and Zr are analyzed with the complete method. Mercury and boron codistill with the fluoride during pyrolysis but do not interfere in the titration. The mercury precipitates in the caustic solution used to collect the pyrolysate and is filtered off. The boron-fluoride complex is dissociated during the digestion with cerium(III).

Anions are not separated from fluoride during the pyrolysis. The titration procedure, however, has a high tolerance for most common anions. The tolerances expressed as mole ratio to fluoride are: acetate, 4; chloride, 19; perchlorate, 16; silicate, 0.5; and tetraborate, 0.25. Anions that complex cerium(III) interfere. Two such common ones are sulfate and phosphate. Method F-Color-1 of this manual tolerates them.

The range of the titrimetric procedure is 3 to 40 mg of fluoride. The maximum aliquot volume is about 20 ml; thus, the lowest determinable fluoride concentration is about 0.15 mg/ml. When the pyrolysis separation is used, the maximum aliquot volume is 3 ml for aqueous samples and about 3 g for most solid samples. The lower limit is, therefore, 1 mg/ml or 1 mg/g. For solid samples such as ZrO_2, ZrF_4, ZrO_2F_2, NbF_5, and UO_2 that do not require the addition of an accelerator (see DISCUSSION), 15- to 20-g portions can be analyzed.

DISCUSSION

In the pyrolysis separation,[1] moist air is passed over a mixture of the sample and the accelerator in a quartz tube furnace at 950°C. The accelerator, tungstic oxide, is added to catalyze the hydrolysis of fluoride salts to volatile hydrofluoric acid. The effluent stream is passed through a caustic absorber where the hydrofluoric acid is trapped. The pyrolysis separation is dependent on such variables as (a) pyrolysis temperature, (b) air flow rate, (c) moisture content of the air, (d) dimensions of the pyrolysis tube and its location in the furnace, (e) location of the sample boat in the pyrolysis tube, (g) sample preparation, and (h) pyrolysis time. These variables must be closely controlled.

The caustic absorber solution is acidified with nitric acid to pH 3.5 before the addition of standard cerium(III). This is necessary to prevent the hydrolysis of the cerium. Monochloroacetic acid is added to catalyze the cerous fluoride precipitation, and gelatin is added to hasten the agglutination of the precipitate. The pH is adjusted to 1.85±0.10 to obtain complete and stoichiometric precipitation. The solution containing the precipitate is placed in a boiling water bath and digested until cloudiness disappears. When boron is present, the precipitation is slow and a digestion period of 20 min is required.

SAFETY PRECAUTIONS

Use care when working around the hot tube furnace to avoid burns. Wear rubber gloves when handling the caustic and strong acid reagents.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, 150-ml.
2. Buret, 15-ml with 0.05-ml divisions.
3. Centrifuge tube, 50-ml, round bottom.
4. Combustion boats, nickel, chamber size 0.6-in. wide x 0.4-in. deep x 3.6-in. long.
5. Fisher Filtrator assembly or equivalent.

6. Flowmeter, Tru-Taper, size 6-15-2.

7. Tube furnace capable of continuous operation at 1000°C, chamber size 1.25-in. diam x 12-in. long.

8. pH Meter with a Thomas combination electrode or equivalent.

9. Pipets, macro and micro, assorted sizes with suction bulb and control syringe.

10. Stirrer, magnetic, with plastic-coated stirring bars.

11. Tamping tool. Weld a 1-in. O.D. x 4-in. aluminum rod to a 0.5-in. x 0.75-in. x 3.5-in. stainless steel bar. Round the edges of the steel bar to fit the combustion boat. See Figure 1.

12. Teflon splatter plate and Teflon cover. See Figure B-7. The splatter plate sets about 1 in. from the top of the pyrolysis collection tube to break up bubbles. The cover sets on top of the collection tube.

13. Tube, pyrolysis, quartz. See Figure B-7.

B. Reagents

NOTE: Prepare all reagents from Analytical Reagent Grade chemicals. Use distilled water for the preparation of all reagents and throughout the analysis.

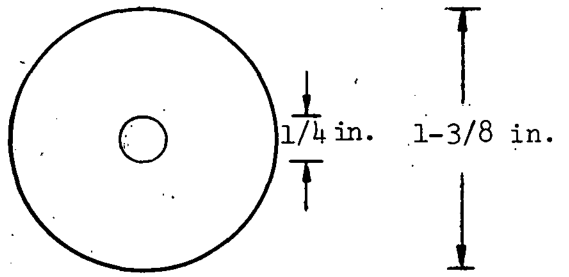
1. Aluminum nitrate, saturated solution, approximately 2M. Prepare in 0.1M HNO_3 using 75 g of $Al(NO_3)_3 \cdot 9H_2O$ per 100 ml of solution.

2. Ammonium hydroxide, conc and 2M.

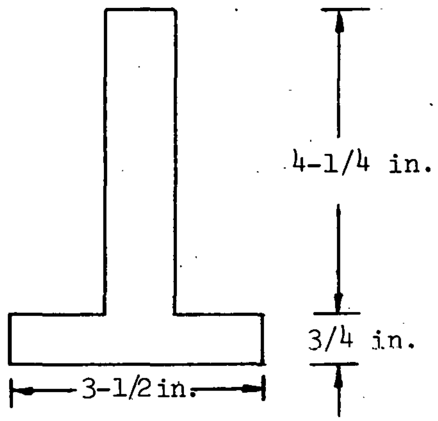
3. Cerium standard solution, 0.075M. Dissolve 65.14 g of $Ce(NO_3)_3 \cdot 6H_2O$ in 1.5 liters of 0.01M HNO_3. Filter through a 0.45-μ membrane filter and dilute to 2 liters with 0.01M HNO_3. Standardize the solution against EDTA per Method Metals-Vol-1 of (INC Analytical Chemistry Manual).

4. Chloroacetic acid, 1M. Dissolve 47.13 g of chloroacetic acid in water and dilute to 500 ml.

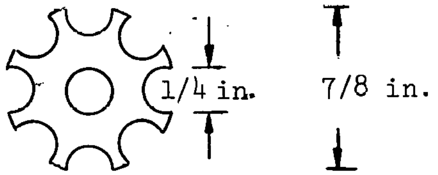
5. EDTA standard solution, 0.05M. Prepare a standard 0.05M solution of the disodium salt per Method EDTA Standard Prep-1 of (INC Analytical Chemistry Manual).



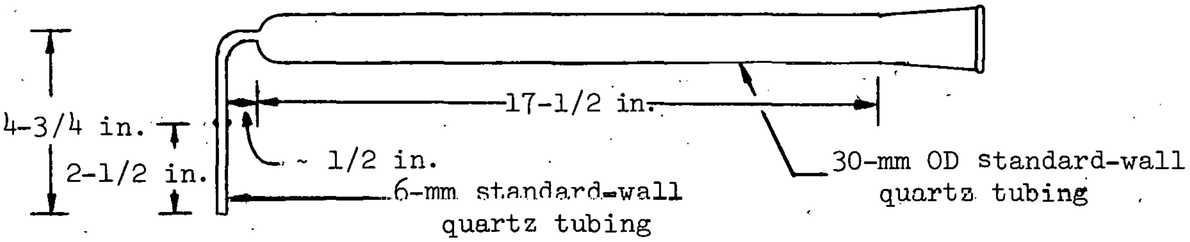
TEFLON COVER PLATE



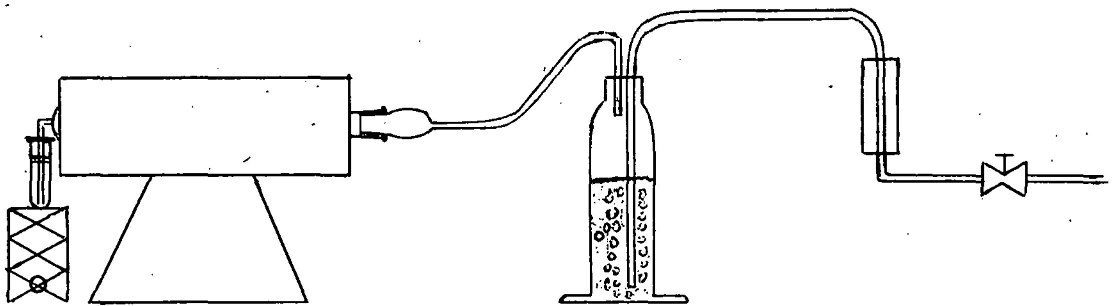
TAMPING TOOL



TEFLON SPLATTER PLATE



PYROLYSIS TUBE



ASSEMBLED APPARATUS

Fig. B-7 Special apparatus for fluoride analysis.

6. Fluoride bench and control standards. A series of standards covering the range of the method will be prepared by the Quality Control Laboratory.

7. Gelatin solution, 1%. Dissolve 1 g of gelatin in 100 ml of water. Prepare a fresh solution each week.

8. Nitric acid, conc and 2M.

9. Phenolphthalein indicator solution, 0.5%. Dissolve 0.500 g of the solid reagent in 100 ml of 90% ethanol.

10. Pyridine.

11. Sodium hydroxide, 3.6M and 2M. Prepare by diluting the commercially obtained 50% (w/w) NaOH.

12. Tungstic anhydride.

13. Xylenol orange indicator, 0.2% in water. Dissolve 0.200 g of solid reagent in 100 ml water.

PROCEDURE

A. Determination of Titration Blank

A blank determination is not necessary.

B. Analysis of Bench and Control Standard

Analyze one of the bench standards by the procedure used for the sample analysis. If the result is out of limits, repeat the analysis. If trouble persists, contact your supervisor.

C. Analysis of Aqueous Samples

1. Weigh 15 g of WO_3 into a 50-ml beaker. Transfer about 10 g to a nickel boat and pack down firmly with the tamping tool.

2. Make a small furrow down the middle of the packed WO_3 bed.

   The sample will be added to this furrow.

3. Pipet 3 ml or less of sample, containing 3 to 40 mg of fluoride, evenly along the length of the furrow.

4. Add 1 ml of the saturated aluminum nitrate solution evenly along the entire length of the boat.	The aluminum aids the conversion of fluoride to hydrofluoric acid.
5. Cover the sample with the remaining 5 g of WO_3.	
6. Pack the WO_3 firmly with the tamping tool.	
7. Add 1 ml of water evenly over the surface of the WO_3 and continue with Procedure <u>E</u>.	The water helps to prevent WO_3 from blowing out of the boat.

D. Analysis of Solid Samples

1. Weigh 15 g of WO_3 into a 50-ml beaker and transfer about 3 g to a mortar.	A small ball mill can be substituted for the mortar.
2. Transfer 3 g or less of sample, containing 3 to 40 mg of fluoride, to the mortar and grind intimately with the WO_3.	Grind the sample until it is as finely divided as the WO_3.
3. Transfer the sample-WO_3 mixture to a nickel boat containing about 2 g of WO_3 spread evenly along the bottom. Use about 5 g of the WO_3 to quantitatively transfer the sample into the boat.	Use several small portions of the WO_3 to transfer the sample.
4. Add 1 ml of saturated aluminum nitrate evenly along the entire length of the boat.	Aluminum aids the conversion of fluoride to hydrofluoric acid.
5. Cover the sample with the remaining 5 g of WO_3 and pack firmly with the tamping tool.	

6.	Add 1 ml of water evenly along the surface of the WO_3 and continue with Procedure E.	The water helps to prevent WO_3 from blowing out of the boat.

E. Separation of Fluoride by Pyrolysis

NOTE: Assemble the pyrolysis apparatus as shown in Figure B-7.

1.	Position the pyrolysis tube in the furnace so that the exit tube is 0.5 in. from the end of the furnace.	If the exit tube is further than 0.5 in. from the furnace, recovery of fluoride may be incomplete.
2.	Add 10 ml of 3.6M NaOH to a 50-ml centrifuge tube and immerse the exit tube in the solution.	The exit tube must extend well below the surface of the NaOH, and the Teflon splatter plate should be about 1 in. from the top of the tube.
3.	Adjust the rate of air flow to 2.5 liters/min.	With a Tru-Taper size 6-15-2 flow meter, a float setting of 2 cm corresponds to a flow rate of 2.5 liters/min.
4.	Place the nickel boat, containing the prepared sample, in the center of the pyrolysis tube.	The temperature of the furnace must be less than 200°C.
5.	Attach the pyrolysis tube to the air supply.	
6.	Turn on the furnace and heat rapidly to 950°C. Maintain this temperature for 10 min.	The total heating time will be about 35 to 45 min.
7.	Turn off the furnace and, with the air flow still on, lower the centrifuge tube.	
8.	Wash the inside of the exit tube with a fine stream of water from a wash bottle equipped with a long hypodermic needle. Finally, rinse down the outside of the exit tube and the Teflon splatter plate.	Some fluoride adsorbs on the inside walls of the exit tube and must be removed by washing with a minimum amount of water. The final volume should not exceed 35 ml after step 9. If there is no precipitate, continue with step 11. A precipitate in the pyrolysate indicates that the sample contains mercury.

9.	Filter the pyrolysate through a 0.45-µ membrane filter using the Fisher Filtrator assembly. Collect the filtrate in a 50-ml centrifuge tube. Wash the residue with a minimum amount of water and collect the washings in the centrifuge tube.	Omit this step and proceed to step 10 if a precipitate does not form.
10.	Remove the pyrolysis tube and while still hot, rinse with water to clean it.	Use an asbestos glove to hold the pyrolysis tube. Pour water slowly down the sides of the tube.
11.	Analyze the pyrolysate per Procedure F.	

F. Titration of Fluoride

NOTE: This procedure is applicable to aqueous samples that do not require pyrolysis. For such samples, pipet 20 ml or less of sample containing 3 to 40 mg of fluoride into a 50-ml centrifuge tube and begin with step 1.

1.	Place the centrifuge tube containing the pyrolysate from Procedure E in an ice bath on a magnetic stirrer, and with the aid of a pH meter, adjust the pH to 3.0 ± 0.5 with conc HNO_3.	
2.	Add 2 drops of 1M monochloroacetic acid.	The monochloroacetic acid catalyzes the precipitation of CeF_3.
3.	Add exactly 10.00 ml of the 0.075M $Ce(NO_3)_3$ solution.	
4.	Add 1 ml of 1% gelatin solution.	Gelatin hastens the precipitation of CeF_3.
5.	Adjust the pH to 1.85 ± 0.10 with 2M HNO_3 or 2M NaOH and stir for 1 min.	CeF_3 precipitation is complete and stoichiometric at pH 1.85.
6.	Remove the electrodes and stirring bar from the sample and rinse with water. Collect the rinsings in the centrifuge tube with the sample.	

7.	Digest the sample in a boiling water bath until the cerium fluoride precipitate settles.	Normally, a 5-min digestion is sufficient. If boron is present, digest for 20 min.
8.	Centrifuge the sample at medium speed for 5 min.	The CeF_3 precipitate will pack at the bottom of the centrifuge tube.
9.	Carefully decant the supernatant solution into a 150-ml beaker.	
10.	Rinse the walls of the centrifuge tube with water and decant the washings into the 150-ml beaker containing the sample.	Use a squeeze bottle and direct the stream of water at the walls of the tube. Do not break up the precipitate in the bottom of the tube. If the precipitate does break up, centrifuge the sample again. Do not transfer any solid material to the 150-ml beaker.
11.	Repeat step <u>10</u> three times.	
12.	Place the beaker on a magnetic stirrer and add 5 drops of xylenol orange indicator.	Place a plastic-coated stirring bar in the beaker.
13.	Add 2 drops of conc HNO_3.	
14.	Add pyridine dropwise to the appearance of a violet color. Count the drops.	
15.	Add two times the pyridine added in step <u>14</u> to bring the pH in the range 5.60±0.25.	
16.	Titrate with EDTA to a yellow end point.	The color change is violet to red to yellow.
17.	Record the data and calculate the results as shown on the sample work sheet. Report all results to three significant figures.	

REFERENCES

1. R. H. Powell and Oscar Menis, "Separation of Fluoride from Inorganic Compounds by Pyrolysis," Anal. Chem., 30 (September 1958) p 1546.

2. Stanley S. Yamamura, Maxine Elliott Kussy, and James E. Rein, "Complexometric Determination of Fluoride with Cerium(III), Anal. Chem., 33 (November 1961) p 1655.

May, 1969
E. M. Fortsch
S. S. Yamamura

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME __________

LOG NUMBER __________

ACTIVITY (mR/hr) __________

DETERMINATION Fluoride

CHARGE NUMBER __________

PROCEDURE F-Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	EDTA, ml	Molarity of EDTA	mmoles $Ce^{=}$ 10(M of Ce)	mg F in Aliquot Analyzed	mg F Corrected For Bias			RESULT mg/ml
# 1	30 ml	5.0	0.0500	0.7500	28.5	29.8±2.0			9.93 ± 0.67

ANALYZED BY __________ DATE __________

CALCULATIONS:

$$D = 57^{*}(C - AB) = 57[0.750 - (5)(0.0500)] = 28.50$$

$$\text{Result} = \frac{E}{\text{Vol. sample}} = \frac{29.8 \pm 2.0}{3.0} = 9.93 \pm 0.67 \text{ mg } F^{-}/\text{ml}$$

* The factor 57 converts mmole cerium to milligrams fluoride.

APPROVED BY __________

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EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM

ABSTRACT

Niobium is extracted as a yellow benzoylphenylhydroxylamine (BPHA)[a] complex into toluene from a 10M HCl medium containing fluoride and thiourea. The yellow Nb-BPHA complex is measured directly at 375 mμ or converted to a more intensely yellow Nb-BPHA-thiocyanate complex and measured at 365 mμ.

APPLICABILITY

This method, based on an Argonne National Laboratory method [1] for the determination of niobium in fissium alloys, is highly selective, hence is applicable to a wide variety of samples including solutions of uranium and solutions of uranium-aluminum, uranium-stainless steel, and uranium-zirconium fuels.

As noted in the abstract, two procedures are described, Procedure D based on measurement of the Nb-BPHA complex and Procedure E based on measurement of the Nb-BPHA-SCN complex. Extensive studies of the effects of diverse ions have been conducted for both procedures. Table B-II lists the tolerance levels of diverse ions for each procedure and Table B-III defines the effects of ions that do or could interfere. For both procedures, the most serious interferences are ions of Ta, Ti, V, and W which cannot be tolerated except in microgram amounts. The observed effects are strong negative interference for high levels of tungsten and all levels of vanadium and strong positive interference for low levels of tungsten and all levels of tantalum and titanium. Nitrate, because of its common occurrence, is a serious potential interference. When its level exceeds 2 mmole, the nitrate must be expelled by evaporating the sample to sulfuric acid fumes per Procedure F.

The working range is 5 to 160 μg of niobium in Procedure D and 1 to 35 μg of niobium in Procedure E. If no preliminary evaporation is made, the maximum sample volume is 4 ml for Procedure D and 5 ml for Procedure E. With these volumes, the lowest determinable concentrations are 1.25 μg Nb/ml and 0.2 μg Nb/ml by Procedures D and E, respectively. With prior evaporation, which is permissible, concentrations down to about 0.02 μg Nb/ml are determinable.

---

[a] Benzoylphenylhydroxylamine also is identified as N-phenylbenzohydroxamic acid.

TABLE B-II

KNOWN DIVERSE ION TOLERANCE LEVELS FOR PROCEDURES D AND E [a]

	Tolerance Level, mMole			Tolerance Level, mMole	
Ion[b]	Procedure D	Procedure E	Ion[b]	Procedure D	Procedure E
Al(III)	1.0	0.75	Ni(II)	1.0	0.3
Actinides[c]	0.5[c]	0.5[c]	Platinum Metals	0.05	0.05
Alkalies(I)	2.0	1.0	Re(VII)	not studied	0.025
Alkaline Earths(II)	1.0	0.5	Si(IV)	not studied	0.04
Bi(III)	0.25	0.05	Sn(II,IV)	3.5	3.5
Cd(II)	1.0	0.2	Ta(V)	interferes; tolerance level not established	
Ce(IV)	0.25	0.1	Th(IV)	0.5	0.25
Co(II)	1.0	0.2	Ti(IV)	not established	0.0002[d]
Cr(III)	1.0	0.6	U(VI)	1.0	1.0
Cr(VI)	0.25	0.1	V(IV,V)	0.005[d]	0.005[d]
Cu(II)	0.5	0.5	W(VI)	0.005[d]	0.0025[d]
Fe(III)	0.5[d]	2.0[d]	Y(III)	0.5	0.1
H(I)	30	30	Zr(IV)	1.0	1.0
Hg(II)	0.25	0.2	Borate	1.0	1.0
In(III)	0.25	0.1	Citrate	5.0	5.0
Lanthanides(III)	0.5[d]	0.5[d]	Fluoborate	8	8
Mg(II)	2.0	0.4	Fluoride	10[d]	10[d]
Mn(II)	1.0	0.2	Nitrate	2[d]	2[d]
Mo(VI)	0.5	0.1	Oxalate	2.5	5.0

TABLE B-II (Continued)

Ion[b]	Tolerance Level, mMole Procedure D	 Procedure E
Perchlorate	12	12
Phosphate	7.5[d]	5[d]
Sulfate	18	18

---

[a] Based on data of R. Villarreal and S. A. Barker of Argonne National Laboratory and also from independent studies by the authors. Except where noted, the tolerance values listed are the highest levels studied and do not represent the maximum tolerance level. In the studies of the effects of diverse ions, the niobium level was maintained at 100 μg for Procedure D and 10 μg for Procedure E.

[b] Metal ions were studied as chloride, sulfate, or alkali metal salts; anions as the acid.

[c] Thorium and uranium were the only actinides studied; neptunium, plutonium, and the transplutonics are not expected to interfere at levels up to about 0.5 mmole.

[d] Maximum tolerance above which interference is observed.

TABLE B-III

EFFECTS OF IONS THAT INTERFERE

	Procedure D[a]		Procedure E[b]	
Ion	Level of Ion	Effect	Level of Ion	Effect
Fe(III)	1.0 mmole	+3.5%		
NO_3^-	>2 mmole	erratic high results	>2 mmole	erratic high results
Ta(V)	1.0 mg	+20%	0.005 mg	+11%
Ti(IV)	0.05 mg	+8%	0.020 mg	+7%
	0.5 mg	+75%		
	10 mg	+125%		
V(IV, V)	0.5 mg	-5.6%	1.0 mg	-20%
	12.5 mg	no extraction of Nb		
W(VI)	5 mg	+12%		
	10 mg	-20%		
	100 mg	no extraction of Nb		

---

[a] Based on studies at a niobium level of 100 μg.

[b] Based on studies at a niobium level of 10 μg.

DISCUSSION

Procedure D, based on measurement of the Nb-BPHA complex, involves an extraction of the Nb-BPHA complex into toluene from a 10M HCl medium containing fluoride and thiourea, a scrub of the toluene extract with 10M HCl, and a spectrophotometric measurement of the Nb-BPHA complex in the toluene. Procedure E is similar to Procedure D except that after the scrub step, the Nb-BPHA-toluene solution is contacted with thiocyanate (SCN^-) in an approximately 3M HCl medium to form the Nb-BPHA-SCN complex. For both procedures, the reactivity of the niobium is very important. The hydrochloric acid concentration must be greater than 9M during the extraction and scrub steps. The 10M HCl scrub is a necessary step in Procedure D.

Although the niobium extracts quantitatively, the Nb-BPHA color is not developed fully during extractions from fluoride media. The full color develops when the Nb-BPHA-toluene solution is scrubbed with 10M HCl devoid of fluoride.

Unless complexed by strong complexers such as oxalate, niobium readily hydrolyzes in dilute acid media including those containing fluoride. Standards and, when possible, solid samples, therefore, should be prepared with an oxalic acid medium. When hydrolysis or polymerization is suspected, an initial fuming with sulfuric acid must be performed.

