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ANNUAL REPORT OF THE ANALYTICAL CHEMISTRY
BRANCH FOR 1966

R. C. Shank & Staff



IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
IDAHO FALLS, IDAHO

U. S. ATOMIC ENERGY COMMISSION

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ANNUAL REPORT OF THE ANALYTICAL CHEMISTRY BRANCH FOR 1966

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ANNUAL REPORT OF THE ANALYTICAL CHEMISTRY BRANCH FOR 1966

SUMMARY - J. M. Crawford

This report presents a general survey of significant work performed by the Analytical Chemistry Branch during 1966. Special service work and research to develop and improve methods and equipment used in the various fields of analytical chemistry are described. All new and revised methods that have been established for regular use during the year are reported in detail in appropriate appendixes. Special analytical work in support of specific AEC-sponsored projects and the continuing development work in maintaining standards and quality control are reported.

This summary is grouped according to the various analytical disciplines represented and may be considered as brief abstracts of the year's accomplishments.

Analytical Development

A colorimetric method, applicable to a wide variety of inorganic and organic samples, has been developed for the determination of mercury. This method includes one basic double-extraction procedure and one single-extraction procedure.

Sixteen unirradiated aluminum-uranium fuel plates were very accurately analyzed for total uranium and isotopic distribution of uranium.

Analytical development service for Westinghouse included: (a) a revised procedure for the colorimetric determination of nickel; and (b) two methods for the determination of citrate and Versenol in an ammonium dihydrogen citrate-Versenol descalant solution.

The dangers of Hengar Granule boiling chips to micro analyses when used in evaporations or acid digestions are described.

Physic Section personnel were given assistance in the separation of short half-life, neutron-deficient radionuclides for decay scheme studies.

A method, designed for glove box operation and applicable to a wide variety of irradiated fuels, has been developed for the separation of plutonium for analysis by isotope dilution mass spectrometry.

The results of a study using the uranium(V) disproportionation reaction in a perchloric acid media were published in Analytical Chemistry.

Instrumentation for electrochemical measurements includes the following: (a) a basic digital system to perform many necessary control and measurement functions, (b) a hybrid analog-digital system with three operational amplifier integrators to improve measurement of electrochemical transients, (c) a new system of all solid-state, operational amplifiers and power boosters to improve by a factor of 10 or more the short time range (10 μ sec) over

which electrochemical reactions can be observed, and (d) a high speed, paper tape punch to improve electrochemical measurements.

To facilitate the large volume of data obtained with the paper tape punch readout system, a data reduction computer program has been written in Fortran language to reduce the electrochemical data by use of a high-speed digital computer.

An in-line plant monitor system is being developed to detect fissionable material in the process equipment waste (PEW) stream in the Chemical Processing Plant. The monitor is to warn of potential nuclear criticality in the noncritically-safe PEW storage tanks.

Because of the instrumentation requirements of the Analytical Branch over the next 5 yrs, a Branch digital computer facility has been proposed, and the specifications and equipment requirements now are being developed.

Attempts to operate the TDD-1 mass spectrometer magnet at currents greater than 200 mA resulted in complete loss of control of the magnet current with the current running to a maximum. After modifying the system, regulation of current in excess of 500 mA was obtained.

In support of the Loss-of-Fluid Test (LOFT) program, development was performed for analytical methods, for fission product inventories in irradiated fuel; for atmosphere analysis, for gas-particulate capsule samplers, and for materials for packaging samples.

A high-level counting system with a NaI(Tl) detector was installed to count radioactive samples up to ~ 5 R/hr. The spectra were resolved by a computer, spectrum stripping program. A procedure is described for the separations of iodine fission product isotopes to obtain their individual gamma-ray spectra. A 10-cc Ge(Li) detector and a 1024-channel memory, 4096-channel ADC analyzer system was installed to reduce the number of chemical separations required for complex mixtures when NaI(Tl) detectors are used. Aluminum, 1/16-in. thick, proved satisfactory for plateout coupon material.

Prior to the installation of the Ge(Li) detector, a dissolution and sequential separation procedure was developed to produce fractions of fission products resolvable by NaI(Tl) gamma-ray spectrometry. The major steps in the procedure are described. Disadvantages, however, were found in the procedure; thus two analytical schemes are being evaluated. One is based on complete analysis by gamma-ray spectrometry with both NaI(Tl) and Ge(Li) detectors. The other involves minimum chemical separations combined with gamma-ray spectrometry.

An inventory of the fission products at meltdown time in the Contamination-Decontamination-Experiment (CDE) has been established based on pre- and post-irradiation uranium isotopic levels.

Analysis of the gases in the reactor vessel can furnish data on metal-water reactions, presence of reducing or oxidizing atmosphere, amount of air entering the vessel, and amount of helium release by ruptured fuel pins.

Hydrocarbon measurements were made of the containment atmosphere before and after the meltdown of an unirradiated fuel element to determine which organic material could contribute to the formation of penetrating iodine.

One of the major sampling devices for LOFT will be the gas-particulate capsule. Laboratory experiments are being performed to test its capability to distinguish between different chemical species of iodine as well as testing the overall performance of the capsule in the CDE Facility.

The sorption of molecular iodine was measured for various particulate filters, charcoal papers, silver-coated copper screens, silver membranes, and assembled filter cartridges.

A procedure was developed and the apparatus designed for the preparation of milligram quantities of I-131 tagged methyl iodide. Various particulate filters, iodine adsorbers, and assembled filter cartridges were tested for sorption of methyl iodide.

The sorption rate of water on charcoal was measured. The complete capsule and assembled cartridges are being evaluated for mechanical and functional operability.

Materials are being tested for packaging analytical samples from LOFT. The leakage rate of molecular iodine and methyl iodide from various materials is described.

Additions and proposed additions to the remotely operated facilities includes the following: (a) a 40 by 40 by 36-in. storage facility for radioactive samples in Cell X, (b) resumption of construction work on the additional alpha handling facility, (c) design of the Remote Analytical Facility Cave, and (d) future RAF installations will consider the use of master-slave manipulators rather than Castle manipulators.

In the continuing program to develop methods for the accurate determination of the burnup of nuclear fuels, details were reported in the quarterly reports, Burnup Determination of Nuclear Fuels.

Spectroscopy

Potassium in scrub solutions and product from the Waste Calcination Facility (WCF) was determined by atomic absorption. The calibration range covers from 0.1 to 1.5 ppm.

An x-ray diffraction study was initiated to determine the change in the lattice parameter of beryllium used as neutron reflectors in nuclear reactors.

An irradiated stainless steel sample was analyzed by emission spectrography for changes in elemental composition. Major decreases were noted in B, Nb, Pb, Si, and Ti concentrations. Major increases were noted in Cu, Mn, Sn, and V concentrations.

A Jarrell-Ash flame spectrometer was converted to a dual atomic absorption flame emission instrument by the addition of atomic absorption accessories.

The stability of UAl_3 at $1000^\circ C$ was determined by x-ray powder camera techniques, and no changes were detected after 250 hr.

A new, demountable, hollow cathode tube was constructed to be used as a sample excitation source for both emission and absorption, or it can be used as a variable light source for atomic absorption by changing cathodes. The hollow cathode tube was used in studies to develop a spectrographic method for fluorine and other nonmetal analyses.

Microwave excitation was used for the spectrographic detection of submicrogram quantities of mercury. A 3 meter Baird spectrograph gives a mercury line at 2537\AA from 0.01 μg of mercury.

Relative fission gas retention properties of irradiated uranium aluminide and uranium dioxide fuel plates were determined using a CEC mass spectrometer.

Acquisition and improvement of equipment are as follows: (a) A CEC 21-620 mass spectrometer from surplus was placed into operating condition, (b) the vacuum-lock drive mechanism on the TDD-1 mass spectrometer was modified, (c) the vacuum-extraction, hydrogen analysis apparatus was modified for remote operation, (d) the mass spectrometer filament bakeout chamber was altered to bake out filaments before installation in the hats which position the filaments in the spectrometer source, and (e) new jigs for forming the filaments have been designed and fabricated.

Chemical Analysis

The methods used by the Chemical Analysis Section and time per analysis are listed in Table V-1.

A white powder was analyzed to determine whether it was Millons base or the nitrate salt of Millons base. The powder was either a mixture of Millons base and the nitrate salt or a polymeric species of the nitrate salt.

Silica particles were dissolved in a mixture of hydrofluoric and sulfuric acid. The dissolution was analyzed spectrophotometrically for the absorbance of neptunium in the silica, and 5.4% was found.

Aluminum alloy powder compacts were analyzed for ruthenium, palladium, and osmium. Palladium was analyzed by x-ray fluorescence, and ruthenium and osmium were analyzed colorimetrically.

Fuel from the Snap-2 reactor contains 10% uranium and 90% zirconium, and the dissolution of the fuel is described.

An Inconel sample was analyzed for Al, Cr, Fe, Ni, P, S, and Ti. Routine laboratory methods were used except for aluminum and titanium.

The identity of a brass fitting was determined by dissolving it in nitric acid and analyzing for Cu, Fe, Pb, Ni, P, Sn, and Zn.

The stability of stored input measurement samples from the processing of enriched uranium fuels is being evaluated. The dissolver samples which were flame sealed in glass vials at the time of processing are being re-analyzed. The data will be analyzed statistically to determine if any significant changes in composition of the samples occurred during storage.

A method for the determination of total and undissolved solids was developed.

A rapid ion exchange method is being studied for the separation of radiocesium. The exchanger is an insoluble potassium salt. Recovery by this method is 98 to 100%.

Two lead barricades were modified for improved gamma-ray analysis of high activity samples. A 3-in. diameter hole was cut in the lids covering the detectors. The detector systems are calibrated for gamma-scanning of samples at distances up to 230 cm.

A fraction separator for chromatographic actinide and lanthanide separations has been assembled for use by the Special Analysis Group.

Standards and Quality Control

The program for the qualification of Umpire Laboratories, which began in 1965, was continued. Several phases were implemented for the program and served as guides for qualification. Table VI-1 summarizes the various phases and the laboratories participating in the Program. Table VI-2 summarizes the status of the uranium and plutonium standards preparation.

The Analytical Chemistry Branch quality control program relating to routine and special methods was continued, and the main features of the program are described.

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ANNUAL REPORT OF THE ANALYTICAL CHEMISTRY BRANCH FOR 1966

I. INTRODUCTION

This is the seventh (1,2,3,4,5,6) annual report of the Analytical Chemistry Branch. Previous to 1960, analytical progress was reported in the ICPP operations weekly and monthly reports and also was reported in the ICPP technical quarterly reports.

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

To provide satisfactory and efficient service, the Analytical Chemistry Branch hopes this report will be of value to management; to those who submit samples, and to all analytical chemists. A summary of this annual report is provided for the benefit of the management.

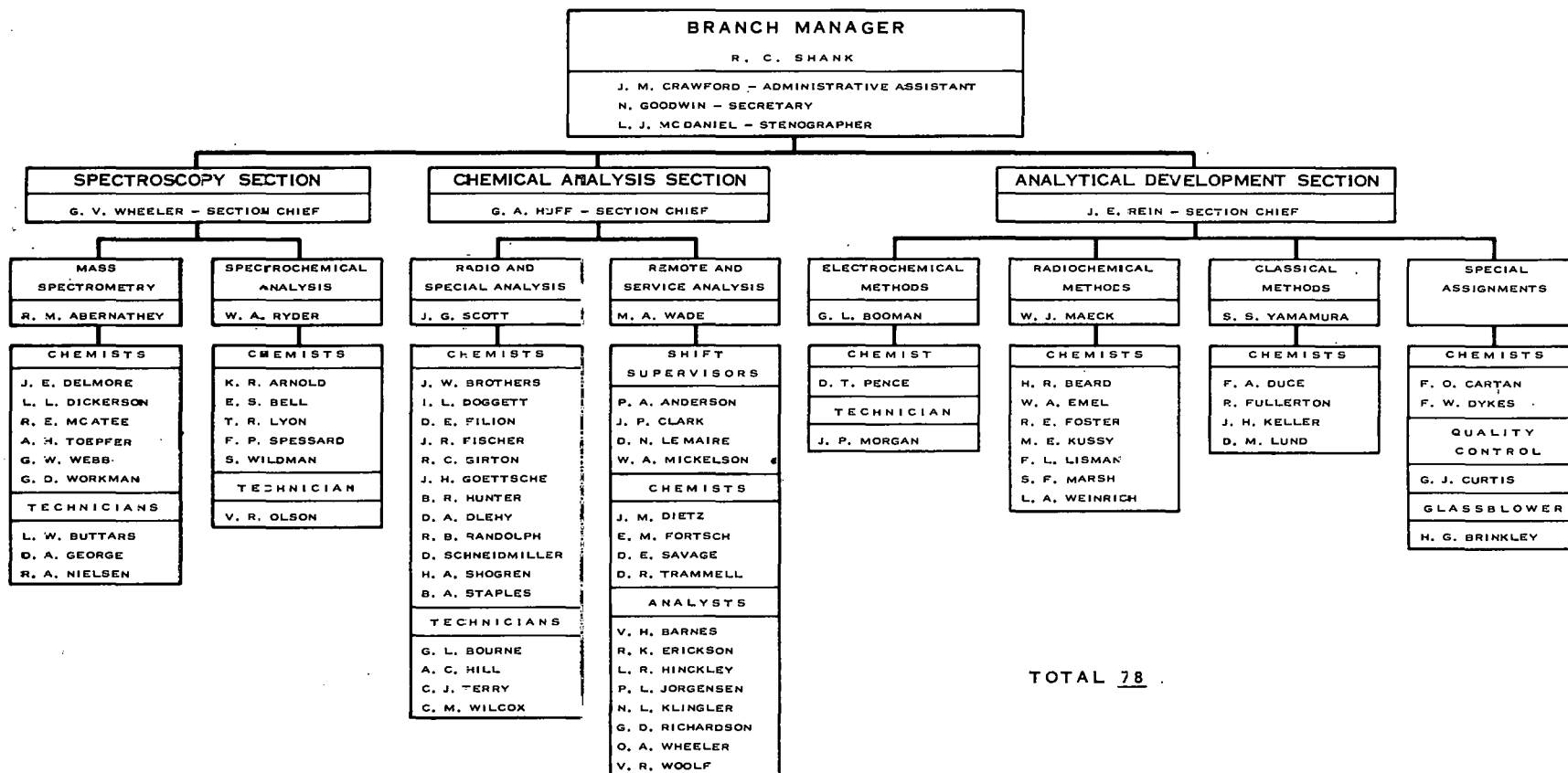
This report has been organized according to analytical disciplines except for the Loss-of-Fluid Test (LOFT) Project and the Burnup Determination of Nuclear Fuel Project.

- (1) R. C. Shank and Staff, Annual Report of ICPP Analytical Section for 1960, IDO-14547 (April 14, 1961).
- (2) R. C. Shank and Staff, Annual Report of ICPP Analytical Section for 1961, IDO-14588 (May 31, 1962).
- (3) R. C. Shank and Staff, Annual Report of Division Analytical Branch for 1962, IDO-14605 (April 25, 1963).
- (4) R. C. Shank and Staff, Annual Report of Division Analytical Branch for 1963, IDO-14636 (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).

II. GENERAL INFORMATION

The organization of the Analytical Chemistry Branch is shown in Figure II-1 and 78 people were employed at the end of 1966. Table II-1 shows the distribution of manpower in 1966, but the time of the Branch manager, the administrative assistant, the two secretaries, and the three section supervisors are not included in the table.

The number of determinations made by the Analytical Branch, and the sample sources are listed in Table II-2.



ANALYTICAL BRANCH
DECEMBER 31, 1966

Fig. II-1. Organization of the Analytical Chemistry Branch

TABLE II-1

DISTRIBUTION OF MANPOWER IN 1966

Section	CPP Operations	CPP Chem Tech	Plant Assistance	Analytical Development	Other INC	Outside INC(a)	Analytical(b)	Total
Spectroscopy	2754.5	1280.5	3559.0	7591.5	6200.0	2430.5	9401.5	33217.5
Chemical Analysis								
Remote and Service Analysis	8861.5	2496.5	5748.0	602.0	4116.0	3211.0	15190.5	40225.5
Radio and Special Analysis	4323.5	66.0	1246.5	668.0	18955.0	879.5	7033.5	33176.0
Analytical Development	194.5	3650.0	843.0	13561.0	8925.5	289.0	9086.5	36549.5
Analytical Branch	16134.0	7493.0	11396.5	22422.5	38200.5	6810.0	40712.0	143168.5
Analytical Percent	11.3	5.2	8.0	15.7	26.7	4.7	28.4	100.0

(a) AEC Contractors other than Idaho Nuclear Corporation.

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

TABLE II-2

DETERMINATIONS MADE BY THE ANALYTICAL CHEMISTRY BRANCH IN 1966

Section	CPP Operations	CPP Chem Tech	Plant Assistance	Analytical Development	Other INC	Outside INC ^(a)	Analytical	Total
Spectroscopy	1898	683	1585	230	3068	2100	489	10053
Chemical Analysis								
Remote and Service Analysis	10921	2941	6466	212	2969	2487	7624	33620
Radio and Special Analysis	4143	99	998	41	18398	538	339	24556
Analytical Development	81	0	0	0	215	5	0	301
Quality Control ^(b)							6565	6565
Analytical Branch	17043	3723	9049	483	24650	5130	8452	68530
Analytical Percent	24.9	5.4	13.2	0.7	36.0	7.5	12.3	100.0

(a) AEC Contractors other than Idaho Nuclear Corporation.

(b) Reagents and controls prepared by this laboratory are not included in the total.

III. ANALYTICAL DEVELOPMENT

1. CLASSICAL METHODS

1.1 Colorimetric Determination of Mercury (R. Fullerton, S. S. Yamamura)

A sensitive, highly versatile colorimetric method has been developed for the determination of mercury. The new method, an adaptation of a British method⁽⁷⁾ for the determination of mercury in organic materials, includes one basic double-extraction procedure and one single-extraction procedure, either of which may be coupled to one of three pretreatment procedures specifically adapted to particular sample types. The single-extraction procedure is provided for samples of known composition. The resulting overall method is applicable to a wide variety of inorganic and organic samples.

The basic procedure resorts to a double dithizone extraction to obtain increased specificity. The mercury is extracted initially into chloroform with dithizone. It is then stripped from the chloroform with an acidic nitrite solution, and after destruction of the excess nitrite with hydroxylamine and aniline, is reextracted for measurement.

Aqueous inorganic solutions, inorganic solids, and organic-containing materials are the types of samples commonly encountered. Three pretreatment procedures have been developed: (a) aqueous inorganic samples are heated with nitric acid to insure oxidation of mercury to the (II) valence state, (b) inorganic solids (excluding metals readily dissolvable in mineral acids) are fused with potassium pyrosulfate and then boiled under reflux with nitric acid, and (c) organic-containing samples are digested with nitric and sulfuric acids.

Details of the method are presented in Appendix B.

1.2 Analytical Development Service For Operations Analysis

1.2.1 Analysis of ETR-Type Fuel Plates for Total Uranium and Isotopic Distribution (S. S. Yamamura, D. M. Lund, R. Fullerton, M. E. Kussy, J. H. Sikes). To calibrate the fuel element scanner, the Operations Analysis Group submitted a total of 16 unirradiated aluminum-uranium fuel plates for the determination of total uranium and isotopic distribution of uranium. The 16 plates, four each of four different types containing between 12 and 30 g of uranium, were dissolved in nitric acid with mercury catalysis; the resulting solutions were weighed; and weighed aliquots were analyzed.

The isotopic distribution of uranium was determined by surface ionization mass spectrometry. Total uranium was determined by redox

(7) Analytical Methods Committee, Analyst 90, (1965) p 515.

titrimetry(8), spectrophotometry(9), and isotope dilution mass spectrometry. NBS U₃O₈ (standard sample 950a) was the primary reference material for the titrimetric and colorimetric methods, and high-purity U-235 metal was the primary standard for the isotopic dilution method.

The precision (standard deviation) of the principal titrimetric method and the supporting colorimetric method, computed from the results of duplicate analyses, was 0.076 g of uranium per plate for a single determination. Based on a "t"-test at the 95% level, there was no significant difference between the titrimetric and colorimetric results. The results of the isotope dilution method with an estimated precision of 0.5 relative percent also agreed with the titrimetric and colorimetric results within statistical limits.

Standards, prepared from 1100S aluminum and NBS U₃O₈ to simulate the composition of the samples, were analyzed concurrently with the samples by the titrimetric method to establish bias. The results for these standards indicated no bias and a precision comparable to that calculated from the results of the samples.

1.3 Analytical Development Service For Westinghouse

1.3.1 Colorimetric Determination of Nickel in Westinghouse ECF Samples (S. S. Yamamura, R. Fullerton). The colorimetric method previously developed for the determination of nickel in Westinghouse ECF descalant solutions has occasionally given erratic results. This method therefore was replaced by a new one patterned after a National Bureau of Standards procedure⁽¹⁰⁾ based on the development of the red nickel(III)-dimethylglyoxime complex at pH 13 in citrate medium. Details of the revised procedure are described in Appendix B.

1.3.2 Analysis of Citrate-Versenol Descaling Solution for Both Components (S. S. Yamamura). Two methods for the determination of citrate and Versenol [(N-hydroxyethyl)ethylenediaminetriacetic acid] were developed for the analysis of an ammonium dihydrogen citrate-Versenol descalant from the Expanded Core Facilities of Westinghouse. Versenol is determined by a direct titration with copper(II) in an aqueous acetate medium at pH 5 to a photometric end point. Citrate is determined by titration with sodium hydroxide after prior removal of Versenol on an acid form cation exchanger⁽¹¹⁾. The cation exchange resin retains Versenol as the +2 Versenol·2H⁺ ion and converts the ammonium dihydrogen citrate to citric acid with three titratable hydrogens.

Details of the procedure are described in Supplement A to Method ECF-1, Mod-1, Appendix B.

(8) R. J. Jones, ed., Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle, USAEC Report TID-7029 (1963) pp 96-107.

(9) R. C. Shank and Staff, Annual Report of Division Analytical Branch for 1965, USAEC Report IDO-14679, Appendix B, pp 109-123 (June, 1963).

(10) O. Menis, National Bureau of Standards, Private Communication (February, 1966).

(11) Suggested by J. S. Fritz, Iowa State University and Ames Laboratory, Private Communication, (October, 1966).

1.4 Analytical Development Studies----General Information

1.4.1 Dangers in the Use of Hengar Granule Boiling Chips in Micro Analyses (S. S. Yamamura). Hengar Granule boiling chips are frequently used in evaporations or acid digestions for their excellent ability to prevent bumping. Bumping can cause losses, particularly with analyses done at micro levels.

Hengar Granule boiling chips appear to be an impure alumina with minor concentrations of iron, sodium, and silicon, and trace levels of silver, copper, magnesium, manganese, molybdenum, and vanadium. They are reasonably stable under neutral conditions but release significant amounts of aluminum and other aforementioned impurities when digested with strong acids or bases.

2. RADIOCHEMICAL METHODS

2.1 Separations of Short-Lived Neutron Deficient Isotopes (S. F. Marsh)

Assistance was given Physics Section personnel in the separation of short half-life, neutron-deficient radionuclides for decay scheme studies. Various Calutron-enriched isotopes were bombarded with high-energy photons from the General Atomic LINAC at LaJolla, California, to yield the (γ, η) and (γ, p) products. Separations of higher than usual purity were required because gamma spectra were taken on a high resolution germanium (lithium) detector, in addition to the sodium iodide (thallium) crystal. These spectra eventually will be published as supplements to the Gamma-Ray Spectrum Catalog of R. L. Heath (Physics Section, Materials Testing Reactor).

The experiments are summarized in the following table.

TABLE III-1

SUMMARY OF SEPARATION PROCEDURES

<u>Target Material</u>	<u>Nuclear Reaction</u>	<u>Isotope Separated</u>	<u>Summary of Separation Procedures</u>
Sc ⁴⁵	(γ, η)	2.5-day Sc ^{44m}	Sequential fluoride, oxalate, and hydroxide precipitations.
Ti ⁴⁸	(γ, p)	3.4-day Sc ⁴⁷	Sequential fluoride, oxalate, and hydroxide precipitations.
Fe ⁵⁸	(γ, p)	1.5-min Mn ⁵⁷	Retain Fe on Dowex-1 from <u>6M</u> HCl while Mn elutes.
Cu ⁶³	(γ, η)	10-min Cu ⁶³	Plate Cu on iron powder from dilute HCl.
	$(\gamma, 2\eta)$	3.3-hr Cu ⁶²	

TABLE III-1 (continued)

<u>Target Material</u>	<u>Nuclear Reaction</u>	<u>Isotope Separated</u>	<u>Summary of Separation Procedures</u>
Br ⁷⁹	($\gamma, 2\eta$)	58-hr Br ⁷⁷	Extract Br ₂ into CCl ₄ . Strip with H ₂ SO ₃ and precipitate AgBr.
Sr ⁸⁴	(γ, η)	36-hr Sr ⁸³	Scavenge with Fe(OH) ₃ , then precipitate Sr(C ₂ O ₄).
Mo ⁹⁷	(γ, p)	25-hr Nb ⁹⁶	Dissolve in hot concentrated H ₂ SO ₄ . Dilute to precipitate Nb. Repeat.
Mo ¹⁰⁰	(γ, p)	3-min Nb ⁹⁹	
Cd ¹¹³	(γ, p)	3.7-hr Ag ¹¹²	Precipitate AgCl. Dissolve in NH ₄ OH. Fume off NH ₄ OH and repeat.
Cd ¹¹⁴	(γ, p)	5-hr Ag ¹¹³	

2.2 Separation of Plutonium for Mass Spectrometric Analysis (S. F. Marsh)

A method has been developed for the separation of plutonium for analysis by isotope dilution mass spectrometry. It is applicable to a wide variety of irradiated fuels. The method, designed for glove box operation, uses simple and inexpensive apparatus which can be discarded to minimize cross contamination.

Sample and spike plutonium, in a hydrochloric acid medium, are reduced to Pu(III) with iodide to obtain chemical species identity. After evaporation to dryness, the residue is dissolved in a nitric acid-sodium nitrite mixture. The resulting Pu(IV) is adsorbed on a column of strongly basic anion exchanger from 8M HNO₃. The column is washed with sequential washes of 8M and 2M HNO₃. The nitric acid washes the column free of the less strongly adsorbed elements which include fission products, uranium, neptunium and higher actinides, and fuel element components. The plutonium then is eluted with 0.2M HNO₃.

The method has been added to the Analytical Manual as Method Pu-Sep-1, and the details are presented in Appendix B.

3. ELECTROANALYTICAL STUDIES

3.1 Uranium(V) Disproportionation Reaction in Perchloric Acid (D. T. Pence)

Work has continued on the investigation of the uranium(V) disproportionation reaction. Results of a study in perchloric acid media were published in Analytical Chemistry⁽¹²⁾ and are summarized by the following abstract.

(12) D. T. Pence, G. I. Rومان, Anal. Chem. 38, (1966) p 1112.

"The correct interpretation of kinetic current measurements that are obtained by the use of controlled-potential polarography at short times requires a thorough understanding of the electrical characteristics of the cell and of the potentiostat. This paper demonstrates the practical application of transfer function measurement of kinetic currents at short times, and methods proposed for their correction are discussed. The uranium(V) disproportionation reaction was studied over the time region of 1 msec to 10 sec using the controlled-potential method. The determined value of the rate constant is $192 \text{ liter}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ for $1M \text{ HClO}_4$ medium."

3.2 Instrumentation for Electrochemical Measurements

3.2.1 Digital Control and Data Collection System (G. L. Booman).

A basic digital system has been constructed to perform many of the necessary control and measurement functions required in an electrochemical study. The following is an abstract of the paper published in Analytical Chemistry. (13)

"A digital instrument has been constructed to perform efficiently the interrelated operations of accurate timing, precise waveform generation, and automated data collection in one integrated unit. Functions such as pulse, square-wave, linear scan, linear-scan-and-hold, stair-step, and bidirectional linear-scan waveforms are obtained easily by changing prewired patchboards. With the flexibility given by patchboard control of the digital logic governing both the waveform generation and the measurement timing, the particular advantages of numerous electrochemical techniques are provided, and the instrument is readily adapted to new techniques. The full information capabilities of electrochemical measurements are closely approached with the measurement time constant of 1 μsec , resolution of 0.01%, and crystal-controlled, logarithmic, multidecade, timing. Relationships between high-speed data processing and rapid data collection are discussed in terms of overall objectives."

3.2.2 Hybrid Integrator for Measurement of Electrochemical Transients (G. L. Booman, D. T. Pence, J. P. Morgan). A hybrid analog-digital system with three operational amplifier integrators has been designed and experimentally verified to give improved measurements for electroanalytical studies.

The time range of a single transient measurement has been extended to seven decades from the previous four decades. During the time period from the initiation of the step input (to the electrochemical cell) to 1 msec, the first integrator accumulates all charge transferred between the electrode and the electroactive species in the electrolyte. At 1 msec, the charge in the first integrator transfers to the second integrator which then accumulates the charge transferred from the cell until 100 msec at which time the charge transfers to the third integrator, and the charge accumulation continues to the completion of the measurement period.

(13) G. L. Booman, Anal. Chem. 38, (1966) p 1141.

