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ANNUAL REPORT OF DIVISION ANALYTICAL BRANCH FOR 1964

Ralph C. Shank & Staff

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by

Ralph C. Shank & Staff

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ANNUAL REPORT OF DIVISION ANALYTICAL BRANCH FOR 1964

SUMMARY - M. S. Anderson

This report presents the work of the Analytical Branch on projects of interest to analytical chemists during 1964. To make the report more useful to those who submit samples, it has been organized by projects rather than by analytical disciplines. Newly developed or updated analytical methods are presented in Appendices B and C.

Improvements on Analytical Methods

This section of the report briefly describes improvements in analytical methods which the Branch made for no specific project. Those improvements which were made for specific projects are presented in Section VI.

Careful regulation of filament temperatures made possible the isotopic analysis of rubidium-cesium and barium-strontium mixtures on the single-filament mass spectrometer.

Two special procedures, oxalate masking to overcome the interference of diverse ions and the use of simulated samples for standards to obtain a correction factor for phosphate, have been added to the routine titrimetric method for the determination of aluminum.

Improvements were made in two different types of procedures for the determination of boron. Fluoride interference in the alkalimetric determination of boron was eliminated by removing the fluoride in a cerous fluoride precipitation. Sensitivity and precision of boron isotopic analysis were improved by using rhenium sample filaments.

Potential sources of error in filtrations with membrane filters include incomplete removal of soluble salts, adsorption of the precipitate on surfaces of the filter holder, mechanical losses during ignition, weight changes of the filter, and reaction of the filter with the solvent. Ways of avoiding these errors are given.

A method for the determination of microgram levels of fluoride was developed, and improvements were made in the method for the determination of milligram quantities of fluoride. Microgram quantities of fluoride are determined spectrophotometrically as the lanthanum(III)-Alizarin Complexone-fluoride complex after separation by distillation from a phosphoric acid medium in a micro still. Specifying the position and size of the pyrolysis tube and using xylenol orange as an indicator in the cerium(III)-EDTA titration improved the determination of milligram levels of fluoride.

Gold was extracted into chloroform as the bromoaurate-trioctylphosphine oxide complex before spectrophotometric determination.

Members of the Analytical Development Section made comprehensive studies of the effects of diverse ions in the spectrophotometric determination of iron with 1,10-phenanthroline in EDTA-citrate medium and in the spectrophotometric determination of milligram amounts of phosphorus by the molybdivanadophosphoric acid method.

Plutonium interference in the extraction-colorimetric determination of microgram amounts of uranium was eliminated by the addition of ferrous sulfamate to the scrub solution.

Electroanalytical Studies

Generalized mathematical solutions have been obtained for the exact analysis of non-linear electrochemical processes. Precise numerical solutions to the partial differential equations describing the theoretical diffusion and kinetic currents of the uranium(V) disproportionation reaction have been obtained by simultaneously solving a series of finite difference equations by Gaussian elimination. An exact mathematical solution was obtained for potentiostatic interpretation of preceding reactions having equilibrium constants equal to or greater than one.

Improved instruments for electrochemical studies were designed. An instrument for the rapid digital recording of electrochemical signals has been completed and is expected to improve speed, accuracy, and precision and allow the study of a larger number of variables. Transistor circuits for the input and output stages in a fast-pulse potentiostat circuit have been constructed for evaluation. A high-power potentiostat circuit was completed using recently-designed, high performance vacuum tubes. A suitable cell was designed and constructed for microsecond response measurements. A design procedure, using computer calculations, was developed for obtaining the stabilizing network parameters giving maximum bandwidth in 3-electrode-cell control systems and for showing the fastest response obtainable across the electrode double-layer with a given amplifier cell system.

Separation of uranium by reversed-phase partition chromatography, using trioctylphosphine oxide supported on glass beads and an acetone elution, was incorporated into a controlled-potential coulometric procedure.

Improvements on Equipment

During 1964 the Analytical Branch continued its general effort to improve its equipment. Improvements and proposed modifications in remotely operated equipment, improvements in counting equipment and

equipment for mass spectrometry, X-ray diffractometry, and infrared spectrophotometry, and a procedure for decontaminating glassware are included in this section of the report.

Remotely operated equipment has been improved, and further improvements have been proposed. An Analytical Alpha Facility (AAF), for work with high alpha and moderate gamma activity, has been proposed for installation in the basement of the building that houses the Analytical Branch. Modifications of the Remote Analytical Facility (RAF) to provide greater versatility for non-routine work have also been proposed. All solid radioactive wastes in the RAF will be handled in sealed cans as soon as equipment for canning is installed. Two systems for the remote collection of fission product gases from fuel capsules have been assembled in the MTR and TAN hot cells.

The capacity and versatility of the Radio and Special Analysis counting room have been increased by additions to and improvements of its equipment. New instruments now in operation are a Beckman Low Beta II and a Nuclear Data Model 180 FMR 512-channel analyzer. The well crystal used with gamma counting equipment was lined with a specially fabricated Teflon insert to protect the crystal from corrosive materials.

Both additions and improvements were also made in mass spectrometric equipment. The focus voltage power supplies of both surface ionization mass spectrometers were revised to improve stability and reduce maintenance. In solving problems encountered in startup of the tandem mass spectrometer, members of the Spectroscopy Section replaced the electron multiplier, revised magnetic scanning circuits, installed a digital voltmeter, revised the accelerating voltage supply circuit, evaluated multiplier mass discrimination, investigated and reduced interference from various impurities in filament materials, and established sample preparation procedures, instrument operating conditions, and sample size requirements.

A special sample cask for transporting samples to and from hot cell facilities was constructed for use with the shielded X-ray diffractometer.

Installation of an Attenuated Total Reflectance accessory for the infrared spectrophotometer has extended its analytical capabilities to include non-transparent materials.

A highly successful procedure for decontaminating glassware has been developed. The glassware is first soaked in a hot solution of 4502 Turco and then it is rinsed with oxalic acid.

Analytical Services

Brief descriptions of some of the new or unusual analytical services which the Analytical Branch provided for other branches of

Phillips Petroleum Company or other AEC contractors are included in this section of the report. Analyses made by established procedures are not described in this report, but their number and source can be seen in Table II-2.

Methods were developed for the analysis of lead and halogens in marking materials for the Electric Boat Company. Lead was separated by two extractions with dithizone and determined colorimetrically. Halogens were separated by distillation and determined by precipitation and titration.

Three entirely different kinds of services were provided for General Electric. Indium in indium-aluminum foils was separated by a sulfide precipitation and determined by an indirect titration. Electrolysis conditions giving greater than 90% recovery were established for the electroplating of thorium, uranium-233, uranium-235, neptunium-237, plutonium-239, plutonium-240, and plutonium-241 on stainless steel. Irradiated metal samples fouled with a flocculant material of unknown composition were cleaned in an ultrasonic bath.