Other potential sources of difficulty are the introduction of color-producing contaminants and the occasional appearance of cloudiness during the absorbance measurements. Glass should not be used in the sample preparation or in the final determination under conditions where the glass is attacked. The occasional cloudiness of the toluene solution, attributed to water-toluene-emulsions, can be minimized by close adherence to the recommended procedures.

SPECIAL SAFETY PRECAUTIONS

Use protective equipment while handling the acids and during the extraction. Toluene is quite volatile and may generate pressure during the extraction. Uncap the extraction bottle cautiously.

APPARATUS AND REAGENTS

A. Apparatus

1. Constant, rapid delivery dispensing equipment, 4-, 10-, and 15-ml, such as Cantipets.
2. Graduated cylinders, 10- and 25-ml.
3. Pipets, macro and micro, assorted sizes with syringe control and rubber suction bulb.
4. Pipets, Mohr, 5- and 10-ml.
5. Pipets, Mohr, 5-ml, plastic.
6. Platinum crucible or dish.
7. Polyethylene bottles, screw-cap, 2- and 4-oz.
8. Spectrophotometer, Beckman Models DU or DK or Cary Model 14 with 1-cm cuvettes made of borosilicate glass or silica (quartz).
9. Vacuum wash train equipped with a 1-liter suction flask and a 2-ft length of plastic tubing terminating with a drawn-out, fine-tipped polyethylene tube.

B. Reagents

Note: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Ammonium thiocyanate (NH_4SCN) solution, 25% (w/v). Dissolve 250 g of NH_4SCN in water and dilute to 1 liter. Transfer the solution to a 2-liter separatory funnel and extract with 100 ml of hexone (methylisobutyl ketone) for 2 to 3 min. Separate and discard the hexone and extract the NH_4SCN solution with 100 ml of chloroform to remove residual hexone. Drain and discard the chloroform, then transfer the solution through a fluted filter paper into a 1-liter reagent bottle.
2. Benzoylphenylhydroxylamine (BPHA) solution, 1% (w/v) in acetone. Dissolve 2.00 ± 0.05 g of BPHA in acetone and dilute to 200 ml with acetone.

3. Diverse ion matrix solution. Prepare 1M solutions of $AlCl_3$, $CrCl_3$, $FeCl_3$, $NiSO_4$, $UO_2(NO_3)_2$, and $ZrOCl_2$, each in 1M HCl. Mix these solutions in the ratio: 15 Zr, 10 Al, 10 Fe, 5 Cr, 5 Ni, and 5 U. This mixture is 0.3M in Zr, 0.2M in Al and Fe, and 0.1M in Cr, Ni, and U.

4. Fluoride complexer solution, 14M in HF and 2M in HBF_4. Dilute 125 ml of 48% HF plus 88 g of 49% HBF_4 to 250 ml with water. Store this solution in an 8-oz polyethylene bottle.

5. Hydrochloric acid, conc(12M), 10M, and 4M.

6. Niobium stock standard, 1.000 mg Nb/ml. Dissolve 0.2500±0.0005 g of pure niobium metal in a 2-oz polyethylene bottle with a minimum of a 4 to 1 mixture of conc HF and conc HNO_3. Using 10 ml of 9M H_2SO_4 for rinsing, quantitatively transfer the niobium solution to a platinum crucible or dish. Evaporate to fumes of sulfuric acid, then let the sample fume for 10 min without spattering. Cool slightly, add 5 ml of conc H_2SO_4 and continue the evaporation until a clear solution is obtained. Cool the sulfuric acid solution, then transfer it to a 250-ml volumetric flask with 0.3M oxalic acid rinses. Dilute to volume with 0.3M oxalic acid and mix thoroughly.

7. Niobium calibration standards I and II, 100 and 125 μg Nb/ml, respectively, for Procedure D. Dilute 20.00 ml and 25.00 ml of the 1 mg/ml stock standard to 200 ml with 0.3M oxalic acid solution.

8. Niobium calibration standards III and IV, 20.0 and 25.0 μg Nb/ml, respectively, for Procedure E. Dilute 4.00 ml and 5.00 ml of the 1 mg/ml stock standard to 200 ml with 0.3M oxalic acid solution.

9. Niobium bench and control standards. Per the calibration standards, prepare dilutions from the 1.000 mg/ml niobium stock standard to cover the concentration range 0.0005 to 0.16 mg Nb/ml.

10. Oxalic acid solution, 1M. Dissolve 22.5 g of oxalic acid in water and dilute to 250 ml with water.

11. Stannous chloride solution, 40% (w/v). Dissolve 40 g of $SnCl_2 \cdot 2H_2O$ in 75 ml of conc HCl, then dilute to 100 ml with conc HCl. If necessary, heat gently to obtain a clear solution. Prepare a fresh solution after 2 weeks.

12. Sulfuric acid, conc.

13. Thiourea, saturated aqueous solution. Add 12 g of thiourea to 100 ml of water and mix until no more dissolves.

14. Toluene.

PROCEDURES

A. Preparation of Reagent Blank

Process a 2-ml portion of water by the same procedure used to process the calibration standards and to analyze the sample(s).

B. Preparation of Calibration Standards

Two pairs of calibration standards are provided: Standard I and II (100 and 125 μg Nb/ml, respectively) for analyses by Procedure D and standards III and IV (20.0 and 25.0 μg Nb/ml, respectively) for analyses by Procedure E. Process an appropriate pair of standards with each series of samples.

Divide the weight of niobium in each standard by its net absorbance to obtain the calibration factor. The difference between the factors for the two standards should not exceed established limits. Also, the average of the two factors should agree with the established calibration factor within specified limits. If either or both of these specifications are not met, reprocess another pair of standards. Consult your supervisor if difficulties persist.

The molar absorptivities of the Nb-BPHA and Nb-BPHA-SCN complexes are 10,900 and 33,875, respectively; hence, the theoretical calibration factors are 171 for Procedure D and 41.0 for Procedure E.

C. Analysis of Bench and Control Standard

Process a bench standard (1 ml of the niobium bench standard plus 1 ml of the diverse ion mixture) each time calibration standards are processed. Separate bench standards are provided for each procedure. If the result for the bench standard does not fall within specified limits, reprocess the bench standard and samples. Notify your supervisor if difficulties persist.

D. Analysis of samples (Nb-BPHA Procedure)

Note: The range of this procedure is 5 to 160 μg of niobium.

1.	With a graduated cylinder or constant-volume dispenser, deliver 15 ml of conc HCl to a 2-oz polyethylene bottle.	If the analysis must be interrupted, stop after step 5. Use Procedure F for samples high in nitrate and for samples that are suspected to contain hydrolyzed species of niobium.
2.	Add 2 ml of the 40% $SnCl_2$ reagent and mix.	
3.	Pipet a sample aliquot of up to 4 ml containing between 5 and 160 μg of niobium.	
4.	Add 4.75 ml of conc HCl for every 1 ml of sample above 2 ml to adjust the HCl concentration to 10M, then mix.	The HCl concentration must be above 9M for quantitative extraction of the niobium. If the sample volume is 2 ml or less, proceed to step 5.
5.	Add 0.5 ml of the 14M HF-2M HBF_4 solution and mix.	Mohr pipets are adequate for steps 5, 6, and 7. Use a plastic pipet for the HF-HBF_4 solution.
6.	Add 0.5 ml of the saturated thiourea solution and mix.	
7.	Add 2 ml of the 1% (w/v) BPHA solution, mix well, and let stand for a minimum of 2 min.	The BPHA must be reacted with the niobium for a minimum of 2 min before extraction. After the 2 min period, the extraction should be carried out without delay. Proceed to step 8 while waiting.
8.	Pipet exactly 20.00 ml of toluene into each bottle.	
9.	Cover the bottle securely with a screw-cap and extract vigorously for 2 min.	
10.	Let the phases separate, then remove the lower aqeous layer with a fine-tipped plastic medicine dropper attached to a vacuum train.	Here as well as in step 14, it is permissible to remove a small portion of the upper toluene phase.

11. With a graduated cylinder or constant-volume dispenser, deliver 15 ml of 10<u>M</u> HCl.	
12. Extract vigorously for 30 sec.	
13. Centrifuge the bottle for several minutes.	
14. Remove and discard the lower layer.	
15. Transfer the clear toluene solution to a dry 1-cm cell (with a micro transfer pipet or by pouring) and measure the absorbance against toluene at 375 mμ.	The Nb-BPHA-toluene solution in the extraction bottle is stable for at least 1 hr. Once transferred to a cell and placed in the spectrophotometer, the color gradually fades; hence, the measurement should be made right away. Transfer the solution to the cell without agitating the solution in the bottle. For best results, flow the solution onto the nonoptical sides of the cell.
16. Record the data and calculate the results as described on the example worksheet. Report all results to three significant figures.	

E. Analysis of Samples (Nb-BPHA-SCN Procedure)

Note: The range of this procedure is 1 to 35 μg of niobium.

1. To a 2-oz polyethylene bottle, deliver 15 ml of conc HCl with a graduated cylinder or constant-volume dispenser.	If the analysis must be interrupted, stop after step <u>5</u>. Use Procedure <u>E</u> for samples high in nitrate and for samples suspected to contain hydrolyzed species of niobium.
2. Add 1 ml of 40% $SnCl_2$ solution.	
3. Pipet a sample aliquot up to 5 ml containing 1 to 35 μg of niobium.	

4.	Add 4.75 ml of conc HCl for every 1 ml of sample above 2 ml and mix.	This adjusts the HCl concentration to the necessary 10M level. If the sample volume is 2 ml or less, proceed to step 5.
5.	Add 0.5 ml of the 14M HF-2M HBF_4 solution and mix.	A Mohr pipet is adequate for steps 5, 6, and 7. Use a plastic pipet for step 5.
6.	Add 0.5 ml of the saturated thiourea solution and mix.	
7.	Add 1 ml of the 1% BPHA solution, mix well, and let stand for a minimum of 2 min.	After the 2-min reaction, the extraction should be carried out as soon as possible. Perform step 8 while waiting for the BPHA to react.
8.	Pipet exactly 15.00 ml of toluene into the bottle.	
9.	Cover the bottle securely with a screw-cap and extract vigorously for 2 min.	
10.	Let the phases separate, then with a fine-tipped plastic medium dropper attached to a vacuum train, remove and discard the lower layer.	Here and in steps 12 and 16, it is permissible to remove a small amount of the upper toluene phase.
11.	Let the phases separate and remove and discard the lower phase.	
13.	With a graduated cylinder or dispenser, deliver 15 ml of 4M HCl to the bottle.	
14.	Deliver 4 ml of the 25% thiocyanate solution to the bottle.	
15.	Extract vigoroucly for 1 min to develop the Nb-BPHA-SCN complex.	
16.	Centrifuge for several minutes and remove the lower aqueous phase.	

17.	Transfer the clear toluene solution (with a micro transfer pipet or by pouring) into a 1-cm cell and measure the absorbance against toluene at 365 mμ.	Transfer the solution to the cell without agitating the solution in the bottle. For best results, flow the solution onto the non-optical sides of the cell. The color is stable for at least 1 hr.
18.	Record the data on the worksheet and calculate the results as described on the example worksheet. Report all results to three significant figures.	

F. Analysis of Samples That Require Prior Sulfuric Acid Fuming

1.	Pipet a suitable aliquot (i.e., suitable for either Procedure <u>D</u> or <u>E</u>) into a platinum dish or crucible.	This procedure is designed to expel nitrate and to dissociate hydrolyzed niobium species. A platinum vessel is recommended because most niobium samples will contain fluoride. The use of platinum limits this procedure to solutions other than aqua regia. In the absence of fluoride, aqua regia solutions can be processed with glass apparatus.
2.	Add 1 ml of conc H_2SO_4, evaporate the sample to the appearance of SO_3 fumes without spattering, then fume for 5 min.	
3.	Chill the crucible, then cautiously add 2 ml of water and 5 ml of conc HCl.	
4.	Heat the crucible <u>GENTLY</u> and swirl the contents of the crucible to dissolve the salts.	Strong heating causes undesirable excessive volatilization of HCl.
5.	Quantitatively transfer the clear solution to a 2-oz polyethylene bottle using 10 ml of conc HCl for the rinses.	
6.	Add 2 ml of 40% $SnCl_2$ (Procedure <u>D</u>) or 1 ml of 40% $SnCl_2$ (Procedure <u>E</u>) and continue per Procedure <u>D</u> or <u>E</u> beginning at step <u>5</u>.	

REFERENCES

Robert Villarreal, Spencer A. Barker, "A Rapid and Selective Method for the Spectrophotometric Determination of Niobium", Paper is to be published in Analytical Chemistry.

January, 1969
S. S. Yamamura
M. E. Kussy

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME ____________________

LOG NUMBER ____________________

ACTIVITY (mR/hr) ____________________

DETERMINATION Niobium

CHARGE NUMBER ____________________

PROCEDURE Nb-Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance vs Toluene	Net Abs.	Calib Factor	µg Nb in Test Aliquot	µg Nb Corr'd for Bias			RESULT mg Nb/ml
Rgt Blank		0.012							
Std, 100 µg Nb		0.611	0.599	166.9					
Std, 125 µg Nb		0.757	0.745	167.8					
				$\bar{x}_2 = 167.3_5$ µg Nb/abs unit					
Sample X	0.50ml /100ml /4.00ml	0.392	0.380		63.6	64.0 ± 0.6			

ANALYZED BY ____________________ DATE ____________

CALCULATIONS:

$$\text{Calib Factor} = C = \frac{\mu g\ Nb}{\text{Net abs}} = \frac{100}{0.599} = 166.9\ ;\ C' = \frac{125}{0.745} = 167.8$$

$$\bar{X}_2 = \frac{166.9 + 167.8}{2} = 167.3_5\ \mu g\ Nb/\text{abs unit}$$

$$D = BC = (0.380)(167.3_5) = 63.6\ \mu g\ Nb$$

$$\text{Result} = \frac{E}{0.50}\frac{(100)}{(4)} = \frac{64.0 \pm 0.6}{0.50}\frac{(100)}{(4)} = 3200 \pm 30\ \mu g\ Nb/ml$$

$$= 3.20 \pm 0.03\ mg\ Nb/ml$$

APPROVED BY ____________________

SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS

ABSTRACT

In this versatile method for the determination of microgram amounts of phosphorus, orthosphosphate phosphorus is extracted selectively as the yellow phosphomolybdic acid complex into methyl isobutyl ketone (hexone) from a 2M $HClO_4$ medium. The yellow complex is then reduced to the more sensitive molybdenum blue complex and measured at 625 mμ. A perchloric acid digestion converts organophosphorus compounds and inert phosphates to determinable orthophosphate. Prior extraction with cupferron eliminates such interferences as vanadium(V) and zirconium(IV).

APPLICABILITY

The basis of this method is the extraction of orthophosphate as the phosphomolybdic acid complex into hexone, reduction of the yellow complex with stannous chloride, and spectrophotometric measurement of the molybdenum blue reduction product at 625 mμ[1]. This extraction - spectrophotometric procedure, Procedure F, is used in various combinations with a perchloric acid digestion pretreatment, Procedure D, and a cupferron extraction pretreatment, Procedure E, for different types of samples (Figure B-8).

The applicability of the method and the effect of diverse ions are different for each analysis scheme (Table B-IV). These differences arise depending on whether the perchloric acid pretreatment (Procedure D) and the cupferron extraction (Procedure E) are used in the analysis scheme. Analysis schemes 2 and 3 include the perchloric acid treatment while analysis schemes 1 and 4 do not. Analysis schemes 3 and 4 include a cuperron extraction whereas schemes 1 and 2 do not. The perchloric acid digestion, Procedure D, converts silicate to silica; converts organophosphorus compounds, metaphosphate, pyrophosphate, and other phosphorus species to determinable orthophosphate; depolymerizes hydrous metal polymers to cupferron-reactive monomers; expels volatile acids; destroys organic complexing agents; and oxidizes certain elements to higher oxidation states. The cupferron extraction, Procedure E, removes metal ions such as V(V) and Zr(IV) that interfere by tying up phosphate.

With reference to Table B-IV, the effect of niobium and tungsten in analysis schemes 3 and 4 and the effect of chromium(III) require further clarification. Niobium and tungsten at a level of 25 μg interfere seriously despite the application of the cupferron extraction. The difficulty with niobium is attributed to the coprecipitation of phosphate by the niobium precipitate that forms in acidic medium devoid of suitable complexing anions. The difficulty with tungsten is that it is not extracted quantitatively by cupferron from a 2M

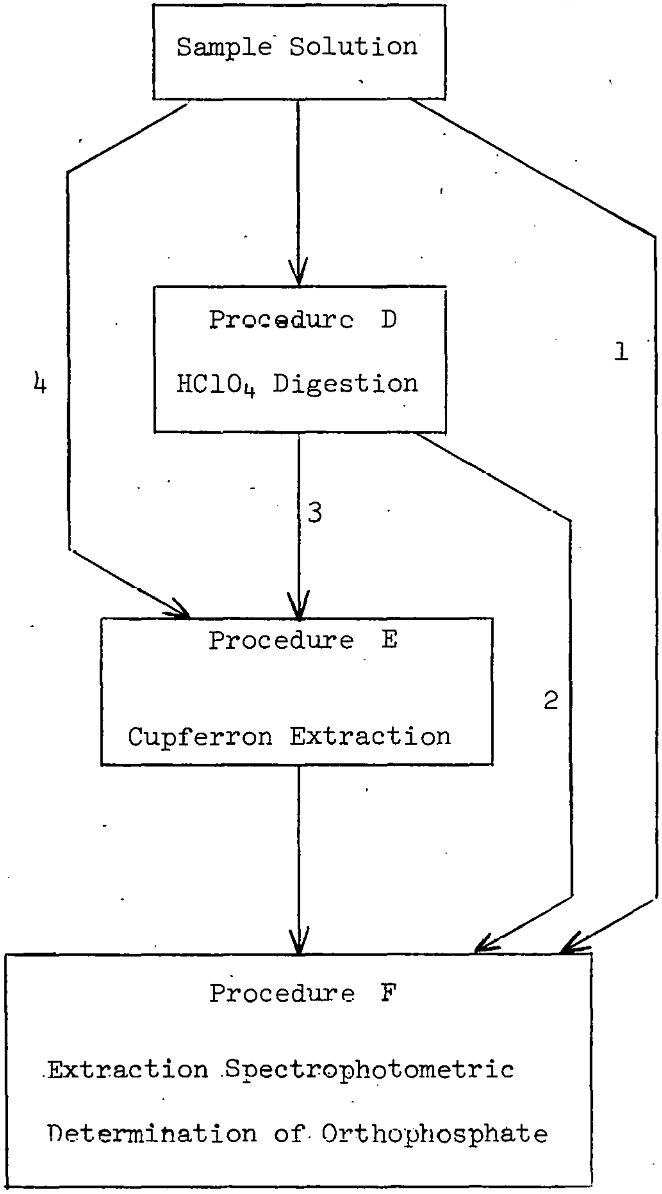

Fig. B-8 Diagram of Analysis Schemes.

TABLE B-IV

APPLICABILITY OF THE VARIOUS ANALYSIS SCHEMES

Analysis Scheme	Applicability	Summary of Diverse Ion Effects[a]
1. Procedure F	Selective determination of orthophosphate in aqueous solutions which do not contain metallic interferences and which may or may not contain organophosphorus compounds such as TBP.	The tolerance expressed as mole ratio of impurity to phosphate is 50,000 for U(VI); 3,500 for Al; at least 1,400 for Na and Mg; at least 550 for Ba, Bi(III), Co, Cr(III, VI), Cs, Cu, Fe, Hg(II), K, Lanthanides(III), Mn(II), Ni, Pb, Th, and Zn; and at least 175 for Si. This tolerance for Hg(II) is based on centrifuging the hexone phase before absorbance measurement as explained in the APPLICABILITY section. As for common anions, the tolerances in terms of mmole per sample aliquot are 8 mmole for Cl^-, NO_3^-, and SO_4^{-2} and 4 mmole for F^-. The metals Hf, Nb, Ti, V, W, and Zr interfere seriously even at a 1:1 metal to phosphate weight ratio.
2. Procedures D + F	Determination of total phosphorus in organic and inorganic samples that do not contain interfering metal ions.	Same as analysis scheme 1 with the following exceptions: a. Cr(III) tolerance is only 0.01 mmole (See Text) b. Perchloric acid fuming expels volatile anions such as Br^-, Cl^-, F^-, and NO_3^-. c. High levels of silicate may interfere in analysis scheme 1. Perchloric acid fuming converts silicate to noninterfering silica.

TABLE B-IV (Continued)

Analysis Scheme	Applicability	Summary of Diverse Ion Effects [a]
3. Procedures D + E + F	Determination of total phosphorus in all types of organic and inorganic samples.	Same as analysis scheme 1 except a. Hf, V, and Zr do not interfere at a 550 to 1 metal to phosphate molar ratio. b. The comments for analysis scheme 2 apply. Niobium, Ti, and W interfere despite the cupferron extraction (See Text).
4. Procedures E + F	Selective determination of orthophosphate in aqueous solutions which contain interfering metal ions and which may contain organophosphorus compounds such as TBP.	Same as analysis scheme 1 except that Hf, V, and Zr do not interfere at a 550 to 1 metal to phosphate molar ratio. Niobium, Ti, and W still interfere (See Text).

---

[a] In the study of the effects of diverse ions, the phosphate level was maintained at 34 μg (4×10^{-4} mmole). The diverse metal ions were added as chloride or nitrate salts or, in the case of Nb, V, and W, as alkali metal salts of the oxyanions. The anions were introduced as the acid.

$HClO_4$ medium. Extraction from 0.3M $HClO_4$ medium yields satisfactory results with 25 μg of tungsten; however, this condition is not satisfactory for zirconium and is not used in this method.

The tolerance of the method for chromium(III) depends on whether the perchloric acid fuming is performed and whether iron(III) is present. In the absence of iron(III), chromium(III) does not interfere at a 550 to 1 chromium(III) to phosphate molar ratio if the sample is not fumed. If it is fumed, the chromium(III) tolerance is only about 25 to 1 or about 0.01 mmole per sample aliquot. In the presence of phosphate, chromium(III) apparently is not oxidized quantitatively to chromium(VI) by fuming perchloric acid. Heating promotes the formation of stable chromic phosphate which does not react with molybdate to form the extractable phosphomolybdic acid complex. When sufficient iron(III) is present, the initial perchloric acid fuming has no effect on the behavior of chromium(III). The explanation is that iron(III) reacts preferentially with phosphate and prevents the formation of nonreactive chromic phosphate.

As stated in Table B-IV, a minor modification in the method, centrifugation of the hexone phase before reading the absorbance, is necessary when mercury is present in the sample. Mercury extracts into the hexone phase, then is reduced to mercury(I) when the hexone phase is contacted with the chlorostannous reagent. This produces a suspension of insoluble mercurous chloride in the hexone phase which, if not centrifuged out, would cause high absorbance readings.

The range of this method is 5 to 100 μg of phosphate (1.6 to 33 μg of phosphorus); however, with extreme care, the range can be extended to 1 μg of phosphate. Both 1- and 5-cm cells are used to cover this range. The maximum sample size is 0.5 ml or 0.5 g for organic samples and about 25 ml for aqueous solutions. Therefore, the minimum determinable phosphate concentrations are 2 ppm with organic samples and 0.04 ppm with aqueous samples.

DISCUSSION

The principal operations involved in this method are:

(1) digestion of samples with perchloric acid

(2) removal of certain metal ions by cupferron extraction

(3) formation of the phosphomolybdic acid complex

(4) extraction of the phosphomolybdic acid complex into hexone

(5) reduction of the yellow complex to molybdenum blue with a hydrochloric acid solution of stannous chloride

(6) measurement of the intensity of the blue complex at 625 mμ.