High measurement precision is maintained by having each integrating capacitor larger by a factor of 10 than that of the preceding integrator. Also, noise is minimized because noise components of longer period than the output sampling interval are averaged out, and the effective bandwidth of the measuring system follows the logarithmically increasing readout periods. Further, the integral measurement gives the full history of the transient, even though a limited number of output measurements is recorded by the digital data logger.

A special diode network was designed to permit linear discharge-charge cycles of the capacitors, thus allowing closer spacing of the data points than is possible with simple exponential charge transfer.

The integrating capacitors have been calibrated, and transfer ratios have been obtained under dynamic test conditions. Initial tests on uranium solutions indicate satisfactory operation.

3.2.3 Fast Response Potential Control (G. L. Booman, D.T. Pence, J. P. Morgan). A new system of all solid state, operational amplifiers and power boosters has been placed in operation to improve, by a factor of 10 or more, the time range over which electrochemical reactions can be observed. This is compared to the solid state controllers previously used. With the 10-V, 0.5-A capacity of the new control system, the approximate 5- to 10- μ sec time constant of the electrochemical cell will be the limiting factor on the measurements. At times less than about 10 μ sec, special techniques are required for resistance compensation and for generation of fast-rise, large-current charging pulses. A separate system will be used for these very short time measurements.

3.2.4 Paper Tape Readout for Electrochemical Data Collection System (J. P. Morgan, G. L. Booman). A high-speed, paper-tape punch has been added to improve the electrochemical measurement capabilities. With this equipment, the manual transcription of data for computer reduction has been eliminated, and the increased data output rate will permit many more data points to be collected on each experimental transient; hence, improving the reliability of the data and of its interpretation. The control logic for the paper tape punch has been wired to produce output tapes in the standardized format for radiochemical data, permitting some data processing (signal averaging, background subtraction, and data plotting) to be accomplished during slack time periods of the multichannel analyzer equipment. Data and identification numbers are punched at the beginning of each paper tape record. Detailed logic and timing diagrams are being prepared.

3.3 Data Reduction Computer Program (D. T. Pence)

A data reduction program has been written in Fortran language to reduce electrochemical data by use of a high-speed digital computer. The program was developed to facilitate the handling of the large volume of data obtained with the paper tape readout, electrochemical collection system described above. The program was written to accomplish the following functions: (a) test all input data and retain only on-scale data, (b) calculate an average value of the blank for the voltage measurements at each time, (c) subtract the blank from each voltage

measurement, (d) test the corrected data for outliers and reject them if the specified confidence level is exceeded, (e) average the corrected and tested data, (f) calculate the variance and standard deviation of the corrected and tested data, and (g) calculate correlation coefficients to establish freedom of bias due to slow introduction of contaminants, oxygen, or adsorbants.

The data reduction program is expected to reduce by 80% the time normally required for data reduction of the experimental electrochemical data. The program also provides additional tests of data reliability which are too time-consuming for desk calculations.

3.4 Fissionable Material Monitor in the PEW System (G. L. Booman, J. P. Morgan, W. J. Maeck, F. L. Lisman)

An in-line plant monitor system is being developed to detect U-235 in the Chemical Processing Plant process equipment waste (PEW) stream. Measurement of delayed neutrons has been selected based on a preliminary investigation of two promising methods. The other method that had been investigated was x-ray fluorescence. The purpose of the monitor system is to warn of potential nuclear criticality in the noncritically-safe PEW storage tanks.

Briefly, the neutron monitor is to operate as follows: a bypass of the PEW stream flows into a chamber in which is located a Pu-238 beryllium neutron source with a flux level of approximately 4×10^8 n/sec. The stream then flows to a second chamber in which is located a series of BF₃ neutron detectors. The neutrons detected are the energetic, delayed neutrons from certain of the fission products. The number of delayed neutrons is proportional to the number of fissionable atoms.

A small digital computer will be the central data processor element of the pulse-counting system. The pulse-count data from the detector-tube, preamplifier system will be entered directly into the computer input through buffer registers. The computer will then convert this digital input information to a typewritten form which can be interpreted easily by a plant operator without complex calculations or reference to extensive tabulations of sensitivity correction factors. Optimized counting periods will be selected under processor control; trend predictions will be established based on data stored in the processor memory; variable term data integration will reduce effect of random noise; statistical evaluation will be presented on the output typewriter of fissionable material level; and the detection limit of the measurement will be available as a function of the time-dependent level of neutron absorbing material in the stream. Sensitivity and calibration checks will be possible under computer programmed control at periodic intervals and off-normal conditions could be checked as they arise. The recent availability of low cost, digital computers has made this approach less costly as well as more informative in terms of fissionable material level in the plant process stream as compared to special wired-logic systems.

3.5 Proposed Analytical Branch Digital Computer Facility (G. L. Booman, J. P. Morgan, D. T. Pence)

The need for on-line data collection facilities at CPP has been made evident from a study of instrumentation requirements of the Analytical Branch over the next 5-yr period. The proposed data acquisition system facilities would accept analog and digital signals through multiplexers, perform necessary normalizations and conversions of these signals, and would produce digital information in the form of typewritten reports immediately after receiving the measurements from the mass spectrometers, x-ray diffraction, radiochemical, spectrographic, and other sources. Functions to be performed include: (a) conversion of raw measurements to concentrations, composition, peak heights, or peak ratios, (b) improvement of signals by programmed data averaging, (c) statistical calculations, radioactive decay, geometry, and dilution corrections, and (d) formatting of data for transmission to the centralized computer facilities. A very large amount of data handling is evident in the preparation of over 5,000 analysis reports each month at the current work load. Supplying analytical results quickly and retaining high reliability, indicates the need for digital data processing techniques. Detailed specifications and equipment requirements are now being developed to meet the needs of the Analytical Chemistry Branch.

3.6 Improvement in Equipment

3.6.1 Improvement of TDD-1 Magnet Regulator Electronics (G. L. Booman, J. P. Morgan). Attempts to operate the TDD-1 mass spectrometer magnet at currents greater than 200 mA resulted in complete loss of control of the magnet current with the magnet current running to a maximum. In troubleshooting the system, the control amplifier was found to be marginally stable and parasitic oscillations at frequencies near 100 Mc existed in the Eimac-series passing tube.

A frequency-gain analysis of the complete control system showed the principal method used to obtain stability was to shunt the Eimac plate to ground with a 4- μ F capacitor. This method is not entirely satisfactory and can be detrimental to tube life.

To eliminate the 4- μ F capacitor and to obtain a wider margin of stability, it was necessary to reshape the gain-frequency characteristics of the control amplifier and to insert an operational type feedback around the entire system. The parasitic oscillations were eliminated by proper bypassing of the Eimac tube.

With the above modifications, regulation of current in excess of 500 mA has been obtained.

4. DEVELOPMENT IN SUPPORT OF LOFT PROGRAM

4.1 Analytical Methods

4.1.1 Gamma-Ray Spectrometry (W. J. Maeck, J. G. Scott, S. F. Marsh, H. R. Beard, W. A. Emel)

4.1.1.1 Generation of Iodine Isotope Spectra. To resolve a multicomponent spectra by spectrum stripping, the spectrum of each nuclide must be available. In cooperation with the Physics Section, individual nuclides are being separated and their spectra are being recorded. Iodine isotopes, 8-day I-131, 2.3-hr I-132, 21-hr I-133, 53-min I-134, and 6.7-hr I-135 were isolated and their spectra were recorded for NaI(Tl) and Ge(Li) detectors. The I-134 and I-135 isotopes were separated from 1 mg of irradiated uranyl nitrate soon after discharge from the reactor. Iodine was chemically separated 5 min after reactor discharge. After 6 hr, to allow I-134 to decay, the iodine fraction was essentially pure 6.7-hr I-135. Ten minutes after the initial separation, the separation was repeated and the iodine fraction containing the remainder of the I-135 and I-133 grown in from the 2-min Te-133 isomer was discarded. A third separation was performed 30 min later. The iodine fraction was >95% I-134 activity with I-133 as the remainder. After 21 hr, the pure spectrum of I-133 remained. The spectrum of 8-day I-131 was obtained on a ORNL I-131 sample. The spectra of I-132, Te-132, and I-133 were obtained by separating the iodine from 10 mg of U-235 which had been irradiated for 0.5 hr and cooled for two days. After the decay of I-132, the spectrum was mainly I-133 with ~20% I-131. The I-131 spectrum was subtracted by a computer program. The Te-132 also was separated from the U-235, passed through a silver chloride column to remove iodine contamination, and the Te-132 spectrum was recorded immediately. After grow-in of I-132, its spectrum was obtained.

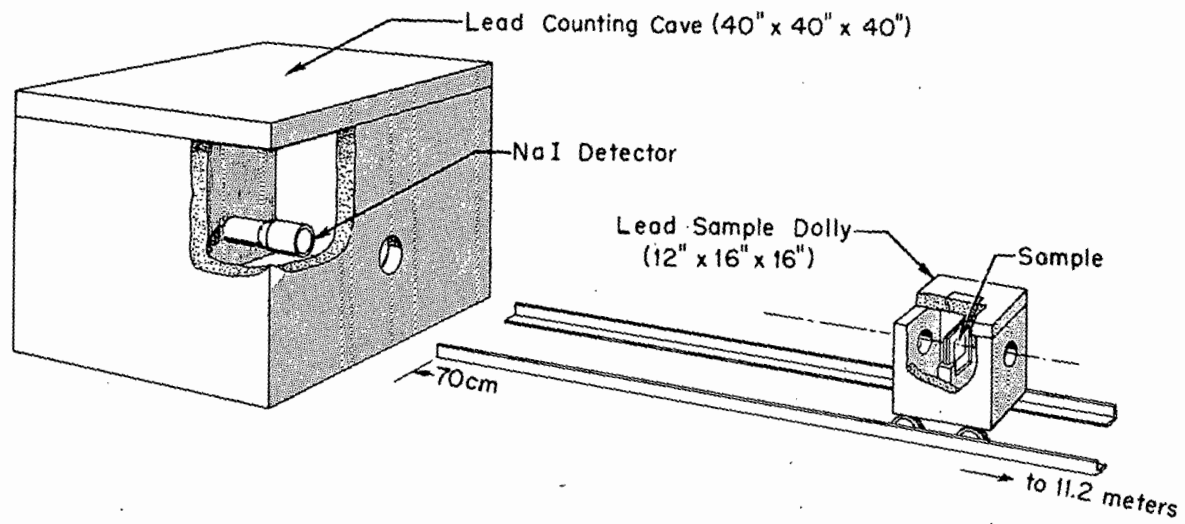
4.1.1.2 High-Level Gamma-Ray Facility. A NaI(Tl) detector was installed for the counting of samples with activities up to ~5 R/hr. The facility, Figure III-1, consists of a standard shielded cave with⁽¹⁴⁾ a 3- by 3-in. detector mounted on its side. A smaller shielded pig that contains the sample travels on tracks outside the detector cave to a maximum distance 11 m from the detector. Holes in the sample pig and detector cave are aligned over the entire distance of travel. A hole also is placed in the backside of the sample pig to minimize backscatter. The detector was connected to a 512-channel analyzer located 600 ft away, and a self-powered preamplifier drove the signal.

The facility was calibrated for distance at gamma-ray energies of 0.11 and 0.21 MeV (Lu-177), 0.41 and 0.68 MeV (Au-198), and 0.9 and 1.1 MeV (Sc-46). Standard spectra were obtained on punch tape for six nuclides for use by a computer (Shifty III) spectrum stripping program. The nuclides were Mo-99, Tc-99, I-131, Te-132 (I-132), I-133 and Xe-133. These isotopes are volatile and therefore predominate in gas and plateout samples from fission product releases.

(14) R. L. Heath, IDO-16880, 1964.

Fig. TTT-1 High-Level Gamma Ray Counting Facility

HIGH LEVEL γ -RAY COUNTING FACILITY



The facility and spectrum stripping program gave highly acceptable results on a series of 250 plateout coupons, particulate filters, and gas samples collected from a fission product release of a U-235 sample melted in a steam atmosphere 6 hr after discharge from the MTR.

4.1.1.3 Effect of Substrate Material and Thickness on Gamma-Ray Spectrometry. The early design of LOFT plateout coupons specified 3/16-in. thick steel. The absorption of the lower energy gamma-rays was too great to permit measurement of such isotopes as Mo-99 (Tc-99) and Xe-133. The backscatter also severely distorted the low energy portion of the spectrum. Decreasing the thickness to 1/16-in. gave little improvement in the absorption effect. Aluminum, 1/16-in. thick, proved satisfactory and was specified as the coupon material.

4.1.1.4 Germanium(Li) Detector System. An Ortec 10-cc Ge(Li) detector and a 1024-channel memory, 4096-channel ADC analyzer system was placed into operation. The resolution for the entire system using a special 4 FET preamplifier is 3 keV at 661 keV. Based on experience with this system, essentially the whole analytical program for samples from LOFT can be performed without chemical separations by combining a high-level NaI(Tl) counting facility for early measurement of the volatile fission products and a Ge(Li) detector system for subsequent measurement of the longer-lived, less-volatile fission products. These later measurements are proposed after decay periods of 5 days to about 3 months. This proposal is discussed in greater detail in Section 4.1.3.

4.1.2 Fission Product Separation Procedures (L. A. Weinrich, S. F. Marsh, M. E. Kussy, W. J. Maeck)

Prior to receiving the Ge(Li) detector, the fission product analyses were based on chemical separations followed by NaI(Tl) gamma-ray spectrometry. The majority of the samples were plateout coupons which consisted of 3/4- by 1 1/2-in. iron or aluminum plates coated with corrosion-resistant paints with bases of vinyl, epoxy, and rubber.

A dissolution and sequential separation procedure was developed. The procedure was designed to produce fractions of fission products resolvable by NaI(Tl) gamma-ray spectrometry. Some cross-contamination of fission products between fractions was expected, especially of iodine (and tellurium) into the other fractions. The activity ratio of iodine to other fission products on samples was extremely high because its release from melted fuel is great and because it preferentially plates on organic surfaces. For this reason, the procedure includes an early separation of iodine and a second later separation to remove that additional iodine grown in from tellurium parents.

At the time the samples were analyzed, the fission products were 1- to 2-week cooled. The fission products normally determined were Zr-Nb-95, Mo-99(Tc-99), Ru-103, -106, I-131, Te-132 (I-132), Cs-137, Ba-140 (La-140), and Ce-141, -144.

The major steps in the procedure were:

- (1) Addition of carriers; Zr, Mo, Ru, I (as iodate), Te, Cs, and La.
- (2) Digestion of the sample and carriers in a specially designed, all-glass, reflux apparatus with a mixture of nitric, perchloric, and sulfuric acids.
- (3) Distillation of iodine, technetium, and ruthenium into sodium hydroxide while the digestion is in progress.
- (4) Separation of the ruthenium from the sodium hydroxide fraction by precipitation as the hydrous oxide with ethanol followed by gamma-scanning of the filtered residue for Ru-103, -106, and the filtrate for I-131 and Tc-99.
- (5) Addition of hydrochloric acid to the undistilled fraction and extraction of tellurium and molybdenum into amyl acetate, stripping both into dilute hydrochloric acid, addition of sodium bromate to oxidize molybdenum to +6, extraction of Mo(VI) into α -benzoinoxime-amyl acetate, and gamma scanning the organic phase for Mo-99 and the aqueous phase for Te-132 (I-132).
- (6) Addition of sodium bisulfite to the aqueous phase from the first extraction in (5) to reduce iodine to -1 and passage through a column of silver chloride to remove the last traces of iodine activity.
- (7) Precipitation of barium as the sulfate followed by gamma scanning for Ba-140.
- (8) Addition of iron(III) to the supernatant solution from the barium sulfate precipitation, addition of sodium hydroxide, gamma scanning the filtered precipitate for La-140, Ce-141, -144, and Zr-Nb-95, and gamma-scanning the filtrate for Cs-137.

4.1.3 Proposed Procedures for Determination of Fission Products in Plateout Samples (W. J. Maeck, L. A. Weinrich)

The longest step in the procedure described in the previous section (4.1.2) is sample dissolution. Another disadvantage is the need for custom-fabricated glass apparatus. Leaching experiments have shown that greater than 90% of the fission products, other than iodine, can be removed from organic-material coated coupons with a 4M HCl-2M HNO₃ mixture. Only about 15% of the iodine leaches. The coupon and 30 ml of the acid mixture are placed in a small beaker which is placed in an ultrasonic bath for 20 min.

Two analytical schemes are being evaluated for the determination of fission products on plateout coupons with high, as much as 5 R/hr, activity

levels. One is based on a complete analysis by gamma-ray spectrometry with both NaI(Tl) and Ge(Li) detectors. The other involves minimum chemical separations combined with gamma-ray spectrometry.

For both schemes, the first step is NaI(Tl) gamma-ray spectrometry in the high-level facility (see Section 4.1.1.2) for the major activities of I-131, Te-132 (I-132), I-133, and Mo-99 (Tc-99).

In the all gamma-ray spectrometry scheme, the samples are rescanned on a Ge(Li) detector after decay periods up to 3 months for the low-activities of Zr-Nb-95, Ru-103, -106, Cs-137, Ba-140 (La-140), and Ce-141, -144.

In the scheme using chemical separations, after the high-level NaI(Tl) gamma scan, the coupons are leached with 4M HCl-2M HNO₃ in the ultrasonic bath. The resulting solution is analyzed for the low-level activities by simple separations followed by NaI(Tl) or Ge(Li) scans.

4.2 Fission Product Inventories in Irradiated Fuel (F. L. Lisman, W. J. Maeck)

Based on pre- and postirradiation uranium isotopic levels, the numbers of fissions were computed for the fuel samples melted in the Contamination-Decontamination-Experiment (CDE) facility. This information was fed into a computer program to establish the inventory of the fission products at meltdown time. Both U-235 and Pu-239 fissioning were taken into account.

The overall material balance of fission products in CDE tests has generally been low. The melted fuel, low enrichment UO₂ clad with Zircaloy, has been dissolved with nitric and hydrofluoric acids. For most fission products, especially those with high boiling points and hence remain in the melted fuel, the material balance is controlled by the dissolution and analysis of the melted fuel. The dissolved fuel solution from one test was filtered through 0.45- μ filters to establish whether fission products might exist as insoluble particulate matter. A residue was isolated that contained about 50% of the total strontium activity, no zirconium-niobium activity, 12% of the ruthenium activity, and 81% of the cerium activity.

4.3 Atmosphere Analysis (L. L. Dickerson, G. W. Webb, R. M. Abernathey, G. V. Wheeler)

4.3.1 Reactor Vessel

Analysis of the gases in the reactor vessel can help explain events taking place during the LOFT experiment by furnishing data on: (a) extent of metal-water reactions, (b) presence of reducing or oxidizing atmosphere at any given time to effect release of fission products from the fuel, and (c) time and amount of air entering the vessel.

Since the atmosphere in the vessel immediately after blowdown will be mostly steam, experiments are under way to study analysis of hydrogen,

oxygen, and nitrogen in steam. Mass spectrometer analysis was selected since early investigation indicated that it offered the most feasible means of analysis of steam atmosphere.

Samples of atmosphere were taken from CDE Runs 2 and 3. Setups are being prepared to install the mass spectrometer in CDE for future runs to obtain continuous analysis of CDE conditions and gain operating experience for LOFT.

4.3.2 Hydrocarbon Detection

Hydrocarbon measurements were made of the containment atmosphere before and after the meltdown of an unirradiated fuel element prior to CDE Run 3 in a search for the release of organic material from the fuel which could contribute to the formation of "penetrating" iodine. Data for the atmosphere, as taken with the flame ionization hydrocarbon detector, are as follows: (a) containment vessel, blank run (with heat, but no fuel) 4.7-ppm methane equivalent, (b) containment vessel, after "cold" meltdown 7.0-ppm methane equivalent, (c) outside containment vessel 3.1-ppm methane equivalent. The steam condensate from the CDE containment vessel showed less than 2-mg extractable aliphatic hydrocarbon from either the blank run or the cold element meltdown run. The condensate was contacted with carbon tetrachloride and then the carbon tetrachloride extract was analyzed by infrared absorption.

4.4 Gas-Particulate Capsule Studies (F. O. Cartan)

A major sampling device in LOFT is the gas-particulate capsule. It samples the containment atmosphere to obtain fission product concentrations classified according to particulate matter, iodine activities differentiated by chemical species, and krypton-xenon. A total of 219 capsules is scheduled to be installed which will sample the atmosphere on a preset time sequence from 30 minutes after blowdown through the fifth day.

The capsule basically is a hollow aluminum sphere which contains a cartridge consisting of particulate filters, silver membranes, and activated charcoal. At the preset time, vacuum is applied to pull the atmosphere sample at a flow rate of 0.1 cfm through the cartridge and the hollow space. Krypton and xenon are the only fission products that should pass through the cartridge into the hollow space.

Laboratory experiments are underway to evaluate cartridge components for their sorption properties for various iodine species. The overall performance of the capsule is being tested in the Contamination-Decontamination-Experiment (CDE) Facility.

4.4.1 Sorption of Iodine Species on Particulate Filters and Various Adsorbers, (J. H. Keller, F. A. Duce, R. Fullerton, F. W. Dykes, P. A. Anderson)

4.4.1.1 Molecular Iodine. The sorption of molecular iodine was measured for various particulate filters, charcoal papers, silver-coated copper screens, silver membranes, and for assembled filter cartridges. The test conditions were a flow rate of 0.1 cfm for 20 min, temperature from room to 94°C, and flow gas of water-saturated air containing molecular iodine with I-131 tracer. The results are summarized in Table III-2 for all components except the assembled cartridge.

Ideal characteristics of the particulate filters for the cartridge are complete retention of particulate matter (hence small pore size), zero sorption of gaseous (especially iodine) species, high bursting strength under a steam environment, and low pressure drop. Bursting strengths and pressure drops were measured for those filters with low iodine sorption. The filter that best meet the four criteria stated above is the Flanders F-700. The next best is the Flanders F-600. Both these filters are sufficiently strong to be used without supporting screens. Supporting screens have been shown to adsorb iodine and their removal is desirable. Of concern is the fact that the characteristics of the filters can change between lots. This probably is due to a change in binder material or to a change in the manufacturing process. A striking example of this is that a previous lot of the Hollingsworth-Vose filters adsorbed less than 2% of the incident molecular iodine (15) whereas in this test, another lot adsorbed essentially all the iodine (Table III-2).

Ideal characteristics of iodine adsorbers (charcoal papers, silver-coated copper screens, and silver membranes) for the cartridge are complete retentions of incident gaseous iodine, low pressure drops, and high bursting strength. Based on these criteria, the best one is the Flotronics 3- μ silver membrane. The Gelman AC-1 charcoal paper is next best.

4.4.1.2 Methyl Iodide. A procedure was developed and apparatus was designed for the preparation of milligram quantities of I-131 tagged methyl iodide. Methyl sulfate and I-131 tagged potassium iodide are mixed in an aqueous medium. The methyl iodide which forms is swept from the reaction vessel with helium and is collected in a liquid nitrogen trap. The product is pure and the yield is essentially complete.

Various particulate filters and iodine adsorbers, as well as assembled filter cartridges, were tested for sorption of methyl iodide. The test conditions were a flow rate of 0.1 cfm for 25 min, temperature of 35°C except for one assembled cartridge at 90°C, and flow gas of water-saturated air containing I-131 tagged methyl iodide.

(15) R. C. Shank and staff, IDO-14679, (1965) p 36.

TABLE III-2

SORPTION OF MOLECULAR IODINE ON VARIOUS FILTERS AND ADSORBERS

Percent Sorbed on Filters^[a,b]

<u>< 2%</u>	<u>2 to 5%</u>	<u>5 to 20%</u>	<u>20 to 90%</u>	<u>> 90%</u>
Reeve Angel 934 AE; all temp.	Reeve Angel 984 H; 94°C.	Flanders F-700; 36°C.	Gelman VF-6; all temp.	Gelman Versapor; all temp.
Flanders F-600; 34°C.	Flanders F-600; 36°C.	Reeve Angel 984 H; 36°C.	Millipore WHWP; all temp.	Hollingsworth-Vose (HV-70); all temp.
	Flanders F-700; 94°C.	Gelman A; all temp.		

Percent Sorbed on Charcoal Papers and Silver Adsorbers^[b]

<u>50 to 98%</u>	<u>98 to 99.5%</u>	<u>Essentially 100%</u>
Ag-plated Cu screens, total sorbed on series of 4 screens; all temp.	Whatman ACG/B Charcoal paper; 94°C.	Whatman ACG/B charcoal paper; 36°C.
		Gelman AC-1 charcoal paper; all temp.
		Flotronics 3-μ silver membrane; all temp.

[a] Usually three filters were tested in series. When the sorption was low, each of the three filters sorbed about equal amounts of iodine. When the sorption was high, the first filter sorbed almost all the iodine.

[b] The filters and adsorbers were exposed to a level of 20 to 600 μg of iodine in these tests. Very recent studies show that the percentage of iodine sorbed on some filters and silver adsorbers increases with decreasing incident iodine.

The sorption was less than 1% for all the tested particulate filters: Flanders F-600, Flanders F-700, Reeve Angel 934 AH, Hollingsworth-Vose 70, and Gelman Versapor. The sorption also was less than 1% on the tested iodine adsorbers Flotronics 3- μ silver membrane, Gelman AC-1 charcoal paper, and silver-plated copper screens. Of interest is that the Gelman AC-1 charcoal paper sorbed 16% of the incident methyl iodide from a slowly flowing helium stream. This demonstrates that tests of this nature, to be valid for the LOFT program, must be performed with LOFT-simulated conditions.

Also tested were glass wool, Teflon wool, and a short column of Dowex-1 ion exchange resin in the iodide form. The sorption was less than 1% on the glass wool and Teflon wool, and was 5% on the Dowex-1 column.

Coconut charcoal, 12/30 PCB, loaded with two different impregnants, 5% triethylenediamine and 1% I_2 - 1% KF, was tested. A 3/4-in. dia by 1-in. long (4.5 g) cylinder of the 5% triethylenediamine-impregnated charcoal retained 93% of the incident methyl iodide. The I_2 -KI impregnated cylinder, 3/4-in. dia by 2/3-in. long (3 g), retained 97% of the incident methyl iodide.

Two assembled cartridges were tested, one at 35°C and the other at 90°C. The cartridges contained an aluminum dummy inlet, three Flanders F-700 filters, five silver-coated copper screens, five Gelman AC-1 charcoal papers, two 1% I_2 - 1% KI impregnated 12/30 PCB charcoal beds, and one Flanders F-700 cleanup filter. Essentially no methyl iodide sorbed on the dummy inlet, the particulate (Flanders F-700) filters, silver-coated screens, nor any of the nonactive parts at both temperatures. The pack of five charcoal papers sorbed 14% of the methyl iodide at 35°C and 8% at 90°C. The charcoal beds sorbed all the methyl iodide incident on them at both temperatures.

4.4.2 Sorption Rate of Water on Charcoal (F. W. Dykes)

Activated charcoals have a large capacity for water, as much as 50% by weight, which changes their sorption characteristics. Of importance to LOFT is that the retention time for krypton and xenon is reduced and methyl iodide is less efficiently trapped.

Weighed cartridges of 12/30 PCB charcoals impregnated with 1% I_2 - 1% KI were tested for water sorption with flows of 0.1 cfm of water-saturated air at temperatures of 30°, 50°, 70°, and 90°C. The results, Figure III-2, show that saturation was not reached for 20-min flows even at 90°C.

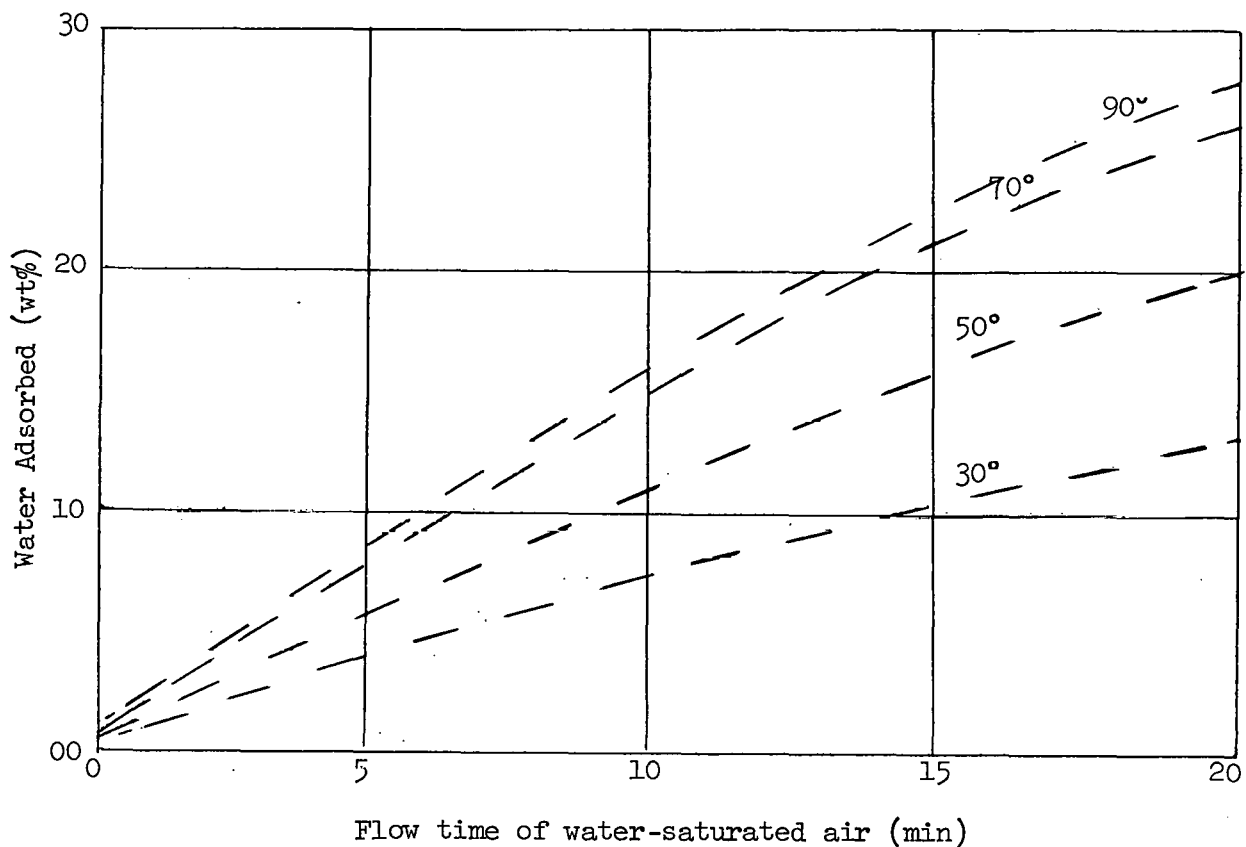


Fig. III-2 Water Sorption by Impregnated Charcoal

4.4.3 Testing of Complete Capsules (F. O. Cartan)

Complete capsules and assembled cartridges are being evaluated for mechanical operability and for functional operability in the Contamination-Decontamination-Experiment (CDE) Facility in which fission products are released under LOFT-simulated conditions.