Methods for the analysis of decontamination solutions from the Expended Core Facility were developed for Westinghouse. In addition to the procedures for the determination of chromium, cobalt, iron, manganese, nickel, oxalic acid, acidity, potassium permanganate, sodium hydroxide, diammonium citrate, ethylenediaminetetraacetic acid, and hydrazine, an ion exchange method for the determination of manganese-54, cobalt-58-60, and iron-59 was developed. An emission spectrographic method for the determination of nickel in alkaline permanganate solutions was also developed.

Wear metals in MIL-1 lubricating oils were determined spectrochemically for Aerojet General Nucleonics.

The Analytical Branch provided services to both the Chemical and Process Development Branch and the Chemical Processing Plant Operations Branch in support of the program for the calcination of radioactive wastes. Procedures and apparatus for the remote determination of bulk density and particle size were developed specifically for Waste Calcining Facility (WCF) product, and the apparatus was successfully operated during the 10-month run of the WCF.

The Analytical Branch provided services useful in obtaining information about the release of ruthenium from the WCF. Radioactive ruthenium was determined in off-gas polyethylene chip filters by gamma spectrometry. Millipore filters were dissolved in nitric acid and analyzed for ruthenium and other radioactive isotopes. Similar analyses were performed on samples prepared by leaching the activity from asbestos filters with hot concentrated nitric acid. Spectrophotometric identification of ruthenium chemical species indicated that ruthenium in scrub solutions from WCF silica gel columns is in an oxidation state no higher than +4. Total nitrogen oxides in WCF off-gas samples were determined to see if competitive adsorption of nitrogen oxides on silica gel

adsorber beds might be the reason for the erratic release of ruthenium from the beds.

Services provided by the Analytical Branch have aided in the development of calcining processes. In support of the program for the calcination of zirconium fuel wastes, procedures for the dissolution of product samples and of a precipitate in the feed samples and the determination of aluminum, fluoride, calcium, and zirconium were developed. The addition of sugar to second- and third-cycle waste solutions necessitated checking the interference of sugar in routine analytical methods and developing a procedure for the analysis of sugar. Phosphate present in the wastes made a study of the interference of phosphate in the routine methods for the determination of mercury and boron necessary. In support of the program for the conversion of calcine to glass, the Analytical Branch has developed procedures to dissolve glass samples, determine the distribution of lead in the glass, determine the concentrations of aluminum, mercury, and phosphate in the glass, and determine the concentration of aluminum in water samples from glass solubility studies.

Services not concerned with the Waste Calcining Facility were also requested by the Chemical Process and Development Branch. One such service was the emission spectrographic determination of microgram quantities of boron in solutions from the electrolytic dissolver process. The rotating disk technique was used in this determination.

Two different types of services were provided for the Materials Testing Reactor Operations Branch. Radioactive waste storage tank solutions containing large amounts of permanganate were analyzed for chloride by a Volhard titration after reduction of the permanganate with oxalic acid. The extent of radiation damage to the MTR graphite pebble bed was determined by comparing the stored energy, changes in crystal structure, ignition point, hydrocarbon content, weight loss, annealing rate, and control of release rate of stored energy of samples from several depths in the VG12 and VG20 positions with graphite balls irradiated for one fuel cycle in the MTR 55 "in tank" position.

Methods for the analysis of samples from the Test Area North were developed for the Health and Safety Branch. An ion exchange method was developed for the determination of tantalum-182 on contaminated smears. An emission spectrographic method for the analysis of beryllium and lead on microsorban air monitor filters was also developed.

For the Reactor Engineering Branch, silicon, tungsten, and copper in U_3Si were determined by an emission spectrographic method using the rotating disk technique. Tantalum in a sample of scandium metal was determined spectrophotometrically as the pyrogallol complex.

Manganese, thorium, Pa^{233} , and total and isotopic uranium were determined in a sample of aluminum-clad $Pa^{233}-ThO_2-MnO_2$ for the Chopper Spectrometry Group of the Nuclear Technology Branch. Manganese was determined by X-ray fluorescence and absorption spectrophotometry, thorium was determined spectrophotometrically as the thorin complex,

Pa²³³ was separated by extraction and determined by gamma spectrometry, and total and isotopic uranium were determined by isotope dilution mass spectrometry.

Three services were provided for the Reactor Physics Section of the Nuclear Technology Branch. In the determination of thorium, lead, and uranium in PbO₂-ThO₂ and PbO₂-UO₂-ThO₂ mixtures, thorium and lead were separated by a sulfide precipitation, lead was determined chelometrically, thorium was determined by reverse EDTA titrimetry, and uranium was determined by isotope dilution mass spectrometry. For another program, thorium was determined by EDTA titration after dissolution in nitric, perchloric, and hydrofluoric acids, and gold, boron, and beryllium were determined spectrophotometrically in the analysis of thorium metal and alloys. The Leco Hydrogen Analyzer was modified so that hydrogen (ppm) can be determined in zirconium reactor materials.

For the Reactor Experiments Section, the apparent crystallite size was determined on irradiated and unirradiated graphite by X-ray diffraction. Also, an emission spectrographic method was developed for determining holmium and thulium in holmium-aluminum and thulium-aluminum alloys.

The Analytical Branch provided services for one other section of the Nuclear Technology Branch. Ultra-violet light was used in the emission spectrographic measurement of the characteristic emission and the width of the band produced by five phosphors for use in alpha scintillators for the Radiation Measurements Section.

Analytical services for the Safety Test Engineering Program during 1964 included the analysis of samples from the SNAPTRAN 2/10A-3 reactor and assistance in planning various phases of the LOFT program.

Samples from the SNAPTRAN 2/10A-3 reactor came from the sampling grid surrounding the reactor environmental tank and from the environmental tank containing the test package. Grid samples included beryllium filter samples, cyclone samplers, Anderson samplers, fallout plates, water tray samples, high volume air samplers, and particle catch cans. Environmental tank samples included environmental water, wafers cut from fuel pieces, debris from the reactor fuel, and selected reactor vessel components other than fuel. Radiochemical determinations of strontium-89-90, zirconium-95, iodine-131, ruthenium-103, cesium-137, barium-140, cerium-141, krypton-85, and cobalt-58 were made. Other analyses included the determination of beryllium, sodium, uranium, zirconium, and hydrogen and microscopic studies for material identification and the determination of particle size distribution. Most of the analyses for SNAPTRAN were made using established procedures. However, techniques for the dissolution of fallout plates and stainless steel and Hastaloy reactor component samples and for the determination of hydrogen in finely divided fuel particles were especially developed for use on SNAPTRAN samples.

Analytical Branch personnel are assisting in planning many phases of the LOFT program. Techniques for the analysis of organic impurities in the atmosphere of the containment shell and oxygen, nitrogen, and hydrogen in the reactor vessel are being investigated. To evaluate proposed gas samplers, the sorption of krypton and xenon onto sorber materials for other fission products is being measured. Rapid radiochemical methods are being developed to supplement the proposed gamma spectrometric measurements of fission products on plateout samples. Decomposition data were obtained for hydrogen peroxide-based decontamination solutions. Brief emission and X-ray spectrochemical studies were made to determine the feasibility of these methods for the determination of total iodine. The fission product adsorption behavior of carbon and stainless steels was investigated for the conditions proposed for the LOFT reactor vessel.