The formation and extraction of the phosphomolybdic acid complex is carried out in a 1.8$\underline{M}$ $HClO_4$ medium. Warm dilute perchloric acid oxidizes cupferron to a yellow-green substance which also extracts into the hexone to give high and erratic results. Chilling the solution minimizes this undesirable side reaction. The formation of the phosphomolybdic acid complex is complete in less than 5 min in 1.8$\underline{M}$ $HClO_4$ medium. Only a slight excess of molybdate is necessary. The reduction of the yellow complex to molybdenum blue and the intensity of the blue color are affected by excess molybdate reagent, acidity, and the presence of anions other than that of the acid medium (HCl) used in the reduction. At room temperature, the color development is complete in 15 min and thereafter, the blue color is stable for several hours. Once prepared, the hexone solution of the molybdenum blue complex must not be diluted because the color intensity is sensitive to change in acidity and salt concentration.

In the analysis of zirconium-containing samples that require a perchloric acid digestion, it has been found necessary to deliver the cupferron reagent to the digestion vessel. The cupferron apparently "dissolves" zirconium phosphate adhering to the vessel walls enabling quantitative transfer of the phosphate to the separatory funnel.

Phosphate contamination through glassware is a constant problem. Many detergents contain phosphate or phosphate-bearing chemicals. All glassware should be soaked initially in 7±1$\underline{M}$ NH_4OH, then thoroughly rinsed with distilled water.

This method, though aimed primarily at liquid samples, can be used to determine phosphorus in solids. Dissolution of metallic samples should be carried out under oxidizing conditions to prevent loss of phosphorus as phosphine.

SAFETY PRECAUTIONS

Perchloric acid digestion of organic matter can be hazardous. Nitric acid should be present during the initial oxidation stage. As a further precaution (especially for easily oxidizable material; alcohols, aldehydes, etc.) nitric acid should be added to the sample before the perchloric acid. If large amounts of easily oxidizable organic matter are to be analyzed, a preliminary oxidation with nitric acid should be made. The digestion should be conducted in a hood behind safety glass.

APPARATUS AND REAGENTS

A. Apparatus

NOTE: All apparatus that contacts the sample prior to the stannous chloride reduction must be cleaned thoroughly before use. Soak the items in 7±1$\underline{M}$ NH_4OH, then rinse well with distilled water.

1. Absorbance cells, borosilicate glass or silica, 1- and 5-cm.
2. Beakers, assorted sizes.
3. Centrifuge tubes, 50-ml.
4. Cylinders, graduated, assorted sizes.
5. Glass beads.
6. Hot plate.
7. Pipets, macro and micro, assorted sizes, with suction bulb and syringe controls.
8. Pipets, Mohr, 5- and 10-ml.
9. Separatory funnels, 125-ml, with Teflon stopcocks.
10. Spectrophotometer, Beckman DU, DK, or equivalent.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Chloroform.
2. Chlorostannous acid solution. Dissolve 2.38 g of $SnCl_2 \cdot 2H_2O$ in 170 ml of conc HCl and dilute to 1 liter with water. Add several pellets of metallic tin and store in a polyethylene bottle. Prepare a new solution every 2 weeks. Because of instability, it might be advisable to cut the recipe by at least 2.
3. Cupferron solution, 0.25<u>M</u>. Dissolve 3.88±0.05 g of ammonium cupferrate in 100 ml of water. Store in a refrigerator in a dark bottle. Prepare a fresh solution after 2 weeks.
4. Diverse ion matrix for phosphate bench standards analyzed by schemes 3 and 4 (Table I). Dissolve 5.0±0.1 g of $ZrOCl_2 \cdot 8H_2O$ and 1.0±0.1 g of NH_4VO_3 in 75 ml of 2<u>M</u> HCl and dilute to 100 ml with water.
5. Hexone (4-methyl-2-pentanone).
6. Molybdate solution. Dissolve 73±0.5 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in water. Filter if turbid, dilute to 1 liter with water, and store in a polyethylene bottle.

7. Nitric acid, conc.

8. Perchloric acid, conc, phosphate-free. Vacuum distill reagent grade perchloric acid.

9. Phosphate standard stock solution, 1.000 mg PO_4^{-3}/ml. Dissolve 0.7165±0.0005 g of KH_2PO_4 in water and dilute to 500 ml with water.

10. Phosphate calibration standards I and II, 50.0 and 75.0 µg PO_4^{-3}/ml, respectively. Dilute 10.00 ml and 15.00 ml of the stock standard to 200 ml with water

11. Phosphate (PO_4^{-3}) bench and control standards. Dilute the 1.000 mg PO_4^{-3}/ml standard with water to the desired concentrations.

PROCEDURE

A. Blank

Process a 5-ml aliquot of water by the same analysis scheme as that used to analyze the samples. The usual blank absorbance is about 0.020 compared against water. If the blank absorbance greatly exceeds this, check first the perchloric acid, then the glass apparatus.

B. Calibration

The use of four calibration standards is intended to promote efficiency by reducing repeat analyses. If only samples with similar concentrations are being analyzed, the use of two appropriate standards will suffice.

Process at least one pair of calibration standards with each series of samples. Use 1.00-ml portions of the 50 and 75 µg/ml phosphate standards for measurements in 1-cm cells and 200-µl portions of the same standards for measurements in 5-cm cells. Record the absorbance for each standard and the blank. Divide the micrograms of phosphate by the net absorbance to obtain the conversion factor. The difference between the two conversion factors for each pair of standards should not exceed limits set by the Quality Control Laboratory. Also, the average of the two conversion factors should agree with the established conversion factor for each group within the specified limits. If either or both specifications are not met, reprocess the pair or pairs of calibration standards. Report problems to your supervisor if difficulties continue.

C. Analysis of Bench-Control Standards

Analyze a bench standard each time samples are analyzed. Process the bench standard by the same analysis scheme used to analyze the samples. If the analysis scheme involves a cupferron extraction, add 1 ml of the diverse ion matrix to the bench standard. The result obtained must fall within specified limits. If it does not, process another bench standard. If trouble continues, report to your supervisor.

D. Digestion of Samples with Perchloric Acid

1. Pipet a sample aliquot containing 5 to 100 μg of total phosphate (1.6 to 33 μg P) into a 150-ml beaker.	Organic samples should be 0.5 ml (0.5 g) or less. Aqueous samples can be as much as 25 ml.
2. Using a Mohr pipet, add 6 ml of conc HNO_3.	For safety, add the HNO_3 before the $HClO_4$. When the sample is predominantly organic, digest the sample with conc HNO_3 for awhile, then admit the conc $HClO_4$. Perform the digestion in a perchloric acid hood equipped with safety glass. If the sample does not contain organic matter, omit step <u>2</u>.
3. Using a Mohr pipet, add 6 ml of conc $HClO_4$.	
4. Place a cover glass on the beaker, evaporate to fumes of perchloric acid, and fume for 5 min.	
5. Cool the sample to room temperature. If the sample contains Hf, V, or Zr, proceed to step <u>6</u>. If these metals are not present, quantitatively transfer the digested sample to a 125-ml separatory funnel with 25 ml of water, then continue with the analysis per Procedure <u>F</u> beginning at step <u>3</u>.	

6. Rinse the cover glass and the beaker walls with 15 ml of water, mix by swirling, then chill the solution in an ice bath for 2 to 3 min.

   The solution must be chilled to minimize perchloric acid oxidation of cupferron to yellow-green products that coextract and interfere.

7. Add 5 ml of 0.25M cupferron solution, swirl the beaker to mix the solution and to wet the beaker walls with the reagent, then let stand for 3 min to permit the cupferron to break up insoluble metal phosphates.

8. Transfer the solution quantitatively with 10 ml of water to a 125-ml separatory funnel.

9. Continue per Procedure E beginning at step 5.

E. Removal of Interfering Metals by Cupferron Extraction

1. To a 125-ml separatory funnel, add 6 ml of conc $HClO_4$ and 15 ml of water.

2. Pipet a sample aliquot (10 ml or less) containing 5 to 100 μg of orthophosphate

3. Dilute to 30 ml with water, mix by swirling the solution, then immerse the funnel in an ice bath for 3 min.

   The solution must be chilled to minimize perchloric acid oxidation of cupferron to yellow-green products that coextract and interfere.

4. Add 5 ml of 0.25M cupferron mix, and let stand for 3 min.

5. Add 30 ml of chloroform, extract vigorously for 1 min, and discard the lower chloroform phase.

6. Repeat step 5.

7. Rinse the walls of the funnel with about 5 ml of chloroform, swirl the funnel to settle the chloroform, then drain the chloroform completely without removing any of the aqueous phase.

8. Continue the analysis per Procedure F beginning with step 3.

F. Extraction-Spectrophotometric Determination of Orthophosphate

1. Pipet a sample aliquot of 25 ml or less containing 5 to 100 µg of orthophosphate into a 125-ml separatory funnel.

2. Add 6 ml of conc $HClO_4$ and dilute to 35 ml with water.

   Measurements at steps 2, 3, 6, 7, and 9 are not critical. Either Mohr pipets or appropriate graduated cylinders are adequate.

3. Add 5 ml of the ammonium molybdate reagent, mix by swirling, then let stand for 5 min.

4. Pipet exactly 25.00 ml of hexone and extract vigorously for 1 min.

5. Let the two phases separate, then drain and discard the lower aqueous layer.

6. Add 15 ml of water, contact gently for 30 sec, then drain the lower phase.

   In the absence of acids or salts, hexone-water mixtures form a difficult-to-separate emulsion when shaken vigorously. Use a gentle rocking motion to mix the two phases.

7. Repeat step 6.

8. Swirl the hexone solution to settle water droplets clinging to the walls of the funnel. Drain the water completely.

9. Add 15 ml of the chlorostannous acid reagent, extract vigorously for 15 sec, and drain and discard the lower aqueous layer.

10. Wait 15 min for color development.

11. Measure the absorbance against hexone at 625 mμ.

If the solution is cloudy, centrifuge it in a 50-ml centrifuge tube.

Use 5-cm cells for samples in the 1- to 15-μg phosphate range and 1-cm cells for samples in the 20- to 100-μg range. In between 15 and 20 μg, either cell may be used.

12. Record the data and calculate the results as shown on the example worksheet.

REFERENCES

1. D. F. Boltz, Colorimetric Determination of Nonmetals, New York: Interscience, 1951, pp 32-36.

February, 1969

P. A. Anderson
F. A. Duce
S. S. Yamamura

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME ____________________

LOG NUMBER ____________________

ACTIVITY (mR/hr) ____________________

DETERMINATION Phosphate

CHARGE NUMBER ____________________

PROCEDURE P- Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance Vs Hexone	Net Absorbance	Conversion Factor μg/abs. unit	$\mu g\ PO_4^{-3}$ in Aliquot	$\mu g\ PO_4^{-3}$ corrected for Bias			RESULT $\mu g\ PO_4^{-3}/ml$
Blank		0.022							
Std, 50 $\mu g\ PO_4^{-3}$		0.474	0.452	110.62					
std, 75 $\mu g\ PO_4^{-3}$		0.710	0.688	109.01					
			$\bar{X}$	109.82					
Bench Std	1.00 ml	0.644	0.622		68.31	69.11 ± 2.4			69.1 ± 2.4

ANALYZED BY ____________________ DATE ____________________

CALCULATIONS:

$$\text{Conversion Factor} = \frac{\mu g\ PO_4^{-3}}{\text{Net abs.}} = \frac{50}{0.452} = 110.62 \qquad C' = \frac{75}{0.688} = 109.01$$

$$\bar{X} = \frac{110.62 + 109.01}{2} = 109.82$$

$$D = BC = (0.622)(109.82) = 68.31\ \mu g\ PO_4^{-3}$$

$$\text{Result} = \frac{E}{\text{Sample vol.}} = \frac{69.1 \pm 2.4}{1.00} = 69.1 \pm 2.4\ \mu g\ PO_4^{-3}/ml$$

APPROVED BY ____________________

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PLUTONIUM SEPARATION FOR THE ISOTOPE DILUTION MASS SPECTROMETRIC ANALYSIS OF IRRADIATED FUELS

ABSTRACT

This method is designed to separate plutonium from irradiated fuel dissolver samples in a form suitable for analysis in surface ionization mass spectrometers. The sample aliquot, and Pu-242 spike added for the isotope dilution concentration analysis, is made 10$\underline{M}$ in hydrochloric acid; the plutonium is stabilized at the (IV) valence state by sequential treatments with iodide and bromate, and is adsorbed on an anion exchange resin column as the negatively charged chloride [$PuCl_6^=$] complex. The column is washed sequentially with 8$\underline{M}$ HCl, 8$\underline{M}$ HNO_3, and 2$\underline{M}$ HNO_3 to remove diverse ions including fission products, neptunium, and transplutonics[1,2]. The plutonium then is eluted with 0.2$\underline{M}$ HNO_3, evaporated to dryness, and dissolved in 3$\underline{M}$ HNO_3 for transfer to the filament of the mass spectrometer.

APPLICABILITY

This method is applicable to existing nuclear fuels including UO_2 pellets, uranium metal alloys, various uranium cermets, and uranium-plutonium mixed fuels. The known tolerance for uranium is 1000 times the plutonium. Dissolution schemes are not included; however common inorganic acids and fusion melts are acceptable. The procedure is designed for high decontamination of fission products rather than for the quantitative recovery of plutonium. Before separation, the isotope spike which normally is Pu-242 is added, and treatments are included to guarantee isotopic identity. The procedure is designed to separate about 0.5 to 5 μg of total plutonium which is the amount used for triple filament mass spectrometer sources. Smaller amounts can be separated with no changes; larger amounts require scaleup of reagents.

The procedure may be used to separate plutonium solely for isotopic distribution analysis merely by omitting the spike isotope. Because Pu-242 is formed by consecutive neutron captures on Pu-239, highly irradiated fuels require an unspiked analysis to correct the Pu-242 spike addition for the Pu-242 in the sample.

DISCUSSION

Based on quality control samples and on the results of duplicate sample analysis, the main source of error is the remote pipetting apparatus used to deliver the sample. The relative standard deviation at the 1-μg/ml Pu level with a fully automatic remote pipetter[3] delivering 500 μl is 0.8%, and for hand-operated, 500-μl micropipets (Ultrapette-type) is 0.37%. Bias for both the remote pipetter and micropipets is insignificant.

A shielded alpha-tight facility is required to protect personnel against beta-gamma penetrating radiation and alpha contamination when the fuel dissolver sample is handled. This facility need not be elaborate because the only special equipment required is the remotely operated pipetter for the delivery of the initial sample aliquot. Other operations can be performed with simple tong-type manipulators. After the ion exchange column separation of the plutonium from the fission products, an unshielded glove box can be used.

A successful isotope dilution analysis requires chemical identity of the determined component in the sample and added spike before the separation is initiated. In this method, the mixture of sample and spike in a 10<u>M</u> HCl medium is treated sequentially with iodide and bromate. Iodide reduces the plutonium(V) and-(VI) oxidation states to the (IV) state and bromate oxidizes the (III) state to the (IV) state. The (IV) state is stabilized as the hexachloro plutonium(IV), $PuCl_6^=$, complex in this medium.

SAFETY PRECAUTIONS

The samples will contain plutonium and higher transuranics. Take every precaution possible to prevent absorption through the skin or ingestion of these materials (See DISCUSSION).

APPARATUS AND REAGENTS

A. Apparatus

1. Heat Lamp.

2. Ion Exchange Column. A polyethylene column, about 5-mm diam, 25-mm long with a 2.5-ml reservoir at the top, is recommended. A convenient source is the Nalgene Unitary Dropper, manufactured by the Nalge Company, which has a molded bulb. The bulb is easily snipped with a scissors to provide the 2.5-ml

reservoir. Place a small wad of glass wool at the delivery end and add the resin slurry to occupy 1 ml. Wash the resin with 4 ml of 10M HCl.

3. Medicine droppers.

4. Pipets, micro, assorted sizes with control syringe.

5. Pipets, transfer (throwaway type).

6. Stoppers, polyethylene or rubber, size 0.

7. Test tube, centrifuge, 5-ml.

B. Reagents

Note: Prepare all reagents with Analytical Reagents Grade chemicals and distilled water.

1. Anion exchange resin. Use a distilled water slurry of Bio-Rad AG-1 X8, 100 to 200 mesh, chloride-form resin, or equivalent.

2. Hydriodic acid. Dilute 25 ml of 57% HI to 100 ml with water. Keep well stoppered. Discard when the brown color of elemental iodine, caused by air oxidation, is visible.

3. Hydrochloric acid, conc, 10M, and 8M.

4. Nitric acid, 8M, 3M, 2M, and 0.2M.

5. Plutonium-242 spike solution. Pu-242 is obtained through the Division of Research, AEC. The material usually is in the form of a low-fired oxide. Dissolve a quantity of the material in a minimum amount of hot, concentrated perchloric acid and dilute with 6M HCl to a final plutonium concentration of 1 μg/ml. Mix until homogeneous. Distribute the solution to 5-ml glass ampoules and flame seal. This provides long-term storage stability. When aliquots are desired, break open an ampoule and deliver the entire contents, as 500-μl aliquots, into 5-ml test tubes. Evaporation of the solvent hereafter causes no error; however, polyethylene stoppers should be placed in the test tubes to minimize the contamination hazards.

6. Potassium bromate solution. Prepare a saturated solution in water.

7. Standard plutonium solution. Transfer about 500 mg (one issue unit) of highly pure plutonium metal (NBS sample 949) to a 500-ml volumetric flask. The weight of each issue unit is provided with the sample. Dissolve the plutonium in 6M HCl using slight heat after the violent reaction subsides. Dilute to volume with 6M HCl and mix until homogeneous. Transfer a 1000-µl aliquot to a 1000-ml volumetric flask, dilute to volume with 6M HCl, and mix until homogeneous. Distribute this solution to 5-ml glass ampoules and flame seal for storage stability.

   Calculate the exact concentration of the standard plutonium solution by:

   $$C = \frac{WP}{500}.$$

   where

   C = µg/ml of plutonium

   W = weight in mg of the plutonium metal

   P = fractional purity of the plutonium metal.

PROCEDURE

A. Calibration of Pu-242 Spike Solution

Pipet 500 µl each of the Pu-242 spike solution and the standard plutonium solution into a clean 5-ml centrifuge tube. The same dry-filmed pipet is recommended for both solutions to obtain maximum accuracy. Rinse the inside walls of the tube with 6M HCl to ensure that no droplets of the solutions remain unmixed. Evaporate slowly, without spattering, nearly to dryness and transfer the tube to the mass spectrometry laboratory. A minimum of six mixtures is recommended for this calibration.

B. Separation of Plutonium

Note: Steps 2 through 11 require a shielded, alpha-tight facility designed to handle irradiated fuel dissolver solutions. See DISCUSSION.

1. Pipet 500 µl of the Pu-242 spike solution into a 5-ml test tube.	Omit this step if only the isotopic distribution of the plutonium is to be determined.

2.	Add 1.5 ml of conc HCl.	
3.	Transfer the tube to the shielded facility. Pipet a sample aliquot containing from 0.5 to 5 µg of plutonium into the tube.	The volume of the aliquot should be 200 to 1000 µl. If the concentration of plutonium in the original sample exceeds 25 µg/ml, first prepare accurate dilutions using 10M HCl as the diluent.
4.	Add 3 drops of the HI solution, then swirl the tube to mix the contents until homogeneous.	Iodide reduces the (V) and (VI) oxidation states of plutonium to the (IV) state in 10M HCl.
5.	Heat the solution to about 80°C for 10 min under an infrared lamp.	
6.	Let the solution cool for about 10 min; and while slightly above ambient temperature, add 5 drops of saturated potassium bromate solution, swirling the solution between each drop.	Plutonium(III) is oxidized to Pu(IV) giving chemical identity of the plutonium in the sample and the Pu-242 spike. The potassium bromate causes gas formation. Swirling between added drops relieves the gas pressure.
7.	Transfer the solution to the ion exchange column collecting the effluent in any convenient container for disposal.	
8.	Pass three 1-ml portions of 8M HCl through the column and discard the effluent.	Most extraneous ions, fission products and fuel components, elute from the column.
9.	Pass ten 1-ml portions of 8M HNO_3 through the column and discard the effluent.	Uranium elutes from the column in this step and step 10.
10.	Pass three 500-µl portions of 2M HNO_3 through the column and discard the effluent.	
11.	Place a 5-ml centrifuge tube under the column and elute the plutonium with four 500-µl portions of 0.2M HNO_3.	

12. Slowly evaporate to dryness under an infrared lamp.

13. Dissolve the residue in 1 drop of 3<u>M</u> HNO_3, stopper with a polyethylene stopper, and transfer the tube to the mass spectrometry laboratory.

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3. F. W. Dykes, J. P. Morgan, W. G. Rieder, The Remote Analytical Facility Model "B" Pipetter, USAEC Report IDO-14456, Atomic Energy Division, Phillips Petroleum Company, (October 1958).

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April 1969

SPECTROPHOTOMETRIC DETERMINATION OF SILICON

ABSTRACT

Silicon, as monosilicic acid and disilicic acid, is reacted with molybdate in an acid medium to form silicomolybdate. The yellow silicomolybdate is reduced to molybdenum blue and measured at 810 mμ. This basic procedure is used alone or in various combinations with three pretreatments to accommodate different sample types. Selective determinations of reactive (monosilicic and disilicic acids) silicon, total soluble silicon (reactive silicon species plus polysilicic acids), and total silicon (reactive silicon plus polysilicic acids plus particulate silicon) are possible.

APPLICABILITY

This method, designed for maximum versatility, is applicable to natural and plant water and to solutions of aluminum, stainless steel, and zirconium salts with or without uranium. Silicon exists as monosilicic acid, disilicic acid, a variety of higher polysilicic acids, and colloidal silica in aqueous medium. This method, with a few exceptions, can be used to determine total silicon and to selectively determine the sum of the reactive monosilicic acid and disilicic acid.

The great versatility of this method stems from the use of a cation resin treatment (Procedure E), a sodium hydroxide treatment (Procedure F), and a boric acid-cation resin treatment (Procedure G) in conjunction with the familiar molybdenum blue colorimetric measurement of silicon (Procedure H). The molybdenum blue procedure is used alone and in various combinations with Procedures E, F, and G to provide five analysis schemes (Figure B-9 and Table B-V). Table B-V defines the applicability of each analysis scheme and summarizes the effects of diverse ions on each. Careful study of Table B-V shows that analysis scheme IV (Procedures E plus F plus H) is limited to the determination of total soluble silicon, rather than total silicon and that scheme V (Procedures G plus H) is limited to the determination of total silicon only. The limitation on analysis scheme IV is imposed by the resin treatment which employs a filtration that removes particulate silica. In fluoride solutions, silicon exists predominantly as a fluosilicate which yields the reactive monomer upon the addition of boric acid. Therefore, analysis of fluoride solutions by scheme V is assumed to give total silicon only.