Prior to this, the time required for complete replacement of the air in the hollow space of the capsule was determined to be less than 2.5 min with a flow rate of 0.05 cfm. Thus at the LOFT flow rate of 0.1 cfm and a sampling time of 20 min, the gas originally present in the hollow space should be completely replaced with a sample of the LOFT atmosphere that passed through the filter cartridge.

At the time of this writing, little CDE data were available. Important findings have been that all incident iodine activity has been trapped in the capsule and that all particulate activity was collected on the particulate filter.

4.5 Testing of Materials for Packaging Analytical Samples (R. Fullerton)

In LOFT, the various samples will be dismantled in a remotely operated facility and the components will be sent to the analytical

laboratories. The components must be packaged in containers which are impermeable to fission products including iodine. This is necessary for health physics reasons and to prevent contamination of gamma-ray counting apparatus. Various materials were tested for permeability to molecular iodine and methyl iodide. The results are summarized in Table III-3.

Polyethylene-coated polyester films are apparently impermeable to molecular iodine but measurably permeable to methyl iodide. Strong, transparent packages can be made from this type of film by heat sealing. Such packages should be satisfactory for all samples, except those expected to release significant amounts of free methyl iodide during storage. Of the other materials tested, Aluminum and Aclar 33C seem satisfactorily impermeable to molecular iodine. Aluminum sample packages, if obtainable with wall thicknesses thin enough to minimize distortion of low energy gamma spectra, are probably satisfactory.

5. REMOTELY OPERATED FACILITIES

5.1 Cell X Storage Facility (F. W. Dykes)

A storage facility for radioactive samples was installed in Cell X. The facility (40 by 40 by 36 in.) provides space for 48, 500-ml volumetric flasks and 4 in. of lead shielding. A "lazy-susan" arrangement permits individual access to samples through a single 4-by 8-in. opening.

5.2 CPP Additional Alpha Handling Facility (F. W. Dykes)

Construction began on this project in March 1966. However, a 6-month strike by construction workers has delayed completion. Work resumed in November 1966. Delivery of the shielded cave continues to be the determining factor for the completion date. Delivery is now scheduled for February 1967.

5.3 RAF Cave (F. W. Dykes)

This project (referred to in last year's report as the "RAF Hot Cell") was approved by the AEC in March 1966. The F. C. Torkelson Co. is the architect-engineer. The Title II design review was completed in November 1966. It is anticipated that final approval of drawings and specifications will soon be forthcoming, and that construction will begin early in 1967. The construction area, which was highly contaminated, has been decontaminated satisfactorily.

5.4 Master-Slave Manipulators for RAF Boxes (F. W. Dykes)

The "castle" manipulators used in the RAF boxes are inefficient devices requiring both skilled operators and complex apparatus for many operations. The versatility of master-slave manipulators could reduce costs through increased operator efficiency and simplified apparatus. A study was made to determine whether master-slave manipulators could be installed in an RAF box. The conclusion was that the installation

TABLE III-3

LEAKAGE OF MOLECULAR IODINE AND
METHYL IODIDE THRU VARIOUS MATERIALS

Material	Thickness (mls)	Test duration (days)	Leakage (%)	
Polyethylene-coated polyester film	5	30	0.0	(I ₂)
		15	1.8	(CH ₃ I)
Polyethylene-coated polyester film	4	14	0.0	(I ₂)
		15	2.8	(CH ₃ I)
Polyethylene-coated polyester film	2	14	0.0	(I ₂)
		15	6.4	(CH ₃ I)
Aluminized polyethylene coated polyester film	2	14	0.0	(I ₂)
		13	0.42	(CH ₃ I)
Polyethylene	2	2	11.0	(I ₂)
Aclar 22C	1.5	16	5.5	(I ₂)
Aclar 33C	2.0	16	0.0	(I ₂)
Aluminum can with aluminum plug		18	0.0	(I ₂)
Surlyn A		4	33.0	(I ₂)

was feasible, provided a larger box was used. The conversion cost was estimated at less than \$10,000 with over two-thirds of this amount being the cost of the manipulators.

Future RAF installations will consider the use of master-slave manipulators for lower total cost (installation and operation).

6. BURNUP DETERMINATION OF NUCLEAR FUELS

In this continuing program to develop methods for the accurate determination of the burnup of nuclear fuels, absolute thermal fission yields were determined for many stable and long-lived fission products for U-233, U-235, and Pu-239. These values, summarized in Table III-4, are tentative. Additional measurements are in progress to produce refined values.

Alpha, capture-to-fission ratio, values corrected to 2200 m/sec also were determined. These are $\alpha_{\text{O}}\text{U-233} = 0.0984$, $\alpha_{\text{O}}\text{U-235} = 0.1728$, and $\alpha_{\text{O}}\text{Pu-239} = 0.356$. These values also are tentative.

Details of the above are reported in a series of three quarterly reports (16,17,18) and in a fourth report which now is being prepared.

Methods were developed for a highly specific, extraction-spectrophotometric determination of microgram amounts of technetium and for the separation of individual lanthanides which are applicable to irradiated nuclear fuels. These are detailed in one of the quarterly reports(17).

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- (16) W. J. Maeck, F. L. Lisman, J. E. Rein, (eds), "Burnup Determination of Nuclear Fuels", Project Report for the Quarter January 1 - March 31, 1966, IDO-14678.
 - (17) W. J. Maeck, J. E. Rein, (eds), "Burnup Determination of Nuclear Fuels", Project Report for the Quarter April 1 - June 30, 1966, IDO-14681.
 - (18) F. L. Lisman, W. J. Maeck, R. E. Foster, Jr., J. E. Rein, (eds), "Burnup Determination of Nuclear Fuels", Project Report for the Quarter July 1 - September 30, 1966, IN-1064.

TABLE III-4

ABSOLUTE THERMAL FISSION YIELDS OF STABLE AND
LONG-LIVED FISSION PRODUCTS FOR U-233, U-235, AND Pu-239

<u>Mass Number</u>	<u>Element</u>	<u>Fission Yield</u>		
		<u>U-233</u>	<u>U-235</u>	<u>Pu-239</u>
83	Kr	1.07		
84	Kr	1.79		
85	Kr (10.76 y)	0.534		
86	Kr	3.01		
99	Tc	5.18	6.21	
101	Ru	3.36		
102	Ru	2.59		
104	Ru	1.10		
106	Ru	0.269		
131	Xe	3.55		
132	Xe	5.00		
134	Xe	6.28		
137	Cs (30.3 y)	6.98	6.28	6.56
140	Ce	6.62	6.32	
142	Ce	6.82	5.89	
143	Nd	5.95	5.90	
144	Nd+Ce	4.79	5.43	
145	Nd	3.44	3.85	2.84
146	Nd	2.59	2.95	2.34
147	Sm	1.97	2.15	
148	Nd	1.34	1.69	1.58
149	Sm	0.806	1.02	
150	Nd	0.509	0.64	0.91
151	Sm	0.376	0.456	
152	Sm	0.201	0.231	

IV. SPECTROSCOPY

1. SPECTROCHEMICAL ANALYSIS

1.1 Potassium Determination in WCF Samples by Atomic Absorption (F. P. Spessard, W. A. Ryder)

Atomic absorption was used to determine potassium in scrub solutions and product from the Waste Calcination Facility. Initial studies using emission spectrographic and x-ray fluorescence techniques showed that these methods did not have the required sensitivity. The greater sensitivity of the atomic absorption technique permitted dilution of the samples thereby reducing their radiation level. Product samples are leached in 6M HNO₃ and diluted so that the potassium content is about 1 ppm. The scrub solutions are diluted similarly. The calibration range covers from 0.1 to 1.5 ppm.

1.2 Beryllium Lattice Parameter (R. E. Winchell)⁽¹⁹⁾

An x-ray diffraction study was initiated to determine the change in the lattice parameter of beryllium used as neutron reflectors in nuclear reactors. Precision of $\pm 0.0002\text{\AA}$ is required. The problem is complicated by the comparatively broad lines in the diffraction pattern and the high film background caused by radioactivity from the sample.

Specimens are powdered after cooling with liquid nitrogen and then are mixed with spectrographic pure silicon metal powder used as an internal standard. Exposures of about 16 hr are required. In order to achieve the required degree of precision, it is necessary to read each film at least 10 times.

1.3 Irradiated Stainless Steel Analysis (T. R. Lyon)

An irradiated stainless steel sample submitted by Battelle Memorial Institute was examined by emission spectrographic analysis for changes in its elemental composition. The total thermal and fast flux accumulated by the sample was approximately 4×10^{22} nvt and 2.1×10^{22} nvt respectively. The sample was excited in the emission spectrograph hot cell and the spectrum compared with that from an unirradiated control sample. Major decreases were noted in the boron, niobium, lead, silicon, and titanium concentrations. Major increases were noted in copper, manganese, tin, and vanadium concentrations.

1.4 X-Ray Absorption Edge Determination of Uranium (T. R. Lyon)

A study was made to determine the feasibility of using x-ray absorption edge techniques for the on-stream monitoring of uranium in variable composition, radioactive waste streams in the Chemical Processing Plant. Secondary radiation from pelleted Mo-Nb metal powders was used because

⁽¹⁹⁾ Summer employee.

their characteristic emission energies bracket the uranium absorption edge. In aqueous solutions the detection limit was found to be 30 ppm for a 4-cm cell and 60 ppm for a 3-cm cell. The 4-cm cell, however, had a lower tolerance for other ions.

1.5 Installation of Atomic Absorption Unit (F. P. Spessard, T. R. Lyon, W. A. Ryder)

The Jarrell-Ash flame spectrometer was converted to the dual atomic absorption/flame emission instrument by the addition of atomic absorption accessories. Mercury, selenium, boron, sodium-potassium, calcium-magnesium-aluminum, iron, nickel, chromium, cobalt, and manganese hollow cathode lamps were obtained for various studies. Because some of the solutions to be analyzed are radioactive, the instrument was installed in a hood and a chimney attached from the burner enclosure to the top of the hood. During operation, hood windows are closed to the point that 125 cfm of air is flowing through the opening.

1.6 High Temperature Study of UAl_3 (W. A. Ryder, E. S. Bell)

A study to determine the stability of UAl_3 at $1000^\circ C$ was undertaken at the request of the Metallurgical Development Section. Initial tests were made using vacuum and inert gas atmospheres in conjunction with an MRC high temperature x-ray diffractometer attachment. These were unsuccessful in that some oxidation of uranium to UO and UO_2 always occurred resulting in the formation UAl_2 and aluminum. The aluminum alloyed with the platinum and tantalum heating stages causing them to fail.

Subsequent tests were made using small conglomerates of UAl_3 powder placed on alumina plates in a small tube furnace. The samples were surrounded by Zr-Ti getter and dry argon gas was passed slowly through the tube. Using x-ray powder camera techniques no changes could be detected in samples after 250 hr at $1000^\circ C$.

1.7 Spectrographic Excitation Source (R. A. Woodruff)⁽²⁰⁾

1.7.1 New Hollow Cathode Tube. Studies of excitation sources useful in spectrographic analysis were started. Initially, a new demountable hollow cathode tube was designed and constructed in collaboration with H. C. Brinkley (Analytical Branch glassblower). It has windows at both ends, and the cathode itself is open at both ends. The cathodes can be changed by merely sliding them into the tube after removing one of the end windows. Electrical connections with the cathode are made by spring contacts. Inlet gas sweeps across the windows before entering the tube proper, thus preventing the windows from darkening. The tube is constructed of vycor glass, and the cathode is surrounded by a water jacket for cooling. It can be used as a sample excitation source for both emission and absorption or can be used as a variable light source for atomic absorption by changing the cathodes.

(20) Summer ARMU employee.

1.8 Emission Spectrographic Analysis for Fluorine (R. A. Woodriff)

A promising spectrographic method for the analysis of fluorine and other non-metals was briefly investigated using the hollow cathode tube (section 1.7.1) and a 3 meter Baird spectrograph. Samples of sodium fluoride were introduced into the cathode and the spectra recorded on type N photographic plates. It was found that the type N plates gave better intensities and furthermore, gave other more intense lines than had previously been reported. The chemical combination of the fluoride seriously affects the intensities and needs to be studied further.

1.9 Microwave Excitation of Mercury for Spectrographic Analysis (R. A. Woodriff)

Microwave excitation was used for the spectrographic detection of submicrogram quantities of mercury. The sample is introduced into a 6-mm tube about 10-cm long. This tube is slipped into an O-ring connection on a tee tube so that helium can be circulated through it. The tube is evacuated and filled with helium several times to pump off any water or other gases. The microwave generator is turned on after the helium pressure is adjusted to 3 or 4 mm and both the entrance and exit slits closed. If the discharge does not start spontaneously, it is started with a Tesla coil. Exposures of 4 or 5 min using a 3 meter Baird Spectrograph gives a good mercury line at 2537\AA from 0.01 μg of mercury.

2. MASS SPECTROMETRY

2.1 Fission Gas Retention of Test Reactor Fuels (L. L. Dickerson)

In a joint effort by the Analytical Chemistry and Chemical Technology Branches, a study was undertaken to determine the relative fission gas retention properties of irradiated uranium aluminide and uranium dioxide fuel plates.

The irradiated fuel plates were heated to various temperatures approaching the melting point of the aluminum cladding material for various times. The volume of the gases evolved were determined by collecting them in a known volume and determining their pressure by means of a McLeod gauge. The CEC mass spectrometer was used to determine their composition. Forty-three samples were collected from the six fuel plates and analyzed. Components other than fission products krypton and xenon which were identified and determined were hydrogen, helium, water, nitrogen, oxygen, carbon monoxide, nitric oxide, argon, carbon dioxide, and miscellaneous hydrocarbons.

2.2 Improvement in Equipment

2.2.1 Gas Mass Spectrometer Acquisition (A. H. Toepfer, L. L. Dickerson, G. W. Webb). A CEC 21-620 mass spectrometer has been acquired from surplus. Accompanying accessories include a strip chart recorder, peak selector,

micromanometer, liquid sample introduction system, and a heatable, continuous-stream, sampling system.

Because the equipment had been idle for several years, it was thoroughly inspected and serviced before startup was attempted. The recording system, which required servicing, was placed into operating condition with a signal simulator. Several vacuum leaks were located and corrected. The instrument now appears to be operable, and satisfactory spectra have been recorded. Its first applications will be to CDE, LOFT semiscale blowdown tests, and methods development for LOFT.

2.2.2 Tandem Mass Spectrometer Vacuum Lock (A. H. Toepfer). The vacuum-lock drive mechanism on the TDD-1 mass spectrometer was modified for improved operation. The main drive screw, of brass, was replaced with a carefully fitted bronze screw, fabricated by Special Maintenance. The drive motor was mounted on rubber to reduce the vibration transferred to the vacuum system. The original micro switches, which stop the lock at the pumping stations during introduction, have failed frequently due to breakage of the small plastic actuators. These were replaced by heavier switches equipped with roller actuators for more dependable operation.

2.2.3 Modification of Hydrogen Analysis Apparatus (L. L. Dickerson, G. D. Workman). The vacuum-extraction, hydrogen analysis apparatus was modified for remote operation. A square plastic handle with a "lock-on" mechanism was installed on the induction heater switch, and the glassware was modified to permit manipulator handling. The induction heater was located in the MTR hot cell, and the transfer pump, calibrated reservoir, and McLeod gauge were located outside the cell.

Seven samples from a zircaloy in-pile tube and five zircaloy tensile specimens were analyzed for hydrogen. The activity of the samples was as high as 5R/hr through the glassware.

2.2.4 Mass Spectrometer Filament Bakeout Apparatus (A. H. Toepfer). The filament vacuum bakeout chamber has been altered so the filaments can be baked out before they are installed in the hats which position the filaments in the mass spectrometer source. Previously, the filaments had been installed in the hats which were mounted on a support fixture in the bakeout chamber. During bakeout, material evaporated from the filaments, deposited on the hats, and was thus introduced into the source. The improvements with the new equipment are: (a) filaments can be handled more conveniently, (b) present limited supply of hats is adequate since they are no longer required for the bakeout operation, (c) hats placed in the source are clean, and (d) several types of filaments can be kept ready for use.

Fixture and filament support bars were made up for the vacuum bakeout chamber. Each bar can hold nine filaments which have been formed and welded to the Kovar seals. Four bars can be placed in the chamber at one time. Four additional bars have been made up to permit either the making of new filaments in advance or for storage in a heated vacuum oven.

Fixtures have been made to support the bars rigidly while mounting newly made filaments and to support the filaments safely in the vacuum oven while awaiting use.

2.2.5 Mass Spectrometer Filament Forming Fixture (A. H. Toepfer). New jigs for forming mass spectrometer filaments have been designed and built. About 5000 filaments per year are used in the triple-filament TDD-1 mass spectrometer. The jig supplied with the instrument was made of aluminum and brass and has worn out. The new jigs are made of stainless steel in all forming parts. Provisions are made for adjusting alignment. The jaws are replaceable when necessary because of wear, damage, or when V-grooved filaments are required. The vises can be opened and closed without the use of tools. With these jigs, filaments are prepared more rapidly and accurately, and the lifetime should be much greater than that of the original jig.

V. CHEMICAL ANALYSIS

1. MANPOWER REQUIREMENTS FOR DIFFERENT ANALYSES

Table V-1 shows some of the general methods and average time required for analysis. These methods are used in the Chemical Analysis Section, and time per analysis was obtained from total analyses and total hours accumulated from 1966 daily time records. The time per analysis applies only if three or more samples are analyzed for the same constituent at the same time. Time per single determination would be higher.

TABLE V-1

1966 ANALYTICAL METHODS AND TIME REQUIRED FOR ANALYSIS

<u>Method</u>	<u>Hrs/Det</u>
Acid, oxalate, pH titrimetric	0.3
Acid, oxalate, pH titrimetric ^[a]	0.3
Acid, phenolphthalein, volumetric	0.3
Activity, gross α , β , γ	0.5
Aluminum, fluoride complexing, titrimetric	0.4
Ammonia, titrimetric	0.5
Barium, radiochemical	1.1
Biochemical oxygen demand	0.3
Boron, mannitol, titrimetric	0.5
Boron, flame photometric	0.2
Cadmium, radiochemical	4.5
Carbon	0.6
Carbonate, titrimetric	0.2
Cerium, radiochemical	2.2
Cesium, radiochemical	1.4
Chloride, colorimetric	0.7

TABLE V-1 (continued)

Chloride, volumetric	0.4
Chromium, diphenylcarbazide, colorimetric	0.6
Chromium, titrimetric	0.4
Chromium, redox, titrimetric	0.6
Cobalt, colorimetric	0.7
Cobalt, radiochemical	0.9
Conductivity	0.1
Fluoride, macro, cerium trifluoride, titrimetric	1.0
Fluoride, micro, distillation, colorimetric	0.7
Gamma, nullification	0.9
Iodine, radiochemical	0.8
Iron, colorimetric	0.3
Iron, radiochemical	1.8
Iron, volumetric	0.7
Manganese, colorimetric	0.5
Manganese, radiochemical	1.0
Mercury, dithizone, colorimetric	0.7
Mercury, thiocyanate, titrimetric	0.4
Moisture analysis	1.7
Molybdenum, radiochemical	3.5
Neptunium, radiochemical	3.2
Nickel, colorimetric	0.6
Nickel, volumetric	0.7
Nitrate, Devarda alloy reduction, distillation, titrimetric	0.4

TABLE V-1 (continued)

Nitrate, phenoldisulphonic, colorimetric	0.6
Particle density	0.6
Plutonium, radiochemical	3.2
pH	0.3
Rare earth, actinide and lanthanide, radiochemical	5.9
Reducing normality	0.3
Ruthenium, colorimetric	0.8
Ruthenium, radiochemical	2.5
Sample particle size	0.3
Sample particle size[a]	1.0
Solids, density absolute	0.3
Solids, density bulk	0.7
Solids, density bulk[a]	0.7
Solids, total	0.6
Solids, undissolved	0.7
Specific gravity, falling drop[a]	0.4
Specific gravity, Westphal balance	0.2
Strontium, radiochemical	1.6
Thorium, radiochemical	7.4
Tributylphosphate, acid saturation, titrimetric	0.4
Uranium, extraction, fluorophotometric	0.4
Uranium, extraction, fluorophotometric [a]	0.4
Uranium, extraction, spectrophotometric	0.5
Uranium, mass, isotopic distribution[b]	0.4
Uranium, mass, isotopic distribution [a,b]	0.5
Uranium, gravimetric	0.8
Uranium, radiochemical	2.6
Viscosity	0.7
Zirconium, cupferron, amperometric	0.8
Zirconium, radiochemical	1.3

[a] Method performed in Remote Analytical Facilities.

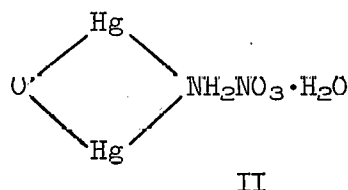
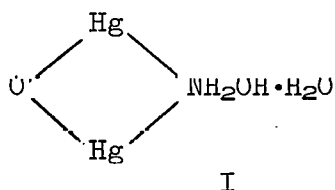
[b] Separation of uranium by solvent extraction before mass assay.

2. ANALYTICAL SERVICES

2.1 Chemical and Process Development Branch

2.1.1 Identification of Millons Base (M. A. Wade, W. A. Ryder)

A white powder, synthesized by the reaction of mercuric oxide with ammonium nitrate, and assumed to be either Millons base or the nitrate salt of Millons base, was submitted for identification. Millons base is represented by formula I and the nitrate salt by formula II.



Millons base is reported to be yellow, but x-ray analysis of the white powder gave a pattern identical to the pattern listed for Millons base. The white powder was insoluble in water, nitric acid, and caustic. However, it reacted with sodium hydroxide to form a yellow compound. The reaction consumed 1 mmole of hydroxyl ion per gram of compound and was not reversed by subsequent treatment with nitric acid.

Analysis of the white compound showed a mercury to ammonia ratio of two to one, a mercury to nitrate ratio of four to one, and an ammonia to nitrate ratio of two to one. The data indicates that the white compound is either a mixture of Millons base and its nitrate salt or a polymeric species of the nitrate salt.

2.2 Chemical Processing Plant Operations Branch

2.2.1 Neptunium Retention by Silica (B. A. Staples, J. G. Scott)

Samples from the neptunium recovery process contained solid silica particles, and it was necessary to determine the amount of neptunium absorbed by these particles. The silica was filtered from the 1M HNO₃ sample solution, then dissolved in a mixture of hydrofluoric and sulfuric acids. The neptunium was determined by a spectrophotometric measurement of the 1.23- μ neptunium(VI) peak. The original sample contained 1.3 mg of solids per milliliter of sample solution, and the neptunium concentration in the solids was 5.4% by weight.

2.3 Nuclear Technology Branch

2.3.1 Analysis of Powder Compacts (I. L. Doggett)

Powder compacts, received from the Reactor Physics Section, were analyzed for ruthenium, palladium, and osmium. These compacts were aluminum alloys containing from 0.5 to 6.0% palladium, ruthenium, or osmium.

The aluminum-palladium compacts were dissolved in aqua regia and analyzed for palladium by x-ray fluorescence.

The aluminum-ruthenium samples were treated with concentrated hydrochloric acid to remove the aluminum. The resulting ruthenium residue was filtered, then fused with sodium hydroxide and potassium nitrate. The fused melt was dissolved with sodium hypochlorite and water, and the solution was analyzed colorimetrically for ruthenium.

The aluminum-osmium samples also were treated with concentrated hydrochloric acid to dissolve the aluminum. The residue, which contained the osmium, was dissolved with a mixture of concentrated sulfuric-nitric acids. The osmium was distilled into 10M NaOH, and the distillate was analyzed using a thiourea colorimetric method⁽²¹⁾. The values obtained for the osmium concentration were significantly lower than the estimated concentration. To verify the results, a second set of samples was analyzed. The aluminum was removed, and the osmium residues were fused with a mixture of sodium hydroxide and potassium nitrate. The melts were dissolved in water, and these solutions were analyzed using the thiourea method. The results checked with those from the distillation procedure and confirmed the difference between estimated and analyzed osmium concentrations.

Standards were made by using pure metals of both osmium and aluminum. Osmium recovery was complete by both methods.

2.4 Phillips Petroleum Company Engineering and Test Branch

2.4.1 Dissolution of Snap-2 Fuels (I. L. Doggett, B. A. Staples, J. G. Scott)

Fuel from the Snap-2 reactor contains 10% uranium and 90% zirconium. Fuel samples from the reactor were dissolved by heating with concentrated hydrofluoric acid until the reaction ceased. The uranium tetrafluoride and fluorozirconates formed during dissolution were put into solution by adding 300 ml of concentrated nitric acid containing 1 g of chromium trioxide and 3 g of boric acid. The chromium trioxide oxidizes the uranium(IV) to the (VI) valence state, and the boric acid dissolves the fluorozirconates. After heating for 15 min, an equal volume of water was added and the sample again heated until a clear solution was obtained.

2.5 Westinghouse

2.5.1 Analysis of Inconel (D. R. Trammell, W. A. Mickelson, M. A. Wade)

An Inconel sample was analyzed for aluminum, chromium, iron, nickel, phosphorus, sulfur, and titanium. Existing laboratory procedures were used for all analyses except aluminum and titanium.

(21) G. H. Ayers, W. N. Wells, Anal. Chem., 22 (1950) p 317.

Aluminum and titanium were separated from the other metallic constituents by mercury cathode reduction. The dissolved sample was treated with peroxide to reduce chromium, then fumed with sulfuric acid to remove nitrate. The sample was adjusted to approximately 0.4M sulfate, then electrolyzed in a mercury cathode cell for 30 min using a 9-V dry cell power source. Aliquots of the electrolyzed solution were analyzed for aluminum and titanium.

Aluminum was determined colorimetrically as the 8-hydroxyquinolate at 395 m μ after first extracting the complex into chloroform from an ammonium chloride-ammonium hydroxide (pH 10) buffered solution containing both cyanide and triethylenetetramine as complexing agents. Titanium at twice the level found in the sample did not interfere in the aluminum procedure. Titanium was determined colorimetrically with Tiron (disodium 1,2-dihydroxy-benzene-3,5-disulfonate) at 380 m μ in a sodium acetate acetic acid buffered medium (pH 3.8) containing thioglycolic acid as a complexing agent. One hour is required for color development, and the color is stable for several hours.

2.5.2 Analysis of Brass Fitting (D. R. Trammell)

A brass fitting was analyzed for copper, iron, lead, nickel, phosphorous, tin, and zinc. These analyses were requested to identify the brass.

During the dissolution of the sample in nitric acid, tin hydrolyzed and precipitated as metastannic acid. The precipitate was filtered and tin was determined gravimetrically after ignition to the oxide. Copper and lead in the filtrate were determined by electrolysis after adjusting the solution to about 0.2M in sulfate and 1M in acid with sulfuric and nitric acids. The electrolysis took approximately 6 hr at 0.9 A. Copper was weighed as the metal on the cathode, and lead was weighed as lead dioxide on the anode. An aliquot of the electrolyzed solution was adjusted to 0.01M in acid and the zinc was precipitated as the sulfide. Following dissolution of the sulfide, zinc was determined volumetrically with EDTA. Nickel, iron, and phosphorous were determined on the electrolyzed solution by standard laboratory colorimetric procedures.

2.6 Development For Chemical Analysis

2.6.1 Stability Evaluation of Stored Input Measurement Samples From Dissolved Irradiated U-235 Fuel Elements (D. R. Trammell, M. A. Wade, G. A. Huff)

A program to evaluate the stability of stored input measurement samples resulting from the processing of enriched uranium fuels was initiated. Dissolved samples from the Materials Testing Reactor, the Engineering Test Reactor, the Vallecitos Boiling Water Reactor, the Pressurized Water Reactor, the General Electric Test Reactor, and Swedish and National Aeronautics Space Authority fuels were sealed in glass vials at the time of processing and are being used for this study.