Quality Control

A table of the precision data for thirty-seven routine analytical methods is given. The effects of various kinds of containers, stoppers, and solvents on the storage stability of standard solutions are being evaluated.

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ANNUAL REPORT OF DIVISION ANALYTICAL BRANCH FOR 1964

I. INTRODUCTION

This is the fifth^(1,2,3,4) annual report of the Analytical Branch. Until 1960, analytical progress was included in ICPP Operations weekly and monthly reports and in ICPP Technical quarterly reports. For 1964, work performed on budgeted programs has been included in monthly reports of the Phillips Petroleum Company Nuclear and Chemical Technology Branch.

This report presents a complete year's work on projects of interest to analytical chemists. Work that has been published is only abstracted here to allow space for presenting details of both positive and negative results not published elsewhere. Updated routine methods used by the Analytical Branch are included in Appendix B, along with newly developed methods. New or updated radiochemical methods are included in Appendix C.

It is hoped that this report will be of value to management, to those who submit samples, and to all analytical chemists. A summary of the entire report is provided for the benefit of management. To make this report more useful to those who submit samples, it has been organized by projects, although previous annual reports were organized according to analytical disciplines.

- (1) R. C. Shank et. al., Annual Report of ICPP Analytical Section for 1960, IDO-14547 (April 14, 1961).
- (2) R. C. Shank et. al., Annual Report of ICPP Analytical Section for 1961, IDO-14588 (May 31, 1962).
- (3) R. C. Shank et. al., Annual Report of Division Analytical Branch for 1962, IDO-14605 (April 25, 1963).
- (4) R. C. Shank et. al., Annual Report of Division Analytical Branch for 1963, IDO-14636 (June, 1964).

II. GENERAL INFORMATION

The organization of the Analytical Branch at the end of 1964 is shown in Figure II-1. At the end of 1964, 65 people were employed in the Analytical Branch. Table II-1 shows the distribution of manpower in 1964, but the time of the branch manager, two secretaries, and three section chiefs is not included in the table.

The number of determinations made by the Analytical Branch and the sources of samples are shown in Table II-2. Methods used by the Branch may be found in IDO-14316, (5) IDO-14613, (6) previous annual reports, and Appendices B and C of this report. Table II-3 is a list of some of the methods most frequently used and the average time required for an analysis by each method.

Analytical service at Test Reactor Area facilities was made available for the first time this year. Sponsors in that area may obtain this service by requests through Project Engineering.

(5) M. J. Shepherd Jr., J. E. Rein, eds, Manual of the Analytical Methods Used by the Control Laboratory at the Chemical Processing Plant. Parts I and II, IDO-14316 (January 1955). Supplement 1 (November 1956). Supplement 2 (March 1957). Supplement 3 (October 1957).

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

Figure II-1. ORGANIZATION OF ATOMIC ENERGY DIVISION ANALYTICAL BRANCH

TABLE II-1

DISTRIBUTION OF MANPOWER IN 1964

Section	ICPP Operations	ICPP Chem. & Proc. Dev.	Plant Assistance	Analytical Development	Other PPCo.	Outside PPCo. ^(a)	Analytical ^(b)	TOTAL
Spectroscopy	1401.5	1068.0	2158.0	6027.0	6106.5	6228.5	8231.5	31221.0
Chemical Analysis								
Remote & Service Analysis	7042.0	4777.5	7593.0	69.5	6195.5	4352.5	14517.5	44547.5
Radio & Special Analysis	965.0	1061.5	5712.5		4658.5	2513.0	5991.0	20901.5
Analytical Development	189.0	691.5	834.0	15512.0	3176.5	522.0	6854.5	27779.5
Analytical Branch	9597.5	7598.5	16297.5	21608.5	20137.0	13616.0	35594.5	124449.5
Analytical %	7.7	6.1	13.1	17.3	16.3	10.9	28.6	100.0

(a) AEC Contractors other than Phillips Petroleum Company.

(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 BRANCH IN 1964

Section	ICPP Operations	ICPP Chem. & Proc.	Plant Dev. Assistance	Analytical Development	Other PPCo.	Outside PPCo. ^(a)	Analytical	TOTAL
Spectroscopy	935	914	852	293	4494	3513	601	11602
Chemical Analysis								
Remote & Service Analysis	7286	5966	9707	18	4645	3477	8075	39174
Radio & Special Analysis	913	944	4935	30	3741	1429	323	12315
✓ Analytical Development			36		63			242
Quality Control ^(b)	117	15	4	655	142	46	6874	-
Analytical Branch	9134	7824	15530	341	12943	8562	8999	63333
Analytical %	14.4	12.4	24.5	0.6	20.4	13.5	14.2	100.0

(a) AEC Contractors other than Phillips Petroleum Company.

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

TABLE II-3

ANALYTICAL METHODS AND TIME REQUIRED FOR ANALYSIS

Method	Hours
Acid, oxalate pH titrimetric	0.33
Acid, oxalate, pH titrimetric(a)	0.38
Acid, simple volumetric	0.33
Aluminum, fluoride complexing, titrimetric	0.43
Biochemical oxygen demand	0.30
Boron, mannitol titrimetric	0.42
Carbonate, titrimetric	0.25
Cerium, radiochemical	1.67
Cesium, radiochemical	2.15
Chloride, thiocyanate titrimetric	1.00
Chromium, diphenylcarbizide, colorimetric	0.52
Chromium, redox, titrimetric	0.50
Density, bulk	0.58
Density, bulk(a)	0.62
Density, particle, mercury displacement	0.40
Density, absolute, helium displacement	0.33
Dibutylphosphate, colorimetric	0.75
Fluoride, macro, cerium trifluoride, titrimetric	1.25
Fluoride, micro, distillation, colorimetric	0.75
Gamma, spectral	1.17
Gross activity	0.56
Iodine, radiochemical	2.83
Iron, column extraction, orthophenanthroline, colorimetric	0.45
Iron, column extraction, EDTA, complexometric	0.50
Mercury, dithizone, colorimetric	0.75
Mercury, thiocyanate, titrimetric	0.42
Nickel, dimethylglyoxime, colorimetric	0.50
Nickel, dimethylglyoxime, precipitation, EDTA titration	0.58
Nitrate, Devarda alloy reduction, distillation, titrimetric	0.48
Ruthenium, radiochemical	1.75
Sample size, mass mean particle diameter, by air flow(a)	0.83
Solids, undissolved, by filtration	0.50
Specific gravity, falling drop(a)	0.50
Specific gravity, Westphal balance	0.25
Strontium, radiochemical	1.71
Tributylphosphate, acid saturation	0.50
Uranium, extraction, spectrophotometric	0.50
Uranium, extraction, fluorophotometric	0.35
Uranium, extraction, fluorophotometric(a)	0.42
Uranium, mass isotopic distribution(b)	0.67
Uranium, mass isotopic distribution(a,b)	0.67
Viscosity	0.67
Zirconium, cupferron, amperometric	1.00

(a) Method performed in Remote Analytical Facilities.