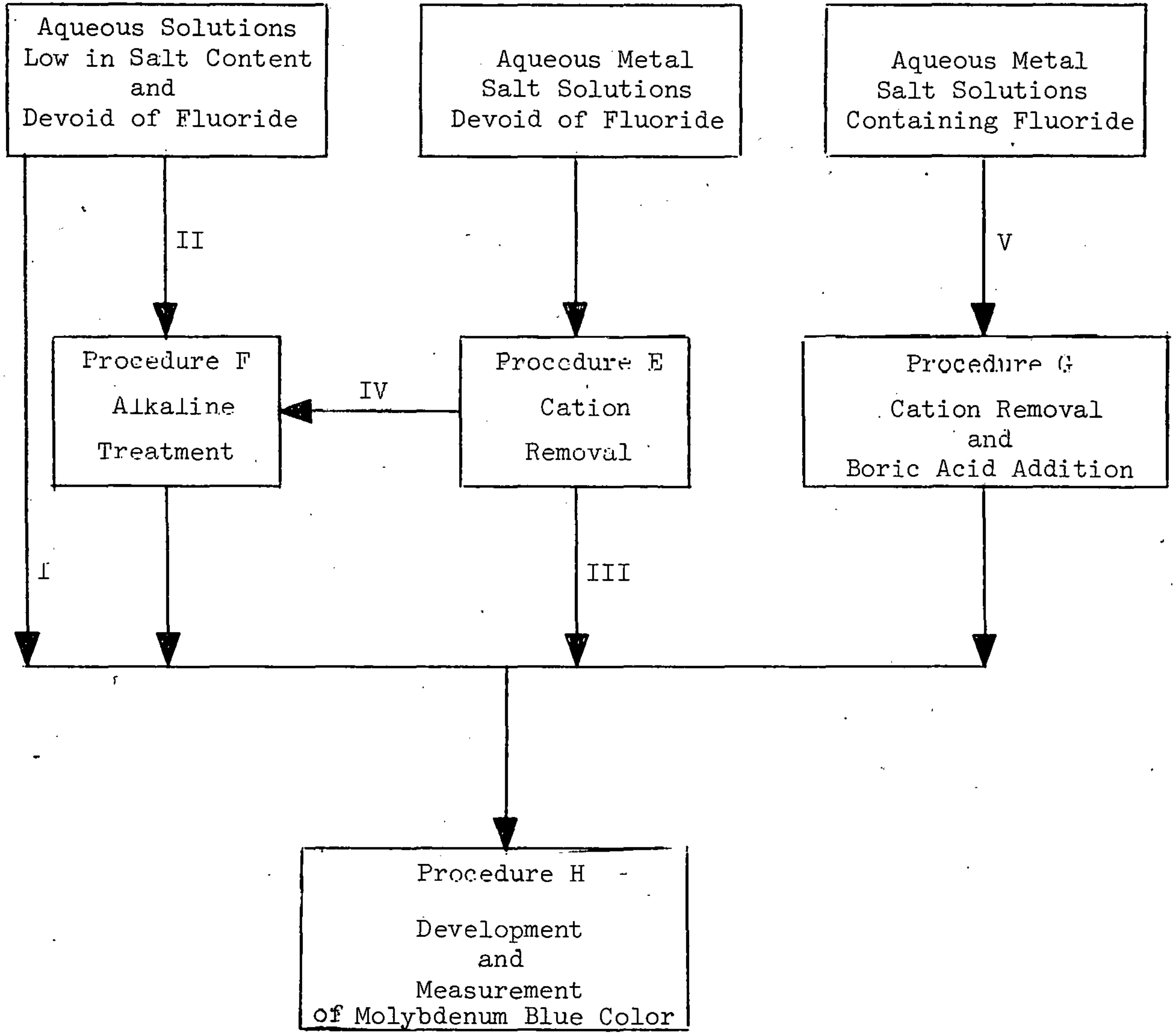

Fig. B-9 Diagram of analysis schemes.

TABLE B-V

APPLICABILITY OF THE VARIOUS ANALYSIS SCHEMES

Analysis Scheme and Application	Diverse Ion Effects[a]
I. Procedure H; Determination of the sum of the reactive monosilicic and disilicic acids in aqueous solutions of low salt content and devoid of fluoride. Samples containing interfering amounts of Cu(II) must be analyzed by analysis scheme III. Samples containing Fe are most conveniently analyzed by analysis scheme III.	The tolerance limits expressed as the diverse ion to silicon molar ratio are at least 950 to 1 for Al; at least 185 to 1 for Co, Cr(III, VI), Fe[b], lanthanides[c], Mn, Ni, and Zn, and at least 25 to 1 for As(V), Hg, Sn(IV), U(VI), and V(V). Copper absorbs at 810 mμ; hence, its tolerance ratio is only 20 to 1. Tin(II) immediately reduces the molybdate and must be absent. Up to 10 mmole of Cl^{-1}, ClO_4^{-1}, NO_3^{-1}, and SO_4^{-2} and 0.005 mmole of PO_4^{-3} per sample aliquot do not interfere. Citrate, fluoride, oxalate, and tartrate must be absent.
II. Procedures F plus H; Determination of total silicon in aqueous solutions of low salt content and devoid of fluoride. Samples containing interfering amounts of Cu(II) must be analyzed by analysis scheme (IV).	Anion tolerance same as analysis scheme I. Cations which form insoluble hydroxides must be absent. Use analysis scheme IV for samples containing cations that form insoluble hydroxides.
III. Procedures E plus H; Determination of the sum of reactive monosilicic and disilicic acids in aqueous mineral salt solutions devoid of fluoride.	Anion tolerance same as analysis scheme I. Metals, except those in the form of anionic complexes, are removed by the cation resin. For example, 2 mmole of Al, 1.5 mmole of an equimolar Fe, Cr, Ni mixture, 0.8 mmole U, and 0.5 mmole Bi are removed sufficiently to enable application of the alkaline treatment. The tolerance for metals that form anionic complexes is the same as analysis scheme I.

TABLE B-V (Continued)

	Analysis Scheme and Application	Diverse Ion Effects[a]
IV.	Procedures E plus F plus H; Determination of total soluble silicon in aqueous metal salt solutions devoid of fluoride.	As analysis scheme III.
V.	Procedures G plus H; Determination of total silicon in metal salt solutions containing fluoride.	Except for those that exist as stable anionic complexes, cations are removed by the resin. This analysis scheme has been applied successfully to fluoride solutions of Zircaloy and to synthetic "Coprocess" Zr-Al fuel solutions. Niobium at 10 to 1 and Sn(IV) and Ti at 25 to 1 molar ratio do not interfere. At least 5 mmole of fluoride can be present in the sample aliquot without adverse effect.

---

[a] Based on diverse ion studies at a silicon level of 30 µg (0.001 mmole).

[b] Because the molybdenum blue color is slow to form, the minimum color development time is 1.5 hr.

[c] Lanthanide oxalates are insoluble, so the sample must be centrifuged or filtered.

The practical range of the method is 5 to 100 µg of silicon; however, the lower limit may be dropped to 1 µg of silicon with extreme care against contamination. The volume of samples analyzed by analysis scheme I is up to 75 ml; hence, the practical lowest determinable silicon concentration is 0.07 µg/ml (2.5×10^{-6}M). The maximum sample volume for schemes II, III, and IV is 25 ml and the lowest practical determinable silicon concentration is 0.2 µg/ml. The maximum sample volume for scheme V is 5 ml and the lowest practical determinable silicon concentration is 1 µg/ml.

A method for the determination of micro concentrations of silicon is Method Si-1, "Gravimetric Determination of Silicon", in INC Analytical Chemistry Manual.

DISCUSSION

The principal pretreatments in the method are (a) the removal of cations with a cation exchange resin in the acid form, (b) the alkaline conversion of all silicon species to the reactive monomer, and (c) the decomposition of silicon fluoride complexes with boric acid in the presence of cation exchange resin. In the color development phase of the method, silicic acid is reacted with molybdate at pH 1.3 to form the yellow silicomolybdate; an oxalic acid-tartaric acid complexing reagent is added; and the yellow silicomolybdate is reduced to molybdenum blue which is measured at 810 mμ. The alkaline pretreatment, step b, is omitted if a selective determination of the sum of monosilicic and disilicic acid is to be performed. Boric acid is added, treatment c, to samples containing fluoride to convert nondeterminable fluosilicates to monosilicic acid.

Cations affect the determination in several ways. They may hydrolyze at pH 1.3, form insoluble molybdates, form insoluble hydroxides that prevent complete conversion of soluble silicon to monosilicic acid, form insoluble oxalates or tartrates, or absorb at 810 mμ. Cation exchange removal is used to circumvent these difficulties. To minimize the introduction of common anions, the cation exchange resin is also used to neutralize the base from the alkaline conversion treatment.

The common anions chloride, nitrate, perchlorate, and sulfate do not interfere at levels up to 10 mmole per sample aliquot. Above this level, they prevent quantitative formation of silicomolybdate and cause low results. Only the monosilicic acid and disilicic acid react with molybdate; hence, the highor polysilicic acids must be converted to monosilicic acid if total silicon is to be determined. This conversion can be accomplished by reaction with hydrofluoric acid, by a basic fusion, or by reaction with a hot sodium hydroxide solution. The decomposition in a hot alkaline solution at pH 12 to 13 was found to be best.

Silicic acid and molybdate react in a dilute acid solution. The optimum pH for this reaction is 1.3±0.1. Because the addition of molybdate to alkaline samples gives low results, the pH of the sample must be adjusted to between pH 1.0 and 1.3 before the molybdate reagent is added. The reaction of molybdate with monosilicic acid and disilicic acid is reported to be complete in 75 sec and 10 min, respectively[1]. These differing reaction rates can be used to establish the presence and approximate level of the monomer and/or the dimer.

In fluoride solutions, silicon exists as a fluosilicate which does not react with the molybdate reagent. The silicon-fluoride complex is decomposed by a saturated solution of boric acid. When boric acid is added to a Zr-Al-F solution such as that from the "Coprocess", a precipitate forms upon the addition of the molybdate reagent. The precipitate formation and low recovery of silicon is avoided by reacting the sample with the boric acid in the presence of cation exchange resin.

The oxalic acid-tartaric acid complexing reagent is added to the sample to complex the excess molybdate reagent and to selectively break up reducible molybdate complexes such as phosphomolybdate. The complexing reagent also slowly breaks up the silicomolybdate complex; therefore, the time interval between the addition of the complexing reagent and the reducing reagent must be controlled between 30 sec and 1 min. If both the complexing and reducing reagents are added together, the phosphomolybdate complex is not completely destroyed.

A tricomponent reducing mixture of bisulfite, sulfite, and 1-amino-2-naphthol-4-sulfonic acid is recommended[2] for this method. It was confirmed to be the most reliable of the many reducing reagents suggested in the literature. Maximum color intensity (complete reduction of the silicomolybdate complex to molybdenum blue) is obtained in 20 min and the color is stable for at least 16 hr.

Variations in temperatures over the range 24°±12°C[3] do not affect the color development.

Silica (glass) is very soluble in alkaline medium and sparingly soluble in water. Basic solutions should be diluted by weight in plastic ware and stored in plastic ware. All reagents must be stored in polyethylene bottles. The cation exchange resin must be freshly charged with 6M HCl, washed with water until the effluent is neutral, then stored in a plastic container.

APPARATUS AND REAGENTS

A. Apparatus

1. Absorbance cells, 1- and 5-cm, of borosilicate glass or silica.
2. Beakers, polyethylene, 50- and 100-ml.
3. Bottles, polyethylene, assorted sizes.
4. Cover glass, polyethylene.

5. Filtrator, Fisher, low form.

6. Flasks, volumetric, 100-ml.

7. Graduated cylinder, pharmaceutical, 10-ml.

8. Hot plate, Chromalox.

9. Magnetic stirrer and plastic-coated magnetic stirring bars.

10. Medicine droppers, polyethylene.

11. Millipore filtering apparatus, 25-mm with 25-mm, 0.45-μ Millipore filters. The stem of the filter holder base is extended with 6- or 7-mm tubing to a total length of 7 in. to facilitate filtrations into beakers or bottles.

12. pH meter with a glass-calomel electrode system.

13. Pipets, macro and micro, assorted sizes, with control syringe and rubber suction bulb.

14. Pipets, polypropylene, assorted sizes.

15. Spectrophotometer, Beckman DU or DK, or Cary Model 14.

B. Reagents

Note: Prepare all reagents with Reagent Grade chemicals and distilled water. Store all reagents in polyethylene bottles.

1. Ammonium hydroxide, silicon-free, 6±1M. Deliver 500 ml of conc NH_4OH to a large crystallizing dish and 250 ml of water to a 1-liter plastic beaker. Place the beaker in the center of the crystallizing dish and add a magnetic stirring bar to the beaker. Place the crystallizing dish plus beaker, enclosed in a sealed polyethylene bag, on a magnetic stirrer and let stand overnight with continuous stirring. Transfer the ammonium hydroxide solution from the beaker to an 8-oz screw-cap, polyethylene bottle.

2. Ammonium molybdate, 10% (w/v) solution. Dissolve 50 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 500 ml of water and filter through a 0.45-μ membrane filter.

3. Boric acid, saturated solution. Add 50 g of H_3BO_3 to 950 ml of water in a 32-oz polyethylene bottle, place the bottle in a hot water bath, stir until dissolution is complete, then cool to room temperature.

4. Buffer, standard, pH 2.00.

5. Complexing reagent, 0.75<u>M</u> oxalic acid-0.75<u>M</u> tartaric acid. Dissolve 49 g of oxalic acid and 56 g of tartaric acid in water and dilute to 500 ml with water.

6. Diverse ion matrix for silicon bench-control standards. Appropriate matrices will be furnished by the Quality Control Laboratory as samples are received for analysis.

7. Nitric acid, 6<u>M</u>.

8. Phenolphthalein indicator solution, 1%. Dissolve 1.0 g of the solid reagent in 100 ml of ethanol.

9. Reducing reagent. Dissolve 27 g of $NaHSO_3$ and 2 g of NaOH in 225 ml of water, add 0.5 g of 1-amino-2-naphthol-4-sulfonic acid, stir until dissolved, dilute to 250 ml, and filter through a 0.45-µ membrane filter.

10. Resin, cation, acid-form. Purify Dowex 50W-X8 (or equivalent), 50- to 100-mesh, resin as described in Procedure <u>D</u>.

11. Silicon standard stock solution, 1.000 mg Si/ml. Fuse 0.5350 g of SiO_2 with 2 g of anhydrous Na_2CO_3 in a platinum crucible. Dissolve the melt in water with mild heating. Meanwhile, dissolve 1 g of NaOH in 50 ml of water in a 100-ml polyethylene beaker. Quantitatively transfer the silicon solution to a 250-ml volumetric flask with water rinses. Dilute the solution to about 200 ml with water, add the sodium hydroxide solution, dilute to volume with water, mix well, then immediately transfer the solution to an 8-oz polyethylene bottle.

12. Silicon calibration standard solution I, 75 µg Si/ml. Pipet 15 ml of the silicon stock solution into a 200-ml volumetric flask. Add about 100 ml of water and 1 g of NaOH dissolved in 50 ml of water, dilute to volume with water, mix well, then immediately transfer the solution to an 8-oz polyethylene bottle.

13. Silicon calibration standard solution II, 50 µg Si/ml. Prepare as above except use 10.00 ml of the silicon stock solution.

14. Silicon bench-control standards. Prepare dilutions of the silicon stock solution in the same manner as for the calibration standards, <u>12</u> and <u>13</u>, to cover the concentration range 5 to 100 µg Si/ml.

15. Sodium hydroxide, 50% (w/w), silicon-free. Fisher's 50% (w/w) NaOH has been found to be satisfactory.

PROCEDURE

Note: Use distilled water throughout the procedure and use plasticware wherever possible.

A. Preparation of Reagent Blank

Process a reagent blank with each set of samples by the same analysis scheme as that used to analyze the sample. Substitute 5 ml of water for the sample aliquot.

B. Calibration

Process a pair of standards with each series of samples. Use 1.00-ml aliquots of standards I and II with sample aliquots containing more than 10 μg of silicon and 200-μl aliquots of the same standards for sample aliquots containing less than 20 μg of silicon. Either set of standards is applicable in the range 10 to 20 μg of silicon. Divide the micrograms of silicon in each standard by its respective net absorbance to obtain the calibration factor. The two factors must agree within specified limits and the average of the two factors must agree with the established conversion factor within the specified limits. If both or either of these specifications are not met, process another pair of standards. Report to your supervisor if difficulties persist.

The method may be used only infrequently so sufficient current calibration data may not be on hand to specify realistic requirements for the calibration. During the development of this method, a precision of 1.25% relative standard deviation was observed by one chemist on measurements of 30- to 40-μg amounts of silicon with a Cary Model 14 recording spectrophotometer. On the basis of this observation, the difference between the two calibration factors should not exceed about 4 relative percent. The observed factor is 113.8±1.4 μg Si/abs unit for 1-cm cell measurements on the Cary Model 14 spectrophotometer. It will be slightly higher if a less sensitive instrument is used.

C. Analysis of Bench-Control Standards

Process the bench standards, spiked with diverse ion matrix when necessary, using the same analysis scheme as that used to analyze the samples. Report the results to the Quality Control Laboratory for calculation of bias and precision.

D. Resin Purification

Fill a large column capable of holding 200 ml of resin to within 3 in. of the top with the resin slurry. Pass 1 liter of 6M HCl slowly through the column, then 1 liter of distilled water. Store the resin in a plastic container.

E. Cation Removal for Analysis Schemes III and IV

1. Add 10 ml of cation resin to a 50-ml polyethylene beaker.	The wet resin is easily dispensed with a small plastic scoop.
2. Pipet a sample aliquot, 25-ml or less, containing 5 to 100 μg of silicon, onto the resin and mix by magnetic stirring for 1 min.	
3. Using a Fisher filtrator and a Millipore filtering apparatus, filter the sample through a 0.45-μ membrane filter. Collect the filtrate in a 100-ml polyethylene beaker for analysis scheme III or in a 2-oz polyethylene bottle for analysis scheme IV.	
4. For analysis scheme IV, proceed to step 2 of Procedure F. For analysis scheme III, proceed to step 2 of Procedure H.	

F. Alkaline Treatment for Analysis Schemes II and IV

1. Pipet a sample aliquot, 25-ml or less, containing 5 to 100 μg of silicon, into a 2-oz polyethylene bottle.	A glass pipet can be used.
2. Add 2 drops phenolphthalein indicator, then add 19M NaOH with a polyethylene medicine dropper until the sample turns pink. Add 5 drops more.	

3.	Heat the sample in a boiling water bath for 20 min.	
4.	Cool the sample to room temperature, add Dowex 50W-X8 resin until the pink color disappears, then add an additional 5 ml.	The wet resin is easily dispensed with a tiny plastic scoop.
5.	Filter the sample through a 0.45-µ membrane filter into a 100-ml polyethylene beaker. Use a Fisher filtrator and a Millipore filtering apparatus.	The sample is acid at this point so glass filtering apparatus may be used. The volume of the filtered sample should not exceed 70 ml.
6.	Proceed to step <u>2</u> of Procedure <u>H</u>.	

G. Cation Removal and Boric Acid Addition for Analysis Scheme V

1.	Add 10 ml of cation resin to a 50-ml polyethylene beaker.	The wet resin is easily dispensed with a small plastic scoop.
2.	With a polyethylene pipet, add a sample aliquot, 5-ml or less, containing 5 to 100 µg of silicon, to the beaker and mix.	
3.	Add 40 ml of the boric acid reagent, mix by magnetic stirring, let stand for 30 min, then mix again.	The boric acid will decompose the silicon-fluoride complex in about 30 min.
4.	Filter the sample through a 0.45-µ membrane filter into a 100-ml polyethylene beaker. Use a Fisher filtrator and a Millipore filtering apparatus.	Boric acid has complexed the fluoride; so a glass filtering apparatus may be used. The volume of the filtered sample should not exceed 70 ml.
5.	Proceed to step <u>2</u> of Procedure <u>H</u>.	

H. Development and Measurement of the Molybdenum Blue Color

1.	Pipet a sample aliquot, 75-ml or less, containing 5 to 100 μg of silicon, into a 100-ml polyethylene beaker.	A glass pipet can be used. Steps 1 through 6 must be completed without interruption.
2.	Adjust the pH to 1.1±0.1 with 6M HNO_3.	
3.	Add 10 ml of the molybdate reagent with a pharmaceutical graduated cylinder.	If a precipitate forms, the sample must be analyzed by analysis scheme IV.
4.	Adjust the pH to 1.3±0.1 with either 6M HNO_3 or 6M NH_4OH. Use a polyethylene medicine dropper.	
5.	Wait 10 min for the yellow silicomolybdate to form.	The silicomolybdate is stable for about 30 min, so proceed to step 6 immediately after the 10-min wait.
6.	With a graduated cylinder, add 10 ml of the complexing reagent. Wait 30 sec and add 2 ml of the reducing reagent. Stir the solution continuously during this step.	The time between the addition of the complexing reagent and the addition of the reducing agent is critical and must be controlled. Low results will be obtained if the interval is much over 1 min.
7.	Wait 20 min for color development.	If the sample contains iron and the iron has not been removed, wait 1.5 hr for color development.
8.	Transfer the sample to a 100-ml volumetric flask and dilute to volume with water.	
9.	Measure the absorbance against water at 810 mμ (infrared source and detector) or at 790 mμ (visible source and detector).	Best results are obtained with an IR source and detector. Use 1-cm cells for samples containing more than 20 μg of silicon and 5-cm cells for samples with less than 10 μg of silicon. In between, either cell may be used; however, standards and samples must be read alike. The color is stable for at least 16 hr.

10. Record the data and calculate the results as described in the example work sheet. Report 3 significant figures but not more than 2 decimal places.

REFERENCES

1. Ralph K. Iler, The Colloidal Chemistry of Silicon and Silicates, Ithaca, New York: Cornell University Press, 1955.
2. Anton B. Carlson, Charles V. Banks, "Spectrophotometric Determination of Silicon in The Presence of Zirconium, Beryllium, Aluminum,and Calcium", Anal. Chem., 24 (1952).
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April, 1969
F. A. Duce
S. S. Yamamura

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME

LOG NUMBER

ACTIVITY (mR/hr)

DETERMINATION Silicon

CHARGE NUMBER

PROCEDURE Si-Color-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance	Conversion Factor	mg Si in Aliquot Analyzed	mg Si corrected for Bias				RESULT mg Si/ml
Si Std 75 mg		0.663	113.12						
Si Std 50 mg		0.447	111.86						
		$\bar{X}$	112.49						
Dissolver Feed	100 ml	0.372		38.47	38.5 ±2.0				385 ±20

ANALYZED BY DATE

CALCULATIONS:

$$\text{Conversion Factor} = \frac{\text{mg Si in Std}}{\text{absorbance}}$$

$$B = \frac{75}{0.663} = 113.12$$

$$B' = \frac{50}{0.447} = 111.86$$

$$\bar{X} = 0.5(B+B') = 0.5(113.12 + 111.86) = 112.49$$

Dissolver Feed:

$$C = AB = 0.372\,(112.49) = 38.47 \text{ mg Si}$$

$$\text{Result} = \frac{D}{\text{Sample vol.}} = \frac{38.5 \pm 2.0}{0.100} = 385 \pm 20 \text{ mg Si/ml}$$

APPROVED BY

COLORIMETRIC DETERMINATION OF SULFUR DIOXIDE IN AIR

ABSTRACT

Air is drawn through a solution of potassium tetrachloromercurate(II) which reacts with sulfur dioxide to form a stable dichlorosulfitomercurate(II) complex[2,3]. A magenta color with an absorbance maximum at 548 mμ develops when this complex reacts with formaldehyde-pararosaniline reagent[5].

APPLICABILITY

This method is specifically designed for air samples; however, it can be applied to other materials (eg metals, fungicides, pharmaceuticals, and agricultural products[1,5]. Heavy metal ions are masked by ethylenediaminetetracetic acid. The range of the method is 5 to 40 μg of sulfur dioxide, and the maximum practical sample aliquot is 10 ml of the air absorbent solution. Therefore, the lowest determinable concentration is 0.5 μg SO_2/ml of this solution. The maximum volume of air passed through the solution is 3600 liters (2.5 l/min for 24 hr). The sensitivity limit, therefore, is 0.0014 μg/ml of air. A common interference is nitrogen dioxide in excess of 2 μg/ml in the final solution[3]. This interference is nullified by adding sulfamic acid[4].