These samples were analyzed for uranium, acid, and specific gravity. The zirconium type fuels also were analyzed for aluminum and zirconium. Following the analytical work, aliquots of the samples were sealed in glass vials by either of two methods. The neck of the vials were heated with an oxygen-propane flame, and the heated area was sealed by either pinching with metal forceps or by pulling the neck out to a fine tip, then flame sealing the tip. The samples contained fission products and read up to 30 R/hr at 3 in. The sealing was done as rapidly as possible to cut down the exposure to personnel.

These samples are being analyzed for the same constituents determined initially as well as gas and solids content. Approximately 20% of the seals were poor, probably due to the haste with which the samples were sealed. These were discarded. Many of the other samples contained small amounts of residue. X-ray diffraction and emission spectrographic analyses identified the residues as being characteristic of the fuel processed. In no case was any detectable uranium found in the residue.

Analyses of the gas from a representative number of samples revealed that combustion products from the sealing flame were trapped in the vials at the time of sealing. The carbon dioxide content, however, was greater than could be attributed to the sealing process. The source of the excess carbon dioxide is unknown. Nitrogen and oxygen also were introduced prior to sampling because the tanks were sparged with either nitrogen or an air-oxygen mixture before the samples were taken. These unexpected variables make an analysis of the gas for radiolysis products impractical.

At the completion of the study, the data will be analyzed statistically to determine if any significant changes in sample composition took place during storage.

3. IMPROVEMENTS IN METHODS AND EQUIPMENT

3.1 Determination of Solids (F. A. Duce, M. A. Wade)

A procedure for the determination of total solids and undissolved solids (Calcliner Solids-1) was added to the Analytical Methods Manual. Total solids are determined gravimetrically by evaporating a known volume of solution to dryness in a tared beaker. Undissolved solids are determined gravimetrically by filtering a known volume of solution through a tared filter. If the undissolved solids are determined at elevated temperatures, the filter is transferred to a tared quartz beaker and heated. Details of the method are presented in Appendix B.

3.2 Cesium Separation by Ion Exchange (J. R. Fischer, J. G. Scott)

A rapid ion exchange method is being studied for the separation of radiocesium. The exchanger is an insoluble potassium salt, dipotassium cobalt(II)hexacyanoferrate(II), $K_2CoFe(CN)_6$ (22). The exchanger,

(22) W. E. Prout et al, J. Inorganic Chemistry, 27, (1965) pp 473-479.

abbreviated KCFC, exchanges potassium for cesium, and also exchanges potassium for rubidium by the same means but less completely.

Previous work with KCFC has been in the form of columns. Though effective, the column technique⁽²³⁾ is time consuming to prepare columns and for the separation. Conditions are being studied to adapt KCFC to a rapid separation using a disc⁽²⁴⁾ which then is gamma-counted directly above a sodium iodide thallium [NaI(Tl)] crystal.

A sample, pipetted into a 50-ml plastic vial, is adjusted with hydrofluoric and hydrochloric acids to 0.1M HF-4.0M HCl. Three hundred milligrams of 50-100 mesh KCFC is added, and the tube is capped and vigorously agitated with a vortex mixer for 10 min. The KCFC then is filtered on an acid resistant Metrical filter in a modified Millipore filtering apparatus, and the resulting disc is counted with a multichannel gamma analyzer.

Experimental data indicates cesium recovery by this technique is between 98 and 100%. Rubidium recovery is approximately 95%. Other acid and caustic media were investigated, but the hydrofluoric-hydrochloric mixture gave better decontamination from niobium, ruthenium, and zirconium.

Large amounts of sodium or potassium do not interfere. Interfering nuclides are those of cobalt, technetium, and zinc.

Sample analysis time can be reduced from 2 hr for the present perchlorate method⁽²⁵⁾ to about 20 min.

3.3 Modification of Barricades and Calibration of Detector Systems for High Activity Level Samples (A. C. Hill, C. M. Wilcox, J. G. Scott)

Two lead barricades in the Analytical Branch counting room were modified by cutting a 3-in. diam hole in the lids covering the detectors. Each hole was cut so it would align directly with the 3-by 3-in. NaI(Tl) detector inside the barricade and the sample holder which moves along a track to a height of 230 cm above the detector. Each hole is lined with cadmium and copper to reduce backscatter effects of gamma rays and x-rays. This modification eliminates the backscatter peaks from the walls of the barricade and also reduces the background by a factor greater than 10 from that obtained with open barricades. The barricades are still suitable for counting low level samples shielded within the barricade by inserting a 3-in. removable lead plug in the hole.

The detector systems in the modified barricades are calibrated for gamma scanning of samples at distances up to 230 cm from the detectors. Standard sources of Ce-144, I-131, Cs-137, and Sc-46 were used to obtain the calibration factors. Gamma-ray photopeak areas from various distances

(23) A. L. Boni, Anal. Chem., 28 No. 1 (January 1966) pp 89-92

(24) W. J. Maeck, Idaho Nuclear Corporation, Private Communication (Sept 1966).

(25) D. G. Olson, IDO-14613, Manual of Radiochemical Methods (January 1964).

can be corrected to a standard 10-cm distance. Samples with activity levels of 2- to 6-R/hr, depending on the energy of the major isotopes, can be counted. There is no appreciable change in spectrum shapes from samples counted at the 10-cm distance.

3.4 New Fraction Separator (B. A. Staples, J. P. Morgan, S. F. Marsh)

A fraction separator for chromatographic actinide and lanthanide separations has been assembled for use by the Special Analysis Group.

The effluent from a chromatographic column is separated into collecting tubes by an automatic fraction collector. Gamma activity in the effluent is detected by a flow-through scintillation detector coupled with a logarithmic count rate meter. A strip chart recorder connected to the rate meter gives a continuous recording of activity detected from the column. Thus, chemical species separated and eluted from a chromatographic column can be collected in separated fractions. From a knowledge of the elution order of the elements and the strip chart activity record, chemical species in each collected fraction can be determined.

VI. STANDARDS AND QUALITY CONTROL

1. QUALIFICATION OF UMPIRE LABORATORIES

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

The Umpire Qualification Program was started in April 1965 at the request of the Division of Nuclear Materials Management of the AEC. During 1966, this Program was continued through June under Phillips Petroleum Company, then thereafter under Idaho Nuclear Corporation. This report describes the status of the Program as of December 31, 1966.

1.1 Participation of AEC, U. S. Commercial, and Foreign Laboratories

Eight AEC and AEC-contractor laboratories, nine commercial U. S. laboratories, and six foreign laboratories are participating in various segments of the Program. This information is summarized in Table VI-1.

1.2 Preparation of Standards

Laboratories that wish to qualify as an umpire laboratory for the analysis of a given material will be tested on their technical ability to analyze a standard of that material. Eight types of standard materials will be used for the tests. Table VI-2 summarizes the preparatory work that must be done, the AEC and AEC-contractor laboratories that are helping the preparatory work, and the present status of the project.

1.3 Distribution of Standards to U. S. Commercial and Foreign Laboratories

As shown in Table VI-1, a total of 15 U. S. commercial and foreign laboratories have expressed definite interest in the uranium segment of the Program. Appropriate standards of the uranium nitrate and uranium hexafluoride materials have been sent to them. Some of these laboratories, primarily those participating only in the isotopic determination of uranium, have completed the analysis. The statistical evaluation of the results is scheduled for early 1967.

1.4 Future Plans

With reference to the foregoing, the following activities are planned for the next one-year period: (a) preparation and distribution of uranium oxide standards, (b) distribution of the three plutonium standards, (c) preparation and distribution of the U-233-enriched uranyl nitrate standard, and (d) assignment of the preparation of the uranium metal standard.

TABLE VI-1

AEC, U. S. COMMERCIAL, AND FOREIGN LABORATORY PARTICIPATION^[a]

<u>Laboratory</u> ^[b]	U-233													
	<u>UFe</u>		<u>UN</u>		<u>UO</u>		<u>UN</u>		<u>PuN</u>		<u>PuO</u>		<u>Pu</u>	
	<u>Std</u> <u>Prep</u>	<u>Anal</u>	<u>Std</u> <u>Prep</u>	<u>Anal</u>	<u>Std</u> <u>Prep</u>	<u>Anal</u>	<u>Std</u> <u>Prep</u>	<u>Anal</u>	<u>Std</u> <u>Prep</u>	<u>Anal</u>	<u>Std</u> <u>Prep</u>	<u>Anal</u>	<u>Std</u> <u>Prep</u>	<u>Anal</u>
<u>AEC</u>														
ORGDP (K-25)	X	X		X		X		X						
NEL		X		X		X		X		X		X		X
GAT		X		X		X		X						
PAD ^[c]		X		X										
INC (CFP)			X	X	X	X	X	X						
RF									X	X	X	X		X
Isochem										X		X	X	X
LASL										X		X		X
<u>U. S. Commercial</u>														
Avco		X		X		X		X		X		X		X
Eberline				X		X				X				
GE-Val		X		X		X		X		X		X		X
Isotopes, Inc.		X		X		X		X						
Nat'l Lead				X		X								
NFS				X		X		X						
Numec		X		X		X				X		X		X

TABLE VI-1 (continued)

Laboratory ^[b]	U-233													
	U ²³⁵		UN		UO		UN		PuN		PuO		Pu	
	Std Prep	Anal	Std Prep	Anal	Std Prep	Anal	Std Prep	Anal	Std Prep	Anal	Std Prep	Anal	Std Prep	Anal
Tracerlab			X		X			X						
Westinghouse			X		X									
<u>Foreign</u>														
CBNM		X		X		X		X		X		X		X
CEA				X		X				X		X		X
CEN-BN		X		X		X				X		X		X
MH-IN		X		X		X								
NUKEM		X		X		X								
ALKEM				X		X				X		X		X

[a] Uranium metal is being added to the Program. Its preparation and standardization has not been assigned, and the interest of U. S. commercial and foreign laboratories have not been established.

[b] Laboratories: ORGDP = Oak Ridge Gaseous Diffusion Plant
 NEL = New Brunswick Laboratory
 GAT = Goodyear Atomic Corporation
 PAD = Paducah Gaseous Diffusion Plant
 INC = Idaho Nuclear Corporation at
 (CPP) Chemical Processing Plant
 RF = Dow Chemical Company, Rocky Flats
 LASL = Los Alamos Scientific Laboratory
 GE-Val = General Electric Company at
 Vallecitos, Calif.
 NFS = Nuclear Fuels Service
 CBNM = Bureau Central de Mesures, Nucleaires
 (Geel, Belgium)

CEA = Commissariat a l'Energie Atomique
 (Grenoble, Fr.)
 CEN-BN = Central de Nucleaires-Belgonucleaire
 (Mol, Belgium)
 MH-IN = Metallurgie Hoboken (Associated with)
 L'Industrie Nucleaire (Hoboken,
 Antwerp, Belgium)
 NUKEM = Nukem, Nuklear-Chemie und-Metallurgie
 (Hanau (Main), West Germany)
 ALKEM = Alken, Alpha-Chemie und-Metallurgie
 (West Germany)

[c] PAD is being considered for the preparation of the uranium metal standard.... PAD, ORGDP, GAT, and CPP for the standardization.

TABLE VI-2

STATUS OF URANIUM AND PLUTONIUM STANDARDS PREPARATION

Description of Work	Laboratory Assigned	Remarks
Uranyl Nitrate		
Preparation	CPP	Completed.
Standardization	CPP	Incomplete; estimated completion date, 2-1-67.
	GAT	Incomplete; estimated completion date, 2-1-67.
	K-25	Completed.
	NBL	Incomplete; estimated completion date, 2-1-67.
	PAD	Completed.
Uranium Hexafluoride		
Preparation	K-25	Completed.
Standardization	GAT	Incomplete; estimated completion date, 2-1-67.
	K-25	Completed.
	NBL	Incomplete; estimated completion date, 2-1-67.
	PAD	Incomplete; estimated completion date, 2-1-67.
Uranium Oxide (U ₃ O ₈)		
Preparation	CPP	The preparation will be started in February 1967. Estimated completion date, 6-1-67.
Standardization	CPP	
	GAT	
	K-25	
	NBL	
Uranyl Nitrate (U-233 enriched)		
Preparation	CPP	To be undertaken in first quarter of FY 1968.
Standardization	CPP	
	GAT	
	K-25	
	NBL	
Uranium Metal ^[a]	Unassigned	To be undertaken in FY 1968.

TABLE VI-2 (continued)

Description of Work	Laboratory Assigned	Remarks
Plutonium Nitrate Preparation	RF	Incomplete; the instability of the nitrate solution is preventing the use of sealed-glass-ampoule containment. RF is considering the use of thick-walled ampoules and conducting studies to improve stability. Not started.
Standardization	Isochem LASL NBL RF	
Plutonium Oxide Preparation	RF	Incomplete; estimated completion date, 4-1-67. Not started.
Standardization	Isochem LASL NBL RF	
Plutonium Metal Preparation	Isochem	Incomplete; estimated completion date, 6-1-67.
Standardization	Isochem LASL NBL RF	

[a] PAD is being considered for the preparation of the uranium metal standard, PAD, K-25, GAT, and CPP for the standardization.

2. QUALITY CONTROL (G. J. Curtis, F. A. Duce, J. E. Rein)

The comprehensive quality control program relating to both routine and special methods was continued. The main features of this program are: (a) the preparation of all reagents and standards for the methods, (b) the submission of standard samples (of unknown content to the analysts) and statistical treatment of the results to compute bias corrections and error limits, (c) the submission of standard samples and statistical treatment of the results to establish whether new analysts are qualified to use the various methods, (d) the maintenance of "bench" standards and control charts, and (e) the continuous surveillance of all control data to ensure that methods remain reliable. "Bench" standards of known values are processed prior to samples to prevent the use of faulty apparatus or reagents.

2.1 Bias and Precision Data

Tables of current bias and of precision for routine methods, based on computer-calculated regression equations computed from standard sample results, are provided at 3-month intervals by Operations Analysis personnel. These tables provide a rapid means to correct results for bias and to associate a precision uncertainty over the entire range of the methods. They are applied by laboratory personnel to all analysis results. Additional information available from these tables is a comparison of the current bias and precision to similar data from the previous period and the range of the method for best precision. The latter guides the analyst to select aliquot sizes to obtain minimum errors.

Table VI-3 is a summary of the current precision for routine methods.

2.2 Training and Testing Program

New analysts in the Chemical Analysis Section are tested for their ability on each method by analyzing a series of nine standard samples. A rapid statistical test⁽⁶⁾ both for accuracy and precision establishes qualification. If they fail, they are retrained and retested.

2.3 Standards and Reagents

The numbers of standard solutions, reagents, and quality control samples prepared this year are summarized in Table II-2.

2.3.1 Storage of Standard Solutions

Standard solutions are now stored in flame-sealed glass ampoules. This prevents concentration changes due to evaporation and hence provides stability over long time periods.

(6) R. C. Shank and Staff, Annual Report of Division Analytical Branch for 1965, IDO-14679, Section VI-2.2.2 (June 1966).

TABLE VI-3

PRECISION OF ROUTINE ANALYTICAL METHODS

<u>Methods</u>	<u>Range and Units</u> ^[a]	<u>Precision</u> ^[b]
Acid, visual indicator titrimetric	0.5 to 4.5 meq	0.01 to 0.09 meq
Acid, oxalate, pH titrimetric	0.5 meq base to 1.2 meq acid	0.01 meq, constant
Acid, oxalate, pH titrimetric, remote	0.5 meq base to 1.2 meq acid	0.02 to 0.03 meq
Aluminum, fluoride complexing, titrimetric	5 to 11 mg	0.16 to 0.19 mg
Beta activity, gross	45 to 355 d/m	7 to 44 d/m
Boron, mannitol com- plexing, titrimetric, high level	0.5 to 5.0 mg	0.01 to 0.20 mg
Boron, mannitol com- plexing, titrimetric, low level	0.1 to 1.5 mg	0.03 mg, constant
Cs-137	5×10^4 to 9.9×10^5 d/m	1.2×10^4 to 1.3×10^5 d/m
Chromium, redox titrimetric	1.6 to 15.6 mg	0.07 to 0.25 mg
Chromium, diphenyl- carbazide colorimetric	0.005 to 0.05 mg	0.0005 to 0.0040 mg
Fluoride, pyrolysis, Ce(III) titrimetric	6 to 40 mg	1.3 to 2.4 mg
Iron, column extraction, EDTA titrimetric	2 to 25 mg	0.12 to 0.59 mg
Iron, orthophenan- throline colorimetric	2 to 98 μ g	1.0 to 4.4 μ g
Iron, column extraction, orthophenanthroline colorimetric	4 to 100 μ g	1.4 to 3.9 μ g
Mercury, titrimetric, Hg(II) with KSCN	96 to 300 mg	2.4 to 4.5 mg

TABLE VI-3 (continued)

<u>Methods</u>	<u>Range and Units</u> ^[a]	<u>Precision</u> ^[b]
Mercury, dithizone colorimetric	50 to 300 µg	12 to 21 µg
Nickel, dimethyl-glyoxime colorimetric	0.01 to 0.1 mg	0.001 to 0.003 mg
Nickel, dimethyl-glyoxime precipitation, EDTA titrimetric	2 to 28 mg	0.3 to 1.1 mg
Nitrate, Devarda reduction, distillation, titrimetric	0.2 to 4.5 mmole	0.03 to 0.15 mmole
Phosphate, extraction, colorimetric	1 to 100 µg	1.4 to 4.6 µg
Reducing normality, dichromate titrimetric	0.1 to 0.9 meq Fe(II)	0.01 meq, constant
Specific gravity Westphal	0.79 to 1.59 specific gravity units	0.001 to 0.003 specific gravity units
Specific gravity falling drop, remote	1.05 to 1.32 specific gravity units	0.001 to 0.005 specific gravity units
Tin, pyrocatechol violet colorimetric	15 to 150 µg	6.5 to 9.9 µg
Tributylphosphate, bromthymol blue titrimetric	1.5 to 12% TBP	0.1 to 0.2% TBP
Uranium, extraction, tetrapropylammonium uranyl trinitrate spectrophotometric	1 to 30 mg	0.17 to 0.91 mg
Uranium, extraction, tetrapropylammonium uranyl trinitrate spectrophotometric	0.5 to 35 mg	0.12 to 0.53 mg
Uranium, mass isotopic distribution, hand pipetted	1.008% U-234 93.129% U-235 0.180% U-236 5.683% U-238	0.007% 0.053% 0.008% 0.002%

TABLE VI-3 (continued)

<u>Methods</u>	<u>Range and Units [a]</u>	<u>Precision [b]</u>
Uranium, isotopic-dilution mass-spectrometric, hand pipetted	1.00 mg	0.008 mg
Uranium, mass isotopic distribution, remote pipetted	1.010% U-234	0.007%
	93.120% U-235	0.062%
	0.182% U-236	0.008%
	5.690% U-238	0.041%
Uranium, isotopic-dilution mass-spectrometric, remote pipetted	1.00 mg	0.014 mg
Uranium, mass isotopic-distribution, high precision	1.0157% U-234	0.0096%
	93.1457% U-235	0.0445%
	0.1814% U-236	0.0079%
	5.6565% U-238	0.0243%
Uranium, isotopic-dilution, mass-spectrometric, high precision	1.00 mg	0.0039 mg
Uranium, extraction, dibenzoylmethane colorimetric	0.005 to 0.075 mg	0.001 to 0.003 mg
Uranium, ignition to U ₃ O ₈ , spectrographic impurity correction	220.0 to 230.0 mg	0.17 mg
Uranium, extraction, pellet fluorophotometric	5x10 ⁻⁵ to 0.1 mg/ml	1.5x10 ⁻⁵ to 3x10 ⁻² mg/ml
Zirconium, cupferron amperometric	0.01 to 0.1 mmole	0.001 to 0.002 mmole

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

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

2.3.2 Comparison of Uranium Materials for the Standardization of U-233

Three uranium materials were used to standardize a U-233 solution to be used as the added isotope for the isotope-dilution, mass-spectrometric method for the determination of uranium. The materials were natural uranium U_3O_8 (NBS sample 950a), fully enriched uranium metal (obtained from the Oak Ridge National Laboratory), and natural uranium metal (obtained from the Argonne National Laboratory).

Solutions at the 2 mg/ml level were prepared for each uranium material by dissolution of a weighed sample in nitric acid and dilution to volume in NBS-calibrated volumetric flasks. Six mixtures of each solution with a U-233 solution were prepared using the same dry-filmed pipet for all deliveries. These 18 mixtures then were analyzed for the U-233 concentration on a surface ionization mass spectrometer. The U-233 concentration was computed on the basis of the made-up concentrations of the three uranium material solutions.

The results are summarized in Table VI-4.

TABLE VI-4

STANDARDIZATION OF U-233 SOLUTION

<u>Standardizing Solution</u>	<u>Results, mg U-233/ml</u>	<u>Average Result</u>	<u>Standard Deviation</u>
ORNL U-235 Metal	0.9916	0.9934	0.0025
	0.9971		
	0.9932		
	0.9929		
	0.9947		
	0.9907		
NBS U_3O_8 [a]	0.9940	0.9936	0.0012
	0.9926		
	0.9956		
	0.9922		
	0.9938		
ANL Natural U Metal	0.9952	0.9940	0.0008
	0.9947		
	0.9930		
	0.9951		
	0.9932		
	0.9931		

[a] One sample lost.

The averages, based on statistical "t" tests, are not significantly different indicating that all three uranium materials are stoichiometric and of the purity claimed for them.

The weighted average value for the U-233 concentration is 0.9938 with a standard deviation of 0.0005. The four uranium solutions have been flame sealed in glass ampoules for long-term storage.

APPENDIX A

PUBLICATIONS AND OTHER ACTIVITIES

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PUBLICATIONS AND PAPERS FOR 1966

1. U. S. ATOMIC ENERGY COMMISSION REPORTS

- | | | |
|-----------|---|--|
| IDO-14678 | W. J. Maeck
F. L. Lisman
J. E. Rein | <u>Burnup Determination of Nuclear Fuels Project Report for the Quarter January 1 - March 31, 1966.</u> |
| IDO-14679 | R. C. Shank
and Staff | <u>Annual Report of Division Analytical Branch for 1965.</u> |
| IDO-14681 | W. J. Maeck
J. E. Rein | <u>Burnup Determination of Nuclear Fuels Project Report for the Quarter April 1 - June 30, 1966.</u> |
| IN-1064 | F. L. Lisman
W. J. Maeck
R. E. Foster
J. E. Rein | <u>Burnup Determination of Nuclear Fuels Project Report for the Quarter July 1 - September 30, 1966.</u> |

2. JOURNAL ARTICLES

D. T. Pence, G. L. Booman, "Kinetic Current Measurements with Controlled Potential," Anal. Chem. 38 (August 1966) pp 1112-1119.

G. L. Booman, "A Digital Data Collection, Waveform Generation, and Timing Instruction for Electrochemical Measurements," Anal. Chem. 38 (August 1966) pp 1141-1148.

3. PAPERS

G. L. Booman, K. D. Smith, "Kinetic Current Measurements at Short Times Using Controlled Potential Polarography," 150th National American Chemical Society Meeting, Phoenix, January 1966.

R. E. Foster, Jr., "Separation and Determination of Krypton and Xenon in Irradiated Nuclear Fuel Samples," 17th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, February 1966.

F. L. Lisman, W. J. Maeck, J. E. Rein, "Accurate Measurement of the Capture to Fission Ratio for U-235 and U-233," 151st National American Chemical Society Meeting, Pittsburgh, March 1966.

F. W. Dykes, "A High Level Cave Designed to Replace Shielded Boxes," 10th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, September 1966.

G. A. Huff, "Improvements in Remote Analytical Chemistry Apparatus Used at the National Reactor Testing Station," 10th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, September 1966.

B. C. Laney, L. L. Dickerson, "Remote Fission-Gas Sampling," 10th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, September 1966.

APPENDIX B

METHODS ADDED TO THE ANALYTICAL
MANUAL IN 1966

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DETERMINATION OF PRINCIPAL COMPONENTS OF ECF DESCALING
SOLUTIONS: ANALYSIS OF CITRATE-VERSENOL
SOLUTION FOR BOTH COMPONENTS

I. Introduction

Section G-1 (ECF-1, Mod-1, p 37) describes the seven solutions that ECF-Westinghouse has been investigating for descaling STR fuel elements. They have now added an eighth descalant, a 1:1 ammonium dihydrogen citrate-Versenol [(N-hydroxyethyl)ethylenediamine triacetic acid] mixture which will be submitted for verification of makeup.

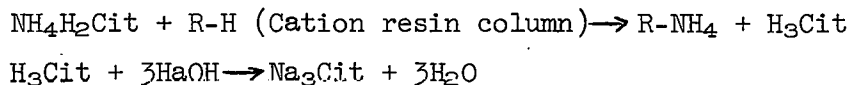
Although ammonium dihydrogen citrate and Versenol are chemically similar to diammonium citrate and EDTA, respectively, the citrate and EDTA methods described in sections G:4, and G:5 (ECF-1, Mod-1, pp 41-46) are not applicable for citrate-Versenol mixtures. Each component interferes in the determination of the other.

This supplement describes two new methods for the determination of citrate and Versenol (also EDTA) in mixtures of the two. Citrate is converted to citric acid and separated from Versenol by passing the sample through a cation exchange column in the hydrogen form. Versenol is retained by the resin. The citric acid in the column effluent is titrated with standard base to a phenolphthalein end point. Versenol is determined on a separate sample aliquot by titration with copper to a photometric end point. Under the conditions, pH 5.0, acetic acid-acetate buffering, citrate does not interfere.

II. Determination of Ammonium Dihydrogen Citrate

II:A. Discussion

The determination of ammonium dihydrogen citrate is based on the reactions:



Versenol is retained by the cation exchange resin as a dipositive Versenol $\cdot 2\text{H}^+$ cation.

The ammonium dihydrogen citrate is prepared at Westinghouse-ECF by combining citric acid and diammonium hydrogen citrate in a 1:1 molar ratio. If necessary, the stoichiometry of the ammonium dihydrogen citrate can be confirmed by a total citrate determination (per this procedure) and a labile-ammonia determination (distillation of ammonia from basic medium and titration with standard acid).

Expected interferences are acidic substances, salts that are converted to acidic substances by the cation resin, and metal ions that are complexed by Versenol. Acidic substances such as mineral acids and acetic acid are not retained by the resin and produce high results. Nitrilotriacetic acid, a common minor contaminant of Versenol and EDTA, bleeds through the column and likewise produces high results. Metal ions, by complexation, promote the downward displacement and elution of Versenol, a tribasic acid.

II:B. Apparatus and Reagents

1. Apparatus

- a. Ion exchange column, 12-mm o.d. x 6-in. column with a 1-mm Teflon-plugged stopcock (with a 1-in. stem) and a 38-mm o.d. x 3-in. reservoir. Use a glass wool plug to support the resin. This column is identical to that described and used in Method Fe-4 of the Analytical Manual.
- b. Pipet, volumetric, assorted sizes.
- c. Buret, 10-ml, with 0.05-ml or smaller graduations.
- d. Beakers, assorted sizes.
- e. Graduated cylinder, 10-ml.
- f. Magnetic stirrer and stirring bars.
- g. Ringstand with Fisher burette holder.

2. Reagents

- a. Citrate-Versenol bench standard. Dissolve 7.539 ± 0.001 g of diammonium citrate and 9.267 ± 0.001 g of Versenol in water and dilute to 1 liter. This solution is $0.0333M$ in citrate (6.973 g/liter as ammonium dihydrogen citrate) and $0.0333M$ (9.267 g/liter) in Versenol.
- b. Sodium hydroxide; 0.1000N. A 0.1000N solution standardized against potassium acid phthalate will be supplied by the Quality Control Laboratory.
- c. Phenolphthalein, 0.5%, in ethanol-water medium.

II:C. Bench Standard

Process a 5-ml aliquot of the citrate-Versenol bench standard per II-D. Limits will be specified by the Quality Control Laboratory.

II:D. Procedure

<u>Steps</u>	<u>Remarks</u>
1. Transfer sufficient Dowex 50W X 8, 50-100 mesh, hydrogen-form resin to the ion exchange column to form a bed 5.5 in. high.	The column should be free of channeling.
2. Wash the resin with distilled water until 25 ml of the column effluent requires not more than 0.01 ml of 0.100N NaOH to reach a phenolphthalein end point. Drain the water until its surface is at the top of the resin column.	
3. Place a clean 150-ml beaker beneath the column and pipet 5.00 ml of the citrate-Versenol descaling solution into the column reservoir.	The citrate-Versenol solution is prepared to be approximately 0.033M in citrate and in Versenol.
4. Pass the sample through the column (as fast as it will go) and wash the citric acid through with four 5-ml portions of distilled water. Collect the sample and washings in the beaker.	The interstitial volume of the column is 5 ml.
5. Add 1 to 2 drops of 0.5% phenolphthalein indicator solution and titrate with 0.1000N NaOH to the appearance of a pink color that persists for at least 30 sec.	
6. Calculate the results as described in <u>II:E</u> .	
7. Transfer the used resin to a large wide-mouth jar for subsequent regeneration.	