(b) Separation of uranium by solvent extraction before mass assay.

III. IMPROVEMENTS ON ANALYTICAL METHODS

The Analytical Branch continued its general effort to improve its analytical methods during 1964. Details of many of the methods described in this section can be found in Appendix B. Other method improvements which were developed for specific projects are described in Section VI.

1. SIMULTANEOUS ISOTOPIC ANALYSIS OF ALKALIES AND ALKALINE EARTHS - R. A. Nielsen

Isotopic analyses of rubidium and cesium were made on a single sample containing 1 $\mu\text{g.}$ of rubidium and 10 $\mu\text{g.}$ of cesium as chlorides, using the single-filament mass spectrometers. The sample filament temperature was carefully increased until the Rb^+ ions were observed. After they were recorded, the temperature was then increased until the Cs^+ ions could be recorded. A similar procedure was used to analyze barium-strontium mixtures. Slightly greater amounts of sample were required and the nitrates were found to be more satisfactory.

2. VOLUMETRIC DETERMINATION OF ALUMINUM - M. A. Wade, S. S. Yamamura

The routine titrimetric method for the determination of aluminum, based on the complexation of aluminate ions by fluoride followed by acidimetric titration of the released hydroxide ions with standard acid, was improved to handle a greater variety of samples. Two special procedures have been added. In one, oxalate masking is used to overcome the interference of many diverse cations including Bi(III) , Ca(II) , Ce(III,IV) , Cu(II) , Hg(II) , La(III) , Mo(VI) , Pb(II) , Th(IV) , V(V) , U(VI) , and Zr(IV) . In the other procedure, designed specifically for alumina calcine, lead phosphate, glass samples, the interference of lead and phosphate is minimized by a combination of oxalate masking for lead and the use of simulated known standards to obtain a correction factor for phosphate.

Details of the two special procedures as well as details of the general procedure are described in Appendix B, Method A1-1, Mod-6.

3. DETERMINATION OF BORON IN THE PRESENCE OF FLUORIDE - S. S. Yamamura, J. H. Sikes

Since fluoride interferes in most available procedures for the determination of boron, the removal of fluoride from boron samples by precipitation as cerous fluoride was investigated briefly. The fluoride was precipitated with a 7.5-fold excess of cerium(III) at pH 4.75 in the presence of acetate to catalyze the precipitation. The excess cerium then was removed on a cation exchange column, and the boron in the column effluent was determined alkalimetrically.

by a routine mannitol procedure. On three boron standards (4 mg. of boron) which contained fluoride at a 10:1 fluoride to boron molar ratio, the boron recoveries ranged from 95 to 98%.

4. ISOTOPIC ANALYSIS OF BORON - R. A. Nielsen, R. M. Abernathy

Sensitivity and precision of boron isotopic analyses were improved by the use of rhenium sample filaments. Rhenium does not appear to react with boric acid or borax as does tantalum, so less sample is required. Very small samples can be analyzed by first fusing sodium hydroxide on the rhenium filament and then adding the boric acid solution. Samples containing 40 μg of boron provide stable NaBO_2^+ ion beams for extended periods.

5. POTENTIAL SOURCES OF ERROR IN THE USE OF MEMBRANE FILTER PAPERS FOR GRAVIMETRIC DETERMINATIONS - S. S. Yamamura, M. A. Wade

As reported in Section VI, a membrane filtration procedure for the determination of total solids in WCF quench solutions was found to be giving erroneously high answers. Investigation of the procedure revealed two sources of error. These and other potential sources of error that may be encountered in the use of membrane filters for gravimetric determinations are discussed below.

The analytical procedure for the determination of suspended solids in the nitric acid-aluminum nitrate (WCF) solution consisted of filtering the solids onto a tared membrane (Millipore) filter, washing with ethanol, and weighing after air drying. The two observed sources of error were incomplete washing of soluble salts from the periphery of the filter paper and partial dissolution of the filter paper during the ethanol wash. Of these two, the former, which introduced a large positive bias, was more serious than the latter, which introduced a small negative bias.

In the usual filtration with membrane filters, the filter is sandwiched between a filter base and a "chimney" or reservoir. During filtration, dissolved salts are drawn by the filter into the area between the contacting surfaces of the filter base and the reservoir, and conventional washing by the addition of wash solutions to the reservoir does not remove the absorbed salts completely. These salts contribute to the weight of the filtered solids. With solutions of high salt concentrations, as in the case cited above in which the aluminum nitrate concentration was about 1M, the salt absorption on a 47-mm. diameter filter can be as much as 20 mg., which is highly significant when small amounts of solids are being weighed. Satisfactory removal of absorbed salts can be accomplished by removing the reservoir and applying the wash solution dropwise to the periphery of the filter paper.

In many gravimetric separations, particularly radiochemical separations, organic solvents are used to dry the precipitate. This may partially dissolve the filter, causing small negative errors.

There are other potential sources of error that may be encountered in the use of membrane filters for quantitative analytical filtrations and gravimetric determinations. These include:

1. Losses through adsorption of the precipitate on the surfaces of the filter holder.
2. Mechanical losses during ignition, caused by the deflagration of the membrane filter.
3. Weight changes of the filter, caused by gain or loss of water under laboratory conditions or at elevated temperatures.
4. Incomplete filtrations caused by dissolution, because of swelling, or distortion of the filter paper by acids, bases, and organic solvents.

Losses through adsorption on filter holder surfaces can be avoided by collecting the adsorbed precipitate on a piece of moistened ashless filter paper. Losses during ignition can be minimized by wrapping the membrane filter and precipitate in a conventional ashless filter paper. Proper selection of the filter paper can prevent errors caused by weight change of the filter or reaction of the filter with solvents. Many new types of membrane filters have recently been made available, and a suitable filter can usually be found.^(7,8)

6. MICRODETERMINATION OF FLUORIDE USING AN IMPROVED DISTILLATION PROCEDURE - M. A. Wade, S. S. Yamamura

The following is an abstract of a paper that is being submitted for publication in Analytical Chemistry. Details of the method are reported in Appendix B, Method F-3.

A versatile distillation-spectrophotometric measurement procedure has been developed for the determination of microgram levels of fluoride in complex inorganic samples. The fluoride

(7) Gelman Filtration Catalog 10-64, Gelman Instrument Company, Ann Arbor, Michigan.

(8) Millipore Filter Corporation, Bedford, Massachusetts.

is distilled from a phosphoric acid medium with an improved micro still and determined spectrophotometrically as the lanthanum(III)-Alizarin Complexone-fluoride complex. Comprehensive data on the effects of 42 diverse ions are included.