DISCUSSION

The magenta complex formed by the reaction of formaldehyde and pararosaniline with sulfur dioxide (in the form of dichlorosulfito-mercurate(II) in this method) is complete in 30 min and is stable for at least 1 hr. For best results, samples should be measured within this 30- to 60-min period[5]. Increasing concentrations of tetrachloromercurate suppress the color formation and thus, its level is fixed in the method[5]. Dichlorosulfitomercurate solutions are unstable with time and exhibit sulfur dioxide losses of 1% per day. When analyses are delayed after sample collections, this correction should be made.

SAFETY PRECAUTIONS

Tetrachloromercurate is highly poisonous. If spilled on the skin, flush immediately with large amounts of water.

APPARATUS AND REAGENTS

A. Apparatus

1. Absorbance cells, 1-cm, Pyrex.
2. Flasks, volumetric, 25-ml.
3. Pipets, macro and micro, assorted sizes with control syringe and suction bulb.

4. Spectrophotometer, Beckman Model DU or DK, or Cary Model 14.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water unless otherwise specified.

1. Formaldehyde solution, 0.2%. Dilute 0.5 ml of 40% formaldehyde to 100 ml with water. Prepare fresh daily.

2. Hydrochloric acid, conc.

3. Pararosaniline, purified 0.2% stock solution. In a separatory funnel, equilibrate 100 ml of 1-butanol and 100 ml of 1M HCl. Weigh 100 mg of pararosaniline hydrochloride (PRA) (Fisher P-389 or equivalent) in a small beaker, then add 50 ml of the equilibrated 1M HCl and let the solution stand for several minutes. To a 125-ml separatory funnel, add 50 ml of the equilibrated 1-butanol. Transfer the PRA solution to the funnel and extract. A violet impurity transfers to the upper 1-butanol phase. Transfer the lower (aqueous) phase into another separatory funnel, add 20 ml of equilibrated 1-butanol and extract again. Repeat the extraction with three separate 10-ml portions of equilibrated 1-butanol. This procedure removes most of the violet impurity that contributes to the blank. After the final extraction, filter the aqueous phase through a cotton plug into a 50-ml volumetric flask and dilute to volume with 1M HCl. This stock reagent is yellowish red. The concentration of the PRA stock solution is determined once for each batch as follows: 1 ml of the stock solution is diluted to 100 ml with distilled water; a 5-ml aliquot from the 100-ml solution is transferred to a 50-ml volumetric flask; 5 ml of 1M sodium acetate-acetic acid buffer (pH 4.69) is added; and the mixture is diluted to 50 ml with distilled water. After 1 hr, the absorbance is determined in a 1-cm cell at 540 mμ with air as a reference. Calculate the percent "purity" of the PRA by

$$\%\text{PRA "purity"} = (10)(K)(\text{absorbance})$$

For 1-cm cells and 0.04-mm slit width in a Beckman DU spectrophotometer, K = 21.3[5]. K for other systems can be determined by comparison with a solution measured as described above or 100% PRA can be assumed on material that has been purified as above and then recrystallized several times from a caustic solution[5].

4. Pararosaniline reagent, 0.016%. Add 20 ml of the stock PRA solution to a 250-ml volumetric flask plus an additional 0.2 ml of stock solution for each percent that the PRA assays below 100%. Add 25 ml of 3<u>M</u> H_3PO_4, dilute to volume with distilled water and store in an amber bottle. This reagent is stable for at least 9 months.

5. Potassium tetrachloromercurate (TMC) absorbing reagent, 0.04M. Dissolve 10.90 g of $HgCl_2$, 5.96 g of KCl, and 0.07 g of ethylenediaminetetracetic acid disodium salt (EDTA) in water and dilute with water to 1 liter in a volumetric flask.

6. Sulfamic acid, 0.6%. Dissolve 0.60 g of sulfamic acid in 100 ml of distilled water. This reagent should be prepared daily.

7. Sulfur dioxide standard stock solution, 400 µg SO_2/ml. Dissolve 0.650 g of $NaHSO_3$ and 2 g of NaOH in 500 ml of water. Add 50 ml of glycerine to stabilize the solution and dilute to 1 liter with water.

8. Sulfur dioxide calibration standards. Prepare aqueous dilutions of the sulfur dioxide standard stock solution as follows:

   a. Standard I, 20 µg SO_2/ml. Dilute 5.00 ml of the stock solution to 100 ml with 5% glycerine-0.05<u>M</u> NaOH solution.

   b. Standard II, 30 µg SO_2/ml. Dilute 7.50 ml of the stock solution to 100 ml with 5% glycerine-0.05<u>M</u> NaOH solution.

<u>PROCEDURE</u>

A. Blank

Prepare the reagent blank per procedure <u>D</u> beginning at step <u>2</u>.

B. Calibration

Process 1.00-ml aliquots of each of the two standards with each series of samples starting at step <u>2</u> of procedure <u>D</u>. Divide the micrograms of sulfur dioxide in each standard by its corresponding absorbance to obtain the conversion factors. The difference between the two factors should not exceed limits set by the Quality Control Laboratory. The average factor should agree with the established conversion factor within specified limits. When the absorbance is read at 548 mµ against the reagent blank, the conversion factor should be about 36 µg/absorbance unit. If both of these specifications are not met, reprocess the pair of calibration standards. Contact your supervisor if difficulties still are experienced.

C. Sampling

Pipet exactly 10 ml of 0.04M potassium tetrachloromercurate solution into a midget impinger. Aspirate the air sample through the absorber at a rate of 0.2 to 2.5 liter/min. The sampling time period may be a few minutes to 24 hr. If the period is lengthy, add water at the end of the period to restore that lost by evaporation. A 0.05M NaOH-5% glycerine solution can be used instead of the potassium tetrachloromercurate solution as the absorbent. Its disadvantage is that it foams at high flow rates.

D. Determination of Sulfur Dioxide

NOTE: Use distilled water throughout the procedure.

1. Pipet a sample aliquot containing the equivalent of 5 to 40 μg of SO_2 into a 25-ml volumetric flask.	
2. Add a volume of the TMC solution equal to 10 ml minus the sample aliquot volume.	Add 10 ml if the absorbent solution is not the TMC solution. Neutralize with NaOH or HCl to pH 7 if the solution is not TMC.
3. Add 1 ml of 0.6% sulfamic acid and allow a 10-min reaction.	This destroys nitrite formed from oxides in nitrogen.
4. Add 2 ml of the 0.2% formaldehyde solution.	Prepare this solution fresh daily.
5. Add 5 ml of the 0.016% PRA reagent.	
6. Dilute to volume with water and mix to obtain a homogeneous solution.	Shake and invert the flask at least 10 times.
7. Let stand for 30 min and measure the absorbance within 1 hr in a 1-cm cell at 548 mμ against the reagent blank.	Adjust the slit width and sensitivity on the spectrophotometer so the reagent blank reads zero.

8. Record the data and calculate the results as shown on the example worksheet. Report all results to three significant figures.

REFERENCES

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June 1969

I. L. Doggett

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME ____________

LOG NUMBER ____________

ACTIVITY (mR/hr) ____________

DETERMINATION Sulfur Dioxide

CHARGE NUMBER ____________

PROCEDURE SO_2 - Color-1

SPECIAL INSTRUCTIONS:

SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	A Absorbance	B conversion Factor	C µg SO_2 in Aliquot Analyzed	D	E	F	G	RESULT µg SO_2/ml
Rgt Blank		0							
Std, 20 µg		0.552	36.23						
std, 30 µg		0.835	35.93						
		$\bar{X}$ =	36.08						
001	10 ml	0.380		13.7					1.37

ANALYZED BY ____________ DATE ____________

CALCULATIONS:

$$B = \frac{\mu g\ SO_2 \text{ in std}}{\text{net Abs}} = \quad B' = \frac{20}{0.552} = 36.23$$

$$B'' = \frac{30}{0.835} = 35.93$$

$$\bar{X} = 0.5(B' + B'') = 0.5(36.23 + 35.93) = 36.08$$

Sample 001

$$C = 0.380(36.08) = 13.7 \ \mu g\ SO_2$$

$$\text{Result} = \frac{C}{\text{Samp Vol}} = \frac{13.7}{10} = 1.37 \ \mu g\ SO_2/ml$$

APPROVED BY ____________

INC Analytical Chemistry Manual
TBP-Vol-1; January 1969

TITRIMETRIC DETERMINATION OF TRIBUTYLPHOSPHATE IN KEROSENE BY AN ACID SATURATION METHOD

ABSTRACT

When contacted with 8M HNO_3, a tributylphosphate (TBP)-kerosene solution extracts nitric acid in amounts directly proportional to the TBP concentration. Titrimetric measurement of the extracted acid with standard base gives a measure of the TBP concentration. The proportionality is constant for TBP concentrations in the range 3 to 12 volume percent. Above this range, a correction is required. TBP-kerosene solutions containing interfering levels of extractable metal ions are scrubbed with a 0.1M ammonium citrate solution before analysis.

APPLICABILITY

This method based on the procedures of Allen and DeSesa[1] and Brown[2] is designed specifically for the determination of tributylphosphate (TBP) in kerosene medium. Tributylphosphate concentrations between 3 and 50 (v/v)% are determinable. Most metal ions are not extracted into TBP-kerosene solutions at high enough concentrations to cause interference. Exceptions are Np(IV, VI), Pa(V), Pu(IV,VI), Th(IV), and U(IV, VI). Uranium, for example, interferes at concentrations exceeding 0.5 g/liter and must be scrubbed out initially with a 0.1M citrate solution.

DISCUSSION

A TBP-kerosene solution extracts nitric acid in amounts proportional to the TBP concentration. This relationship holds for TBP concentrations up to about 12% when the TBP-kerosene solution is contacted three times with 8±0.5M HNO_3. At TBP concentrations above 10%, results tend to be slightly low and corrections based on quality control data are applied. This is caused by a significant increase in the volume of the TBP-kerosene phase due to the extraction of nitric acid; hence, less than a proportionate amount of acid is present in a unit volume of the acid-contacted TBP-kerosene solution that is titrated with the standard sodium hydroxide.

Two potential sources of error are incomplete separation of the TBP-kerosene and 8M HNO_3 phases and too rapid titration near the bromthymol blue end point. As the end point is approached, the blue color appears, then fades slowly. The titration must be taken to a blue color that remains for 2 min.

SPECIAL SAFETY PRECAUTIONS

The extraction of the TBP-kerosene sample with 8M HNO_3 is potentially hazardous. Wear rubber gloves and tightly secure the stopper of the separatory funnel. Release the pressure in the separatory funnel periodically to eliminate excessive pressure build up.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, Griffin, low form, 250-ml.
2. Buret, 10-ml, graduated in 0.05-ml increments.
3. Buret, 25-ml, graduated in 0.10-ml increments.
4. Funnels, separatory, 125-ml, with Teflon-plugged stopcocks.
5. Magnetic stirrer and plastic-coated stirring bars.
6. Pipets, volumetric, 5- and 25-ml.

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water.

1. Ammonium citrate solution, 0.1M. Dissolve 5.65 g of diammonium hydrogen citrate in water and dilute to 250 ml.
2. Bromthymol blue indicator, 0.05 (w/v)%. Triturate 0.1 g of the dry indicator with 7.5 ml of 0.02M NaOH and dilute to 200 ml with water.
3. Nitric acid, 8.0±0.5M.
4. Sodium hydroxide, standard, 0.200N.
5. Tributylphosphate standard 5.0 (v/v)%. Measure 50 ml of reagent grade TBP in a 50-ml volumetric flask. Transfer the TBP to a 1-liter volumetric flask with kerosene rinses and dilute to volume with kerosene.
6. Tributylphosphate bench standards. Prepare four bench standards with TBP concentrations in the range of 2 to 15 (v/v)%. Measure the appropriate volume of TBP for each standard and dilute to 1 liter with kerosene.

PROCEDURE

A. Determination of Titration Blank

A blank determination is not required for this method.

B. Determination of TBP Conversion Factor

The TBP conversion factor must be determined in duplicate by each shift for every new batch of 8M HNO_3. Use 25-ml aliquots of the 5.0 (v/v)% TBP standard and follow Procedure D. Report the results to the Quality Control Laboratory which will assign a TBP conversion factor to the 8M HNO_3.

$$\text{TBP Conversion Factor} = \frac{(\text{TBP conc of std, in \%})}{(\text{ml } 0.2N \text{ NaOH})(\text{Normality of NaOH})} = \frac{\%\ \text{TBP}}{\text{meq NaOH}}$$

C. Analysis of Bench Standard Control

Analyze one of the bench standards with each series of samples. The result obtained must fall within the specified limits. If the result is outside the limits, reprocess the bench standard. Contact your supervisor if difficulties persist.

D. Analysis of Samples

1. Pipet a 25-ml aliquot of the sample into a 125-ml separatory funnel. Proceed to step 2 if the sample contains interfering levels of metal ions. If not, proceed to step 3.
2. Add 10 ml of 0.1M diammonium hydrogen citrate solution, extract vigorously for 2 min, let stand for 5 min, then drain and discard the lower aqueous phase.

   If the sample contains enriched uranium, follow the established salvage procedures.
3. Contact the sample with three 25-ml portions of 8M HNO_3; each time, extract vigorously for 2 min, let the phases separate, then drain the lower phase.

4. Wait 15 min to obtain complete phase separation.	
5. Pipet 5.00 ml of the TBP-kerosene solution into a 250-ml beaker containing a plastic-coated stirring bar.	Do not transfer any of the aqueous phase. Let the pipet drain for 30 sec.
6. Add 100 ml of distilled water and 10 drops of the bromthymol blue indicator solution.	
7. Place the beaker on a magnetic stirrer and adjust the stirring to give good mixing of the two phases without loss of solution.	
8. Immerse the tip of the buret into the sample and titrate with the 0.2N NaOH to the permanent blue color of the yellow to blue bromthymol blue end point that remains for 2 min.	Use the 10-ml buret for samples containing 10% TBP or less. Use the 25-ml buret for samples containing greater than 10% TBP. Titrate slowly in the vicinity of the end point to avoid undertitration. The blue color appears, then slowly fades.
9. Record the data and calculate the results as described on the example worksheet. Report 3 significant figures.	

REFERENCES

1. Robert J. Allen and Michael A. DeSesa "Determination of Tributyl Phosphate", U. S. Atomic Energy Commission, WIN-52 (1956).

2. E. A. Brown, "The Determination of Tributyl Phosphate By An Acid Saturation Method", U. S. Atomic Energy Commission, FMPC-66 (1952).

3. R. A. Schneider and K. M. Harmon, "Analytical Solvent Extraction", Chemical Processing Department Analytical Technical Manual, U. S. Atomic Energy Commission, HW-53368 (1957).

January 1969

D. M. Lund

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME ____________________

LOG NUMBER ____________________

ACTIVITY (mR/hr) ____________________

DETERMINATION % TBP

CHARGE NUMBER ____________________

PROCEDURE TBP-Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Volume of NaOH required ml	Normality of NaOH	TBP Conversion Factor %/meq	% TBP	% TBP Corrected for Bias			RESULT % TBP
IAS		8.24	0.201	5.43	8.99	8.99±0.10			8.99± 0.10
IBS		14.15	0.201	5.43	15.4	15.6±0.1			15.6± 0.1

ANALYZED BY ____________________ DATE ____________________

CALCULATIONS:

Sample IAS:

D = ABC

D = 8.24 x 0.201 x 5.43 = 8.99

E = 8.99 ± 0.10

Sample IBS:

D = ABC

D = 14.15 x 0.201 x 5.43 = 15.4

E = 15.6 ± 0.1

APPROVED BY ____________________

EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF MILLIGRAM AMOUNTS OF URANIUM

ABSTRACT

A rapid, highly selective method is described for the determination of milligram amounts of uranium in a wide variety of inorganic and organic samples. For aqueous samples, the uranium is extracted directly into hexone as the neutral tetrapropylammonium trinitratouranate ion pair from an acid-deficient aluminum nitrate salting medium, then measured at 452 mμ on a recording spectrophotometer. For organic solvent samples, the uranium first is stripped with an ammonium citrate solution, then extracted as aqueous samples. For both cases, standards are processed simultaneously and the uranium concentration of the samples is determined by comparison.

APPLICABILITY

This versatile method is applicable to a wide variety of inorganic samples including those of the aluminum, stainless steel, and Zircaloy types. It is also applicable to liquid organic samples such as hexone and tributylphosphate (TBP)-kerosene. Two basic analysis procedures, D and E (see comparison of the two in Table B-VI), are used. Procedure D which uses smaller volumes of samples and reagents is simpler, more adaptable to remote use, and more economical. Its sensitivity limit is 1 mg U/ml. Procedure E is especially suitable for samples either with complex unknown compositions or with low levels of uranium. Its sensitivity is 0.1 mg/ml. A special Procedure F is provided for the analysis of water-immiscible organic solvent samples[1]. This procedure, based on a citrate strip of the uranium, is coupled with Procedure E.

The range is 1 to 40 mg of uranium for Procedures D and E. As written, the maximum sample aliquot for aqueous samples is 1 ml for Procedure D and 10 ml for Procedure E; hence, the lowest concentration determinable is 1 mg U/ml by Procedure D and 0.1 mg U/ml by Procedure E. When highest precision is desirable, Procedure E should be used for samples with uranium concentrations less than 5 mg/ml. For organic solvent samples, a limit of 25 ml is specified and the lowest concentration that can be determined is 0.04 mg U/ml.

The effects of diverse ions have been studied extensively under the conditions of Procedure D [2,3] and Procedure E; and on the basis of these studies, the tolerance levels of 43 metal ions and 18 anions have been established (Table B-VII). Careful examination of Table B-VII will show that most ions do not interfere even at high levels. Some identified in Table B-VII by the letter "b" may interfere under given conditions and maximum tolerance levels are listed for these. The maximum tolerance level is defined as that level where the observed effect becomes 1%. The effects of a number of the interfering ions at levels above the maximum tolerance

TABLE B-VI

COMPARISON OF PROCEDURES D AND E

Item Compared	Procedure D	 E
Volume of salting solution	6 ml	40 ml
Maximum sample volume	1 ml[a]	10 ml
Maximum volume of water permissible during extraction	1.75 ml	12 ml
Range of procedure	1 to 40 mg U for "cold" samples 5 to 40 mg U for samples that require remote handling	1 to 40 mg U
Lowest concentration determinable	1 mg U/ml ("cold" samples) 5 mg U/ml (samples that require remote handling)	0.1 mg U/ml
Diverse ion tolerance	Excellent, but generally less than Procedure E; greater than moderate amounts of chloride interfere	Excellent, including high levels of chloride

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[a] The sample volume can exceed 1 ml if the sample is evaporated prior to extraction.

TABLE B-VII

EFFECTS OF DIVERSE IONS[a]

Ion	Tolerance Level, mmole		Ion	Tolerance Level, mmole	
	Procedure D	Procedure E		Procedure D	Procedure E
Metal Ions					
Al(III)	2.0[c]	15.0	Mg(II)	0.75	5.0
Ag(I)	1.2	2.0[c]	Mn(II)	0.50	5.0
Au(III)	Expected to Interfere		Mn(VII)	1.0[d]	1.0[d]
Ba(II)	0.025	1.0[c]	Mo(VI)	0.10[b]	0.35[b]
Be(II)	1.0	2.0[c]	Na(I)	1.2	5.0[c]
Bi(III)	0.025	0.05[b]	Nb(V)	0.1[b]	0.1[b]
Ca(II)	0.75	5.0[c]	Nd(III)	0.10	0.55
Cd(II)	0.50	5.0	NH_4(I)	0.5[c]	3.0
Ce(III)	0.50	5.0	Ni(II)	1.0	5.0
Ce(IV)	0.008[b]	0.025[b,d]	Np(VI)	Expected to Interfere	
Co(II)	1.2	5.0	Pb(II)	0.25	5.0
Cr(III)	1.5	5.0	Pt(IV)	0.0003[c]	0.024
Cr(VI)	0.1[b,d]	0.5[b,d]	Pu(IV,VI)	Expected to Interfere[f]	
Cu(II)	1.0	5.0	Ru(III,IV)	0.01[c]	0.13
Dy(III)	0.10[c]	0.55	Sm(III)	0.10	0.52
Er(III)	0.10[c]	0.52	Sn(II,IV)	0.02[c]	0.05[b]
Fe(III)	0.50	5.0	Sr(II)	0.50	5.0
H(I) as HNO_3	10[b]	50[b]	Th(IV)	0.008[b]	0.025[b]
			V(V)	0.012[b]	0.025[b]
Hg(I,II)	0.50	2.5	W(VI)	0.01[c]	0.06[b]
Ho(III)	0.015[c]	0.025[b]	Y(III)	0.02[c]	0.10
K(I)	0.50	8.0	Zn(II)	1.0	2.5
La(III)	0.50	5.0[c]	Zr(IV)	0.25	2.5

TABLE B-VII (Continued)

Ion	Tolerance Level, mmole Procedure D	Tolerance Level, mmole Procedure E	Ion	Tolerance Level, mmole Procedure D	Tolerance Level, mmole Procedure E
Anions					
Acetate	1.2	8.7[b]	I^{-1}	0.05[c,e]	0.10[b,e]
BO_3^{-3}	0.025	3.0	NO_3^{-1} (as acid)	10	50
BrO_3^{-1}	0.50	1.0[c]	Oxalate	0.050	4.0
Br^{-1}	0.2[c]	1.0	ClO_4^{-1}	0.10[b]	0.50[b]
Cl^{-1} (low Fe samples)	0.25	24.2[b]	Peroxide (H_2O_2)	0.10[b]	0.50[b]
Cl^{-1}(high Fe samples)	Expected to Interfere	6.0[b]	$S_2O_8^{-2}$	0.25	---
Citrate	0.25	2.5[b]	PO_4^{-3}	0.25[b]	1.0[b]
CN^{-1}	0.25	0.25[c]	SO_4^{-2}	0.25[b]	12[b]
F^{-1}	5.0	20	Tartrate	0.05[c]	2.5
Formate	1.2	5.0[c]			

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[a] Unless noted otherwise, the tolerance level listed is the highest level studied and does not represent the maximum tolerance level.

[b] Maximum tolerance level below which the error is 1% or less.

[c] Conservative estimate based on the chemical properties of the elements and the observed effect of the ion in the other procedure.

[d] Tolerance level with no hydroxylamine reduction. With reduction, tolerance is about same as lower valence ion listed.

[e] After the extraction, wait 30 min before color measurement to allow the iodine to bleach out.

[f] The interference of plutonium possibly could be eliminated or reduced by scrubbing the hexone phase with a salting solution containing organic complexing reagents[4].

level also have been studied for Procedure E. The data are summarized in Table B-VIII. Noteworthy is the fact that sulfate does not interfere seriously even at the 24 mmole (1.25 ml of the concentrated acid) level.

The diverse ions that do interfere affect the determination in different ways. Bismuth, perchlorate, tungstate, and vanadate precipitate under the conditions of the analysis and carry uranium. Cerium(IV), chloroaurate ($AuCl_4^-$), perchlorate, vanadate, and Th(IV) form stable complexes with the tetrapropylammonium ion and prevent the complete extraction of uranium. Others such as Ho(III), Np(VI), and Pu (all valences) coextract with the uranium and absorb at 452 mμ, the working wavelength. Complexing anions such as citrate, phosphate, and sulfate above certain levels complex uranium to prevent quantitative extraction. Chloride alone does not interfere except at very high levels; however, when major amounts of iron(III) also are present, the chloride level must be less than 6 mmole for Procedure E and less than 1 mmole for Procedure D. Above these limits, the iron(III)-chloride complex coextracts and interferes by altering the spectrum of the uranium complex. The extraction of iron is strongly dependent on the chloride concentration as well as the total chloride level. In Procedure E, the addition of water effectively reduces the chloride concentration and the coextraction of iron.