II:E. Calculations

$$\text{Citric Acid Molarity} = \frac{0.1000 \text{ (ml NaOH)}}{3 \text{ (Samp Vol in ml)}}$$

Result, grams ADC per liter = 209.2 (Citric Acid Molarity)
where ADC = ammonium dihydrogen citrate and
209.2 is its molecular weight.

III. Determination of Versenol [(N-Hydroxyethyl)ethylenediamine Triacetic Acid]

III:A. Discussion

This procedure for the determination of Versenol is specifically designed for citrate-Versenol descalent. Actually, because of the chemical similarity of Versenol and EDTA (Versene), it is also applicable to the determination of EDTA in citrate-EDTA and hydrazine-Versene (HV) mixtures. For the latter HV-type samples, however, the cerium titration procedure, G:5 (ECF-1, Mod-1, pp 43-45), should be used.

Versenol is determined directly in the presence of citrate by titration with a standard copper(II) solution to a photometric end point (Fig. 1). In an acetic acid-acetate medium at pH 5.0 \pm 0.5 citrate up to a 2 to 1 citrate to Versenol molar ratio does not interfere. Citrate, however, does have sufficient adverse effect on the titration to prevent the use of a visual indicator.

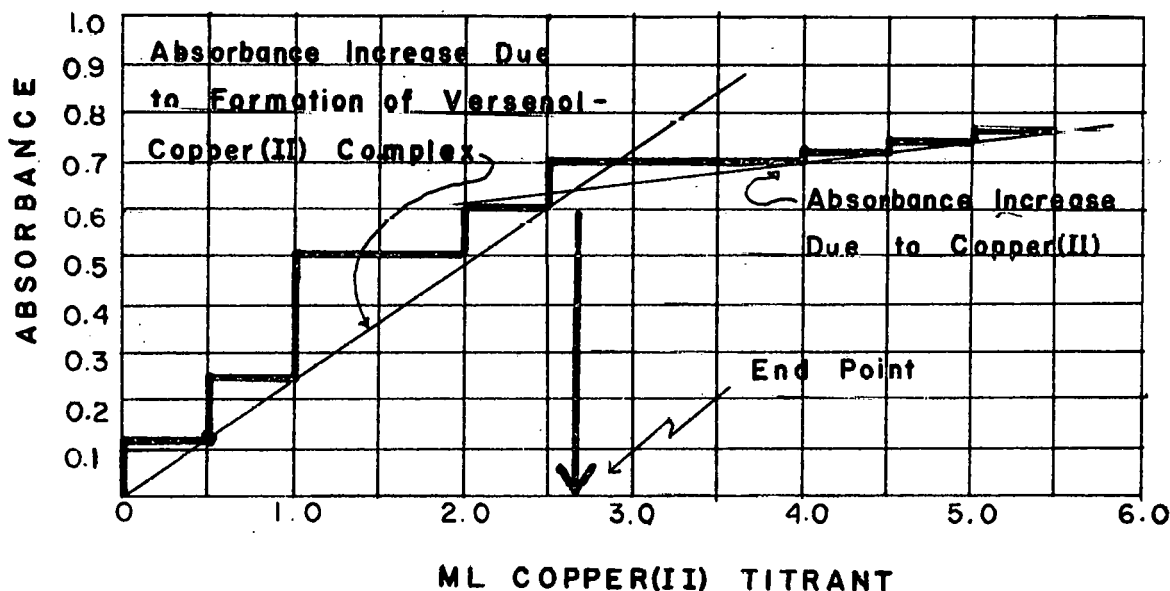


Fig. 1. Photometric Titration of Versenol with Copper(II) in Acetate Medium

A study of interferences has not been made. Expected interferences are metal ions that form stable Versenol complexes and complexons that form stable complexes with copper(II).

III:B. Apparatus and Reagents

1. Apparatus

- a. Recording spectrophotometer such as Beckman DK-2 and Cary Model 14.
- b. Absorption cell, 5-cm, Pyrex.
- c. Beaker, 150-ml.
- d. Magnetic stirrer and stirring bars.
- e. Ringstand and Fisher buret clamp.
- f. Buret, 10-ml, with 0.05-ml or smaller graduations.

2. Reagents

- a. Citrate-Versenol bench standard. Dissolve 7.539 ± 0.001 g of diammonium citrate and 9.267 ± 0.001 g of Versenol in water and dilute to 1 liter. This solution is $0.0333M$ in citrate (6.973 g/liter as ammonium dihydrogen citrate) and $0.0333M$ (9.267 g/liter) in Versenol.
- b. Copper(II) nitrate solution, $0.05M$. Dissolve 60.4 g of cupric nitrate trihydrate in water and dilute to 1 liter. Standardize the solution against 5 ml of standard $0.05M$ EDTA per III:D substituting the standard EDTA solution for the sample. Then:

$$\text{Cu(II) Molarity} = \frac{5.00 (\text{EDTA Molarity})}{\text{ml of Cu(II) sol'n}}$$

- c. Standard EDTA solution, $0.05M$. A standard $0.05M$ EDTA solution (18.62 g disodium EDTA dihydrate per liter) standardized against pure zinc oxide will be provided by the Quality Control Laboratory.
- d. Acetic acid-sodium acetate buffer, pH 5.0. Dissolve 174 g of sodium acetate trihydrate in water, add 41.4 ml of glacial acetic acid, and dilute to 1 liter with water.

III:C. Bench Standard

Process a 5-ml aliquot of the citrate-Versenol bench standard per III-D. Limits will be specified by the Quality Control Laboratory.

III:D. Procedure

Steps	Remarks
1. Pipet 5.00 ml of the citrate-Versenol descalent into a 150-ml beaker.	If made up properly 5 ml of sample will contain 0.15 mmole of Versenol.
2. Add 5 ml of the acetate buffer and dilute the sample with distilled water to 135±5 ml.	A 135-ml dilution is used to keep the absorbance less than one throughout the titration and to minimize the absorbance changes due to dilution of the sample by the copper titrant.
3. Without spilling, fill a 5-cm absorption cell with the diluted sample. Place the cell in the light path of the recording spectrophotometer and set the absorbance at zero.	Use a wavelength setting of 750 mμ. In steps 3 through 5, select an appropriate scale for the horizontal axis (for example, 1 division = 0.1 ml) and plot the absorbance data directly on to the chart (see Fig. 1 under <u>III-A</u>).
4. Return the solution to the beaker, deliver 0.50 ml of the copper titrant to the sample, and mix well. Fill the cell with the sample solution and determine its absorbance.	Do not use water rinses. Use the sample solution itself to rinse the cells; however, be sure to return all rinses to the beaker.
5. Repeat step 4 until about 6 ml of titrant has been introduced and the photometric end point has been established.	
6. Extend the straight line portions of the volume-absorbance plot to the intersection of the two. The volume reading at the intersection represents the end point of the titration.	

III:E. Calculations

$$\text{Versenol Molarity} = \frac{(\text{ml Cu})(\text{Cu Molarity})}{\text{Sample volume in ml}}$$

Result, Grams Versenol per liter = 278.3 (Versenol Molarity)

IV. References

1. Yamamura, S. S., IDO Notebook U-1150, pp 125ff.

S. S. Yamamura

November, 1966

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DETERMINATION OF THE DISSOLVED OXYGEN AND
THE BIOCHEMICAL OXYGEN DEMAND OF SEWAGE

ABSTRACT

The biochemical oxygen demand (BOD) of sewage is the quantity of dissolved oxygen (DO) that is consumed during the oxidation of decomposable organic matter by aerobic organisms. Duplicate samples are received for analysis. On one sample, DO is determined immediately. Two aliquots of the other sample are added to oxygen-saturated water and incubated at 20°C for 5 days. Blanks of the oxygen-saturated water are incubated simultaneously. The decrease in DO between the samples and blanks is computed as the BOD.

The DO is determined by the Alsterberg modification of the Winkler titrimetric redox method. In this procedure, Mn(II) is added to an alkaline solution of the water sample. The DO oxidizes Mn(II) to Mn(III) which then is reacted with iodide in an acidic medium to form elemental iodine. The elemental iodine, equivalent to the DO, is titrated with standard sodium thiosulfate.

APPLICABILITY

The method is applicable to raw and treated sewage, industrial wastes, and river waters. The method also can be used to determine DO in aqueous samples free of reducing and oxidizing components.

DISCUSSION

Samples for DO and BOD analysis usually are received from the MTR, CFA, CPP, and EBR-II areas once each month. A raw input sample to the sewage processing plant and a treated effluent sample from it are received in duplicate. The DO content of the raw input sample is small (the BOD is high); the opposite holds for the treated effluent sample.

One of the duplicate samples is analyzed immediately for DO as described in Procedure D. Two aliquots (differing by a factor of 2 in volume) of the other duplicate sample are first diluted with aerated water and incubated for 5 days as described in Procedure C and then analyzed for DO as described in Procedure D. The aliquot volume selected for incubation depends upon the type and the source of the sample. Table I lists the samples usually analyzed and the recommended aliquot volume. If the operating conditions of the sewage plants change, these recommendations may no longer apply.

IDO-14316
H₂O-DO-BOD-1:2
Mod-1

TABLE I
DILUTION FRACTIONS AND RECOMMENDED ALIQUOT VOLUMES
FOR SAMPLES USUALLY ANALYZED

<u>Source of Sample</u>	<u>Type of Sample</u>	<u>Aliquot Volume, ml^a</u>	<u>Aliquot Fraction^b</u>	<u>Dilution Water Fraction</u>
CFA	Raw	15.0	0.0496	0.9504
		7.5	0.0248	0.9752
	Treated	100.0	0.3311	0.6689
		50.0	0.1656	0.8344
CPP	Raw	15.0	0.0496	0.9504
		7.5	0.0248	0.9752
	Treated	100.0	0.3311	0.6689
		50.0	0.1656	0.8344
MTR	Raw	15.0	0.0496	0.9504
		7.5	0.0248	0.9752
	Treated	100.0	0.3311	0.6689
		50.0	0.1656	0.8344
EBR	Raw	2.0	0.0066	0.9934
		1.0	0.0033	0.9967
	Treated	4.0	0.0132	0.9868
		2.0	0.0066	0.9934

^a Two dilutions with aliquot volumes differing by a factor of 2, as shown, are recommended for each sample.

^b Based on a final volume of 302 ml. For aliquot volumes different than shown, divide the aliquot volumes by 302.

SPECIAL PRECAUTIONS

1. All glassware must be extremely clean. When cleaning glassware with chromic acid cleaning solution, wear rubber gloves.
2. Precaution must be taken throughout the procedure to prevent contamination of samples with air.

APPARATUS AND REAGENTS

A. Apparatus

1. BOD bottles, 300-ml capacity with ground glass stoppers. Determine the volume of each bottle and discard those outside the range of 303 ± 6 ml. Before use, clean the bottles with chromic acid cleaning solution, completely rinse with distilled water, and drain dry.
2. Incubator, thermostatically controlled at $20 \pm 1^\circ\text{C}$. Light must be excluded to prevent the growth of algae.
3. Buret, 10-ml.
4. Glass-covered magnetic stirring bars, uniform size with a displacement volume of 0.8 ml. Clean with chromic acid cleaning solution and completely rinse with distilled water.
5. Pipets, volumetric, assorted sizes.
6. Iodine titration flask, 500-ml capacity with ground glass stoppers.
7. Special 204-ml volumetric flask. Cut off the neck of a 200-ml volumetric flask at a volume of 204 ml and flame seal.

B. Reagents

NOTE: Use Analytical Reagent Grade reagents and distilled water.

1. Phosphate buffer. Dissolve 8.5 g of KH_2PO_4 , 33.4 g of Na_2HPO_4 , and 1.7 g of NH_4Cl in distilled water and dilute to 1 liter.
2. Magnesium sulfate solution, 0.091M. Dissolve 22.5 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, in distilled water and dilute to 1 liter.
3. Calcium chloride solution, 0.126M. Dissolve 27.5 g of CaCl_2 in distilled water and dilute to 1 liter.
4. Ferric chloride solution, 0.001M. Dissolve 0.25 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in distilled water and dilute to 1 liter.

IDO-14316
H₂O-DO-BOD-1:4
Mod-1

5. Dilution water. To a 20-liter bottle previously cleaned with chromic acid cleaning solution, add 15 ml each of the following reagents: phosphate buffer, magnesium sulfate solution, calcium chloride solution, and ferric chloride solution. Dilute to 15 liters with distilled water. Bubble air through this solution for 30 min. Stopper and let set for 3 days before using.
6. Manganous sulfate solution, 1.73M. Dissolve 480 g of MnSO₄·4H₂O in distilled water and dilute to 1 liter. Filter, if necessary.
7. Alkaline iodide-azide solution. Dissolve 475 g of NaOH and 128 g of NaI in distilled water and dilute to about 900 ml. Add 10 g of NaN₃ dissolved in 40 ml of distilled water and dilute to 1 liter.
8. Starch indicator. Add a water slurry of 5 g of starch to 1 liter of boiling water and continue boiling for a few minutes. Cool, transfer to a glass stopped bottle, add a few drops of toluene as a preservative, and store in a refrigerator.
9. Potassium iodate primary standard solution, 0.20N (0.0333M). Dissolve exactly 7.1333 g of KIO₃ in distilled water and dilute to 1 liter.
10. Sodium thiosulfate solution 0.025N. Dissolve 6.2 g of Na₂S₂O₃·5H₂O in distilled water and dilute to 1 liter. Standardize this solution weekly as described in Procedure A.
11. Potassium iodide crystals.
12. Sulfuric acid, 1.8M. Carefully add, with cooling, 100 ml of concentrated sulfuric acid to water and dilute to 1 liter.

PROCEDURE

A. Standardization of Sodium Thiosulfate

Note: Standardize the thiosulfate solution each week in duplicate.

<u>Analysis Step</u>	<u>Remarks</u>
1. Add 100 ml of water to an iodine titration flask.	
2. Add about 1 g of potassium iodide and swirl to dissolve.	
3. Add 5 ml of 1.8M H ₂ SO ₄ .	

Analysis Step

Results

- | | |
|--|--|
| 4. Add exactly 1.0 ml of the 0.20N standard iodate solution. Stopper and swirl the flask to completely mix the solutions. Let stand for 1 min. | The solution turns brown due to the formation of elemental iodine. |
| 5. Remove the stopper and immediately titrate with the standard sodium thiosulfate solution until a pale straw color is reached. | The change in color from brown to a pale straw indicates that the end point is near. |
| 6. Add about 1 ml of the starch indicator solution. | The starch forms an intense blue color with the remaining elemental iodine. |
| 7. Stopper the flask and shake the contents for 15 sec. | This dissolves iodine vapor above the surface of the solution. |
| 8. Rinse the sides of the flask with water and continue the titration until the blue color disappears and the solution remains colorless for 15 sec. | On standing, the blue starch-iodine color reappears due to air oxidation. |
| 9. Determine the normality of the thiosulfate solution as described under <u>CALCULATIONS</u> . | |

B. Test for Stability of Dilution Water.

Two samples of dilution water are analyzed for DO with each series of original samples as described in Procedure D. Two other samples of dilution water are incubated with each series of samples according to Procedure C and then analyzed for DO. The DO in the original dilution water and in the incubated dilution water should be the same. This comparison is not made to apply a blank correction, but rather to test for the stability of the dilution water. The DO content of the original and incubated samples should not differ by more than 0.1 g/l. If this difference is exceeded, use the average for calculations. The probable cause for a difference is organic contamination of the glassware.

IDO-14316
H₂O-DO-BOD-1:6
Mod-1

C. Preparation of Samples for Incubation.

Note: Each sample is received in duplicate. Analyze one bottle immediately for pH and then for dissolved oxygen as described in Procedure D. Make two dilutions from the other bottle and incubate for 5 days as described below. Also incubate two samples of the aerated dilution water with each batch of samples.

1. To each of two clean BOD bottles, add a clean glass stirring bar. (With the stirring bar in place, these bottles hold 302±6 ml of solution.)
All glassware must be cleaned with chromic acid cleaning solution to remove any trace of organic matter.
2. Carefully siphon the bottles half full of dilution water.
Do not allow bubbles to form in the water.
3. Using volumetric pipets, transfer aliquots of the sewage sample to the BOD bottles. Add the sample below the surface of the water.
Refer to Table I for the recommended sample size. Two dilutions are prepared, one at half the concentration of the other.

Two bottles containing only dilution water are to be processed with each batch of samples.
4. Continue siphoning the dilution water into the samples until the bottles are full. Stopper tightly and add water around the stopper to form a seal.
Do not trap any air when the stopper is inserted.
5. Mix the samples on a magnetic stirrer for 5 min.
6. Invert a 50-ml beaker over the top of each bottle to retard evaporation of the water seal. Place them in an incubator at 20±1°C for 5 days.
Check on the fourth day to ensure that the seals are sufficiently wet. Add water as necessary.
7. After 5 days, determine the dissolved oxygen as described in Procedure D.

D. Determination of Dissolved Oxygen

Note: Analyze one duplicate of the sample on the day it is received. Analyze the two dilutions of the other duplicate and the two stability check samples of the dilution water after the 5-day incubation period.

1. Remove the water from the stopper trap. This conveniently can be done by suction.
2. Remove the stopper and carefully add a clean glass stirring bar. (With the stirring bar in place, these bottles hold 302±6 ml of solution.) The incubated samples already contain a stirring bar.
3. Add 2 ml of manganous sulfate and 2 ml of alkaline iodide-azide reagent at least 1 in. below the surface of the liquid.
4. Carefully insert the stopper and remove the sample displaced by the stirring bar and the 4 ml of reagents. Use suction to remove the liquid.
5. Mix on a magnetic stirrer for 5 min. A precipitate of Mn(II) hydroxide forms which the dissolved oxygen oxidizes to Mn(III) hydroxide.
6. Allow the precipitate to settle and carefully remove the stopper. Then carefully add 2 ml of concentrated sulfuric acid below the surface of the liquid.
7. Carefully stopper the bottle and remove the sample displaced by the sulfuric acid. The volume of sample used in the analysis is decreased to 296 ml because 6 ml of reagents displace 6 ml of sample.
8. Mix on a magnetic stirrer for 5 min. The Mn(III) hydroxide dissolves and oxidizes iodide to elemental iodine.

IDO-14316
 H₂O-DO-BOD-1:8
 Mod-1

9. Transfer a 200-ml aliquot of the sample to an iodine titration flask. Stopper the flask to prevent loss of iodine. Use the special 204-ml volumetric flask for the transfer. 204 ml of this solution is equal to 200 ml of sample before the reagents were added.
10. Titrate with the standard sodium thiosulfate solution as described in Procedure A, steps 5 through 8.
11. Determine the DO and BOD as described in CALCULATIONS.

CALCULATIONS

A. Calculations for Standardizing the Sodium Thiosulfate Solution for Determining DO. Record the data on the worksheet and calculate the results as follows:

<u>COLUMN</u>	<u>UNIT TO RECORD</u>
A	Sample code and bottle number.
B	Volume of potassium iodate solution, ml.
C	Normality of potassium iodate solution.
D	Volume of thiosulfate required to titrate the potassium iodate solution, ml.
E	Normality of thiosulfate solution. $E = \frac{BC}{D}$
F	Volume of thiosulfate required to titrate the sample, ml.
G	Result, mg of oxygen/liter. $G = \frac{(E) (F) (8) (1000)}{200}$ $G = 40 EF$

Note: Report DO results to the nearest 0.01 mg/l.

B. Calculations for BOD. Record the data on the worksheet and calculate the results as follows:

<u>COLUMN</u>	<u>UNIT TO RECORD</u>
A	Sample code and bottle number.
B	Dissolved oxygen of original dilution water, mg/l.
C	Dissolved oxygen of original sample, mg/l.
D	Dissolved oxygen of incubated sample, mg/l.
E	Decimal fraction of dilution water used.
F	Decimal fraction of sample used.
G	Dissolved oxygen available in dilution at zero time. $G = (B \times E) + (C \times F)$
H	Result, BOD, mg/l. $H = \frac{G - D}{F}$

Note: Report BOD results to the nearest 0.1 mg/l.

REFERENCES

- (1) Standard Methods for the Examination of Water, Sewage, and Industrial Wastes, 10th ed., Waverly Press, Inc., Baltimore, 1955, pp 252-266.

M. A. WADE

September, 1966

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COLORIMETRIC DETERMINATION OF MERCURY WITH DITHIZONE

ABSTRACT

A sensitive, versatile, colorimetric method based on a dithizone extraction is described for the determination of mercury in inorganic and organic samples. Four procedures are included --- two for inorganic solutions, one for inorganic solids, and one for organic materials and aqueous solutions containing dissolved organic matter. The effects of diverse ions on the method are discussed.

APPLICABILITY

This method is applicable to a wide variety of samples including fuel dissolver product, calciner feeds, and calciner off-gas scrub solutions. Also, with appropriate pretreatment, the method is applicable to such samples as calciner feeds containing sucrose, alumina-zirconia calciner solids, and organic materials such as vegetation, cardboard, polyethylene, inks, and paints.

Four procedures, C, D, E, and F, are recommended for the analysis of the many different types of samples mentioned in the preceding paragraph. Procedures C, D, and E, patterned after a method recently reported⁽¹⁾, are identical except for differences in the initial steps (Figure 1). Procedure C; the principal procedure, is intended for aqueous samples, especially those with unknown compositions where maximum selectivity is desirable. Procedure D is designed for solid inorganic samples (especially waste calciner solids) and Procedure E for organic samples and inorganic samples containing organic matter. In all three procedures, C, D, and E, the mercury is initially extracted into dithizone-chloroform, stripped out of the chloroform with sodium nitrite, then reextracted into dithizone-chloroform after destruction of the excess nitrite with hydroxylamine and aniline. Procedure F is simpler and faster than Procedure C and differs from the latter in that only a single extraction is made using twice as much complexer-buffer solution. It is specifically designed for aqueous inorganic samples of known composition, such as the aluminum nitrate calciner feed samples from the Chemical Engineering Section that are free of interferences, or that contain only noninterfering concentrations of potential interferences such as copper. Procedure F should not be used for uncharacterized samples.

The effect of diverse ions for Procedure F are summarized in Table I which lists the known tolerance levels of numerous ions present individually and in groups that simulate the composition of samples actually encountered. Silver(I) at greater than 0.1 to 1 silver-to-mercury molar ratios and copper(II) at greater than 150 to 1 ratios are the only known cationic interferences. Iodide inhibits the extraction of mercury.

IDO-14316
Hg-Color-5:2
Mod-1

Procedure C is similar to Procedure F except for the use of two dithizone-chloroform extractions in C. The tolerance levels of diverse ions for Procedure C are therefore expected to be higher than those for Procedure F. For example, the tolerance level of copper(II) is 150 to 1 for Procedure F and 750 to 1 for Procedure C.

In all four procedures, strong oxidants that oxidize dithizone interfere when present in high enough concentration. Oxides of nitrogen formed during the digestion of samples and the oxidation of mercury are the most common interferences. These are removed effectively by hydroxylamine hydrochloride and aniline hydrochloride. After the digestion or oxidation step, brown nitrogen oxide fumes are often observed above the solution. These should be removed by gentle suction prior to the addition of the hydroxylamine and aniline.

By the use of both 1- and 5-cm absorption cells, the range of the method is 1 to 35 μg of mercury. The maximum sample size for aqueous solutions is 5 ml; for inorganic solids, 0.1 g; and for organic samples, 2 g. Accordingly, the lower limit of determinability is about 0.2 ppm, 10 ppm, and 0.5 ppm, respectively.

DISCUSSION

Potential sources of error include: (a) use of mercury-contaminated glassware, (b) loss of mercury by volatilization during sample preparation and analysis, (c) use of too large a sample aliquot, and (d) incomplete destruction of nitrate prior to the final extraction.

Use of mercury-contaminated glassware is a frequent and serious source of error. All glassware, including new glassware, should be boiled in 4M nitric acid and rinsed thoroughly with distilled water before use. Do not rely upon the purity of demineralized water. Always use distilled water for all reagents and throughout the method.

Mercury and mercury compounds are quite volatile and can be lost under many conditions. It is volatilized slowly but in significant amounts from boiling acid solutions. It is volatilized quantitatively or nearly so in acidic and basic fusions. Use a reflux condenser for all fusions and lengthy boiling steps.

In this method, the chloroform extract contains blue-green unreacted dithizone and yellow-orange mercury dithizonate, so the observed color varies from blue-green at low levels of mercury to yellow-green when 25 to 35 μg of mercury are present. If the final extract lacks the greenish cast, the capacity of the dithizone could have been exceeded and another, smaller sample should be processed.

Solid Inorganic Samples
(Procedure D-1)

Fuse with $K_2S_2O_7$.
↓
Reflux with HNO_3 .
↓
Dilute to appropriate volume with water.
↓
Pipet aliquot containing 1-35 μg Hg.
↓
Continue per Procedure C, starting at *.

Solid Inorganic Samples
(Procedure D-2)

Fuse sample with $K_2S_2O_7$ and reflux with HNO_3 .
↓
Dilute with water until $N^a \leq 0.75$.
↓
Add $NH_2OH \cdot HCl$ and aniline $\cdot HCl$ and extract Hg(II) with $Dz-CHCl_3$.
↓
Continue per Procedure C, starting at **.

Aqueous Inorganic Samples
(Procedure C)

Pipet aliquot containing 1-35 μg Hg.
↓
Heat with HNO_3 to oxidize all Hg to Hg(II).
↓
*Extract Hg(II) into $CHCl_3$ from EDTA-citrate medium at pH 2.85 ± 0.35 .

**Strip Hg(II) from $CHCl_3$ with $NaNO_2$.

↓
Destroy excess $NaNO_2$ with $NH_2OH \cdot HCl$ and aniline $\cdot HCl$.
↓
Extract Hg(II) into $CHCl_3$ from EDTA-citrate-mono-chloroacetate medium at pH 2.85 ± 0.35 .
↓
Measure absorbance at 495 $m\mu$.

Organic Samples and
Inorganic Samples
Containing Organics
(Procedure E)

Digest sample with $HNO_3 - H_2SO_4$.
↓
Dilute with H_2O until $N^a \leq 0.75$.
↓
Destroy N-oxides with $NH_2OH \cdot HCl$ and aniline $\cdot HCl$.
↓
Extract Hg(II) with $Dz-CHCl_3$.
↓
Continue per Procedure C, starting at **.

Aqueous Inorganic Samples
(Procedure F)

Pipet aliquot containing 1-35 μg Hg.
↓
Digest with HNO_3 to oxidize all Hg to Hg(II).
↓
Extract Hg(II) as the dithizonate into $CHCl_3$ from EDTA-citrate medium at pH 2.85 ± 0.35 .
↓
Measure absorbance at 495 $m\mu$.

Fig. 1. Outline of Procedures C, D, E, and F

IDO-14316
 Hg-Color-5:4
 Mod-1

Table I. EFFECT OF INDIVIDUAL IONS AND ION COMBINATIONS
 ON PROCEDURE F (AND C)

<u>Ion or Mixture Investigated</u>	<u>Tolerance Level, Ion to Hg Molar Ratio^{a,b}</u>
Be(II), Bi(III), Ca(II), Cd(II), Ce(III), Co(II), Cr(III), Cs(I), Fe(III), Ge(II), Ho(III), In(III), La(III), Mg(II), Mn(II), Mo(VI), Ni(II), Pb(II), Sn(II,IV), Sr(II), Th(IV), Ti(IV), U(VI), V(V), Y(III), Zn(II), Zr(IV).	Each ion individually at 1000
Ag(I)	0.1 ^c
Au(III), Pd(II), Pt(IV)	Each ion individually at 50
Cu(II)	150 ^c
Borate	2000
Bromide	1000
Chloride	7.5×10^5
Iodide, thiosulfate	--- ^d
Phosphate	3.0×10^4
Sulfate	1.3×10^5
Simulated aluminum fuel dissolver product	
Al(III), Zr(IV)	Each at 2000
Cr(VI), U(VI)	Each at 50
Cl ⁻ plus NO ₃ ⁻	1×10^4

TABLE I (continued)

Simulated aluminum fuel dissolver product

Al(III)	4×10^4
Cu(II)	150 ^c
Cr(III), U(VI)	Each at 50
Fe(III)	200
Mn(II), Ni(II)	Each at 100
NO_3^{-1}	12×10^4

Simulated calciner product fused with potassium pyrosulfate

Al(III), Zr(IV)	Each at 2000
Cr(VI)	50
K(I)	2.4×10^5
SO_4^{-2}	1.3×10^5

-
- (a) Mercury level maintained at 20 μg (1×10^{-4} mmole).
- (b) Except where noted otherwise, the tolerance level listed is the highest level studied and does not represent the maximum permissible level.
- (c) Maximum tolerance level.
- (d) Iodide and thiosulfate interfere at 1000:1. Both inhibit the extraction of mercury. Iodine coextracts as free iodine. The tolerance levels of iodide and thiosulfate have not been established.

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Hg-Color-5:6
Mod-1

Nitrite and nitrogen oxides (NO_2 and NO) that yield nitrite in the presence of water and air, oxidize dithizone rapidly and cause erratic, low results. The presence of nitrite is indicated by a gradual "bleaching" of the blue-green dithizone to a golden-yellow oxidation product. The function of the hydroxylamine and aniline during the initial and final extractions is to destroy the nitrite.