7. DETERMINATION OF MILLIGRAM AMOUNTS OF FLUORIDE - E. M. Fortsch, S. S. Yamamura

The pyrolysis separation, cerium(III)-EDTA complexometric titration method(9) was improved for the determination of milligram levels of fluoride. Low recoveries of fluoride in the pyrolysis can be caused by allowing the exit section of the quartz pyrolysis tube to extend too far from the furnace or by using too large a diameter tube. By substituting xylenol orange for arsenazo-cresol red, the end point of the titration was sharpened. The method, incorporating these improvements, is presented as Method F-1, Mod-3 in Appendix B.

8. EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF GOLD - W. B. Holbrook

The following is an abstract of the paper published in Analytical Chemistry(10). A detailed procedure also is presented as Method-Au-1 in Appendix B.

This method for gold is based on the extraction of the bromoaurate-tri-octylphosphine oxide complex into chloroform followed by an in situ absorbance measurement. The tolerance for both anions and cations is excellent; no common ions interfere at lower than 100 to 1 mole ratios to gold. Analysis time is 1.5 hours for a series of nine samples. The precision is better than 1% standard deviation.

9. SPECTROPHOTOMETRIC DETERMINATION OF IRON WITH 1,10-PHENANTHROLINE IN EDTA-CITRATE MEDIUM - S. S. Yamamura, J. H. Sikes

The spectrophotometric 1,10-phenanthroline procedure that was developed for the direct determination of iron in the various types of Expanded Core Facility descaling solutions (Section VI) appeared useful as a general method for iron. A comprehensive

(9) S. S. Yamamura, M. E. Kussy, J. E. Rein, Anal. Chem. 33, 1655 (1961).

(10) W. B. Holbrook, J. E. Rein, Anal. Chem. 36, 2451 (1964).

study of the effects of diverse cations and anions was therefore undertaken. This study has shown that most cations and anions do not interfere. Exceptions are silver (-5.2% bias at 200:1 silver to iron molar ratio), cobalt (serious interference even at low ratios), nickel (interferes at ratios greater than 12.5:1), and ruthenium (serious interference at low ratios).

Details of the procedure are described in Appendix B, Method Fe-5.

10. DETERMINATION OF MILLIGRAM AMOUNTS OF PHOSPHORUS - S. S. Yamamura, J. H. Sikes

The molybdivanadophosphoric acid spectrophotometric method⁽¹¹⁾ used for the determination of phosphorus in the calcine glass samples (Section VI) appeared to be widely applicable to a variety of samples. An extensive study was made of the effects of diverse ions at mole ratios several-fold higher than the ratios investigated in the published report. Results of the interference study and details of the procedure are presented in Appendix B, Method P-Color-2.

11. COLORIMETRIC DETERMINATION OF URANIUM - M. A. Wade, S. S. Yamamura

An extraction-colorimetric method⁽¹²⁾ for the determination of microgram amounts of uranium has been modified to eliminate plutonium interference. Details of the method are reported in Appendix B, Method U-Color-4, Mod-3.

In this method, uranium is extracted into hexone and determined in situ colorimetrically with dibenzoylmethane. In the original method, prior to color development, diverse ions were removed from the hexone phase by a scrub with an acid-deficient, aluminum-nitrate salting solution containing citric acid, tartaric acid, and ethylenediaminetetraacetic acid. Under these conditions, plutonium was not scrubbed out completely and introduced a positive error.

The addition of ferrous sulfamate to the scrub solution increased the scrubbing of plutonium to greater than 99.5%. A 2:1 mole ratio of plutonium to uranium can be tolerated without interference.

(11) R. E. Kitson, M. G. Mellon, Ind. Eng. Chem., Anal. Ed., 16, 379 (1944).

(12) W. J. Maeck, G. L. Booman, M. C. Elliott, J. E. Rein, Anal. Chem. 31, 1130 (1959).

IV. ELECTROANALYTICAL STUDIES (G. L. Booman)

The purposes of this project are to develop analysis methods based on electrochemical measurements and to develop a fundamental understanding of the electrochemistry of the species which are of direct concern to the atomic energy program. A detailed study of the electrochemistry of uranium is presently underway to obtain optimum measurement techniques, freedom from interferences, and the prediction of behavior in diverse chemical environments.

Generalized mathematical solutions have been obtained for the exact analysis of non-linear electrochemical processes. Reaction schemes involving the second-order disproportionation of uranium(V) are now for the first time amenable to quantitative study. The solutions were obtained by a numerical method, solving sets of up to 500 different equations simultaneously over four or more decades of normalized time in logarithmic steps.

An exact mathematical solution was obtained for potentiostatic interpretation of preceding reactions having equilibrium constants equal to or greater than one.

Digital instrumentation has been completed for measuring electrochemical signals with a full scale resolution of 0.01%, time resolution to 0.1 μ sec, automatic collection of up to 51 data points separated in time by as little as 40 μ sec, and with typewriter output of the digitized information. Transistor circuits to give high input impedance and up to 1-ampere pulse currents at 1- μ sec rise time have been constructed for evaluation with 20 mc-bandwidth operational amplifiers in a fast-pulse potentiostat circuit. A high-power, 1- μ sec response potentiostat circuit was completed using recently-designed, high performance vacuum tubes. A suitable cell was designed and constructed for microsecond response measurements.

A design procedure, using computer calculations, was developed for obtaining the stabilizing network parameters giving maximum bandwidth in 3-electrode-cell control systems and for showing the fastest response obtainable across the electrode double-layer with a given amplifier cell system.

Separation of uranium by reversed-phase partition chromatography, using trioctylphosphine oxide supported on glass beads and an acetone elution, was successfully incorporated into a controlled-potential coulometric procedure. The electrolyte used in the coulometer cell is an 80% acetone, 1M sulfuric acid solution, which permits the elimination of two quantitative pipettings as compared to procedures using conventional liquid-liquid extraction.

1. MATHEMATICAL ANALYSIS OF ELECTRODE RESPONSES

1.1 Second Order Reactions - D. T. Pence

A method has been developed for a precise numerical solution for the theoretical diffusion and kinetic currents of the second-order uranium(V) disproportionation reaction, using high speed digital computers. The method is based on a generalized approach first developed by Koutecky and Koryta⁽¹³⁾ for obtaining approximate analytical solutions to the partial differential equations describing the uranium(V) disproportionation reaction.

Development of the method involved the transformation of coordinates, derivation of a series of finite difference equations to approximate the equations describing the system, and the mathematical solution of the series of equations. The transformation of coordinates was necessary to convert the spherical system of coordinates of the hanging drop electrode to a linear coordinate system to simplify calculations. The transformation of the time coordinate to one which is a function of the rate constant, concentration of reactants, and real time, is an essential feature of the generalized approach. Because four decades of time were required to adequately follow the disproportionation reaction, a logarithmic time scale was used. By making the space coordinate dependent on $t^{-1/2}$, the concentration per unit cell remains relatively constant as the difference equations are solved for each new time step, automatically compensating for the time dependent growth of the diffusion layer.