The harmful effect of some of the interferences can be minimized or eliminated with simple manipulations. In the recommended procedures, a sequential potassium permanganate-hydroxylamine sulfate treatment is used routinely to guarantee that the uranium is in the extractable (VI) valence state. This treatment automatically reduces Ce(IV), Cr(VI), Mn(VII), and peroxide to eliminate their interferences. Volatile interferences such as perchloric acid can be removed by repeated evaporation of the sample with sulfuric acid. Sulfate, however, tends to suppress the absorbance so that the final fuming should be to a small volume and standards should be processed with the samples through the same treatment. The tolerance for thorium can be increased by the use of a modified salting solution with a higher tetrapropylammonium nitrate (TPAN) concentration.

TABLE B-VIII

EFFECT OF DIVERSE IONS AT LEVELS ABOVE THE MAXIMUM TOLERANCE LEVEL, PROCEDURE E[a]

Metal Ion	Mmole Present	Effect, %	Anion	Mmole Present	Effect, %
Au(III)	0.04	- 9.0	Acetate	17.4	- 1.7
Bi(III)	0.50	- 2.6	Cl^{-1} (low Fe)	36.3	- 1.1
H(I) as HNO_3	63	- 1.1	Citrate	5.0	- 2.0
	78	- 4.3			
Ho(III)	0.10	+ 2.3	I^{-1}	0.5	Iodine Coextracts and Interferes
Mo(VI)	0.70	- 2.0	ClO_4^{-1}	2.0	- 2.7
Sn(II,IV)	0.25	- 2.3	Peroxide (H_2O_2)	1.0	- 3.5
Th(IV)	0.05	- 1.5	PO_4^{-3}	7.3	- 1.5
V(V)	0.05	- 1.5	SO_4^{-2}	18	- 1.5
	0.10	- 4.4		24	- 2.1
W(VI)	0.10	- 4.4			

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[a] The uranium level was maintained at 0.1 mmole (25 mg). Similar effects can be expected for Procedure D at diverse ion levels approximately 20% of the levels listed above.

DISCUSSION

The uranium must be in the (VI) oxidation state to quantitatively extract. A permanganate oxidation step is specified in both Procedures D and E to accomplish this. If the uranium is definitely known to be in the (VI) state only, the addition of potassium permanganate is not necessary. The uranium can be assumed to be totally in the (VI) state when the sample contains strong oxidants such as chromium(VI) and when the prior history of the sample precludes the existence of uranium in oxidation states other than (VI).

The extraction of uranium(VI) and the absorbance of the extracted uranium complex are dependent on temperature, the TPAN concentration, the age and concentration of the salting solution, and the volume of hexone. Thus, standards must be processed each time a sample is processed. Recent studies have shown that the calibration factors for D and E are slightly, but significantly, different so standards must be processed by the same procedure as that used for the analysis of the samples. The reasons for the observed difference between the factors for D and E are thought to be differences in the level and concentration of TPAN in the two extraction systems and differences in the distribution of hexone into the aqueous phase. The latter is particularly important in the analysis of hexone samples wherein uranium is stripped from the hexone sample with 9 ml of 0.1M diammonium hydrogen citrate, reextracted into 6 ml of hexone per Procedure E, then compared against standards also processed via Procedure E. To minimize errors associated with increases or decreases in the volume of the final hexone extract, the calibration standard must be diluted with 9 ml of 0.1M diammonium hydrogen citrate preequilibrated with hexone. This practice is not necessary in the analysis of samples of TBP-kerosene with only limited solubility in water.

Two potentially serious sources of error are the improper measurement of the hexone and the loss of hexone in the extraction process before equilibration is attained. It should be kept in mind that a difference of one drop (~0.05 ml) of hexone will cause an error of nearly 1%. Freshly prepared salting solution contains a significant amount of suspended hexone which seriously effects the results. For this reason, requests for salting solution should be made well in advance so that properly aged salting solutions can be provided.

In Procedure E, up to 75 mg of uranium is extracted quantitatively, so that in emergencies (for example, when resamples are not available), the hexone extract can be diluted with 1 or 2 parts of hexone to enable measurement. This approach will give results within about 3% of the true value....about 1.5% low when diluted twofold and about 2 to 3% low when diluted threefold.

APPARATUS AND REAGENTS

A. Apparatus

1. Absorbance cells, Aminco, 5-cm, 13-mm OD, 4.9-ml capacity. These cells should be fitted with Teflon sleeves with a diameter similar to that of standard 22-mm OD 5-cm cells.
2. Absorbance cells, Corex, 1-cm. Teflon spacers should be placed in the bottom of the cell if scaled-down volumes are used in the method.
3. Beakers, assorted sizes.
4. Cary Model 14 Recording Spectrophotometer, Beckman DK Recording Spectrophotometer, or equivalent.
5. Centrifuge, International Clinical, Model Cl, or equivalent.
6. Culture tubes, 25-ml, with polyethylene-lined screw caps.
7. Dropping bottles.
8. Extraction apparatus for test tubes; pin wheel type[2] is recommended.
9. Graduated cylinder, 50-ml.
10. Hot plate.
11. Pipets, micro, assorted sizes, with control syringe.
12. Pipets, Mohr, 5- and 10-ml, with suction bulb.
13. Pipets, transfer.
14. Pipets, volumetric, assorted sizes, including 6-ml, with suction bulb.
15. Polyethylene stoppers for test tubes and separatory funnels.
16. Separatory funnels, 125- and 60-ml, with Teflon stopcocks.
17. Test tubes, glass, 16- x 150-mm, or slightly larger.

5

B. Reagents

NOTE: Prepare all reagents with Analytical Reagent Grade Chemicals and distilled water. Use distilled or treated water throughout the method.

1. Acid-deficient aluminum nitrate salting solution, 2.8<u>M</u>, 0.8% (0.04<u>M</u>) in TPAN. Dissolve 1050 g of $Al(NO_3)_3 \cdot 9H_2O$ in 75 ml of water and 135 ml of conc NH_4OH with the aid of heating and stirring. Cool to room temperature, dilute to 900 ml with water, add 20 ml of 10% tetrapropylammonium hydroxide (Eastman Organic), and mix well. Extract the solution with 100 ml of hexone for 3 min. Let stand for about 1 hr to allow the phases to separate, then drain off the lower phase into a 1-liter bottle. Finally, add 80 ml of 10% tetrapropylammonium hydroxide and mix well. THE SOLUTION IS SUITABLE FOR USE AFTER 3 DAYS (see the DISCUSSION section). The preparation of a 4-liter batch is recommended. To prepare a 4-liter batch, multiply all additions by four and extract the solution one half at a time with 200-ml portions of hexone.

2. Acid-deficient aluminum nitrate salting solution, 2.8<u>M</u>, 5.0% in TPAN. Neutralize 100 ml of 10% tetrapropylammonium hydroxide solution to pH 7 with 5<u>M</u> HNO_3. Transfer to a large evaporating dish and allow the TPAN solution to stand until a thick slurry of crystals forms. This may take as long as 4 days. Transfer the crystals to a 400-ml beaker with 20 ml of water. Add 210 g of $Al(NO_3)_3 \cdot 9H_2O$. Stir and add water until a volume of approximately 165 ml is reached. Add 27 ml of conc NH_4OH and stir without heating until solution is complete. Filter and dilute to 200 ml with water.

3. Ammonium citrate solution, 0.1<u>M</u>. Dissolve 22.62 g of diammonium hydrogen citrate in water and dilute to 1 liter.

4. Hexone (methyl isobutyl ketone, 4-methyl-2-pentanone).

5. Hydroxylamine sulfate, 1<u>M</u>. Dissolve 32.8 g of $(NH_2OH)_2 \cdot H_2SO_4$ in water and dilute to 200 ml.

6. Nitric acid, conc.

7. Potassium permanganate solution, 0.2<u>M</u>. Dissolve 3.16 g of $KMnO_4$ in 100 ml of water. Store in a dark bottle.

8. Uranium stock solution, 250 mg U/ml. Ignite approximately 300 g of NBS U_3O_8 at 900°C for 1 hr. Let cool, then weigh to the nearest 0.001 g, 295±1 g of the oxide into a 500-ml Erlenmeyer flask. Cover the flask with a reflux head and dissolve the U_3O_8 in nitric acid with the aid of heat. Lengthy digestion

may be necessary to completely dissolve the oxide. When the dissolution is complete, evaporate the solution to the appearance of uranyl nitrate crystals. Cool slightly, then quantitatively transfer the contents of the Erlenmeyer flask with water rinses to a tared (to ±0.001 g) 1-liter volumetric flask. Cool the flask and contents to room temperature, dilute to volume with water, mix thoroughly, and weigh. Store the solution in sealed ampoules in 50-ml units. From the weight of the U_3O_8, its purity, and the weight of the solution, calculate the uranium concentration in mg/g. Label the ampoules accordingly.

9. Uranium calibration standards I and II, ~25 and ~20 mg U/ml, respectively. Dilute 25 ml and 20 ml (weighed to ±0.001 g) of the stock solution to 250.0 ml with 0.1<u>M</u> HNO_3. Calculate the concentration of uranium of the two solutions from the weight of the aliquot and the concentration of the stock solution.

10. Uranium bench-control standards. Prepare a series of dilutions of the stock solution, per item 9 above, to cover the concentration range 1 to 40 mg U/ml.

A. Blank

A blank is not necessary in this method. All absorbances are measured against air.

B. Calibration

To cover the range of 1 to 40 mg U, both 1- and 5-cm cells are used — 5-cm cells for the range 1 to 9 mg U and 1-cm cells for the range 5 to 40 mg U. If samples of widely varying uranium concentrations are being analyzed, the preparation of four calibration standards, 200 μl and 1.00 ml of standard I and 200 μl and 1.00 ml of standard II, will assure the presence of one suitable pair of comparison standards and minimize repeat analyses. If only samples with similar concentrations are being analyzed, two appropriate standards will suffice.

Calibration standards should be processed with each series of samples by the same procedure as that used to analyze the samples. Process the appropriate standards as follows:

1. Aqueous samples that do not require fuming. Use Procedure D or E with reference to samples.

2. Aqueous samples that require sulfuric acid fuming. Because high levels of sulfate exert a slight lowering effect, standards must be carried through the same treatment to compensate for the effect. Process the standards per Procedure G.

3. TBP-kerosene samples. Pipet the calibration standard into a 125-ml separatory funnel, add 5 drops of conc HNO_3 and 9 ml of 0.1$\underline{M}$ ammonium citrate, and process the mixture per Procedure E beginning at step 4.

4. Hexone samples. Contact 50 ml of 0.1$\underline{M}$ ammonium citrate with 10 ml of hexone in a 125-ml separatory funnel for 3 min. Let the two phases separate then drain the hexone-equilibrated 0.1$\underline{M}$ ammonium citrate into a 100-ml beaker. Pipet the calibration standard into a 125-ml separatory funnel, add 5 drops of conc HNO_3 and 9 ml of hexone-equilibrated 0.1$\underline{M}$ ammonium citrate and then process the mixture per Procedure E beginning at step 4.

Divide the milligrams of uranium in each standard by its respective absorbance to obtain the conversion factor. For each of the two groups of standards, the difference between the two factors should not exceed limits set by the Quality Control Laboratory and the average of the two factors should agree with the established conversion factor within the specified limits. If either or both of the specifications are not met, reprocess the pair or pairs of calibration standards immediately. Contact your supervisor if difficulties still are experienced.

C. Analysis of Bench-Control Standards

Each time samples are analyzed by Procedures D, E, or G, process one of the bench-control standards by the same procedure used to analyze the samples. The result obtained must fall within specified limits. If it does not, process another standard. Report to your supervisor if further difficulties are encountered.

The analysis of organic solvent samples is expected only at infrequent intervals. When such samples are received, request special bias controls from the Quality Control Laboratory.

D. Analysis of Aqueous Samples (Procedure D)

NOTE: Procedure D is recommended for radioactive samples that require remote handling and for all other samples except those with complex unknown compositions or those with appreciable amounts of chloride. For samples requiring analysis, the uranium concentration must be at least 1 mg/ml. For samples requiring remote analysis, only 1-cm cells can be used for the absorbance measurement. Thus the uranium concentration must be greater than 5 mg/ml. If greater sensitivity is needed, concentrate the sample initially by evaporation or use Procedure E. The tolerance of

Procedure D for diverse ions and the recommended pretreatment for volatile interferences are discussed under APPLICABILITY.

1. Pipet a sample, 1 ml or less, containing 1 to 40 mg of uranium and less than 10 meq of acid, into a 16- x150-mm test tube or a 25-ml screw-cap culture tube.	If the extraction of uranium is done remotely, the sample aliquot must contain at least 5 mg of uranium. If the evaporation step is used in step 5, the sample can be slightly larger than 1 ml. For best precision, select a sample aliquot with at least 10 mg of U.
2. Add 1 drop of conc HNO_3.	If it is known definitely that the uranium is in the (VI) valence state only, omit step 3 and continue with step 4.
3. While swirling the tube continuously, add 0.2M $KMnO_4$ one drop at a time until the pink color persists for 30 sec.	
4. Add 0.2 ml of 1M $(NH_2OH)_2 \cdot H_2SO_4$ and mix.	The purpose of the $(NH_2OH)_2 \cdot H_2SO_4$ is to reduce oxidants such as $KMnO_4$, Cr(VI), and Ce(IV).
5. Using the approximation that one drop ≈0.05 ml to determine the volume of reagents added in steps 2 to 4, estimate the total volume of the treated sample. If the volume exceeds 1.5 ml, evaporate the sample to less than 1.5 ml, then cool it to room temperature.	
6. Add 6 ml of the 0.8% TPAN, aluminum nitrate salting solution with a Mohr pipet.	If the sample contains interfering levels of thorium, use the 5.0% TPAN salting solution.
7. Pipet exactly 6.00 ml of hexone, stopper, and extract for 3 min with the extraction wheel or manually.	Erratic results will be obtained when there is inadequate mixing. Preferably, extract vigorously by hand for 2 min.

8. Centrifuge for 1 min to separate the two phases.	
9. With a transfer pipet, transfer the hexone phase to a 5-cm (1 to 9 mg of U) or a 1-cm (5 to 40 mg of U) optical cell.	Select the cell on the basis of the yellow color of the hexone phase. In doubtful cases, select the 5-cm cell for this will enable subsequent measurement in a 1-cm cell. For best results, the observed net absorbance should be 0.1 or higher.
10. Place the cell in the recording spectrophotometer and adjust the instrument so that the absorbance versus air is 0.0 to 0.5 at 480 mμ.	One cell is recommended for a series of measurements of standards and samples. Clean the cell between measurements by rinsing it three times with water and three times with acetone, then dry the cell with clean air. After the final measurement, rinse the cell thoroughly with water, then acetone, and then air dry.
11. Scan the sample versus air from 480 mμ to 440 mμ at a scan speed of 0.5 mμ (5A) per sec.	
12. Determine the uranium concentration of the sample by comparison to the standards as described under CALCULATIONS.	

E. Analysis of Aqueous Samples (Procedure E)

NOTE: This procedure is intended primarily for samples that contain between 0.1 and 2 mg of uranium per ml; however, it also is applicable to samples with higher uranium concentrations. Procedure E is recommended for samples with unknown compositions and samples that contain large amounts of chloride. The effects of diverse ions and the recommended pretreatment for volatile interferences are discussed under APPLICABILITY.

1. Pipet a sample aliquot containing 1 to 40 mg of uranium and less than 50 meq of acid into a 60-ml separatory funnel.	For best precision, select an aliquot with more than 10 mg of uranium.

2. Add 5 drops of conc HNO_3.	
3. If the aliquot volume is less than 5 ml, dilute to 5 ml with water. Otherwise, proceed to step 4 or 5 (see note).	If it is known definitely that uranium is in the (VI) valence state only, omit step 4 and continue with step 5.
4. While swirling the funnel continuously, add 0.2M $KMnO_4$ one drop at a time until the permanganate color persists for 30 sec.	
5. Add 0.5 ml of 1M $(NH_2OH)_2 \cdot H_2SO_4$ to reduce excess permanganate and other oxidants such as Cr(VI) and Ce(IV). Mix by swirling.	If the sample contains high concentrations of Cr(VI) or Ce(IV), warm the funnel in a hot water bath to hasten reduction, then chill to room temperature. The total volume of sample plus added reagents must be less than 12 ml at this point. If the volume exceeds 12 ml, start again with a smaller aliquot. If a resample is not available, evaporate the sample to less than 12 ml under a heat lamp, chill to room temperature, then proceed with step 6.
6. With a graduated cylinder, add 40 ml of the 0.8% TPAN aluminum nitrate salting solution.	
7. Pipet exactly 6.00 ml of hexone, stopper, and extract fairly vigorously for 1 min.	Low results will be obtained if the extraction is performed too gently.
8. Let the two phases separate, then drain off the lower aqueous phase.	
9. Pour (or transfer with a transfer pipet) the hexone phase to a 5-cm (1 to 9 mg U) or a 1-cm (5 to 40 mg U) optical cell. If a precipitate or emulsion persists, drain the organic phase	Select the cell on the basis of the yellow color of the hexone phase. In doubtful cases, select the 5-cm cell first for this will enable subsequent measurements in 1-cm cells. For best results, the

	into a clean 16- x 150-mm test tube and centrifuge for 1 min.	observed net absorbance should be 0.1 or higher.
10.	Place the sample in the recording spectrophotometer and adjust the instrument so that the absorbance versus air is 0.0 to 0.5 at 480 mμ.	One cell is recommended for a series of measurements of standards and samples. Clean the cell between measurements by rinsing it three times with water and three times with acetone, then dry the cell with clean air. After the final measurement, rinse the cell thoroughly with water, then acetone, and then air dry.
11.	Scan the sample versus air from 480 mμ to 440 mμ at a scan speed of 0.5 mμ (5A) per sec.	
12.	Determine the uranium concentration of the sample by comparison to the standards as described under CALCULATIONS.	

F. Analysis of Organic Samples

NOTE: This procedure is designed specifically for the analysis of hexone and TBP-kerosene samples.

1.	Pipet a sample aliquot (25 ml or less) containing 1 to 40 mg of uranium into a dry 60-ml separatory funnel.	For best results, select a sample with greater than 10 mg of uranium.
2.	If the aliquot volume is less than 5 ml, dilute to 5 ml with the solvent.	Use hexone for hexone samples and kerosene for TBP-kerosene samples.
3.	Pipet 5 ml of the 0.1<u>M</u> ammonium citrate solution, stopper, and extract for 2 min.	

4. Let the two phases separate, then drain the lower aqueous phase into a clean, dry 60-ml separatory funnel.	The phase separation must be complete. Carryover of the organic solvent to the aqueous phase causes low results.
5. Repeat steps <u>3</u> and <u>4</u>, except use 2 ml of the 0.1<u>M</u> ammonium citrate solution. Combine the aqueous strip with the first 5-ml strip.	
6. Repeat step <u>5</u>.	The total volume of the aqueous strip must not exceed 12 ml after step <u>7</u>. Do not use more than 2 ml of water to rinse the tip of the separatory funnel.
7. Add 5 drops of conc HNO_3 to the combined aqueous citrate strip and mix.	
8. Complete the determination per Procedure <u>E</u> beginning at step <u>5</u>.	

G. Analysis of Aqueous Samples Requiring Sulfuric Acid Fuming

NOTE: This treatment is designed to remove volatile interferences such as chloride, perchlorate, and peroxide. Occasionally for reasons not known, the uranium spectra climbs sharply away from the base line as the wavelength decreases. Sulfuric acid fuming has been found to correct this.

1. Pipet a sample aliquot containing 1 to 40 mg of uranium into a small beaker.

2. Add 0.5 ml of conc HNO_3 and 1 ml of conc H_2SO_4, evaporate the sample to sulfuric acid fumes, and fume for 5 min.

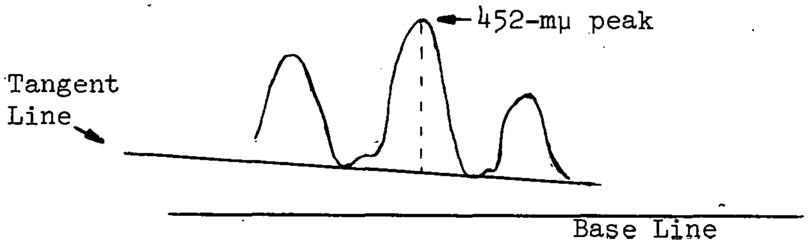
3. Cool the sample, add 5 ml of water, and heat gently until the salts dissolve completely. Additional water may be added to effect dissolution and to replenish that lost through evaporation.

4. Evaporate the solution slowly to a volume of 3 ml or less, then transfer the sample quantitatively to a 125-ml separatory funnel with small water rinses. The volume of the solution should not exceed 12 ml after the transfer.

5. Continue with the determination per Procedure E beginning at step 6.

CALCULATIONS

A. Determine the absorbance of the calibration standards and the samples by drawing a line tangent to and connecting the absorbance minimums on each side of the 452-mμ peak as shown below.



The absorbance is the height of the peak in absorbance units and is equal to the difference between the absorbance reading at the 452-mμ peak and the absorbance reading on the tangent line at 452 mμ.

B. Record the sampling and absorbance data and calculate the results as shown on the example work sheet. Report all results to three significant figures.

The calibration standards are prepared with natural uranium so a correction must be applied for enriched uranium samples. The factor for this correction is the ratio of the average atomic weight of the uranium in the sample to the average atomic weight of the natural uranium (238.04). Table B-IX lists corrections factors for different enrichment levels. The effects of varying U-236 and U-234 are considered negligible.

TABLE B-IX

CORRECTION FACTORS FOR DIFFERENT U-235 LEVELS

U-235 Isotope Abundance, %	Correction Factor	U-235 Isotope Abundance, %	Correction Factor
		50	0.9937
100	0.9875	40	0.9950
90	0.9887	30	0.9962
80	0.9900	20	0.9975
70	0.9912	10	0.9987
60	0.9925	0	1.0000

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1. F. A. Duce, Idaho Nuclear Corporation, Private Communication (October 1967).

2. W. J. Maeck, G. L. Booman, M. C. Elliot, J. E. Rein, "Spectrophotometric Extraction Methods Specific for Uranium," Anal. Chem., 31 (July 1959) p 1130.

3. W. J. Maeck, G. L. Booman, M. C. Elliot, J. E. Rein, "Separation of Uranium from Diverse Ions, Methyl Isobutyl Ketone Liquid-Liquid Extraction System," Anal. Chem., 30 (December 1958) pp 1902-1907.

4. R. C. Shank et al, Annual Report of Division Analytical Branch for 1964, IDO-14655 (April 1965) pp 73-79 and J. E. Rein, This Manual, Method U-Color-2 (October 1967).

April, 1969
S. S. Yamamura

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME ____________________

ACTIVITY (mR/hr) ____________________

CHARGE NUMBER ____________________

LOG NUMBER ____________________

DETERMINATION Uranium

PROCEDURE U-Color-1, Procedure E

SPECIAL INSTRUCTIONS:

The sample is a dilute solution of product uranyl nitrate with 84.5% U-235 enrichment.