SAFETY PRECAUTIONS

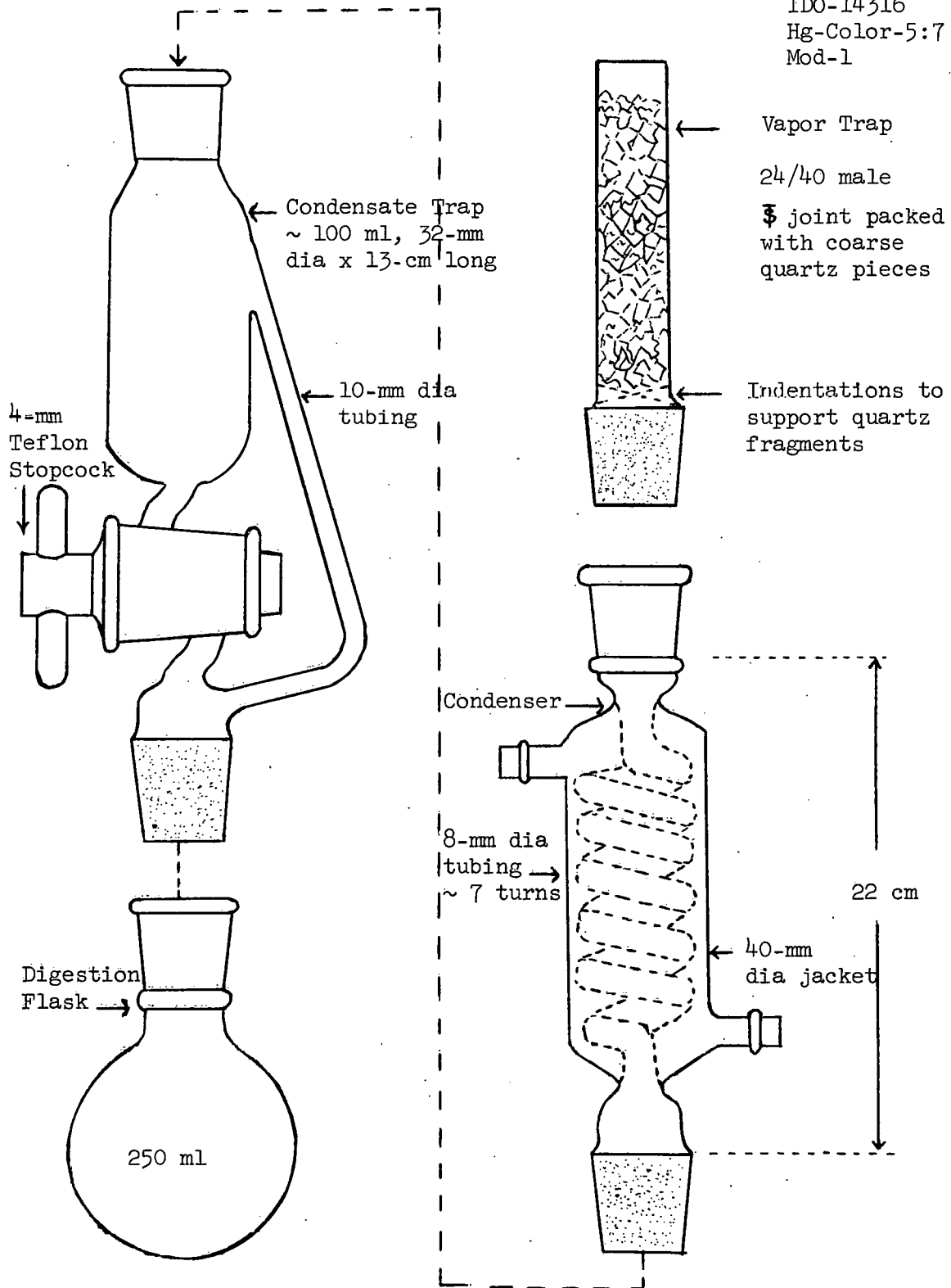
1. Carry out the digestion of organic samples in a hood behind a safety shield to guard against possible explosion and to confine the nitrogen oxide fumes evolved during the digestion. Wear safety glasses.
2. After each extraction, remove the separatory funnel stoppers carefully to avoid spattering of chloroform or the acidic aqueous solution. This precaution applies to the extractions carried out with the large separatory funnels in Procedures D and E.
3. Wear latex gloves when handling concentrated acids.

APPARATUS AND REAGENTS

A. Apparatus

1. Spectrophotometer, Beckman Model DU, DK, or B, or Cary Model 14.
2. Absorption cells, matched pairs, 1-cm and 5-cm, with covers.
3. Separatory funnels, 500-ml, with ground glass stoppers and Teflon stopcocks.
4. Separatory funnels, 60-ml, with Teflon stopcocks.
5. Pipets, micro, assorted sizes, with control syringe.
6. Pipets, macro, volumetric, assorted sizes.
7. Graduated cylinders, 10-ml.
8. Pipets, Mohr, 5- and 10-ml.
9. Centrifuge tube, 50-ml.
10. pH Meter, Leeds and Northrup with capillary glass-calomel electrodes or Beckman with a single-probe glass-calomel electrode.
11. Digestion apparatus for organic samples (Figure 2).
12. Volumetric flasks, assorted sizes.

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Hg-Color-5:7
Mod-1



Construction: Pyrex or Kimax 24/40 § joints throughout

Fig. 2 Digestion Apparatus for Organic Samples

IDO-14316
Hg-Color-5:8
Mod-1

13. Quartz fusion apparatus for inorganic solids. Use a 100-ml round bottom quartz flask or a 35-mm dia x 6-in. quartz test tube with a 2⁴/₄₀ outer joint in conjunction with the condenser illustrated in Figure 2.

B. Reagents

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

1. Mercuric nitrate solution, 500 µg/ml. Dissolve 0.5000 g of redistilled mercury metal in 20 ml of 7.5M HNO₃ with heating. Boil gently for 10 min, cool, then dilute to 1 liter with water. Store as 40-ml units in sealed glass ampoules.
2. Mercury calibration standard solutions.
 - a. Standard I, 30.00 µg Hg per ml. Dilute 15.00 ml of the mercury stock solution to 250 ml with 0.25M HNO₃.
 - b. Standard II, 20.00 µg Hg per ml. Dilute 10.00 ml of the mercury stock solution to 250 ml with 0.25M HNO₃.
 - c. Standard III, 8.00 µg Hg per ml. Dilute 4.00 ml of the mercury stock solution to 250 ml with 0.25M HNO₃.
 - d. Standard IV, 6.00 µg Hg per ml. Dilute 3.00 ml of the mercury stock solution to 250 ml with 0.25M HNO₃.
3. Sodium nitrite solution, 0.75M. Dissolve 51.76 g of sodium nitrite in 500 ml of water and dilute to 1 liter with water. Prepare a fresh solution every month. Store in the dark.
4. Hydroxylamine hydrochloride, 2.5M. Dissolve 174 g of hydroxylamine hydrochloride in 800 ml of distilled water. Filter the solution through a 0.45-µ membrane filter and dilute to 1 liter with water.
5. Aniline hydrochloride solution, 0.5M. Add 45 ml of concentrated hydrochloric acid to 500 ml of water. Add 46 ml of freshly-distilled aniline SLOWLY with efficient stirring. Transfer to a 1-liter volumetric flask and dilute to volume with water. The final solution should be colorless or have only a faint pink or yellow tinge. Store in the dark and prepare a fresh solution every month.

NOTE: The aniline must be added slowly to dilute hydrochloric acid solution to avoid excessive coloration of the solution.

6. Buffer-complexer reagent. Dissolve 37.22 g of disodium ethylenediamine tetraacetate dihydrate (EDTA), 94.50 g of mono-chloroacetic acid, and 90.48 g of ammonium citrate in a 2-liter beaker with 1500 ml of distilled water. Use sufficient concentrated ammonium hydroxide to adjust the solution to pH 4.0. Dilute to 2 liters with water.
7. Dithizone stock solution, 0.0105 (w/v)% ($4 \times 10^{-5}M$). Dissolve 0.0525 g of dithizone in chloroform and dilute to 500 ml with chloroform. Store in a refrigerator when not in use.
8. Dithizone solution, 0.00105 (w/v)% ($4 \times 10^{-6}M$). Pipet 50.00 ml of the 0.0105% stock solution into a 500-ml volumetric flask and dilute to 500 ml with chloroform. Store in a refrigerator when not in use.
9. Hydrochloric acid, 1.0M. Dilute 86 ml of concentrated hydrochloric acid to 1 liter with water.
10. Nitric acid-sulfuric acid digestion mixture. Mix, as needed, concentrated sulfuric acid and concentrated nitric acid in the ratio 1:5.
11. Potassium pyrosulfate.
12. Sodium hydroxide, .85M. Dissolve 34.0 g of sodium hydroxide in water and dilute to 1 liter with water.
13. Ammonium hydroxide, concentrated.
14. Nitric acid, concentrated and 1M.

PROCEDURES

NOTE: Use distilled water throughout the procedure.

A. Blank

Process a reagent blank with each set of samples per the procedure selected for the analysis of samples. For aqueous samples, use 3 ml of distilled water in place of the sample. With inorganic solids and organic samples, omit the addition of a sample substitute, but introduce all reagents used for the samples in amounts equal to those used for the samples.

B. Calibration and Bench Standard

Four standards are recommended for this method --- two for the high range (to be measured in 1-cm cells) and two for the low range (to be measured in 5-cm cells). If only one type of sample is to be analyzed, two appropriate standards will suffice. However, if the mercury concentrations of the samples vary over a wide range, the use of all four calibration standards will minimize repeat analyses.

Process calibration standards with each run by the same procedure as that used to analyze the samples. Use 1.00-ml aliquots of the appropriate standards. Divide the observed absorbance by the micrograms of mercury in the standard to obtain the conversion factor. For each of the two groups of standards the difference between the two factors should not exceed established limits and the average of the two factors should agree with the established conversion factor within specified limits. If either of these requirements is not met, reprocess the pair or pairs of calibration standards. Contact your supervisor if difficulties are still experienced.

C. Analysis of Aqueous Inorganic Samples

<u>Steps</u>	<u>Remarks</u>
1. Pipet an aliquot, 5 ml or less, containing 1 to 35 μg of mercury into a 50-ml centrifuge tube.	The use of a wide-mouth test tube such as a 50-ml centrifuge tube facilitates pH adjustment in step 6. Refer to the APPLICABILITY section for information on tolerance levels for diverse ions.
2. Add 1 ml of concentrated nitric acid and immerse the centrifuge tube in a boiling water bath for 5 min.	Nitric acid oxidizes Hg(0,I) to Hg(II). Prolonged digestion will lead to loss of mercury by volatilization. If brown nitrogen dioxide fumes are observed, aspirate the fumes with mild suction before adding the hydroxylamine hydrochloride.
3. Cool, add a small stirring bar, dilute to about 15 ml with water, add 2 ml of 2.5M hydroxylamine hydrochloride, then let stand for 5 min with intermittent stirring with a magnetic stirrer.	
4. Add 1 ml of 0.5M aniline hydrochloride.	

5. Add 5 ml of the buffer-complexer solution.
6. With the aid of a pH meter adjust the pH to 2.85 ± 0.35 with concentrated ammonium hydroxide.
7. Transfer the sample quantitatively to a 60-ml separatory funnel with water rinses. Use polyethylene stoppers.
8. Add approximately 15 ml of 0.00105% dithizone-chloroform solution and extract for 30 sec. Let the two layers separate, then swirl the separatory funnel to settle the floating droplets of chloroform. Shake vigorously.
9. Drain the lower chloroform layer into a new 60-ml separatory funnel. Do not transfer any of the aqueous phase. Observe the color of the chloroform solution. If it is golden-yellow or nearly so with very little blue-green color of free dithizone, extract the residual aqueous phase in the original separatory funnel with 10 ml of the 0.00105% chloroform-dithizone solution and drain the chloroform extract into the new separatory funnel. If the second extract still lacks the blue-green color of free dithizone, discard the sample and process a new, smaller aliquot.
10. Extract the residual aqueous phase in the original separatory funnel with 5 ml of chloroform and drain the chloroform into the new separatory funnel. Discard the aqueous phase. The two organic phases (steps 9 and 10) are combined.

11. To the dithizone-chloroform extract, add exactly 10 ml of 1.0M HCl and 1 ml of 0.75M sodium nitrite solution. Stopper and shake for 30 sec. The nitrite destroys the dithizone and returns the mercury to the aqueous phase.
12. Let the two phases separate, then drain and discard the lower chloroform layer. Take care that none of the aqueous layer is lost in the separation.
13. To the residual aqueous phase, add 2 ml of 2.5M hydroxylamine. React for 5 min with intermittent swirling. Complete the destruction of nitrite is necessary. In steps 13 and 14, rinse the neck of the separatory funnel with water, then add the hydroxylamine hydrochloride and the aniline hydrochloride.
14. Rinse the separatory funnel with a little water, then add 1 ml of 0.5M aniline hydrochloride solution. Swirl to mix.
15. Add 5 ml of the buffer-complexer solution, swirl to mix, then add 10 ml of 0.85M NaOH to adjust the pH to the range 2.85 ± 0.35 . With the buffer-complexer solution at pH 4.0 and the HCl and NaOH additions as specified, the final pH will be in the required range 2.85 ± 0.35 .
16. Pipet precisely 15.00 ml of 0.00105% dithizone-chloroform solution, stopper, and extract for 15 sec. The extraction time must be kept short to minimize the extraction of copper.
17. Let the phases separate, then drain the lower chloroform phase into a 25-ml screw-cap culture tube. Measure the absorbance of the chloroform phase at 495 m μ against the reagent blank in 1-cm (5 to 35 μ g of mercury) or 5-cm (1 to 10 μ g of mercury) cells. When in doubt, measure the absorbance with 5-cm cells first. This will permit subsequent measurements with 1-cm cells.

The color of the chloroform-dithizone extract should show the presence of excess unreacted dithizone, i.e., a bluish-green cast. If not, discard the sample and process a new smaller aliquot.

The walls of the tube adsorb water droplets which otherwise interfere. If necessary, centrifuge the tube.

Under proper conditions, the color of the chloroform extract is stable for at least 2 hr. If slow but noticeable "bleaching" is observed, the nitrite probably was not destroyed adequately in steps 13 and 14. Discard the sample and process a new one.

18. Record the data on the work sheet and calculate the results as described under CALCULATIONS.

D. Analysis of Inorganic Solids

1. Procedure for samples with greater than 100 ppm levels of mercury.

<u>Steps</u>	<u>Remarks</u>
a. Transfer a 0.1-g sample containing greater than 10 μg of mercury to the quartz fusion apparatus.	This procedure is intended primarily for inorganic solids such as alumina and alumina-zirconia calcined materials that are difficult to dissolve. Dissolve metals and alloys under reflux in appropriate mineral acids and analyze them per Procedure C.
b. Add 3.0 g of potassium pyrosulfate.	
c. Assemble the fusion apparatus. Tilt it to about a 45° angle.	
d. With a Meker burner, fuse the sample repeatedly until the melt clears.	
e. Turn off the cooling water and return the apparatus to the upright position.	

- f. Add 6 ml of concentrated nitric acid through the condenser and heat the mixture with a micro burner until the point of condensation just reaches the top of the condenser or until the start of bumping. During fusion, mercury is volatilized into the condenser possibly as metallic mercury. The purpose of the nitric acid reflux is to recover the volatilized mercury.
- g. Cool slightly, turn on the cooling water and rinse the condenser with 20 to 25 ml of 1M HNO₃.
- h. Remove the fusion flask or tube and place it in a boiling water bath until the liquid clears and most of the solids are dissolved. It is not necessary to dissolve the solids completely.
- i. Cool the solution and filter it through a 0.45- μ membrane filter directly into a 250-ml volumetric flask. Use at least three 10-ml portions of 1M HNO₃ for the transfer and washing and a Fisher filtrator-Millipore setup for the filtration.
- j. Dilute to volume with water and mix well.
- k. Pipet an aliquot, 25 ml or less, containing 1 to 35 μ g of mercury into a 50-ml beaker.
- l. Continue per Procedure C beginning at step 3. If the observed net absorbance of the sample corresponds to less than 1 μ g of mercury, select a larger aliquot (if this is permissible) in step k. With a 25-ml aliquot of the diluted sample, the lower limit of determinability

is 100 ppm of mercury in the original solid sample. If greater sensitivity is required, reanalyze the original solid sample per Procedure D-2.

2. Procedure for samples with less than 100 ppm levels of mercury.

<u>Steps</u>	<u>Remarks</u>
a. Dissolve a 0.1-g sample per steps <u>a</u> through <u>h</u> of Procedure <u>D-1</u> .	
b. Cool the solution then filter the solution through a Whatman 41 filter paper into a 500-ml separatory funnel. Use three 10-ml portions of 1M HNO ₃ to rinse the fusion flask and the filter paper.	
c. Dilute to 250 ml with distilled water.	The acidity must be reduced to 0.75N or less.
d. Add 5 ml of 2.5M hydroxylamine hydrochloride and let stand for 5 min with intermittent swirling.	
e. Rinse the separatory funnel with water, then add 2 ml of 0.5M aniline hydrochloride solution.	
f. Extract for 30 sec with 10 ml of 0.00105% dithi-zone-chloroform solution. Drain the lower chloro-form phase into a 60-ml separatory funnel.	Considerable pressure is often built up within the separatory funnel. Cover the stopper with a tissue paper and remove the stopper carefully.
g. Repeat step <u>f</u> .	

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Mod-1

- h. Repeat step f using 10 ml of chloroform in place of the dithizone-chloroform solution. Discard the aqueous phase.
- i. Continue per Procedure C beginning at step 11.

E. Analysis of Organic samples and Inorganic Samples Containing Organic Matter.

<u>Steps</u>	<u>Notes</u>
1. Weigh or pipet a sample containing 1 to 35 μ g of mercury into the flask of the digestion apparatus (Figure 2).	This procedure has been found to be satisfactory for 2-g samples of organic matter such as vegetation. If larger samples must be processed to reach the desired sensitivity, process separate 2-g samples per steps <u>E-1</u> through <u>E-15</u> , combine the dithizone-chloroform and chloroform extracts of steps <u>E-13</u> through <u>E-15</u> , then complete the determination per step <u>16</u> .
2. Add 15 ml of freshly-prepared nitric acid-sulfuric acid digestion mixture.	
3. Assemble the digestion apparatus per Figure 2 and heat the sample with a heating mantle controlled by a Variac. Boil vigorously and collect the distillate in the condensate trap. Continue the digestion until only 2 to 3 ml of acid remains and sulfuric acid fumes and charring is observed.	A Variac setting of 105-110 is recommended.
4. <u>CAUTIOUSLY</u> return the condensate to the digestion flask through the stopcock. If necessary, swirl the flask to loosen solids adhering to the walls of the flask.	

5. Continue the digestion to the reappearance of sulfuric acid fumes and charring.
6. Repeat steps 4 and 5 until charring is no longer observed. The entire digestion normally requires about 1.5 hr.
7. Return the condensate to the digestion flask, cool slightly then admit about 50 ml of water through the top of the digestion apparatus. Admit the water slowly.
8. Reflux for 5 min, or longer if necessary, to dissolve precipitated sulfate salts.
9. Disassemble the digestion apparatus. Rinse each component with water and collect the rinses in the flask. Rinse the side arm of the condensate trap also.
10. Transfer the contents of the flask quantitatively to a 500-ml separatory funnel with water rinses and dilute to about 400 ml with water. For quantitative extraction of the mercury, the acidity must be 0.75N or less.
11. Add 10 ml of 2.5M hydroxylamine hydrochloride solution, mix well, then let stand for 5 min. Swirl intermittently during the 5-min period.
12. Add 2 ml of 0.5M aniline hydrochloride solution and mix well.
13. Extract the mercury with a 10-ml portion of 0.00105% dithizone-chloroform solution for 30 sec. Drain the lower chloroform layer into a 60-ml separatory funnel. Considerable pressure is often built up during the extraction. Cover the stopper with a tissue paper and remove the stopper carefully.

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14. Repeat step 13.

15. Repeat step 13 using 10 ml of chloroform in place of the dithizone-chloroform solution. Discard the aqueous phase.

Combine this organic phase with the two previous organic phases in the 60-ml separatory funnel.

F. Analysis of Aqueous Inorganic Samples of Known Composition (Single Extraction Procedure).

<u>Steps</u>	<u>Remarks</u>
1. Pipet an aliquot, 5 ml or less, that contains 1 to 35 µg of mercury into a 50-ml centrifuge tube.	The sample must not contain more than 4 mmoles of aluminum nor more than 0.03 mmole of Cu(II). See Table I for the tolerance levels of other ions.
2. Add 1 ml of concentrated nitric acid and immerse the centrifuge tube in a boiling water bath for 5 min.	Nitric acid oxidizes Hg(0,I) to Hg(II). Prolonged digestion will lead to loss of mercury by volatilization.
3. Cool, add a small stirring bar, dilute to about 15 ml with water, add 2 ml of 2.5M hydroxylaminc hydrochloride, then let stand for 5 min with intermittent stirring with a magnetic stirrer.	If much brown nitrogen dioxide fumes is observed, aspirate the fumes with mild suction before adding the hydroxylaminc hydrochloride.
4. Add 1 ml of 0.5M aniline hydrochloride.	
5. Add 10 ml of the complexer-buffer solution and adjust the pH to 2.85-0.35 with concentrated ammonium hydroxide.	
6. Transfer the sample quantitatively to a 60-ml separatory funnel with water rinses.	
7. Add <u>exactly</u> 15.0 ml of 0.00105% dithizone-chloroform solution and extract for <u>exactly 15 sec.</u>	The extraction time must be kept short to minimize the extraction of copper.

8. Drain the lower chloroform layer into a 50-ml culture tube. The walls of the culture tube adsorb water droplets which otherwise interfere. If necessary, centrifuge the tube.
9. Measure the absorbance of the chloroform extract against the reagent blank at 495 m μ in 1-cm (5 to 35 μ g of mercury) or 5-cm (1 to 10 μ g of mercury) cells. When in doubt, measure the absorbance with 5-cm cells first. This will permit subsequent measurements with 1-cm cells. The color of the chloroform-dithizone extract should show the presence of excess unreacted dithizone, i.e., a bluish-green cast. If not, discard the sample and process a new smaller aliquot. Under proper conditions, the color of the chloroform extract is stable for at least 2 hr. If slow but noticeable "bleaching" is observed, the nitrite probably was not destroyed adequately in steps 3 and 4.

CALCULATIONS

Record the data on the worksheet and calculate the results as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Micrograms of mercury in calibration standards.
B	Absorbance of standards.
C	Calibration factor.
	$C = \frac{B}{A}$ $C' = \frac{B'}{A'}$
D	Average calibration factor.
	$D = 0.5 (C + C')$
E	Sample volume in ml or sample weight in g.
F	Dilution factor.

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G Sample absorbance.
H Result, micrograms of mercury per ml or
per g.

$$H = \frac{FG}{DE}$$

Report three significant figures for values greater than 1 and to the nearest second decimal place for values less than 1. Example: 199 $\mu\text{g/ml}$, 1.99 $\mu\text{g/ml}$, and 0.20 $\mu\text{g/ml}$.

REFERENCES

1. Analytical Methods Committee, Analyst 90, 515 (1965).

R. Fullerton
S. S. Yamamura

November 1966

F. Determination of Nickel (Replacement-Insertion to Section F,
ECF, Mod-1)

F:1. Discussion

This procedure, an adaptation of a National Bureau of Standards method⁽¹⁾, is specifically designed for the determination of nickel in descalent solutions. The nickel is determined by developing the red nickel-dimethylglyoxime complex in a highly alkaline, citrate medium containing persulfate and measuring its intensity at 465 m μ . All samples are initially digested with acids and concentrated by evaporation prior to color development.

The range of the colorimetric procedure is 2 to 15 μ g of nickel. The maximum sample sizes that may be taken for analysis are 25 ml for ammonium citrate (AC) and hydrazine-Versene (HV) samples and 100 ml for oxalic-nitric (ON) and water (W) samples. The lower limit of determinability is, therefore, 0.08 ppm nickel for the AC and HV samples and 0.02 ppm for the ON and W samples.

Manganese which is often present in ECF samples precipitates as manganese dioxide in alkaline persulfate medium and interferes seriously. Its interference is avoided by filtering the manganese dioxide just prior to measurement. The precipitation of manganese dioxide is not complete in the 30- to 60-min color development period and continues slowly after the filtration. Filtered samples should therefore be read within 5 min after filtration.

F:2. Apparatus and Reagents

F:2.1 Apparatus

1. Spectrophotometer, Beckman DU or DK-2, Cary Model 14.
2. Absorption cells, 5- and 10-cm Pyrex.
3. Pipets, macro and micro, assorted sizes.
4. "Redy-Dispensers", 5-ml size.
5. Volumetric flasks, 25- and 50-ml sizes.
6. Erlenmeyer flasks, 125- and 250-ml sizes.
7. Reflux heads for 125- and 250-ml Erlenmeyer flasks.
8. Oscillating hot plate.
9. Chromalox hot plate with Transite board.
10. Ice bath.
11. Millipore filtration apparatus, 1-in. dia. with Gelman VM-6, 0.45- μ membrane filters.
12. Fisher filtrator.

F:2.2 Reagents

NOTE: Use distilled water to prepare all reagents.

1. Ammonium citrate, 2.5M aqueous solution.
2. Dimethylglyoxime solution, 1% ($\frac{W}{V}$) ethanolic solution.
3. Potassium persulfate solution, 5% ($\frac{W}{V}$) aqueous solution.

4. NaOH solution, 50% ($\frac{W}{V}$) aqueous solution.
5. Standard nickel stock solution, 1.000 mg Ni/ml. Dissolve 1.000 ± 0.001 g of pure nickel metal in 10 ml of concentrated nitric acid and dilute to 1 liter with water.
6. Nickel calibration standard I, 8 μ g Ni per ml. Dilute 2.00 ml of the stock solution to 250 ml with water.
7. Nickel calibration standard II, 12 μ g Ni per ml. Dilute 3.00 ml of the stock solution to 250 ml with water.
8. H₂SO₄ - HClO₄ - HNO₃ digestion mixture. Add one volume of concentrated H₂SO₄ to a mixture of 2 volumes of HClO₄ and 5 volumes of HNO₃.
9. Miscellaneous acids, H₂SO₄, HCl, and H₃PO₄, concentrated, in dropping bottles.

F:3. Procedure

NOTE: Use distilled water throughout the procedure.

F:3.1 Blanks

1. For calibration standards and samples. Add 10 ml of the triacid digestion mixture to a 125-ml Erlenmeyer flask and process it per Procedure F:3.4 beginning at step 3.
2. For bias controls An appropriate ECF matrix blank must be processed with the bias controls to correct for the nickel introduced via the matrix. The nickel bias control is normally prepared with 15 ml of a given matrix. Therefore, process 15 ml of the appropriate matrix solution per Procedure F:3.4.

F:3.2 Calibration

Pipet 1.00 ml of the 8.00 μ g per ml nickel standard into one 125-ml Erlenmeyer flask and 1.00 ml of the 12.0 μ g per ml nickel standard into another flask. Add 10 ml of the triacid digestion mixture to each and process the two standards per Procedure F:3.4 beginning at step 3.

F:3.3 Cleansing of glassware

All glassware should be cleaned thoroughly before and after each use. Clean new glassware by fuming perchloric acid in them, then rinsing them with water. Rinse used volumetric flasks with water, a 2% ($\frac{V}{V}$) mixture of 30% hydrogen peroxide and 1M nitric acid, and water in that order. Treat all glassware used for the digestion and color development as follows: (a) rinse the glassware with water, then with a 2% ($\frac{V}{V}$) solution of 30% hydrogen peroxide and 1M nitric acid; (b) treat the rinsed glassware for 3 to 4 min with 2 to 3M hydrofluoric acid, then rinse thoroughly with water.

F:3.4 Analysis of samples

<u>Steps</u>	<u>Remarks</u>
1. Pipet a sample containing 2 to 15 μg of nickel, less than 300 μg of iron, and less than 2.5 mg of manganese into an Erlenmeyer flask.	For HV and AC Samples, use a 125-ml Erlenmeyer flask and up to 25 ml of sample. For W and ON samples, use a 250-ml flask and up to 100 ml of sample. Water (W) samples should be evaporated to about 1 ml without the triacid digestion mixture, then processed per steps <u>8</u> through <u>17</u> .
2. Add 0.5 ml of concentrated sulfuric acid, then add 2 ml of the 1:2:5 $\text{H}_2\text{SO}_4\text{-HClO}_4\text{-HNO}_3$ mixture for each 5 ml of sample. Place a reflux head on the flask to minimize sample losses.	For samples less than 5 ml, use 0.5 ml of concentrated sulfuric acid and 2 ml of the triacid mixture.
3. Evaporate the sample on an oscillating hot plate to the appearance of perchloric acid fumes.	Perform, all digestion steps behind a safety shield.
4. Continue the evaporation on a Chromalox hot plate (set on high with a Transite board on it) until evolution of HClO_4 fumes ceases.	If necessary, transfer the sample to a Chromalox hot plate set on high with a sheet of asbestos on the hot plate to completely volatilize the HClO_4 . Use the asbestos sheet-covered hot plate only toward the end of this step after most of the organic has been decomposed. Too rapid evolution of perchloric acid may lead to explosions.
5. Cool. Rinse and remove the reflux head, then continue the evaporation over a small flame (Meker burner) to a volume of about 0.5 ml.	Incline the flask at about 45° to minimize loss of sample. Swirl constantly to prevent local baking.