The finite difference equations are solved simultaneously at each time interval by Gaussian elimination. The accuracy of the solution is dependent on the number of concentration cells and time intervals. The partial differential equations that are approximated by the finite difference equations exactly describe the system so the degree of exactness of solution is a function of computer time used. If a logarithmic time scale had not been used, the computational time required to obtain a satisfactory solution would have been prohibitive. The optimum number of concentration cells and time intervals needed for a given accuracy was estimated by a mathematical error analysis, and more accurately determined by computer calculations.

(13) J. Koutecky, J. Koryta, Collection Czechoslov. Chem. Commun. 19, 845 (1954).

This method is also easily adaptable to other complex reactions, both linear and non-linear. To adapt it to another second-order reaction scheme of similar mechanism, only a few boundary-dependent equations need be changed.

A plot of the ratio of the kinetic and diffusion currents versus the logarithm of normalized time provides a generalized method of data analysis which is more convenient, versatile, and exact than are the methods available for the more classical approaches. Only a few generalized curves need be obtained to allow analysis without recourse to additional calculations. This is a result of using the normalized time coordinate. Therefore, the same generalized curves may be used to analyze experimental data obtained from solutions of varying uranium concentration, acidity, and electrolyte composition. Diffusion coefficients as well as rate constants are readily obtainable using this method of analysis. The electrochemical approach is unique in that unstable species, such as uranium(V), can be generated at the same electrode which is simultaneously measuring its properties. Because part of the hanging mercury drop is shielded by the electrode support, uniform spherical diffusion around the drop is prevented. A method was developed to correct for this time-dependent shielding effect prior to the analysis of the experimental data.

1.2 Preceding Reactions - G. L. Booman

The theoretical equations for a preceding reaction were extended from the work of Koutecky and Brdicka⁽¹⁴⁾ to the cases where the equilibrium constant is equal to or greater than one. For $K = 1$; the ratio of kinetic to diffusion current has been found to be:

$$\frac{i_k}{i_d} = \frac{1}{2(k_f + k_b)t} \left[e^{-(k_f + k_b)t} - 1 \right] + 1$$

For $K > 1$, this ratio is:

$$\frac{i_k}{i_d} = \frac{K}{K^2 - 1} \left\{ K - e^{-mt} - \frac{2\sqrt{mt}}{\sqrt{K^2 - 1}} \left[K e^{-mt} - 1 \right] e^{-\frac{K^2 mt}{K^2 - 1}} \int_0^{\sqrt{\frac{K^2 mt}{K^2 - 1}}} e^{\lambda^2} d\lambda \right\}$$

(14) J. Koutecky, R. Brdicka, Collection Czechoslov. Chem. Commun. 12, 337-55 (1947).

where $m = k_f + k_b$

Satisfactory numerical checks were made on these two equations. These equations will provide the ability to recognize and interpret potentiostatic current-time curves for cases in which the current is significantly controlled by a slow liberation of the electroactive species from a non-electroactive complex.

2. INSTRUMENT DESIGN

2.1 Electroanalytical Fast Data Logger - G. L. Booman

An instrument for the rapid digital recording of electrochemical signals has been completed by the Instrument Development Group (K. D. Smith) and placed in operation. The basic components consist of an analog sample-and-hold circuit with a sampling time uncertainty of less than $0.1 \mu\text{sec}$, and a 0.01% analog-to-digital converter with a $40\text{-}\mu\text{sec}$ conversion time. The digital number corresponding to the cell current is stored in a ferrite-core buffer memory capable of storing 51 4-digit plus sign numbers at a rate of one word every $50 \mu\text{sec}$. The sampling schedule is controlled by digital timing circuits, made of standard plug-in modules, which can be placed in either a linear or quasi-logarithmic mode. When the memory is full or the experiment complete, the stored data are automatically typed on the data sheet. The circuitry uses transistors exclusively.

This new equipment will eliminate the slow and tedious oscilloscope photographic method previously used, greatly improve the experimental precision and accuracy, increase the consistency of the data through the high resolution available, and allow the study of a much larger number of variables than was possible before.

2.2 Electroanalytical Potentiostat Modification - G. L. Booman

Solid-state input and output stages for a transistor, operational-amplifier potentiostat circuit were completed by the Instrument Development Group (Kent Smith). These components were designed for pulse measurements at response times as short as $1\text{-}\mu\text{sec}$. The input stage uses a field-effect transistor to give high input impedance. The output stage uses recently-developed, high-speed, core-driver transistors to produce peak output currents as great as 1 ampere.

Construction of a fast potentiostat circuit using four Eimac 4CX350A vacuum tubes as the primary control circuit was completed. An electrochemical cell for fast response measurements was constructed and tested. Cell design features include: an optically-flat, 2-cm diameter window which permits microscopic observation of electrode placement with solution present; a micro, platinum-wire reference probe which overcomes capacitive errors of salt bridge probes; a very short lead from the hanging mercury drop electrode to the grounded cell support plate which gives the necessarily low lead inductance for sub-microsecond measurements. Stable closed-loop performance with 1-mc. bandwidth was shown using the cell-controller system with an electrolyte of 1M sulfuric acid. Final circuit optimization can now be done with actual cell conditions.

2.3 Transistor Polarograph Design for Optimum Response - W. B. Holbrook

A project has been completed in which the objective was to develop a simple and reliable method for designing a stable polarograph circuit using a 3-electrode electrochemical cell. A circuit using a 3-electrode electrochemical cell makes possible the use of experimental techniques and the collection of data which would be very difficult, if not impossible, to obtain using a 2-electrode electrochemical cell. It was theorized that optimum circuit component values could be determined which would give maximum bandwidth and would simplify electrochemical cell design in a manner significantly different from presently accepted theory.

Methods for obtaining stability in 3-electrode circuits have been reported. However, the selection of optimum circuit component values, considering the polarograph cell combination, has not.

The optimum component values were determined by analysis of the polarographic circuit. Mathematical formulas were derived for this analysis. A FORTRAN-IV program for the IBM-7040 computer was written based on these formulas. A series of optimum circuit component values was calculated and tabulated for a variety of cell and circuit component characteristics.

A transistor polarograph, previously constructed, was modified using the calculated data for the component values. The response and stability of this instrument substantiated the calculated data.

The tabulated optimum circuit component values, with associated related data, will give the conditions for maximum effective bandwidth and control accuracy, and will simplify the electrochemical cell design. These conditions can be determined without tedious, time-consuming calculations.

A paper describing this work has been prepared and submitted for journal publication.

3. CONTROLLED-POTENTIAL COULOMETRIC DETERMINATION OF URANIUM -
W. B. Holbrook

The controlled-potential coulometric method for uranium⁽¹⁵⁾, pioneered in this laboratory, is the most highly precise method for milligram levels. However, it is subject to diverse ion effects and requires a preseparation of the uranium for most samples.

The procedure⁽¹⁶⁾, previously developed in this laboratory and now in routine use, is lengthy, involving an extraction of the uranium into an organic phase, separation and evaporation of an aliquot of the organic phase, and a fusion to remove the last traces of organic matter which interferes in the coulometric determination. Also, three quantitative pipettings are required: the sample aliquot, the added organic solvent, and the aliquot of the organic phase. This is followed by a quantitative transfer from the fusion tube to the coulometric cell. A faster procedure and one that would require only one quantitative pipetting, the sample aliquot, would be to separate the uranium on a reversed-phase chromatographic column (one of the newer separation techniques), elute with an organic solvent, and coulometrically analyze the organic eluate.