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	Absorbance	Conversion Factor	mg U in Aliquot Analyzed	Enrichment Factor	mg U Corrected for Enrichment	mg U Corrected for Bias		RESULT mg U/ml
U std, 20mg		0.384	52.08						
U std, 25mg		0.478	52.30						
		$\bar{x}$ =	52.19						
Prod-UN-1	3.00 ml								
	(Entire Sample used)	0.598	52.19	31.21	0.9894	30.88	31.23±0.65		10.41± 0.22

ANALYZED BY ____________________ DATE ____________________

CALCULATIONS:

$$\text{Conversion Factor} = \frac{\text{mg U in Std}}{\text{Absorbance}} = B = \frac{20}{0.384} = 52.08$$

$$B' = \frac{25}{0.478} = 52.30$$

$$\bar{x} = 0.5(B + B') = 0.5(52.08 + 52.30) = 52.19 \text{ mg U / abs unit}$$

Prod-UN-1

$$C = AB = 0.598\,(52.19) = 31.21 \text{ mg U}$$

$$E = CD = 31.21\,(0.9894) = 30.88 \text{ mg U}$$

$$\text{Result} = \frac{F}{\text{Sample Vol.}} = \frac{31.23 \pm 0.65}{3.00} = 10.41 \pm 0.22 \text{ mg U/ml}$$

APPROVED BY ____________________

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SEPARATION OF URANIUM FOR MASS SPECTROMETRIC ANALYSIS

ABSTRACT

Uranium, with added spike isotope when concentration is to be determined by the isotope dilution technique, is extracted from an acid-deficient aluminum nitrate salting solution into methyl isobutyl ketone. The organic phase is scrubbed with a special complexing solution to remove coextracted plutonium when it is present in significant quantities in the sample. The organic phase either is contacted with hydrogen peroxide to precipitate milligram levels of uranium as uranium peroxide or is evaporated to dryness for microgram levels of uranium. The uranium peroxide or evaporated residue is solubilized with nitric acid for the mass spectrometric analysis.

APPLICABILITY

This method, designed for samples that contain high levels of fission products, is applicable to existing nuclear fuels including the alloying and cladding constituents present in aluminum, various stainless steels, zirconium, and most cermets. The manipulations are simple, being designed for shielded facilities with Castle-type manipulators. The extraction conditions give about 10^5 decontamination of aged fission products such that the separated organic phase that contains the extracted uranium can be moved to a nonshielded hood for the remainder of the procedure. The degree of extraction of uranium is about 90%. As discussed further in the next section, the degree of extraction of such fission products as zirconium and cerium will increase for highly (more than 8 meq per sample aliquot) acid samples. This effect can be overcome by adding ammonium hydroxide to the extraction mixture. However, because the maximum sample aliquot volume is 1 ml, the tolerance level is at least 8<u>N</u> acid. The acidity of fuel dissolver samples rarely exceeds this level.

The usual isotopic compositions of uranium in fuel samples at the time of writing this procedure (1968) are normal and enriched. The added isotope for the isotope dilution determination of uranium concentration, as described in this method, therefore is U-233. Another isotope is required for samples that contain U-233 such as irradiated thorium. The added isotope for these samples usually is U-238. Because of natural uranium contamination, expecially in thorium, samples without added isotope also should be analyzed to provide the means to correct for this contamination. If this natural contamination is high, U-235 may be superior as the added isotope.

Two procedures are described: <u>B</u> is for the uranium concentration range of 0.001 to 0.1 mg/ml and <u>C</u> is for 0.1 to 10 mg/ml. For both procedures, the maximum sample aliquot is 1.0 ml. Above the upper limit, samples should be diluted rather than using very small aliquot volumes. The recommended diluent is 6M HNO_3. Below the lowest limit, samples can be evaporated. Before evaporation, the samples should be acidified with HNO_3, if necessary, to 6M. Either a large volume of sample can be evaporated, diluted to volume, and aliquoted, or larger sample aliquots can be evaporated in the test tube used for the extraction. The latter is preferable because the added isotope can be added and mixed with the sample aliquot prior to the start of evaporation. Spattering losses therefore have negligible effect. After evaporation, any residue should be dissolved in not more than 1 ml of 6M HNO_3.

In the procedures as described, the amount of U-233 added is 0.005 mg for Procedure B and 0.5 mg for Procedure C. Highest reliability is obtained at a ratio of 1 to 1 for the major uranium isotope in the sample to U-233. The reliability decreases significantly when this ratio falls outside the range of 0.2 to 5.

Of the analytical methods used for uranium, this method is the most universal one and, at the same time, is highly reliable. It does, however, require a minimum of 2 man hours. If less reliable results are acceptable, the more rapid spectrophotometric methods (U-Color-1 and U-Color-2, this Manual) can be used.

DISCUSSION

The basis of the extraction procedure is the preferential solubility of the ion association complex $[H]^+[UO_2(NO_3)_3]^-$ in hexone from a highly salted aqueous phase. The concentration of the salt, aluminum nitrate, is at a selected level to give about 90% extraction of the uranium at which level the decontamination factor for aged (>3-month) fission products is 10^5. This level was selected as a compromise of uranium extraction and fission product decontamination. It should be apparent that this extraction condition should not be used as the preliminary separation for methods not based on the isotope dilution technique. The salting solution is acid-deficient to improve the decontamination of such hydrolyzable fission products ions as Zr(IV), Nb(V), and Ce(IV). The acid deficiency of the salting solution is 2N[b]. With 4 ml being used and the sample aliquot restricted to a maximum of 1 ml, this acid deficiency is not completely neutralized until a sample acidity level of 8N. If desired, concentrated ammonium hydroxide can be added after the sample aliquot and added U-233 isotope are mixed to improve the decontamination for highly acid samples. The minimum volume of ammonium hydroxide should be used because its addition dilutes the salting strength and hence the amount of uranium extracted.

The oxidation state of the uranium in the extracted ion association complex is +6. The U-233 added isotope is in this oxidation state. Because the isotope dilution technique depends on chemical identity of the sample isotope species and added isotope species, an oxidation with Cr(VI) (potassium dichromate) is included in the procedures. This oxidation can be omitted only when the uranium in the sample is known to be in the +6 oxidation state. Normally, nitric acid is a sufficiently strong oxidant to provide this oxidation state. However, nitric acid samples of uranium have been encountered which contain +4 uranium stabilized by such complexing agents as fluoride and oxalate.

For easier remote operation, the organic reagent aluminon (aurintricarboxylic acid) is added to the extraction mixture. It forms a deep red complex with the aluminum ion of the salting solution and hence provides an easily seen demarcation of the aqueous and organic phases through the thick, shielded, viewing windows. This aids the analyst to separate more of the organic phase after the completion of the extraction.

The extraction, though highly selective for uranium, will coextract such transuranics as neptunium and plutonium. These elements do not directly interfere in the subsequent mass spectrometric analysis, but do constitute a health hazard in the mass spectrometry laboratory. For this reason, a step is included in the procedures in which the separated organic phase is scrubbed with a mixture of hydrazine, oxalic acid, and EDTA in an aluminum nitrate matrix. This mixture reduces neptunium and plutonium to the low extractable +3 oxidation states and complexes them as aqueous soluble complexes. This scrub step is not necessary for fuels at the CPP in which the initial U-235 abundance is above about 20%. This, of course, is also dependent on the burnup level of the fuel.

Organic matter in the finally separated uranium fraction sent to the mass laboratory causes erratic behavior in the instrument and even loss of material from the filament. Sources of organic matter are: (a) the use of rubber stoppers in the extraction, (b) lint or other packing material in the test and centrifuge tubes, and (c) incomplete digestion of the final uranium fraction in Procedure B. Hexone leaches organic matter from rubber stoppers. This organic matter is removed by an acetone wash. It is important not to let the acetone wash come in contact with the rubber stopper. All tubes should be rinsed with water (and dried) to remove lint. The final uranium fraction from Procedure B that is sent to the mass laboratory should be digested with nitric acid until no visible residue remains.

SAFETY PRECAUTIONS

Samples processed by this procedure usually will contain U-233, plutonium, and higher transuranics. Observe the necessary handling procedures to prevent either absorption through the skin or ingestion of these materials.

Hydrogen peroxide severely burns the skin. Wear rubber gloves when handling this reagent and wash any contacted skin areas immediately with copious quantities of cold water.

APPARATUS AND REAGENTS

A. Apparatus

1. Centrifuge, International Clinical Model CL, with 15-ml head and 5-ml adapter, or equivalent.
2. Centrifuge tubes, glass, 5-ml.
3. Dispensing heads, 4-ml and 2-ml, for adding the salting solution, scrub solution, and hexone.
4. Heat lamp.
5. Meker burner.
6. Phase mixing apparatus, 10-in. disc with clamps to hold four 10-ml tubes mounted on a stand and rotated at 60 rpm by an electric motor.
7. Pipets, micro, calibrated, assorted sizes, with constriction of the calibration mark such as the Ultrapette. Use only pipets calibrated by the Quality Control Laboratory.
8. Pipets, transfer, 1-ml glass, uncalibrated.
9. Pipets, volumetric, assorted sizes, with control syringes and suction bulbs.
10. Stoppers, rubber or polyethylene, size 00.
11. Test tubes, glass, 10-ml, 13- x 100-mm.

B. Reagents

Note: Prepare all reagents with Analytical Reagent Grade chemicals and distilled water.

1. Acetone.
2. Aluminum nitrate salting reagent, 2.0$\underline{M}$ in aluminum nitrate and 2$\underline{N}$ acid-deficient. Dissolve 750 g of $Al(NO_3)_3 \cdot 9H_2O$ in water to give a final volume of about 800 ml. Add 134 ml of conc NH_4OH and stir vigorously until dissolution is complete. Dilute to 1 liter with water. Contact this solution with 100 ml of hexone in a large separatory funnel (with a Teflon-greaseless-stopcock) to remove traces of natural uranium impurity. Discard the organic phase.

3. Ammonium hydroxide, conc.

4. Hexone. Shell Oil Co. methyl isobutyl ketone, Eastman White Label 4-methyl-2-pentanone.

5. Hydrogen peroxide, 30%. Keep in refrigerator when not in use.

6. Nitric acid, conc and 6<u>M</u>.

7. Plutonium scrub solution 2.0<u>M</u> in aluminum nitrate, 2<u>N</u> acid-deficient, 0.25<u>M</u> each in oxalic acid, EDTA, and hydrazine. Dissolve 750 g $Al(NO_3)_3 \cdot 9H_2O$ in water to give a final volume of about 800 ml. Add 134 ml of conc NH_4OH. Stir vigorously to dissolve, and add 31 g of oxalic acid dihydrate, 64 g of EDTA, and 15 ml of 85% hydrazine hydrate. Dilute to 1 liter with water, mix, and contact this solution with 100 ml of hexone in a large separatory funnel (with a Teflon-greaseless-stopcock) to remove traces of natural uranium. Discard the organic phase.

8. Potassium dichromate solution, 0.1<u>M</u>. Dissolve 29.4 g of $K_2Cr_2O_7$ in water and dilute to 1 liter with water.

9. Uranium-233 spike solution I, standardized 1 mg/ml level in 1<u>M</u> HNO_3. This reagent is provided as 500-µl aliquots in test tubes by the Quality Control Laboratory. The reagent is standardized by isotope dilution mass spectrometry with NBS U_3O_8, high-purity natural uranium metal, and high-purity fully enriched U-235 metal. It is stored in flame-sealed 10-ml ampoules. When aliquots are desired, an ampoule is broken open, and the entire contents is distributed in 500-µl aliquots with a calibrated pipet (Ultrapette-type).

10. Uranium-233 spike solution II, standardized, 0.01 mg/ml level, in 1<u>M</u> HNO_3. This reagent is prepared by an exact 100-fold dilution of reagent 9 in NBS-calibrated volumetric ware. It is stored and supplied as described for reagent 9.

NOTE ON REAGENTS 9 AND 10: Store the test tubes containing these reagents in a hood or glove box. Discard any tube that tips over because solution will creep around and adhere to the stopper and will not be available for mixing with the sample. If used, this would cause high bias in the results.

PROCEDURE

A. Bench Standard

No bench standard as such is processed. However, verify the volume delivery of the remote pipetter by processing a 500-µl delivered aliquot of the Method H-Vol-1 bench standard. Limits are provided by the Quality Control Laboratory.

B. Low-Level Uranium Separation

NOTE: See Procedure D for remote operations.

1.	Pipet an aliquot of the sample that contains from 0.0005 to 0.05 µg of uranium into a test tube that contains 500 µl of U-233 spike solution II.	Use a calibrated dri-filmed Ultrapette in the range of 100 to 1000 µl. Select the pipet to give the closest ratio of 1 to 1 for the major uranium isotope to U-233. The amount of U-233 in the tube is 0.005µg. Pipet the sample aliquot deep into the tube but do not let the pipet tip touch the U-233 solutions.
2.	Mix the contents of the tube by swirling and add 2 drops of 0.1M $K_2Cr_2O_7$ to oxidize the uranium in the sample to the +6 oxidation state and again swirl the contents.	The $K_2Cr_2O_7$ addition may be omitted only when the oxidation state of the uranium in the sample is known to be +6.
3.	Add the minimum volume of conc NH_4OH to neutralize acidity in excess of 8 meq added in the sample aliquot.	This step may be omitted if high decontamination from fission products is not essential.
4.	Add 4 ml of the salting (reagent 2) solution, 2 drops of the aluminon reagent, 2 ml of hexone, insert a stopper, and mix the contents for 1 min on the phase mixing apparatus.	Read the next note before continuing.
5.	Transfer as much of the organic phase (with none of the aqueous phase) as	In this step and steps 6 and 7, neptunium, plutonium, and other extraneous elements are scrubbed from the organic phase.

	possible with a new transfer pipet to a 10-ml test tube. Discard the aqueous phase to the hot waste drain.	These steps may be omitted for samples that do not contain significant quantities of these components (See the DISCUSSION section).
6.	Add 2 ml of the plutonium scrub (reagent 7) solution, insert a stopper, and mix the contents for 3 min on the phase mixing apparatus.	Also steps <u>5</u>, <u>6</u>, and <u>7</u> must be used when $K_2Cr_2O_7$ was added and the samples contain chloride. With such a combination, chromium extracts. These steps scrub chromium from the organic phase. If not scrubbed, chromium would carry through the rest of the procedure and cause erratic behavior in the mass spectrometer.
7.	Centrifuge for 1 min at 2/3 full speed.	
8.	Transfer as much of the organic phase (with none of the aqueous phase) as possible from either step <u>4</u> or step <u>6</u> with a new transfer pipet to a new, cleaned 5-ml centrifuge tube. Discard the aqueous phase to the hot waste drain.	
9.	Slowly, without spattering, evaporate the hexone to dryness under a heat lamp with the aid of a gentle stream of air directed into the tube.	Perform this operation in a glove box or hood.
10.	Heat the tube with a Meker burner until the tip of the tube just glows red.	This decomposes all the organic matter.
11.	After the tube cools, add 2 drops of conc HNO_3 and evaporate to dryness as described in step <u>9</u>.	
12.	Repeat step <u>11</u>.	
13.	Insert a clean stopper and measure the gross beta-gamma activity with a portable meter in contact with the tube.	If the reading is less than 30 mR/hr, continue with step <u>16</u>. If more than 30 mR/hr, continue with step <u>14</u>.

14.	Add 0.5 ml of 6<u>M</u> HNO_3 to the tube, swirl it for 1 min, and transfer the solution with the aid of another 0.5 ml of 6<u>M</u> HNO_3 wash to a clean 10-ml test tube.	Use a new transfer pipet for this transfer. Make sure that a new unused 10-ml test tube is used.
15.	Repeat steps <u>4</u> through <u>13</u>.	
16.	Write the log number and sample code on the tube and prepare a work sheet for the mass spectrometry laboratory which includes all data necessary to calculate the final results, such as sample weight and dilutions.	

C. High-Level Uranium Separation

NOTE: See Procedure <u>D</u> for remote techniques.

1.	Pipet an aliquot of the sample that contains from 0.05 to 5 mg of uranium into a test tube that contains 500 µl of U-233 spike solution I.	Use a calibrated dri-filmed Ultrapette in the range of 100 to 1000 µl. Select the pipet to give the closest ratio of 1 to 1 for the major uranium isotope to U-233. The amount of U-233 in the tube is 0.5 mg. Pipet the sample aliquot deep into the tube but do not let the pipet tip touch the U-233 solution.
2.	Mix the contents of the tube by swirling and add 2 drops of 0.1<u>M</u> $K_2Cr_2O_7$ to oxidize the uranium in the sample to the +6 oxidation state and again swirl the contents.	The $K_2Cr_2O_7$ addition may be omitted only when the oxidation state of the uranium in the sample is known to be +6.

3.	Add the minimum volume of conc NH_4OH to neutralize acidity in excess of 8 meq added in the sample aliquot.	This step may be omitted only if high decontamination from fission products is not essential.
4.	Add 4 ml of the salting (reagent 2) solution, 2 drops of aluminon reagent, 2 ml of hexone, insert a stopper and mix the contents for 1 min on the phase mixing apparatus.	Read the next step before continuing.
5.	Transfer as much of the organic phase (with none of the aqueous phase) as possible with a new transfer pipet to a 10-ml test tube. Discard the aqueous phase to the hot waste drain.	In this step and steps 6 and 7, neptunium, plutonium, and other extraneous elements are scrubbed from the organic phase. These steps may be omitted for samples that do not contain significant quantities of these components. (See the DISCUSSION Section).
6.	Add 2 ml of the plutonium scrub (reagent 7) solution, insert a stopper and mix the contents for 3 min on the phase mixing apparatus.	Also, steps 5, 6, and 7 must be used if $K_2Cr_2O_7$ was used and the samples contain chloride. With such a combination, chromium extracts. These steps scrub chromium from the organic phase. If not scrubbed, chromium would carry through the rest of the procedure and cause erratic behavior in the mass spectrometer.
7.	Centrifuge for 1 min at 2/3 full speed.	
8.	Transfer as much of the organic phase (with none of the aqueous phase) as possible from either step 4 or step 6 with a new transfer pipet to a new, cleaned 5-ml centrifuge tube. Discard the aqueous phase to the hot waste drain.	

9.	Add 1 ml of 30% H_2O_2, insert a clean stopper, and mix the contents for 1 min or until the precipitation of uranium peroxide appears complete.	If no precipitate forms, add 1 drop of conc NH_4OH and again mix the contents. This may be repeated, 1 drop at a time, to obtain increased amount of precipitate. However, samples treated with large amounts of conc NH_4OH tend to give erratic behavior in the mass spectrometer.
10.	Centrifuge at 2/3 full speed for 5 min.	
11.	With a clean transfer pipet connected to a vacuum wash train, remove the supernatant solution without disturbing the precipitate.	
12.	Add 2 drops of acetone and vigorously agitate the tube until the precipitate is dispersed.	In steps 12 and 13, do not let acetone contact rubber stopper.
13.	Wash down the tube with 3 ml of acetone.	
14.	Centrifuge at 2/3 speed for 5 min.	
15.	With the transfer pipet used in step 11, remove the acetone without disturbing the precipitate.	If the acetone is highly colored which indicates organic matter, repeat steps 13, 14, and 15.
16.	Insert a clean stopper and measure the gross beta-gamma activity with a portable meter in contact with the tube.	If the reading is less than 30 mR/hr, continue with step 19. If more than 30 mR/hr, continue with step 17.
17.	Add 0.5 ml of 6M HNO_3 to the tube, swirl it for 1 min, and transfer the solution with the aid of another 0.5 ml of 6M HNO_3 wash to a clean 10-ml test tube.	Use a new transfer pipet for this transfer. Make sure that a new unused 10-ml test tube is used.

18. Repeat steps 4 through 16.

19. Write the log number and sample code on the tube and prepare a work sheet for the spectrometry laboratory which includes all data necessary to calculate the final results, such as sample weight and dilutions.

D. Remote Operation Separation

1. Add 2 drops of 0.1M $K_2Cr_2O_7$ to a 10-ml test tube that already contains 500 µl either of U-233 spike solution I or U-233 spike solution II.

   Select the spike solution depending on the uranium content of the sample. See steps 1 in both Procedures B and C.

2. Add 4 ml of the salting (reagent 2) solution and 2 drops of the aluminon reagent to a clean 10-ml test tube.

3. Add 2 ml of hexone to another clean 10-ml test tube.

4. Transfer the 3 tubes prepared in steps 1, 2, and 3 to the Remote Analytical Facility.

5. Deliver an aliquot of the sample that contains from 0.0005 to 0.05 mg of uranium into the test tube that contains the U-233 spike solution II or an aliquot of the sample that contains from 0.05 to 5 mg or uranium into the U-233 spike solution I.

   Adjust the pipetter tip to a height of 1 in. above the liquid in the tube before delivering the sample. Also, adjust the tube position so the pipetter tip is not touching the tube. The recommended delivery volume for dissolved fuel samples from the plant process is 500 µl. Use the calibrated 200 to 700 position of the pipetter to deliver 500 µl.

6.	Wash the pipet tip with 5 to 10 drops of water.	The salting strength will be diluted too much if more than 10 drops is used to result in unsatisfactory low extraction of uranium.
7.	Remove the tube from the pipetter and mix the contents by swirling the tube.	Take care no solution is lost from the tube in this operation.
8.	Add the 4 ml of the salting (reagent 2) solution and 2 drops of aluminon reagent from the transferred (step 2) tube. Discard the empty tube.	
9.	Insert a stopper and mix the contents by swirling the tube.	
10.	Remove the stopper, add the 2 ml of hexone from the transferred (step 3) tube. Set the empty tube aside.	
11.	Replace the stopper and mix the contents for at least 1 min by repeatedly inverting the tube.	Use the tong that has a special bracket to hold the stopper in place.
12.	Decant as much of the organic phase (with none of the aqueous phase) as possible to the empty tube that had contained the hexone.	
13.	Insert a clean stopper and transfer the tube to the Warm Laboratory.	
14.	Continue either with Procedure B, step 6, or with Procedure C, step 6.	

REFERENCES

1. W. J. Maeck, G. L. Booman, M. C. Elliott, J. E. Rein, "Separation of Uranium From Diverse Ions: Methyl Isobutyl Ketone Liquid-Liquid Extraction System", Anal. Chem., 30 (December 1958, pp. 1902-1907.

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TITRIMETRIC DETERMINATION OF ZIRCONIUM WITH CUPFERRON

ABSTRACT

Zirconium is titrated with cupferron in a 3.6M $(NH_4)_2SO_4$-2M H_2SO_4 medium to an amperometric end point[1].

APPLICABILITY

Though quite selective, cupferron (ammonium salt of nitrosophenylhydroxylamine) reacts[1,2] with a number of common metal ions in 2M H_2SO_4 medium (Table B-X). This method, therefore, is limited to samples that contain only negligible amounts of metallic interferences. Examples of samples that can be analyzed are solutions of zirconium salts, solutions of Zircaloy and Zircaloy-clad fuels, and solutions such as those encountered in fuel processing and waste calcination that contain zirconium and aluminum or aluminum plus calcium.

Other potential interferences are strong oxidants that destroy the cupferron and complexing anions that keep the zirconium from reacting quantitatively and rapidly with cupferron. Examples of oxidants are nitrate above 10 mmole per sample aliquot, cerium(IV), chromium(VI), and large amounts of perchlorate. Cupferron forms an extremely stable complex with zirconium so most anions including chloride, citrate, fluoride, nitrate, oxalate, sulfate, and tartrate can be tolerated at mmole levels[1]. Fluoride which often is present in zirconium-containing solutions, is tolerated up to a molar ratio of 30 to 1. Phosphate at 1 to 1 seriously retards the formation of zirconium cupferrate but can be tolerated if sufficient time is allowed for equilibrium to be established[1].

The harmful effects of oxidants and large amounts of fluoride can be reduced or eliminated by evaporating the sample to sulfuric acid fumes initially, then reducing residual oxidants with hydroxylamine. The addition of aluminum also removes fluoride interference[1].

The overall range of this method is 0.01 to 0.10 mmole of zirconium Best precision is obtained above 0.025 mmole.

TABLE B-X

PRECIPITATION OF METAL IONS BY CUPFERRON IN 2M H_2SO_4 MEDIUM

Metal Ions	Extent of Precipitation and Effect of Ion on the Method
Bi(III), Fe(III), Ga(III), Hf(IV), Mo(V,VI), Nb(V), Sb(III), Sn(IV), Ta(V), Ti(IV), U(IV), V(IV,V), W(V,VI).	Complete or nearly complete precipitation; Serious positive interference.
Cu(II), lanthanides(III), Th(IV), Tl(III).	Partial precipitation; Positive interference increases as level of ion increases.
Alkali metals(I), alkaline earths (II), Al(III), Ag(I), As(III), Be(II), Ca(II), Cd(II), Co(II), Cr(III), Fe(II), Hg(II), In(III), Mg(II), Mn(II), Ni(II), Pb(II), Ru(III,IV), Sc(III), Tl(I), U(VI), Y(III).	No precipitation; No interference expected even at high levels except that some ions may precipitate as the sulfate and carry down Zr. Examples of these are the alkaline earths and Pb(II).