6. Cool. Rinse down the walls of the flask with 2 to 3 ml of water, then add 1 ml (one medicine dropper full) of concentrated hydrochloric acid and 3 drops of concentrated phosphoric acid.
7. Evaporate the sample over a Meker burner to the appearance of SO_3 fumes, then maintain the sample (with intermittent heating) at this "just beginning to fume" stage for about 30 sec.

The purpose of steps 7 and 8 is to solubilize the metal sulfates that precipitate in the digestion. The HCl digestion coupled with the $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ digestion does this effectively. Swirl the flask constantly during this entire step to prevent localized overheating. Strong heating results in the formation of insoluble phosphoric acid polymers.
8. Cool, then rinse down the walls of the flask with 5 ml of water.

Use a wash bottle.
9. Add 5 ml of 2.5M ammonium citrate.
10. Add 5 ml of 5% potassium persulfate. Mix by swirling.
11. Chill in an ice bath.

The sample is chilled to prevent the reaction of persulfate on citrate which produces a yellow interfering coloration.
12. Add 5 ml of 50% ($\frac{W}{W}$) sodium hydroxide. Swirl to mix.
13. Chill to 250°C or less, then remove the flask from the ice bath.
14. Add 1 ml of 1% ($\frac{W}{V}$) dimethylglyoxime. Swirl.
15. Let the color develop for 30 min. Swirl the contents of the flask now and then to wet the walls of the flask with the reagent.

The color development period can be extended to 1.5 hr with no adverse effect.

- | | |
|--|---|
| 16. Filter the sample quantitatively with water rinses through a 0.45- μ membrane filter directly into a 25-ml volumetric flask. | The main purpose of the filtration is to remove manganese dioxide which interferes; however, all samples should be filtered regardless of their appearance. |
| 17. Dilute to volume with water and mix well. Measure the absorbance of the solution against water within 5 min. Use a 5-cm cell. | Filtered solutions should be read within 5 min because precipitation of the manganese dioxide is not complete in the 0.5- to 1.5-hr color development period and continues slowly after filtration. |

F:4. Calculations

Record the data and calculate the results as shown in the following example work sheet.

Report results to three significant figures for values greater than 1 μg per ml and to the nearest 0.001 μg for values less than 1 μg per ml. Ex: 10.6, 1.06, and 0.011 μg Ni per ml.

F:5. Reference

1. Menis, O., National Bureau of Standards, Personal Communication, February, 1966.

S. S. Yamamura

December, 1966

IDO-14316
ECF-1, Mod-1:36

Determination							Nickel	
A	B	C	D	E	F	G	H	
Sample Identification	Sample Vol., ml	Absorb vs Water	Net Absorb.	Calib Factor For Stds	Average Calib. Factor	µg Ni in Test Sample	Result µg Ni per ml	
Rgt Blank	--	0.060						
Standard I, 8 µg Ni		0.436	0.376	0.0470	0.0472			
Standard II, 12 µg Ni		0.629	0.569	0.0474				
AC-1114	10	0.440	0.380			8.05	0.805	
Control-Blk AC Bias		0.075						
Control-1		0.436	0.361			7.65		

Calculations:

$$E = \frac{D}{A} = \frac{0.376}{8} = 0.0470$$

$$G = \frac{D \text{ for Sample}}{F} = \frac{0.380}{0.0472} = 8.05 \text{ µg Ni in test sample}$$

$$E' = \frac{D'}{A'} = \frac{0.569}{12} = 0.0474$$

$$H = \frac{G}{B} = \frac{8.05}{10} = 0.805 \text{ µg Ni/ml}$$

$$\begin{aligned} \bar{F} &= 0.5 (E + E') = 0.5 (0.0470 + 0.0474) \\ &= 0.0472 \end{aligned}$$

TITRIMETRIC DETERMINATION OF NITRIDE NITROGEN
IN ALLOYS HIGH IN NICKEL AND CHROMIUM

ABSTRACT

A modified Kjeldahl procedure is described for the determination of micro amounts of nitride nitrogen, N^{-3} , in nickel-chromium alloys. The sample is dissolved with a mixture of perchloric and phosphoric acids. The nitrogen, converted to ammonium in the dissolution process, is then distilled as ammonia into boric acid and titrated with standard acid to a visual indicator end point (1, 2).

APPLICABILITY

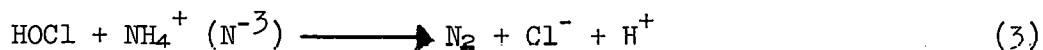
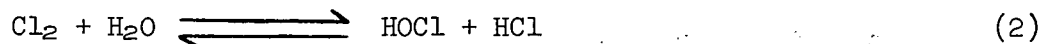
This method is applicable to samples dissolvable by a perchloric acid-phosphoric acid mixture. These samples include Hastelloy X (22% Cr, 24% Fe, 9% Mo, and 45% Ni) for which the method was developed and NBS Sample 161, a nickel-chromium casting alloy.

The lower limit of the titration procedure is 100 μ g of nitrogen. The maximum sample size that can be processed in the distillation is about 1.5 g. Consequently, the lower limit of this method is 0.0065 wt% nitrogen in the original alloy.

At the 0.025 wt% level, the observed precision is \sim 10 relative %.

DISCUSSION

For accurate results, the sample must be dissolved without any loss of nitrogen. In the perchloric acid-phosphoric acid dissolution procedure, nitride nitrogen, N^{-3} , will be oxidized to volatile, non-determinable, elemental nitrogen unless proper precautions are taken to prevent this. The relevant reactions are:



Perchloric acid and its decomposition product chlorine do not oxidize N^{-3} to nitrogen but hypochlorous acid, one of the products of the reaction of chlorine with water (reaction 2), does. Reaction 2 is acid-dependent...low acidity (water dilution) favors the formation of hypochlorous acid; high acidity favors the reverse of this.

The formation of hypochlorous acid and the accompanying oxidation of N^{-3} to nitrogen can be prevented by reducing the chlorine with sulfite

IDO-14316
Nitrogen-1:2

before the highly acidic dissolved sample is diluted with water. The excess sulfite is destroyed with peroxide.

SPECIAL SAFETY PRECAUTIONS

The mixed perchloric acid-phosphoric acid dissolver solution, the 30% hydrogen peroxide, and the 9.4M NaOH can cause severe burns. Use rubber gloves to avoid contact with the skin, and if these chemicals do come in contact with the skin, wash immediately with copious amounts of water. The dissolver solution can react explosively with organic matter. Store it in a glass bottle away from combustible organic matter.

APPARATUS AND REAGENTS

A. Apparatus

1. Kjeldahl distillation apparatus, Fig. 1.
2. Buret, 10-ml, with at least 0.05-ml graduations.
3. Magnetic stirrer and Teflon-coated stirring bars.
4. Heating mantle and variac.
5. Erlenmeyer flask, 500- and 125-ml.
6. Round bottom flask, 500-ml.
7. Hot plate.
8. Pipets, volumetric, macro and micro, assorted sizes.
9. Graduated cylinders, assorted sizes.
10. Medicine droppers.
11. Volumetric flask, assorted sizes.

B. Reagents

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

1. Bench standard, NBS sample 161 containing 0.027 wt% nitrogen.
2. Perchloric acid-phosphoric acid solution. Mix 80 volumes of 70% perchloric acid with 20 volumes of 85% phosphoric acid.

IDO-14316
Nitrogen-1:3

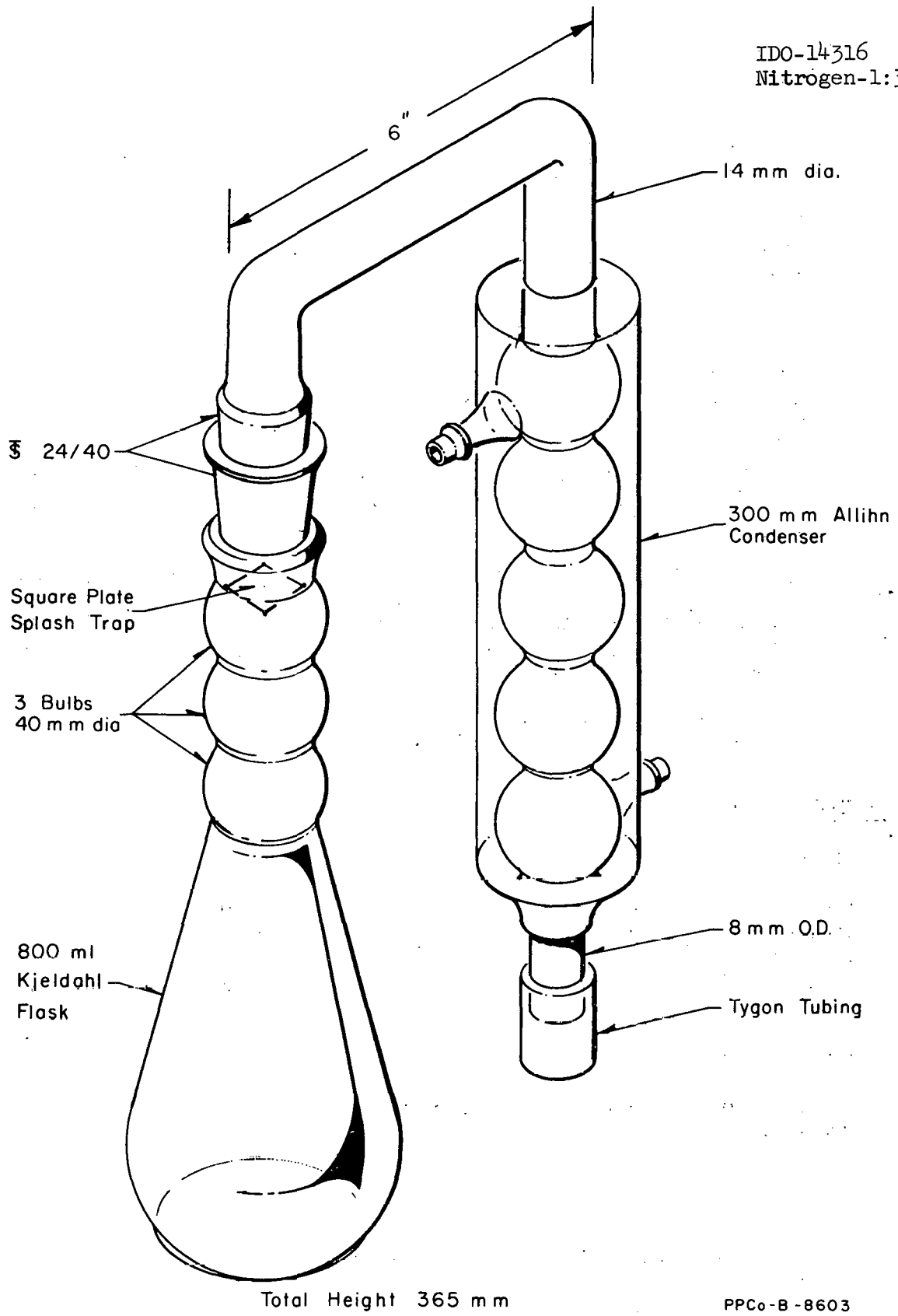


Fig. 1 Kjeldahl Distillation Apparatus

3. Sodium sulfite solution, 10% (W/V). Dissolve 10 g of sodium sulfite in water and dilute to 100 ml.
4. Doubly-distilled ammonia-free water. Add 10 ml of sulfuric acid to one liter of distilled water in a quartz flask, and distill.
5. Hydrogen peroxide, 30%.
6. Sodium hydroxide, 9.4M, ammonia-free. Dissolve 680 g of sodium hydroxide in 2 liters of water. Add 0.5 g Devarda alloy and reduce the volume to 1.8 liters by boiling.
7. Boric acid-mixed indicator. Dissolve 20 g of boric acid in hot water. Add 7.5 ml of alcoholic 0.1% bromocresol green and 4 ml of alcoholic 0.1% methyl red and dilute to 1 liter.
8. Hydrochloric acid, 0.005N. Standardize against 0.400-ml aliquots of 0.1000N NaOH. Pipet the sodium hydroxide into a 125-ml Erlenmeyer flask containing 25 ml of the boric acid-mixed indicator solution plus 75 ml of water. Titrate with the acid solution to a change from blue to reddish brown.

$$\text{Normality of HCl} = \frac{0.0400}{\text{Vol of HCl}}$$

PROCEDURE

A. Blank

The blank is extremely important and should be processed in duplicate with each set of samples. Process the blank per C using the same quantities of all reagents (perchloric acid-phosphoric acid mixture, sodium sulfite, hydrogen peroxide, sodium hydroxide, etc.) as that used for the sample.

B. Bench Standard

Process the NBS sample 161 bench standard per C before analyzing samples. Results should be within the limits specified by the Quality Control Laboratory.

C. Analysis of Samples

1. Accurately weigh a 1.5 g or less sample and place it in a 500-ml Erlenmeyer or round bottom flask. The sample should contain 100 to 1200 μ g of nitrogen. It is also possible to dissolve

a sample larger than one gram, then carry a portion of it through the distillation and titration. If this approach is used, always add the sodium sulfite solution to the acidic dissolved sample before it is diluted with water.

Use doubly-distilled water throughout the procedure.

2. Dissolve the sample with a minimum of perchloric acid-phosphoric acid dissolver solution. Add the dissolver solution in 10-ml increments and heat to dissolve the sample. Note the volume of dissolver solution used.

Some samples tend to become passive and nonreactive. Decant the supernatant acid solution to the Kjeldahl distillation flask, then continue the dissolution with fresh 10-ml portions of the dissolver mixture.

3. Cool, then quantitatively transfer the dissolved sample to the Kjeldahl distillation flask. Use 5-ml portions of the 10% sodium sulfite solution for the transfer. Mix well.

Use 5 ml of the sulfite solution for each 10 ml of perchloric acid-phosphoric acid dissolver solution.

4. Heat the solution to boiling and boil for 2 min. Allow to cool.

5. Cautiously add 1 ml of 30% hydrogen peroxide for each 25 ml of sodium sulfite admitted in Step 3. Boil gently until the hydrogen peroxide is completely decomposed.

The complete decomposition of hydrogen peroxide is indicated by a change in the boiling characteristics of the solution. Small bubbles indicate the presence of peroxide.

6. Assemble the distillation apparatus. Immerse the condenser tip in 25 ml of the boric acid-mixed indicator solution contained in a 125-ml Erlenmeyer flask.

IDO-14316
Nitrogen-1:6

7. Calculate the milliequivalents of acid introduced in step 2 and add an equal amount of sodium hydroxide (use the 9.4M NaOH solution).
8. Add 30 ml more 9.4M NaOH.
9. Add exactly 100 ml of water.
10. Distill and collect 75 ml of distillate. Control the heating to minimize bumping. The total volume of the distillate plus absorber solution is 100 ml.
11. Titrate the distillate with the 0.005N standard HCl solution to a color change of blue to reddish brown. Titrate to the same reddish brown color as that obtained during the standardization of the hydrochloric acid.

CALCULATIONS

Record the data on the work sheet and calculate the results as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Sample wt, g.
B	Dilution factor.
C	Sample titer, ml.
D	Blank titer, ml.
E	Acid normality.
F	Result, wt% nitrogen.

$$F = \frac{1.4 BE(C-D)}{A}$$

Report results to three significant figures but never more than the nearest 0.0001, for example: 0.0709, 0.0071 wt% N.

REFERENCES

1. H. J. Anderson, and J. C. Langford, Anal Chem 35 1093 (1963).
2. F. B. Moore, and H. Diehl, Anal Chem 34, 1638 (1962).

D. K. Oestreich

June, 1966

SEPARATION OF PLUTONIUM FOR
MASS SPECTROMETRIC ANALYSIS

ABSTRACT

A procedure is described for the separation of plutonium for analysis by isotope dilution mass spectrometry. Sample and spike plutonium, in hydrochloric acid, are first reduced with iodide to ensure chemical identity. After evaporation to dryness, the residue is dissolved in nitric acid containing nitrite. The resulting plutonium(IV) is retained on a column of strongly basic anion exchange resin from 8M nitric acid. After washing the column free of impurities, the purified plutonium is eluted with dilute nitric acid.

APPLICABILITY

The procedure is designed to separate plutonium from other actinide elements, fission products, and fuel cladding materials. To facilitate glove box operation, the procedure requires only simple and inexpensive equipment which should be discarded after a single use. Sample aliquots are chosen to contain 0.1 to 1 μg of plutonium.

DISCUSSION

The specificity of this procedure is achieved through the high distribution of tetravalent metal-nitrate complexes on strongly basic anion exchange resin. The reported distribution coefficient for plutonium(IV) in 8M nitric acid is $\sim 10^4$, while values for uranium(VI), neptunium(V), americium(III), and all aged fission products are much lower.⁽¹⁾

As is true with all isotope dilution measurements, quantitative recovery is unnecessary. This procedure is neither intended nor should be used whenever complete recovery of plutonium is essential.

SAFETY PRECAUTIONS

Because of the presence of alpha-emitting actinides in the samples, work will ordinarily be performed in a glove box. Follow Health Physics procedures for the particular type and intensity of radiological hazard.

APPARATUS AND REAGENTS

- A. Apparatus
1. Pipets; microliter, assorted sizes.
 2. Pipets; transfer (throwaway type).

IDO-14316
Pu-Sep-1:2

3. Test tubes; 5-ml conical.
4. Heat lamp.
5. Medicine droppers; small size.
6. Anion exchange resin; Dowex 1-X4, 200-400 mesh, nitrate form.
7. Stoppers; polyethylene, size 0.

B. Reagents

1. Nitric acid; 8M, 2M, 0.2M.
2. Hydrochloric acid; 6M.
3. Hydroiodic acid; concentrated.
4. Sodium nitrite; 1M.
5. Pu spike solutions. Standardized Pu-239 and Pu-242 solutions, sealed in glass ampoules, are available from the Quality Control Laboratory. The concentrations are about 1 µg/ml.

PROCEDURE

Pretreatment. The first step in the procedure requires a hydrochloric acid system for the iodide reduction of plutonium; therefore:

- A. If a large dilution of the original sample is necessary, dilute with 6M HCl.
- B. If little or no dilution is necessary, add an excess of hydrochloric acid and heat, under a heat lamp, to reduce the nitrate present.

1. Add a pretreated known aliquot of the sample to an exact amount of the appropriate plutonium spike. The sample and spike plutonium amounts should be approximately equal, totaling 0.2 to 2 µg.
2. Add 2 or 3 drops of hydroiodic acid and mix thoroughly. Iodide reduces all plutonium to (III), thus ensuing chemical identity.
3. Heat carefully under a heat lamp to near dryness.
4. When cool, add 1 ml of 8M HNO₃ and 2 drops of 1M sodium nitrite. Mix well. Plutonium(III) is reoxidized to (IV).
5. Transfer the nitric acid solution to a small (medicine dropper), 5-X 25-mm column of Dowex 1-X4, 200-400 mesh anion exchange resin (nitrate form) which has been equilibrated with 8M HNO₃. The plutonium(IV) nitrate complex is strongly retained on the column from 8M HNO₃.

6. Wash the column with 2 ml of 8M HNO_3 . Discard the effluent. Fuel cladding impurities, fission products, and americium are eluted.
7. Wash the column with 2 ml of 2M HNO_3 . Discard the effluent. Other actinides are eluted.
8. Elute plutonium with 2 ml of 0.2M HNO_3 . Collect the effluent in a 5-ml conical tube.
9. Evaporate the solution to near dryness, stopper the tube, and transfer it to the mass laboratory for analysis. If there is any chance of external contamination on the tube, place it in another container, such as a plastic bag or ice cream carton, to protect personnel.

(1) J. P. Faris, R. F. Buchanan, Anal. Chem. 36, 1157 (1964).

S. F. Marsh
October, 1966

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DETERMINATION OF UNDISSOLVED AND TOTAL SOLIDS

ABSTRACT

Gravimetric methods are described for the determination of undissolved solids and of total solids in aqueous solutions. Undissolved solids are separated from a sample aliquot on a tared filter, then washed and dried to constant weight at selected temperatures. Total solids are determined by evaporating a sample to dryness and heating the residue to constant weight.

APPLICABILITY

These methods are generally applicable to aqueous samples, but are written to be specifically applicable to samples from the waste calcination process, both from pilot plant studies and from the CPP Waste Calcination Facility (WCF).

DISCUSSION

A serious error in the method for undissolved solids can result from incomplete washing of dissolved salts from the periphery of the filter. The sample diffuses to the periphery of the filter which is sandwiched between the top and bottom sections of the Millipore filtration apparatus. The dissolved salts can only be effectively removed by thorough rinsing of the filter after the top section of the Millipore apparatus has been removed. Water is added dropwise from a medicine dropper around the periphery of the filter while suction is applied.

Two errors often encountered in weighing the solids are the use of improper marking inks to identify the drying containers and failure to desiccate the heated samples. Any material used to mark a container must not change weight when the container is heated. Most laboratory marking inks lose weight or even completely disappear when heated in a furnace. The only acceptable methods of marking are to permanently etch the container with hydrofluoric acid or to use an engraving vibratory tool. The amount of moisture in the atmosphere affects the weight of an object. For this reason, heated samples must be placed in a desiccator. The heated samples should be allowed to cool to about 60°C before being placed in the desiccator and remain in the desiccator for 1 hr before being weighed.

The solids will be dried to constant weight at specified temperatures ranging from room temperature to 900°C. The temperature determines the types of filter and the type of container. At room temperature, either Millipore or glass fiber filters can be used. Above room temperature to 400°C, glass fiber filters should be used. At these temperatures, the filters do not lose weight. However, the glass fiber filters must be

tared at the temperature used for the sample. Above 400°C, the Millipore which will completely disintegrate, should be used. Quartz beakers must be used above 400°C; borosilicate glass beakers can be used at lower temperatures. Their tare weight must be determined at the temperature to be used for the samples.

SPECIAL PRECAUTIONS

1. Wear asbestos gloves when handling high temperature items.
2. Plant (WCF) samples will contain fission product activities. Handle them in conformance with health physics regulations.
3. Use only the filtration apparatus located in the hot (No. 1) hood.
4. Decontaminate the filtration apparatus at regular intervals. The recommended decontamination reagents are Turco 4502 and Turco 4521.
5. The balance is located in the open laboratory. Take necessary precautions, such as placement of masking tape on the controls, to prevent its contamination.

APPARATUS AND REAGENTS

Use distilled water throughout the procedures.

1. Beakers, quartz, 100-ml, etched with a permanent number (see Discussion Section).
2. Beakers, borosilicate glass, 100-ml, etched with a permanent number (see Discussion Section).
3. Millipore filters, 4.7-cm, 0.45- μ , Type HA.
4. Glass fiber filters 5-cm, Reeve-Angel.
5. Millipore filtration apparatus.
6. Centrifuge tubes, plastic, 50-ml.
7. Graduated cylinders, 100-ml.
8. Heat lamps.
9. Muffle furnace.
10. Desiccators, glass with air release valve. The recommended desiccant is Indicating Dryrite. As it becomes exhausted, the color changes

from blue to red. Regenerate it by heating at 100°C for 24 hr in a large Petri dish with the depth of the Dryrite not exceeding 1 in.

11. Balance, analytical, sensitivity of 0.1 mg.
12. Watch glasses, Speedyvap type.
13. Aluminum weighing dishes, 2-in. diam.
14. Vacuum pump.

PROCEDURE

A. Selection of Proper Filter and Beaker

The type of filter to be used for determining undissolved solids depends upon the temperature selected for the drying as follows:

<u>Drying Temperature, °C</u>	<u>Filter</u>
Room	Millipore or glass fiber
Room to 400	Glass fiber
400	Millipore

Use quartz beakers above 400°C. Borosilicate beakers can be used below 400°C.

B. Determination of Constant Weight

The quantity of undissolved solids will range from a few milligrams to several grams. The time required to obtain constant weight depends on the nature of the sample, the size of the sample and the heating temperature. A weight is defined as constant when a repeated heating cycle produces a weight that agrees with the previous weight by 0.5 mg or less or within 1% of the sample weight for samples weighing more than 50 mg.

C. Determination Undissolved Solids

1. Select the proper filter. Select the filter according to Procedure A.
2. Tare either the filter if the solids are determined below 400°C or a quartz beaker if the solids are determined above Desiccate the filters or beakers before weighing. Place the Millipore filters directly in the desiccator using marked aluminum

- 400°C. Obtain a constant tare weight as described in Procedure B.
3. Mark the sample bottle at the liquid level.
 4. Filter with a dry Millipore apparatus into a clean, dry filter flask.
 5. Transfer the filtrate (before washing the solids with water) to a clean, dry bottle.
 6. Label the bottle with the log number and sample code and identify it as filtrate. Set it aside for additional analyses.
 7. Replace the collection flask. Transfer the remainder of the sample from its bottle to the filter paper with water rinses.
 8. Wash the solids thoroughly with water.
 9. Remove the chimney from the filtration apparatus and, with the vacuum still applied, wash the periphery of the filter with 15 ml of water applied dropwise from a medicine dropper. Allow each drop to fall half on the paper and half on the filtering base.

dishes to identify the filter. Heat the glass fiber filters or the quartz beakers to the temperature of the analysis for 1 hr and cool to about 60°C before disiccation.

Make a fine mark at the bottom of the meniscus of the liquid.

The filtrate is to be used for additional analyses. Dry apparatus must be used so that the concentration of the filtrate is not changed. The filtration may be speeded by first centrifuging the sample.

When the filtration is slow, collect only enough filtrate for the requested analyses. If the sample is subjected to the negative pressure of the filtering process for long periods of time, the liquid evaporates to change the concentration of the filtrate.

Dissolved salts are trapped on the periphery of the filter between the two halves of the filtration apparatus. These must be removed by thorough washing with water.

10. Remove the filter and dry at the specified temperature to constant weight.
- a. If the solids are to be dried at room temperature, put the filter in a marked aluminum dish and set in a desiccator for 3 hr.
- b. If the solids are to be determined from room temperature to 400°C, put the glass fiber filter in a borosilicate or quartz beaker and heat at the specified temperature for 2 hr.
- c. If the solids are to be determined at temperatures above 400°C, put the filter in a quartz beaker and char under a heat lamp. Transfer the sample to a furnace and heat at the specified temperature for 3 hr.
11. Determine the volume of the sample by measuring the volume of water required to fill the original sample bottle to the mark made in step 3.
12. Calculate and report undissolved solids as g/l.
- See Procedure B for an explanation of constant weight.
- The drying time can be reduced if vacuum is applied to the desiccator. Put a Speedyvap watch glass on the dish to protect the sample from direct air flow when the vacuum is released.
- The beaker must be tared at the specified temperature. See step 2.
- Add water slowly until the bottom of the meniscus is at the mark made in step 3.
- See Calculations Section.

D. Determination of Total Solids

1. Tare a 100-ml borosilicate beaker if the solids are to be dried at 400°C or less. Tare a 100-ml quartz beaker if the solids are to be dried at temperatures above 400°C.
2. Mark the sample bottle at the liquid level.
- Heat the beakers to the temperature of the analysis for 1 hr, cool to about 60°C, and then desiccate them. Obtain a constant tare weight as described in Procedure B.
- Make a fine mark at the bottom of the meniscus of the liquid.

3. Quantitatively transfer the sample to the tared beaker with the aid of water rinsings.
4. Cover the beaker with a Speedy-vap watch glass, heat under a heat lamp until dry, and then heat to a constant weight at the specified temperature.

If the analysis is to be made at room temperature, evaporate the sample to near dryness and then set aside to dry at room temperature. When the sample appears to be completely dry, place it in a desiccator until constant weight is obtained as defined in Procedure E.
5. Determine the volume of the sample by measuring the amount of water required to fill the original sample bottle to the mark made in step 2.

Add water slowly until the bottom of the meniscus is at the mark made in step 2.
6. Calculate and report total solids as g/l.

See Calculations Section.

CALCULATIONS

Record the data on the worksheet and calculate the results as follows.

<u>Column</u>	<u>Unit to Record</u>
A	Vol of sample, ml.
B	Time of tare weight. ^a
C	Tare weight, g.
D	Time of gross weight. ^a
E	Gross weight, g.
F	Sample weight, g.
	F = E-C
G	Result, g/l
	$G = \frac{1000 F}{A}$

Report results to three decimal places 0.001 g/l.

^aThe time at which consecutive weights are taken is recorded so that the length of time a sample is heated between weights can be calculated. This will aid in changing the validity of the constant weight. It will also give an indication of how long a specific type of sample must be timed in order to obtain a constant weight.

F. A. Duce
M. A. Wade

April, 1966

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DETERMINATION OF SULFUR BY COMBUSTION

ABSTRACT

A method is described for the determination of sulfur in metal alloys using the Leco Model 532 induction furnace and the Model ET-20 automatic photometric titrator. The sample is ignited in a stream of oxygen and the resulting sulfur dioxide is passed into a titration vessel where it bleaches a starch-iodine complex. This solution then is titrated automatically with potassium iodate back to the original photometric intensity of the starch-iodine complex.

APPLICABILITY

This method is designed primarily for the determination of sulfur in ferrous alloys. With modifications, however, various materials, such as coal, coke, oil, rubber, limestone, slag, and iron ore, can be analyzed. With the usual 1-g sample of ferrous alloys, the range of the method is 0.001- to 0.200-% sulfur. The precision is on the order of $\pm 0.002\%$ sulfur.