Trioctylphosphine oxide (TOPO)^(17,18) was selected as the uranium-complexing agent to be suspended on the inert support of the reversed-phase chromatographic column, and sulfuric acid^(15,16) was chosen as the electrolyte to be mixed with the organic eluate for the coulometric analysis. About 12 organic solvents were selected for evaluation as the eluting agent. Criteria for their selection were high solubility for TOPO, miscibility with sulfuric acid, and stability (no formation of coulometrically-interfering degradation products) when

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- (15) G. L. Booman, W. B. Holbrook, J. E. Rein, Anal. Chem. 29, 219 (1957).
(16) G. L. Booman, W. B. Holbrook, Anal. Chem. 31, 10 (1959).
(17) J. W. O'Laughlin, C. V. Banks, U. S. Atomic Energy Commission Rept. IS-737, 1963.
(18) J. C. White, W. J. Ross, U. S. Atomic Energy Commission Rept. NAS-NS-3102, 1961.

mixed with sulfuric acid. The evaluation was made by studying the polarographic waves of uranium in sulfuric acid mixtures of these solvents using the transistor polarograph described in the previous section. Five solvents, acetone, methanol, ethanol, p-dioxane, and acetonitrile were found to be satisfactory. The system adopted was a mixture of 4 volumes of acetone and 1 volume of 2.5M sulfuric acid. The acetone, reagent-grade, was purified of trace impurities which give high and erratic residual currents. The purification consisted of an agitation with freshly-precipitated silver oxide, removal of water by contact with anhydrous sodium sulfate, filtration, and distillation.

The overall procedure, with 1-mg. aliquots of a uranium standard, was found to be highly precise with a relative standard deviation of better than 0.1%. The effects of diverse ions, especially nuclear fuel alloy constituents and fission products, are being determined.

V. IMPROVEMENTS ON EQUIPMENT

1. REMOTELY OPERATED EQUIPMENT

1.1 High-level Analytical Facilities - F. W. Dykes

The decision to modify existing remote facilities to serve the chemical analysis needs of the LOFT program indicates that approval of a high-level, general-purpose analytical facility will not be forthcoming in the foreseeable future. Consequently, the emphasis has been changed to providing facilities for specific projects by either constructing small remote facilities in existing buildings or modifying existing facilities. An Analytical Alpha Facility (AAF) has been proposed for installation in the basement of the building that houses the Analytical Branch. This facility would be used by the Remote and Service Analysis group for work with high alpha and moderate gamma activity. A preliminary proposal also has been made to remodel a portion of the Remote Analytical Facility to provide greater versatility for non-routine work.

1.2 Canning of Solid Radioactive Waste - F. W. Dykes

The canning of solid radioactive waste has reduced contamination in the Remote Analytical Facility. This method was used in the disposal of samples obtained from calcined Idaho Chemical Processing Plant waste. It is a cleaner method for handling solid waste materials, and as soon as equipment can be installed all solid radioactive waste will be handled in sealed cans.

1.3 Remote Collection of Fission Product Gases - L. L. Dickerson, R. M. Abernathey

The gas collection apparatus which was in use at ARA before shutdown was remodeled and set up at MTR Hot Cell. A new Toepler pump and McLeod gauge were installed and a rough vacuum manifold was assembled with silver solder joints, since mercury had attacked the old soft solder joints. Another apparatus was assembled at the TAN Hot Cell. Remote punches are set up at both locations. Highly radioactive fuel capsules have been punched and the gases collected and measured at both locations. The volumes of both systems have been calibrated with a precision of 0.3%.

2. COUNTING EQUIPMENT

2.1 Low Beta Counter - A. C. Hill, J. G. Scott

A new Beckman (Sharps) Low Beta II Instrument is in operation in the Special Analysis counting room. The instrument

has an automatic sample changer, an anticoincidence circuit and a shielded five inch detector. The instrument background count is approximately three counts per minute, and the efficiency is better than 50% with a one inch Sr^{90} source. The instrument is adaptable for counting alpha activity also.

2.2 Multichannel Analyzer - A. C. Hill, J. H. Scott

A new Nuclear Data Model 180 FMR, 512 Channel Analyzer was put in service near the latter part of the year. It is equipped with a Tally punch tape and an IBM typewriter. The new analyzer can be used interchangeably with the Model 131 analyzer on any of the detection systems. These now provide a very complete and extensive counting system.

2.3 Teflon Insert for Well Crystal - A. C. Hill

A 3" x 3" NaI(Tl) well crystal was lined with a specially fabricated Teflon insert. The insert is used as a protective measure to prevent damage to the crystal. It has not changed the efficiency of the detection system and has proven effective in preventing corrosive materials from contacting the crystal. It also makes decontamination of the system much easier.

3. MASS SPECTROMETERS

3.1 Revision of Focus Voltage Power Supplies of Surface Ionization Mass Spectrometers - R. A. Nielsen, J. P. Morgan

The focus voltage power supplies of both surface ionization mass spectrometers were revised to improve stability and reduce maintenance. The circuits were simplified by substituting a battery and potentiometer for a much more complicated supply using a cathode follower and a 10-position switch, both of which required excessive maintenance. Instrument down time has been reduced and stability of ion beams has been improved.

3.2 Problems Encountered in the Startup of the Tandem Mass Spectrometer - R. M. Abernathey, G. V. Wheeler, A. H. Toepfer, G. D. Workman, R. E. McAtce

During the startup of the Nuclide TDD-1 mass spectrometer, several defects were encountered which required correction before the instrument was serviceable. The most serious defect was in the electron multiplier detector. When set up to give an output current greater than about 10-10 amps, the multiplier rapidly lost gain, as much as 20 to 30% in a few minutes. When the ion beam was reduced, the gain gradually recovered. The multiplier power supply was rebuilt and then finally replaced. The multiplier was returned to the factory and overhauled, but no improvement was noted. It was then replaced with a new one which has been completely satisfactory.

The magnetic scanning circuits did not provide enough variation in scanning speed for the range of masses encountered in the burnup program, so these were revised to provide scanning speeds of 2.5 to 10% of the atomic mass per minute.

A digital voltmeter was installed and the accelerating voltage supply circuit was revised to provide a stable reference point for measuring the voltage. An accurate voltage measurement combined with a magnetic field strength measurement by nuclear magnetic resonance enables the operator to locate and identify masses exactly.

Tracking of the two magnets was found to be much better than expected, so that magnetic scanning can be used even in tandem operation. This reduces mass discrimination nearly ten times by measuring all beams at the same energy. No mass discrimination was observed when a NBS uranium standard was analyzed by direct collection. Multiplier mass discrimination was therefore evaluated by comparing direct collection data with multiplier data from mass 85 to 240. The discrimination was found not to be linear with mass (m) or with $\sqrt{m}$, and it was concluded that it must be measured for each mass interval of about 10%.