DISCUSSION

Cupferron reacts with zirconium at a stoichiometric 4 to 1 ratio when the zirconium is in the form of the reactive monomer. Fuming the sample with sulfuric acid assures this. The end point of the titration is determined by monitoring the concentration of uncomplexed cupferron amperometrically at a potential of -0.75 V versus the standard calomel electrode. When all available zirconium is complexed and free cupferron appears, the cupferron is reduced at the surface of a dropping mercury electrode resulting in a current that rises linearly with increasing free cupferron concentration. The end point is the intersection of this straight line and the straight line constructed through the current versus volume of titrant points before the appearance of free cupferron. The titration conditions originally recommended by Olson and Elving[1], i.e., titration in 1.8M H_2SO_4 medium at -0.84 V, gave a titration curve characterized by a pre-end point hump that introduced much uncertainty in the location of the end point. This difficulty has been corrected by lowering the potential to -0.75 V[3] and by loading the titration medium with ammonium sulfate[4]. The solidification of the 1% gelatin solution also has been a problem. Solid gelatin, a highly satisfactory substitute[5], therefore is used.

SAFETY PRECAUTIONS

The initial steps of the analysis involve the addition of 9M H_2SO_4 and the evaporation of the sample to sulfuric acid fumes. Wear rubber gloves when handling the sulfuric acid and perform the fuming in a fume hood behind a safety shield. Cool the fumed sample before adding the 4M $(NH_4)_2SO_4$ solution; however, do not immerse the fuming beaker directly into cold water. The beaker is likely to shatter resulting in dangerous spattering.

APPARATUS AND REAGENTS

A. Apparatus

1. Ampot, Sargent, modified with compensator or Model III Sargent Polarograph, or equivalent.

2. Beakers, Berzelius tall-form, 200-ml.

3. Buret, 10-ml, graduated in 0.05-ml increments.

4. Electrode assembly, standard calomel and dropping mercury electrodes (with attached mercury reservoir) mounted through a Teflon plug which fits the 200-ml tall-form beaker. This assembly also contains two polyethylene tubing inlets for the nitrogen purge and sweep gas.

5. Graduated cylinders, assorted sizes.

6. Hot plate.

7. Magnetic stirrer, with plastic-coated magnetic stirring bars.

8. Pipets, macro and micro, assorted sizes with rubber suction bulb and control syringe.

9. Valve, 2-way valve for directing the nitrogen gas to either purge or sweep as desired. Valve is mounted on the Ampot.

B. Reagents

NOTE: Use Analytical Reagent Grade chemicals and distilled water for the preparation of all reagents.

1. Ammonium sulfate solution, 4M. Dissolve 1060 g of $(NH_4)_2SO_4$ in 1800 ml of water and dilute to 2 liters with water.

2. Cupferron solution, 0.0500M. Dissolve 7.7580 g of cupferron in water and dilute to 1 liter. Store the solution in the refrigerator when not in use. Prepare a new solution after 5 days. Cupferron stored over ammonium carbonate as obtained from J. T. Baker is satisfactory. If purification is necessary, purify the reagent as follows:

   Dissolve 25 g of the reagent in 250 ml of water in a 1-liter separatory funnel. Add 15 ml of conc HCl and shake. Add 75 ml of diethyl ether and mix thoroughly by shaking. Reject the aqueous phase. Add ammonium hydroxide until basic to litmus and sufficient water until the precipitate solubilizes. Transfer small portions of the ammonium hydroxide phase to large beakers and precipitate the purified ammonia salt with acetone. Collect the product on a Buchner funnel, rinse several times with acetone, and air dry.

3. Gelatin, solid powder.

4. Hydroxylamine sulfate, 2<u>M</u>. Dissolve 32.8 g of $(NH_2OH)_2 \cdot H_2SO_4$ in water and dilute to 200 ml.

5. Nitrogen, water-pumped, in large cylinders.

6. Sulfuric acid, 9<u>M</u>.

7. Zirconium Bench and Control Standards. Prepare these standards from pure crystal bar zirconium to cover the range 0.01 to 0.1 mmole of zirconium. Dissolve the zirconium metal in a minimum of hydrofluoric acid in a plastic container and dilute to volume with water. The standards are best stored in screw-cap polyethylene bottles.

PROCEDURES

A. Preliminary Operations

1. Connect the black-tipped wire of the Sargent Ampot to the dropping mercury electrode and the red-tipped wire to the Calomel electrode.

2. Start the dropping mercury electrode, making sure that no air bubbles exist in the mercury lines.

3. Open the nitrogen valve and adjust the flow to a rate of about 2 bubbles per sec.

4. Keep the "Rev. Cell" switch on the position (- +).

5. Set the "Current Mult" on "X_1".

6. Leave the "Current" switch on normal.

7. Leave the helipot labeled "App. E.M.F." at "750".

8. Turn "Battery" to "On" and set the "Range E.M.F." to 1.00 V.

9. Leave the "Circuit" "Open" until ready to take readings and then throw the switch to "Damped".

B. Blank

Recent experience indicates that no blank determination is necessary for this method.

C. Analysis of Bench-Control Standard

Process a bench standard with each series of samples per Procedure D. The result obtained must fall within the limits specified. If not, reprocess the standard. Consult your supervisor if difficulties persist.

D. Analysis of Samples

NOTE: The cupferron titrant is stored in a refrigerator. Take it out of the refrigerator enough in advance to allow the solution to warm to room temperature.

1. Pipet a sample aliquot containing 0.01 to 0.10 mmole of zirconium into a 200-ml Berzelius beaker.	For best precision, work at the high end of the range 0.025 to 0.10 mmole.
2. Add 20 ml of 9M H_2SO_4, evaporate to the appearance of sulfuric acid fumes, and fume for 5 min.	Most zirconium samples contain fluoride so do not use a cover glass. Evaporate carefully without spattering the sample.
3. Let the beaker and contents cool to room temperature, add 80 ml of 4M $(NH_4)_2SO_4$, and 1 ml of 2M $(NH_2OH)_2 \cdot H_2SO_4$, and mix by magnetic stirring.	
4. Chill the solution to 25°C or less in a cold water bath.	Above 25°C, cupferron decomposes readily. Measure the temperature with a thermometer.
5. Add about 1/2 micro spatula full of solid gelatin powder.	
6. Rinse the electrode assembly with water and fit it onto the beaker.	

7.	Bubble nitrogen through the solution for at least 5 min with the stirrer on.	The purpose of this step is to remove oxygen.
8.	Change the nitrogen to sweep over the solution and with the stirrer off, measure the mercury drop time. It should be between 2 and 5 sec per drop. If necessary, adjust the height of the mercury reservoir to obtain the required drop time.	If readjustment of the mercury reservoir height fails to give the desired drop time, the length of the capillary electrode must be altered.
9.	Fill the buret with fresh 0.0500<u>M</u> cupferron solution and titrate the sample "amperometrically" with the "Circuit" switch in the "Damped" position.	"Amperometric" titration involves (a) the addition of a constant increment of titrant with the nitrogen bubbling through the solution and the stirrer on, (b) the passage of nitrogen through the solution for another 30 sec with the stirrer on, (c) waiting 60 sec with the stirrer off and the nitrogen sweeping over the solution, and (d) recording the galvanometer (current) reading and the corresponding volume of titrant. This four-step process is repeated until 5 points are obtained beyond the break or end point. The recommended titrant increments are 0.10 ml, 0.25 ml, and 0.50 ml for the zirconium levels 0.01 to 0.025, 0.025 to 0.050, and 0.050 to 0.100 mmole, respectively.
10.	Record the data and calculate the results as described under <u>CALCULATIONS</u>.	

CALCULATIONS

Record the titration (titrant volumes and galvanometer readings) data on a columnar sheet of paper, then determine the end point by plotting galvanometer readings on the vertical axis against titrant volume on the horizontal axis (Figure B-10). The end point is the intersection of the two lines defined by the points before and after the break.

Record the titrant volume and the sampling data on the work sheet and calculate the results as described on the work sheet. Report all results to 3 significant figures.

The factor 0.25 appears in the equation for the calculation of the mmole of zirconium in the sample aliquot. This factor converts mmole cupferron to mmole zirconium, for as noted in the discussion, cupferron reacts with zirconium in the ratio 4 to 1.

REFERENCES

1. E. C. Olson and P. J. Elving, "Amperometric Titration of Zirconium,Application to Fluoride Solution," Anal. Chem., 26 (1954) p 1747.
2. G. E. F. Lundell and J. I. Hoffman, Outlines of Methods of Chemical Analysis, New York: Wiley, 1963.
3. H. Kubota and J. G. Surak, "Automatic, Amperometric, Cupferron Titration of Zirconium in Highly Radioactive Solutions," Anal. Chem., 35 (1963) pp 1715-1718.
4. S. S. Yamamura, J. E. Rein, G. L. Booman, "Amperometric Determination of Tin with Cupferron," Anal. Chem., 31 (1959) pp 1868-1870.
5. E. M. Fortsch, Idaho Nuclear Corporation,private communication (March 1969).

April 1969
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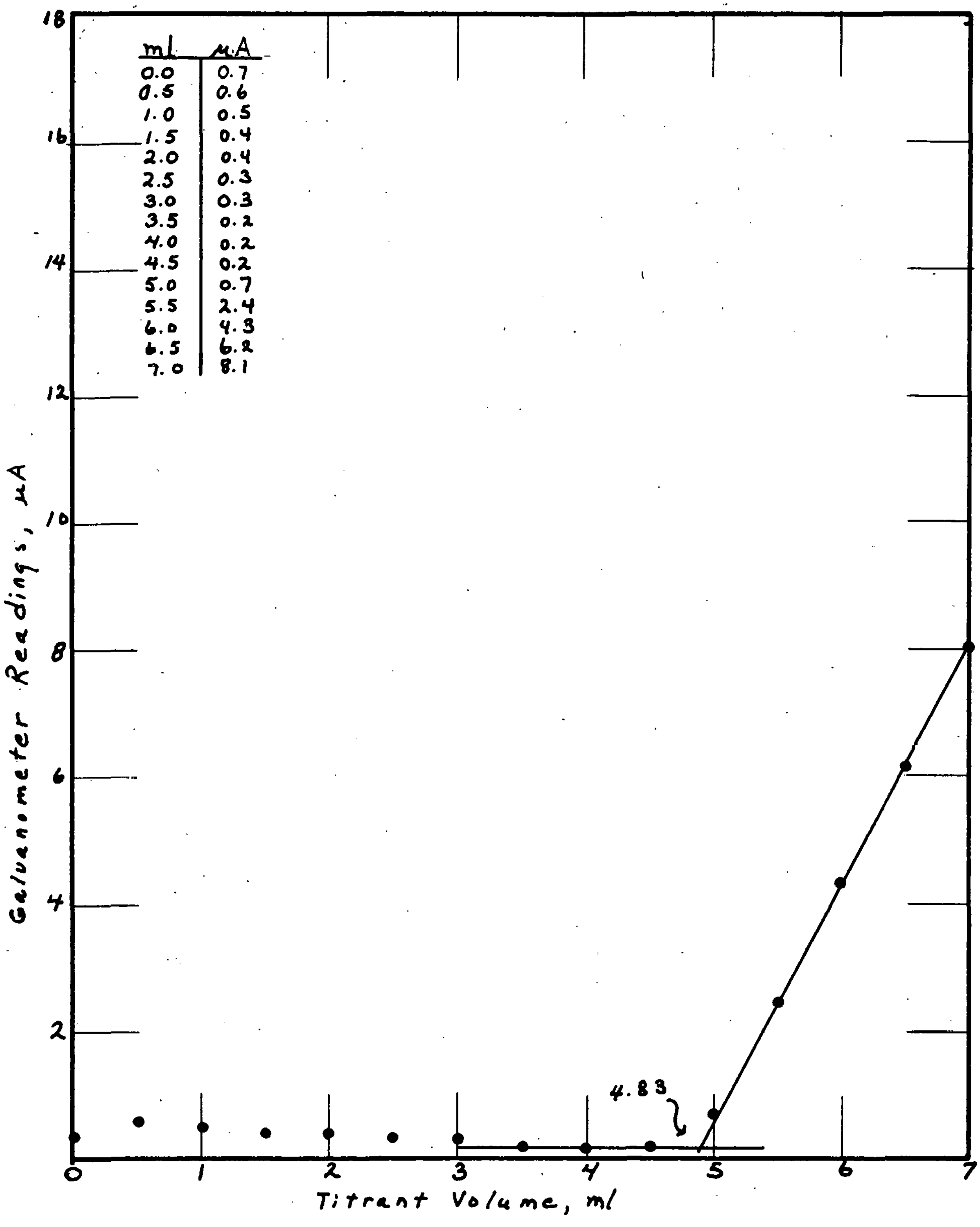

ml	µA
0.0	0.7
0.5	0.6
1.0	0.5
1.5	0.4
2.0	0.4
2.5	0.3
3.0	0.3
3.5	0.2
4.0	0.2
4.5	0.2
5.0	0.7
5.5	2.4
6.0	4.3
6.5	6.2
7.0	8.1

Fig. B-10 Titration data.

FORM INC-121
(REC. 4-67 BACK)

CHEMICAL ANALYSIS WORK SHEET

SAMPLE NAME ______________________ LOG NUMBER ______________________

ACTIVITY (mR/hr) ______________________ DETERMINATION Zirconium

CHARGE NUMBER ______________________ PROCEDURE Zr-Vol-1

SPECIAL INSTRUCTIONS:

		A	B	C	D	E	F	G	
SAMPLE DESCRIPTION	SAMPLING AND DILUTION DATA: $a_0/d_1/a_1/d_2/a_2$	cupferron <u>M</u>	End Point From Graph ml	mmole Zr in Aliquot Analyzed	mmole Zr Corrected For Bias				RESULT <u>M</u>
No. 101	0.100 ml	0.0500	4.83	0.060	0.059±0.002				0.59±0.02

ANALYZED BY ______________________ DATE ______________________

CALCULATIONS:

$$C = AB(0.25) = (0.0500)(4.83)(0.25) = 0.0604 \text{ mmole Zr}$$

$$\text{Result} = \frac{D}{\text{Vol. sample}} = \frac{0.059 \pm 0.002}{0.100} = 0.59 \pm 0.02 \ \underline{M}$$

APPROVED BY ______________________

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APPENDIX C

ANALYSIS OF AN ATR FUEL PLATE FOR TOTAL B-10 AND U-235

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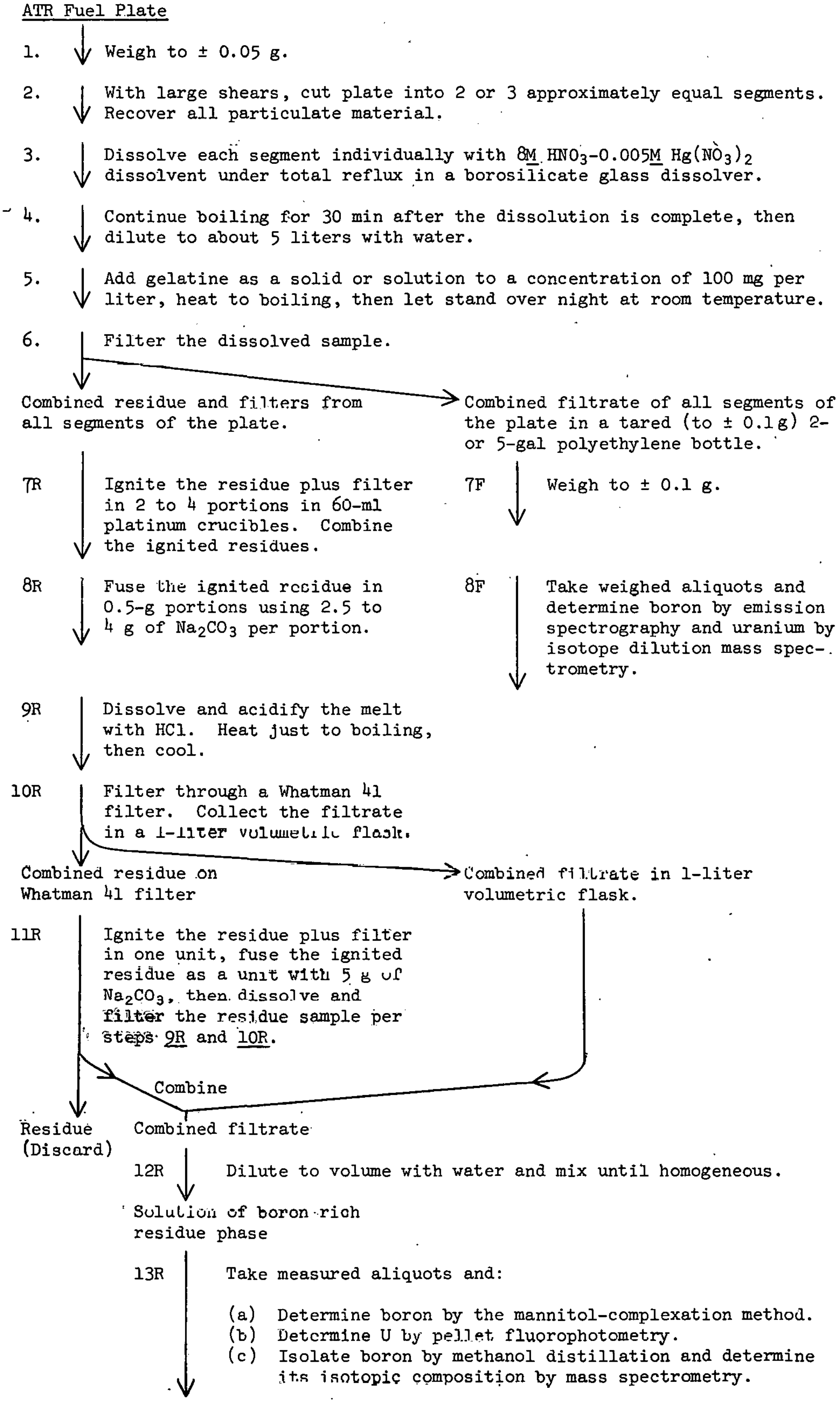
The following, in diagram form for simplicity, is the analysis scheme for the determination of total B-10 and U-235 in ATR-type fuel plate.



ATR Fuel Plate

1. Weigh to ± 0.05 g.

2. With large shears, cut plate into 2 or 3 approximately equal segments. Recover all particulate material.

3. Dissolve each segment individually with 8M HNO_3-0.005M $Hg(NO_3)_2$ dissolvent under total reflux in a borosilicate glass dissolver.

4. Continue boiling for 30 min after the dissolution is complete, then dilute to about 5 liters with water.

5. Add gelatine as a solid or solution to a concentration of 100 mg per liter, heat to boiling, then let stand over night at room temperature.

6. Filter the dissolved sample.

Combined residue and filters from all segments of the plate.

7R Ignite the residue plus filter in 2 to 4 portions in 60-ml platinum crucibles. Combine the ignited residues.

8R Fuse the ignited residue in 0.5-g portions using 2.5 to 4 g of Na_2CO_3 per portion.

9R Dissolve and acidify the melt with HCl. Heat just to boiling, then cool.

10R Filter through a Whatman 41 filter. Collect the filtrate in a 1-liter volumetric flask.

Combined filtrate of all segments of the plate in a tared (to ± 0.1 g) 2- or 5-gal polyethylene bottle.

7F Weigh to ± 0.1 g.

8F Take weighed aliquots and determine boron by emission spectrography and uranium by isotope dilution mass spectrometry.

Combined residue on Whatman 41 filter

11R Ignite the residue plus filter in one unit, fuse the ignited residue as a unit with 5 g of Na_2CO_3, then dissolve and filter the residue sample per steps 9R and 10R.

Combined filtrate in 1-liter volumetric flask.

Combine

Residue (Discard)

Combined filtrate

12R Dilute to volume with water and mix until homogeneous.

Solution of boron-rich residue phase

13R Take measured aliquots and:

(a) Determine boron by the mannitol-complexation method.
(b) Determine U by pellet fluorophotometry.
(c) Isolate boron by methanol distillation and determine its isotopic composition by mass spectrometry.

DETAILS AND NOTES REGARDING THE ANALYSIS SCHEME

Step	Notes
2	The weight of the ATR plates varies from 260 g (Plate 2) to 950 g (Plate 19). Most of this is aluminum with a practical solubility limit of about 1M. If a sufficiently large dissolver-condenser apparatus is available, the plate may be taken as a unit. At CPP, the plate is severed to permit dissolution in existing 6-liter flasks. The inside diameter of the largest, commercially available, male, standard-taper joint is 103 mm (4 in.). It may be necessary, therefore, to bend those plates (Plates 18 and 19) with a width of 4 in. into the shape of an angle iron.
3	Initially, add 500 ml of the dissolvent to the flask, insert the fuel plate segment into it through the condenser, then heat the flask on a hot plate until vigorous reaction starts. Immediately, remove the flask from the hot plate and let the reaction proceed without heating until it subsides. Return the flask to the hot plate and complete the dissolution by the addition of 250-ml increments of dissolvent as required. Control the vigor of the dissolution by adjusting the heating. Throughout the dissolution, keep 500 ml of cold distilled water nearby to quench the reaction when necessary.
5	Gelatine facilitates filtration by precipitating silica.
6	Using a siphon system, siphon the clear supernatant solution first, then the slurry. Membrane filters of 0.45-μ pore size (Gelman α-6 or Millipore HA) supported on a 47-mm diam Millipore filter holder is satisfactory. Frequent filter changes are recommended for rapid filtration. Depending on the size of the plate (See notes for step 2), use a tared 2- or 5-gal polyethylene bottle to store the filtrate.
7R	Dry the residue first in an oven or over a hot plate, then perform the initial ignition over a Meker burner. Complete the ignition in a muffle furnace at 1000°C.
8R	Use 2.5 g of Na_2CO_3 initially, then add another gram later if a clear melt is not obtained. The fusion should be started, with a lid on the crucible, over an air-fed Meker burner (∿ 5 min), then completed in a 1000°C muffle furnace (∿ 10 min). After about 5 min of fusion, spattering is negligible and the lid may be removed for visual inspection of the melt.

8F The isotopic distribution mass spectrometric procedure for the determination of uranium is described in TID-7029, "Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle". The spectrographic method for boron is one in use at CPP employing a vacuum technique. The usual vacuum cup electrode has a convex-shaped head. Altering the head to a crater shape has increased the sensitivity and precision of the method.[1]

9R Wipe the outside of the crucible with a damp tissue and lay it and the lid in a 250-ml Teflon beaker containing 75 ml of water. Add 2 ml of conc HCl for each gram of Na_2CO_3 and cover the beaker with a polyethylene or Teflon cover glass. When the melt disintegrates completely, heat the solution just to boiling, then chill it to room temperature. (The fused residue of ETR-type plates with large amounts of silicon should be decomposed in water without any HCl addition.)

10R Filter all the dissolved solutions through the same filter. Rinse the beaker and filter thoroughly with water.

11R See Notes to step <u>7R</u> through <u>10R</u>. The residue remaining after the second carbonate fusion has been found to contain only insignificant amounts of boron and uranium.

13R The mannitol-complexation method is Method B-Vol-1 in the INC Analytical Chemistry Manual. The pellet fluorophotometric method for the determination of low concentrations of uranium is Method U-Fluor-1 in the same manual. The latter also is described in TID-7029.

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[1] Ted Lyon, Idaho Nuclear Corporation, Private Communication, September, 1968.