DISCUSSION

In establishing a method for materials other than iron and steel, standard samples of the substance under test should be used. Materials must be magnetic to be heated by the induction furnace. For samples that are nonmagnetic, iron chip accelerator is mixed with the sample to allow ignition to take place. If organic substances such as coal or rubber tend to explode, cover them with a layer of powdered alumina to slow the rate at which volatiles are released. Halogens interfere by darkening the starch-iodine complex.

SAFETY PRECAUTIONS

The Leco furnace is a high voltage unit and should not be disassembled while plugged in. Metal should not be brought into close proximity with the induction coil when the unit is in operation.

TROUBLESHOOTING GUIDE FOR INDUCTION FURNACE

Low Sulfur Results

1. Oxygen flow not sufficiently long.

IDO-14316
S-1:2
Mod-1

2. Sample temperature too low. Sufficient sample must be used to obtain the induction heating. If the sample does not heat properly, add iron chip accelerator. Always use the Leco IH-10-550S tube and the Leco crucibles and covers.
3. Furnace failure. See Electronic Service Manual for Leco High Frequency Induction Furnaces.
4. Titration vessel not aligned.
5. Initial color of starch-iodine complex not sufficiently intense. Do not allow the color to fade completely during the evolution of the sulfur dioxide as some will escape. If color completely fades, start over either with less sample or with initial color set more intensely using the endpoint control.
6. Apparatus leaks. Inspect all joints and ring seal.
7. Insufficient accelerator.
8. Potassium iodate solution too strong. The concentration must be exactly 0.444 mg/ml.
9. Sample contains halogens.
10. Rubber tubing connections may absorb sulfur. Use a minimum amount of Tygon tubing for all connections.
11. Potassium iodate solution leaked into titration vessel.

High Sulfur Results

1. Sulfur contamination from crucible or cover.
2. Potassium iodate solution too weak. The concentration must be exactly 0.444 mg/ml.

Erratic Sulfur Results

1. Starch solution too old.
2. Line voltage fluctuation.

APPARATUS AND REAGENTS

A. Apparatus

1. Leco Model 532 induction furnace and Model ET-20 electronic titrator.

2. Leco IH-10-850 crucible and Leco IH-10-950 crucible covers are recommended but any crucibles and covers made by Leco are sulfur free and may be used.
3. Microspatula and tweezers.
4. Oxygen cylinder.

B. Reagents

All reagents used should be C. P. or Analytical Reagent grade. Use distilled water for the preparation of all reagents and throughout the procedure.

1. Potassium iodate solution, 0.00207M. Dissolve 0.444 g of potassium iodate in distilled water and dilute to 1 liter.
2. Starch-iodine solution. Mix 9 g of starch into a paste with 10 ml of distilled water. Pour slowly into 1 liter of boiling water and boil for 1 min. Add 15 g of potassium iodide. Prepare a fresh solution once each week.
3. Hydrochloric acid, 0.2M.
4. Leco iron chip accelerator No. 160.
5. Leco No. 155 tin metal accelerator (20 mesh).

PROCEDURE

A. Bench Standard

Using Procedure C, process NBS samples which approximate the sample composition. Acceptable limits are ± 0.002 wt% sulfur of the stated value.

B. Blank

Using Procedure C, process 1 g of the iron accelerator.

C. Samples

1. Turn on the furnace power and filament switches. Allow at least 45 sec for warmup.
2. Set the oxygen flow at 1 liter/min.

IDO-14316

S-1:4

Mod-1

3. Weigh 1 to 3 g of sample into the crucible and add three microspatulas of tin accelerator.
For high nickel-chromium alloy samples, add 1 g of iron accelerator.
4. Place a cover on the crucible. Place the crucible on the ceramic column and raise them into the quartz combustion tube. Turn the crucible lift control to the left, but not so far left that the firing button is depressed.
Make sure the crucible is centered to avoid breaking the quartz tube.
5. Turn on the titrator power switch. Allow 1 min for warmup.
6. Turn the double throw switch to "neutral" and the end point control knob to the extreme left.
7. Rinse the titration vessel with 0.2M HCl. Close the stopcock after this step.
8. Add 5 ml of the starch-iodine solution to the titrator vessel and fill to the line with 0.2M HCl.
9. Fill the buret with 0.00207M KIO_3 solution.
10. Turn the double throw switch to "titrate" and slowly rotate the endpoint control clockwise until the light begins to flash and a medium blue color is obtained.
The light flashes when the potassium iodate solution flows from the buret.
11. Refill the buret with 0.00207M KIO_3 solution.
12. Turn the crucible lift control on the furnace to the extreme left to depress the firing button.
If the furnace circuit breaker clicks while the sample is burning, press the "reset" button. The circuit breaker opens when the plate current on the furnace exceeds 500 mA.
13. Read the buret after the light stops flashing.

14. Inspect the melted sample in the crucible for homogeneity.

If the melt is not homogeneous, the sample did not burn properly and the results will be low. In this case, start again adding 1 g of iron accelerator.

CALCULATIONS

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Tare weight of crucible, g.
B	Weight of sample plus crucible, g.
C	Weight of sample, g.
	$C = B - A$
D	Titer of sample, percentage units.
E	Titer of blank for 1 g of accelerator, ml.
F	Result, wt% sulfur.
	$F = \frac{D - E}{C}$

Report results to three decimal places 0.001%.

Note that if exactly 1 g of sample is used, the blank-corrected buret reading is the percent sulfur content of the sample.

REFERENCE

1. Laboratory Equipment Corporation, Instruction Manual for Operation of Leco Sulfur Determination No. 400-I and ET-20, Saint Joseph, Michigan (1953).

D. K. Oestreich
April, 1966

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COLORIMETRIC DETERMINATION OF FLUORESCEIN

ABSTRACT

A method is described for the determination of microgram quantities of fluorescein in solid and aqueous samples. The absorbance of an aqueous solution of the sodium salt of fluorescein is measured at 490 m μ .

APPLICABILITY

This method is designed for the determination of pure fluorescein in distilled water solutions or particulate fluorescein trapped on fiber glass filters. The lower limit of detection is 0.5 μ g of fluorescein and the linear range is 0.5 to 80 μ g.

DISCUSSION

The method is based on the absorbance measurement of the sodium salt of fluorescein which has an intense color in an aqueous medium. The color is most intense at a pH greater than 9.0. The maximum absorbance is at 490 m μ . The color is stable for at least 24 hr.

APPARATUS AND REAGENTS

A. Apparatus

1. Assorted pipets.
2. Volumetric flasks, 25-ml.
3. Griffin beakers, 50-ml.
4. Fiber glass filters, 1-in., Reeve Angel, or equivalent.
5. Filter holders for above filters.
6. Beckman Model DU spectrophotometer, or equivalent.
7. Absorption cells, 1- and 5-cm, Corex.
8. Magnetic stirrer and Teflon-coated magnets.

B. Reagents

1. Fluorescein, powder, Eastman Organic Chemicals.

Fluorescein-1:2

2. Calibration and bench standards.
 - a. Standard I, 80 μg of fluorescein per ml. Dissolve 80.0 mg of fluorescein in ethanol, dilute to 1 liter with ethanol, and mix until homogeneous.
 - b. Standard II, 40 μg of fluorescein per ml. Dissolve 40.0 mg of fluorescein in ethanol, dilute to 1 liter with ethanol, and mix until homogeneous.
3. Sodium hydroxide, $\underline{6\text{M}}$ and $\underline{0.01\text{M}}$.
4. Ammonium chloride buffer, $\underline{1\text{M}}$, pH 9.35. Mix two volumes of $\underline{1\text{M}}$ NH_4OH and one volume of $\underline{1\text{M}}$ HCl .

PROCEDURE

A. Blank

Process a reagent blank. Begin with step D-1 substituting water for the sample.

B. Calibration

1. If using 1-cm absorption cells, process a 500- μl aliquot from each of standard I and Standard II beginning with step D-1.
2. If using 5-cm absorption cells, process a 100- μl aliquot from each of Standard I and Standard II beginning with step D-1.
3. Divide the micrograms of fluorescein in each aliquot by its respective absorbance to determine the conversion factor. Before samples are analyzed, the difference between the two conversion factors and the average conversion factor must agree within limits set by the Quality Control Laboratory. Also, the average of the two conversion factors must agree with the established conversion factor within specified limits.

C. Analysis of Filter Samples

<u>Steps</u>	<u>Remarks</u>
1. Leach the sample filter with 10 to 15 ml of $\underline{0.01\text{M}}$ NaOH in a 50-ml beaker with vigorous magnetic stirring for at least 5 min.	The sodium salt of fluorescein is more soluble than fluorescein.

2. Transfer the leach solution to a 25-ml volumetric flask.

3. Add 2 ml of 1M NH_4Cl buffer to the beaker and transfer with small water rinses to the 25-ml volumetric flask. Dilute to 25 ml with water, and mix until homogeneous.

The recommended mixing procedure is to transfer the solution between the volumetric flask and a larger bottle as described in the Remote and Service Analysis Group Operating Manual (PTR-729, p 121, November, 1964).

4. Filter the leach solution through a 1-in. fiber glass filter.

Suspended solids cause high absorbance readings.

5. Measure the absorbance of the filtrate at 490 $\text{m}\mu$ with either 1-cm or 5-cm Corex cells.

If the absorbance in 1-cm cells is greater than 0.75, take an aliquot and process by section D.

D. Colorimetric Analysis

1. Pipet up to 20 ml of a water sample into a 25-ml volumetric flask.

The leached filter sample is in a 25-ml volumetric flask from step C-3.

2. Add 2 ml of the 1M NH_4Cl buffer, dilute to 25 ml with distilled water, and mix until homogeneous.

The recommended mixing procedure is to transfer the solution between the volumetric flask and a larger bottle as described in the Remote and Service Analysis Group Operating Manual (PTR-729, p 121, November, 1964).

3. Measure the absorbance at 490 $\text{m}\mu$ with either 1-cm or 5-cm Corex cells.

If the fluorescein content is unknown, first measure in 1-cm cells. If absorbance values are below 0.1, discard the results and use 5-cm cells.

CALCULATIONS

Record the data and calculate the results as shown in the following example worksheet.

Report results to two significant figures.

CHEMICAL ANALYSIS WORK SHEET

Sample Name _____ Log Number _____
 Activity (mR/hr) _____ Determination Fluorescein
 Charge Number _____ Procedure _____

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 Ys H ₂ O	Net Absorbance	Conversion Factor = μg/abs	μg in Aliquot Analyzed D = BC		Result μg/sample
Reg Blank		0.005					
Std 40 μg		0.410	0.405	98.8			
Std 20 μg		0.215	0.210	97.6			
				\bar{x} 98.2			
Sample	Total sample	0.355	0.350		34.4		34.4 μg/sample

ANALYZED BY: Analyzed by I. L. Doggett Date December 1966

CALCULATIONS:

$$\text{Result} = \frac{D}{\text{sample}} = \frac{34.4}{\text{sample}}$$

Approved by _____

COLORIMETRIC DETERMINATION OF OSMIUM

ABSTRACT

This method, designed primarily for powder metallurgy samples of aluminum containing osmium metal or oxide, involves an initial separation of the osmium metal or oxide from the aluminum by dissolution of the aluminum in hydrochloric acid and filtration of the insoluble osmium fraction. The osmium fraction is dissolved by a sodium hydroxide-potassium nitrate fusion and colorimetrically determined or is dissolved by a nitric-sulfuric acid mixture, distilled as the tetroxide, and colorimetrically determined. The colorimetric method is based on the red, water-soluble complex formed with thiourea.(1,2)

APPLICABILITY

This method was developed specifically for the analysis of relatively pure aluminum-osmium alloys in which osmium is either the metal or the oxide. In one of the two procedures, osmium is separated by distillation as the tetroxide before color development. This increases the specificity of the method. Other elements that distill, such as ruthenium, are potential interferences. The range of the colorimetric procedure is 0.5 to 5 mg of osmium. The lower limit of the overall method for aluminum matrix samples is 0.5 mg of osmium.

DISCUSSION

The aluminum in the sample is dissolved in hydrochloric acid and the insoluble osmium-containing residue is removed by filtration. The hydrochloric acid dissolution foams considerably; thus heat must be applied with caution to avoid loss of solution. Aluminum that contains more than 4% osmium, by weight, will dissolve without applied heat. The membrane filter containing the osmium residue can be dissolved by two procedures. The controlling factor is the presence of metals precipitated by caustic. In the first procedure the residue may be fused in a caustic-potassium nitrate mixture. Fusion is complete when the melt turns brown. The brown color is the result of the oxidation of osmium by the nitrate to the tetroxide. Do not heat after the melt turns brown because insoluble silicates will form from the glass tube. The melt is dissolved in water after fusion. In the second procedure the residue is dissolved in a concentrated nitric acid-sulfuric acid mixture and then is separated by distillation. The distillate is trapped in 10M NaOH. Distillation is complete when the brown color, formed by the osmium tetroxide, disappears from the dissolver solution. Heating an additional 5 min will assure complete distillation.

Os-1:2

The colorimetric determinations are based on the absorbance measurement of the red complex ion, $\text{Os}(\text{NH}_2\cdot\text{CS}\cdot\text{NH}_2)_6^{+++}$, formed by the reaction of osmium tetroxide and thiourea in approximately 1M H_2SO_4 . (1,2) Substances that oxidize thiourea must be absent. The complex has a maximum absorbance at 540 m μ . The color is stable for at least 8 days.

SAFETY PRECAUTIONS

Wear rubber gloves when handling concentrated acids. Rapid addition of sulfuric acid to an aqueous solution will cause spattering. Follow procedures for addition of concentrated acids.

APPARATUS AND REAGENTS

A. Apparatus

1. Assorted pipets and syringe controls.
2. Volumetric flasks, 100-ml.
3. Beckman Model DU spectrophotometer, or equivalent.
4. Absorption cells, Corex, 1-cm, calibrated to ± 0.002 absorbance units with a processed standard in the cells at 540 m μ .
5. Millipore filters, 0.45- μ , 25-mm, type HA, or equivalent.
6. Filter holders for above filters.
7. Ruthenium distillation apparatus.
8. Centrifuge tubes, 50-ml.

B. Reagents

Use distilled water and reagent grade chemicals.

1. Sulfuric acid, conc and 6M.
2. Nitric acid, conc.
3. Sodium hydroxide, pellets.
4. Sodium hydroxide, 10M.
5. Potassium nitrate, crystals.

6. Thiourea, 10% (w/v). Dissolve 10 g of thiourea in water and dilute to 100 ml. This reagent is stable for at least 2 months.
7. Calibration and Bench Standards
 - a. Standard I, 1.000 mg Os/ml. Dissolve 100.0 mg of osmium metal per section D starting at step 2, dilute to volume in a 100-ml volumetric flask, and mix until homogeneous.
 - b. Standard II, 2.000 mg Os/ml. Dissolve 200.0 mg of osmium metal per section D starting at step 2, dilute to volume in a 100-ml volumetric flask, and mix until homogeneous.

PROCEDURE

A. Blank

Process a reagent blank with each series of samples, starting at section D, substituting water for the sample.

B. Calibration and Bench Standard

A calibration is required each day samples are analyzed.

1. Process a 2-ml aliquot of Standard I and a 2-ml aliquot of Standard II. Evaporate to dryness and continue per Procedure D beginning at step 2.
2. Divide the milligrams of osmium in each aliquot by its respective absorbance to determine the conversion factor. Before samples are analyzed, the two conversion factors must agree within limits set by the Quality Control Laboratory. Also, the average of the two conversion factors must agree with the established conversion factor within specified limits.

C. Dissolution of Aluminum

<u>Steps</u>	<u>Remarks</u>
1. Weigh and transfer a sample that contains 0.5 to 100 mg of osmium to a 50-ml centrifuge tube.	The chemical form of the osmium must be metal or oxide.
2. Add 10 ml of conc HCl and gently heat to dissolve the aluminum.	Add the acid in 2- to 3-ml increments and heat gently to initiate the reaction. The reaction proceeds with considerable foaming.

3. Filter the sample on a 25-mm, 0.45- μ membrane filter. Wash the filter three times with 5-ml portions of distilled water. Discard filtrate and washes.
4. Treat the filter and residue by procedure D or E.

Procedure D is faster but cannot be used for samples that contain diverse metals that precipitate with NaOH.

D. Caustic Fusion of Residue

1. Transfer the filter and residue to a 50-ml centrifuge tube.
2. Add six (~ 2g) NaOH pellets and 0.1 g of KNO_3 crystals.
3. Heat gently over a flame until the melt turns brown.
4. Cool, then add 15 to 20 ml of distilled water and heat gently over a flame until the melt dissolves.

The osmium oxidizes to the brown-colored tetroxide.

To avoid bumping, gently heat while continuously swirling the tube.

5. Transfer the solution to a 100-ml volumetric flask, dilute to volume with distilled water, and mix until homogeneous.

The recommended mixing procedure is to transfer the solution between the volumetric flask and a larger bottle as described in the Remote and Service Analysis Group Operating Manual (PTR-729, p 121, November, 1964).

6. Proceed to Procedure F.

E. Acid Dissolution of Residue and Separation of Osmium by Distillation

1. Transfer the filter and residue to a ruthenium distillation apparatus.
2. Add 5 ml of conc HNO_3 and 10 ml of conc H_2SO_4 .

Add the conc H_2SO_4 slowly to prevent spattering.

3. Heat with a flame and trap the distillate in 50 ml of 10M NaOH. Continue heating for 5 min after the brown color disappears.

Osmium oxidizes to the brown-colored, volatile tetroxide. Disappearance of the brown color from the dissolver solution indicates completion of the distillation.

4. Transfer the solution to a 100-ml volumetric flask, dilute to volume with distilled water, and mix until homogeneous.

The recommended mixing procedure is to transfer the solution between the volumetric flask and a larger bottle as described in the Remote and Service Analysis Group Operating Manual (PTR-729, p 121, November, 1964).

5. Proceed to Procedure F.

F. Colorimetric Analysis

1. Pipet an aliquot containing from 0.5 to 5 mg of osmium from the solutions obtained in sections D or E into a 100-ml volumetric flask and dilute with distilled water to ~50 ml.

For the calibration standards, use a 50-ml aliquot.

2. Add the calculated amount of 6M or stronger H_2SO_4 to neutralize the NaOH.

Assume no neutralization of the caustic during distillation. Add the acid slowly with mixing while cooling the flask in an ice bath. Osmium tetroxide may volatilize from a hot acid solution. The final acidity after dilution to volume (step 3) must be $1 \pm 0.5M$.

3. Add 1 ml of 10% thiourea solution, dilute to 100 ml with distilled water, stopper, and mix until homogeneous.

The solution should be at room temperature before dilution. The recommended mixing procedure is to transfer the solution between the volumetric flask and a larger bottle as described in the Remote and Service Analysis Group Operating Manual (PTR-729, p 121, November, 1964).

4. Let the solution stand for at least 10 min for full color development.

The color is stable for at least 8 days.

Os 1:6

5. Measure the absorbance at 540 m μ in a 1-cm Corex absorption cell.

CALCULATIONS

Record the data and calculate the results as shown in the following example worksheet.

Report results to three significant figures.

REFERENCES

1. G. H. Ayers, W. N. Wells, Anal. Chem., 22 (1950) p 317.
2. R. Sauerbrunn, E. B. Sandell, J. Am. Soc., 75 (1953) p 3554.

I. L. Doggett
December 1966

CHEMICAL ANALYSIS WORK SHEET

Sample Name _____ Log Number _____

Activity (mR/hr) _____ Determination Osmium

Charge Number _____ Procedure _____

Special Instructions:

Sample Description	Sampling and Dilution Data: a ₀ /d ₁ /a ₁ /d ₂ /a ₂	A	B	C	D	E	F	G
		Absorbance	Net	Conversion	mg O ₂ in			
		Vs H ₂ O	Absorbance	Factor = $\frac{mg O_2}{Abs}$	Aliquot Analyzed D = C/B			Result mg/g
Rgt Blank		0.010						
std 1.00mg O ₂		0.186	0.176	5.68				
std 2.00mg O ₂		0.362	0.352	5.68				
				$\bar{x} = 5.68$				
Sample	0.4176g/100ml/10ml				2.29			54.8mg O ₂ /g

ANALYZED BY: I. L. Doggett Date December 1966

CALCULATIONS:

$$\text{Result} = \frac{D d_1}{a_0 a_1} = \frac{(2.29)(100)}{(0.4176)(10)} = 54.8 \text{ mg/g}$$

Approved by _____

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APPENDIX C

METHODS ADDED TO THE ANALYTICAL
RADIOCHEMICAL MANUAL IN
1966

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DETERMINATION OF Fe-55 BY
LIQUID SCINTILLATION COUNTING

ABSTRACT

After preliminary treatments to separate diverse activities, the iron is precipitated as ammonium ferriphosphate which is suspended as a gel with powdered silica directly in the liquid scintillation solution. The yield is determined on an aliquot of the treated sample prior to the ammonium ferriphosphate precipitation by a colorimetric procedure.

APPLICABILITY

This method was developed primarily for the determination of Fe-55 in reactor loop decontamination solutions such as alkaline citrate, alkaline permanganate, and hydrazine-Versene.

DISCUSSION

Iron first is precipitated as the hydrous oxide which then is dissolved in 10M HCl. Residual cations are effectively separated by putting the solution through an anion exchange column that has been equilibrated with 12M HCl. The iron is selectively eluted with 0.01M HCl after eluting the other cations with 6M HCl. Iron-59 can be detected readily by its 1.10- and 1.29-MeV gamma rays or by beta emission with E_{max} of 0.27 and 0.46 MeV. Iron-55 decays by electron capture emitting characteristic x-rays of 5.9 keV with a low fluorescence yield of 25%. A liquid scintillation system therefore is required for its measurement.

When aqueous solutions are added to liquid scintillation solutions, considerable quenching of low energy beta emitters occur. To overcome this, the iron is held in suspension as an ammonium ferriphosphate precipitate with a thixotropic silica gel in the scintillation solution. Little color quenching occurs with this white precipitate. However, trapped air and impurities in the reagents will cause quenching.

The ammonium ferriphosphate is precipitated from concentrated H_3PO_4 by adding a solution of 0.1M NH_4Cl in ethanol. The suggested formula for the precipitate is $NH_4H_2[Fe(PO_4)_2] \cdot 2H_2O$. With aqueous samples, quenching decreases the counting efficiency to about 8%. With the precipitate, the efficiency is about 20%.

The yield is determined by analyzing an aliquot of the sample for total iron concentration just prior to the ammonium ferriphosphate precipitation. The procedure used is an orthophenanthroline colorimetric one described as procedure A of Method Fe-3, Mod-2 in the INC Analytical Manual.

SAFETY PRECAUTIONS

Prepare scintillation solutions and samples in a hood as p-dioxane vapors are flammable and toxic. Handle the finely powdered silica in a hood and take the utmost precautions to avoid its inhalation.

APPARATUS AND REAGENTS

A. Apparatus

1. Centrifuge tubes, graduated, 10-ml.
2. Small ion-exchange columns made from 5-ml conical test tubes with the tips removed. (See Reagents, item 10 for preparation.)
3. Special, thin-walled, glass, counting vials, ~ 20-ml volume, Beckman Instruments.
4. Ultrasonic vibrator bath.
5. Micropipets, assorted sizes and syringe controls.
6. Liquid scintillation counting system.
7. Beakers, various sizes.
8. Vortex mixers.

B. Reagents

1. Phosphoric acid, 85%.
2. Hydrochloric acid, conc, 10M, 6M, and 0.01M.
3. Ammonium hydroxide, conc and 6M.
4. Sodium hydroxide, 6M.
5. Ethanol, 95 or 100%.
6. Ammonium chloride, 0.01M, in 95 or 100% ethanol.
7. Hydrogen peroxide, 30%.
8. Iron carrier solution, 2.5 mg Fe/ml.
9. Iron-55 standardized solution.

10. Anion exchange resin column. Place a pad of fiber glass in a 5-ml conical test tube without its tip (see Apparatus, item 2) and two-thirds full with AG-1, x 8, 100 to 200 mesh, resin. Flow 5 ml of concentrated HCl through the column.
11. Scintillation solution. Dissolve 10 g of PPO[2, 5-diphenyloxazole], 150 mg of POPOP[bis(2-(4-phenyloxazolyl))benzene], and 120 g of naphthalene in p-dioxan (scintillation grade) and dilute to 1 liter with p-dioxan (scintillation grade). Mix until homogeneous.

PROCEDURE

A. Blank

1. Pipet 2 ml of the iron carrier solution and process by the same procedure that is used for samples. It is not necessary to determine the yield in the blank because it usually is negligible.

B. Calibration Standards and Calculation of Counting Efficiency

1. Place two aliquots of an Fe-55 standard solution directly into 15 ml of the scintillation solution (with added silica powder) in a counting vial. Choose the aliquots to bracket the estimated activity level of the sample.
2. Calculate the efficiency as the ratio of the observed cpm to the known dpm for each standard aliquot. The difference between the ratios and the average ratio value must agree within limits set by the Quality Control Laboratory.

C. Analysis of Samples

1. Transfer an aliquot of the sample into a 40-ml centrifuge tube. The volume of sample to be used depends on the activity level. If unknown, a 5- to 10-ml volume is recommended.
2. Add 2 ml of the iron carrier solution and mix.
3. Acidify alkaline permanganate samples with conc HCl with the aid of pH paper, add 4 drops of 30% H₂O₂, and heat to just below boiling. For hydrazine-Versene samples, add 6 drops of conc NH₄OH per 5 ml of sample. These treatments increase the chemical yields. No special treatment is required for alkaline citrate samples. Do not heat the hydrazine-Versene samples.

Fe-55--1:4
Tentative Procedure

4. Add 6M NaOH with continuous swirling to precipitate the hydrous oxide of iron.
5. Centrifuge and decant the supernatant solution.
6. Dissolve the precipitate in 10M HCl and transfer the solution with 10M HCl washes to an anion exchange column.

The column has an open tip. Place a 250-ml beaker beneath the column to collect the effluent before the transfer.
7. Wash with two column volumes of 6M HCl followed by two column volumes of 2M HCl. Discard the effluents.

A column volume is about 5 ml.
8. Elute the iron with three column volumes of 0.01M HCl into a graduated, 40-ml centrifuge tube.
9. Heat to near boiling and dropwise add conc NH₄OH while swirling the contents to precipitate the hydrous oxide of iron.
10. Dissolve the precipitate with a minimum volume of conc H₃PO₄ with the aid of heat.

The recommended volume of conc H₃PO₄ is 0.5 ml.
11. Dilute to 5.0 ml with water and mix until homogeneous.

The recommended mixing procedure is to use a vortex mixer.
12. Pipet 100 μl of the diluted, dissolved precipitate into a 25-ml volumetric flask, dilute to volume with 0.01M HCl, and mix until homogeneous.

Analyze an aliquot for iron by the colorimetric procedure (see the Discussion section).
13. Add 25 ml of the 0.01M NH₄Cl-ethanol solution to the 4.9 ml of solution remaining in the 40-ml centrifuge tube with continuous swirling, then add an excess of 3 to 4 ml.

The white precipitate is ammonium ferriphosphate.

14. Centrifuge and decant the supernatant solution.
15. Wash the precipitate with 10 ml of ethanol. Direct a stream of the ethanol to break up the precipitate and mix in an ultrasonic bath.
16. Centrifuge and decant the supernatant solution.
17. Add 5 ml of the scintillation solution and slurry the precipitate in an ultrasonic bath for 3 min.
18. Transfer the slurry to a counting vial which previously has been packed full of silica powder.
19. Rinse the centrifuge tube with three 2-ml fresh portions of the scintillation solution, adding the rinses to the counting vial.
20. Fill the counting vial with scintillation solution and cap it.
21. Vigorously shake the vial to mix the solution and the silica then place the vial in an ultrasonic bath for 1 min. The ultrasonic bath purges trapped air and gives effective mixing.
22. Count in a liquid scintillation counter using two channels.

CALCULATIONS

Record the data and calculate the results as shown in the following example worksheet.

Report results to three significant figures.

CHEMICAL ANALYSIS WORK SHEET

Sample Name _____ Log Number _____

Activity (mR/hr) _____ Determination Fe-55

Charge Number _____ Procedure _____

Special Instructions:

	A	B	C	D	E	F	G	H	
Sample Description	Sampling and Dilution Data: $a_0/d_1/a_1/d_2/a_2$	mg of Carrier Added	Iron Result from Color Procedure $\mu\text{g/ml}$	Correction Factor for Yield	Counting Efficiency	C/m from Sample	C/m from Blank	C/m Corrected for Blank	Result $d/m/ml$
AP-3 Iron Carrier	3/5/4.9	5	3	0.75	0.24	140	40	100	189

Analysed by D. A. O'Leary Date December 1966

CALCULATIONS:

$$C = \frac{8 d_1 b}{1000 a A} = \frac{(3)(5)(25)}{(1000)(0.1)(5)} = 0.75$$

Where:
 d_1 = volume of sample before aliquot removed for color analysis,
 b = volume of dilution taken for color determination,
 1000 = Conversion factor from μg to mg , and
 a = aliquot of d_1 removed for color analysis

$$H = \frac{G d_1}{C D a_0 a_1} = \frac{(100)(5)}{(0.75)(0.24)(3)(4.9)} = 188.9$$

Approved by _____