Impurities in filament material have been a serious problem. Several materials have been examined, and rhenium generally has given least interference. Strong ion beams are observed from the impurities K, Rb, Cs, Ca, Sr, Ba, Mo, and Nb. A vacuum bakeout chamber was constructed for pre-treatment of sample filaments. It reduces but does not eliminate the extraneous ions.

Sample preparation procedures, instrument operating conditions, and sample size requirements were established for Pu, U, Am, Sm, Nd, Zr, and Ru and for U-Pu mixtures. About 1 μg is required for Zr and Ru and for U in the presence of Pu, but 0.1 μg is sufficient for the others.

X-RAY DIFFRACTOMETER

4.1 Sample Cask for Shielded X-ray Diffractometer - W. A. Ryder

A special sample cask for transporting prepared samples to and from hot cell facilities was designed and constructed for use with the shielded X-ray diffractometer. The cask permits the sample to be loaded directly into the instrument without exposing personnel to the sample radiation. It provides 2-3/4 inches of lead shielding.

5. INFRARED SPECTROPHOTOMETER

5.1 ATR Accessory for Infrared Spectrophotometer - L. L. Dickerson, R. M. Abernathey

Infrared analytical capabilities have been extended to include certain non-transparent materials. The new equipment is a Perkin-Elmer Attenuated Total Reflectance accessory for the PE-21 infrared spectrophotometer. The system produces a spectrum similar to an absorption spectrum by measuring the attenuation of infrared radiation reflected from the interface between the sample and an appropriate crystal near the critical angle. Three such successive reflections are made from three portions of a sample, each about 1 x 10 mm. Since only the surface is involved, the sample material need not be transparent to obtain a spectrum. This accessory is particularly useful for such materials as rubber and other plastic materials that cannot be pressed into a thin film, sliced, or ground and pressed in potassium bromide.

6. DECONTAMINATION OF GLASSWARE - I. L. Doggett, E. M. Fortsch

Various laboratory detergents, acids, and commercial decontaminating solutions were tested to develop a glassware decontamination procedure. The solutions were: 1M tartaric acid, 1M nitric acid, Wasco decontaminating reagent, Sparkleen laboratory detergent, Green detergent, Fisher's RPS-25 solution, and 4502 Turco with an oxalic acid rinse. The most successful procedure proved to be soaking glassware in a near boiling solution containing one part of 4502 Turco to 100 parts of water for 20 minutes, and then rinsing it with oxalic acid. Highly contaminated glassware can be decontaminated almost to background levels of activity. Most decontaminated glassware can be reused except in radiochemical analyses of low levels of activity.

VI. ANALYTICAL SERVICES

Some of the unusual services provided by the Analytical Branch during 1964 are described in this section of the report. The number and source of determinations made by established procedures can be found in Table II-2, but no description of these has been provided. Details of new procedures developed in order to provide some of the services described in this section can be found in Appendices B and C.

1. ELECTRIC BOAT COMPANY

The Electric Boat Company at the Naval Reactor Facilities evaluated several crayons and inks as markers to identify materials used in the construction of atomic-powered submarines. A knowledge of the composition of these markers was necessary to determine if they contained substances that were either toxic to personnel or poisonous to the reactor. As part of the program, EBC requested that crayons and inks be analyzed for total halogens, lead, phosphate, and sulfur.

1.1 Determination of Lead - M. A. Wade

Because of unknown sample composition, the requirements of a method for the lead analysis were high specificity and high sensitivity. A combination of two dithizone extraction-colorimetric procedures for lead(19,20) met these requirements. High specificity was obtained through masking and through selective extractions at controlled pH. The sensitivity inherent in the colorimetric method of measurement permitted the determination of lead at the 100-ppm level as requested. Details of the analytical procedure are discussed below.

The lead is extracted into a dithizone-carbon tetrachloride solution from a citrate-cyanide masking medium at pH 10. Under these conditions, bismuth is known to coextract with the lead. Thus, to guard against bismuth interference, the lead is stripped into dilute nitric acid, and contacted at pH 2 with a dithizone-carbon tetrachloride solution which is subsequently discarded. Finally the lead in the aqueous phase is reextracted at pH 10 and measured spectrophotometrically at 520 m μ . The absorbance of the red lead-dithizonate complex is linear with concentration over the range of 3 to 20 μ g. of lead.

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- (19) C. J. Rodden, ed., Analytical Chemistry of the Manhattan Project, p. 379, McGraw-Hill, New York (1950).
- (20) E. B. Sandell, Colorimetric Determination of Traces of Metals, p. 555, Interscience, New York (1959).

1.2 Determination of Total Halogens - M. S. Anderson

In the analysis of total halogens, the sample was decomposed and the halogens were oxidized to the free state by successive oxidations with fuming sulfuric acid, potassium persulfate, and chromic acid or potassium permanganate. The free halogens were removed by distillation and passed into an absorber where they were reduced to the halides by sodium arsenite. The halides were precipitated with a measured excess of silver nitrate, filtered, washed, dried, and weighed. The excess silver nitrate in the filtrate and washings was titrated with potassium thiocyanate. Details of the method are given in Appendix B, Method Hal-1.

2. GENERAL ELECTRIC

2.1 Determination of Indium in Indium-Aluminum Alloys - S. S. Yamamura

In the 710 Reactor Program at General Electric, indium-aluminum alloy foils containing 5 to 10 weight per cent indium are used to measure the resonance flux in the reflector. Samples of foils were submitted for indium analysis to establish the actual indium content and to determine its homogeneity.

A direct X-ray fluorescence measurement of the indium was not feasible because the foils were not "infinitely thick" and the foil thickness varied from sample to sample. Dissolution and X-ray fluorescence measurement of the solutions also was unsatisfactory due to inadequate precision. A chemical method therefore was developed. The following is a brief description of the procedure:

The alloy sample was dissolved in hydrochloric acid, then evaporated to near dryness to remove excess acid. The residue was dissolved in water, and indium was separated as the sulfide at pH 2.5 to 4. After digesting the sulfide precipitate with nitric and perchloric acids, indium was determined by adding an excess of equimolar cerium(III)-EDTA and titrating the cerium(III), liberated in an amount equal to the indium, at pH 5.5 to 6 with EDTA to a xylenol orange end point.

Because a small amount of aluminum was occluded by the indium sulfide precipitate, sulfosalicylic acid was added to mask the aluminum. However, the aluminum still reacted slowly and irreversibly with the xylenol orange indicator, and it was necessary to titrate immediately after pH adjustment and take the first permanent color change from reddish purple to yellow as the end point.

The method was evaluated with known mixtures of 11.64 and 17.46 mg. of indium(III) and 100 to 200 mg. of aluminum(III). The recoveries of indium ranged from 99.7 to 100.2%.

2.2 Preparation of Fission Foils of Electrodeposits of Heavy Elements - M. E. Kussy, W. J. Maeck

A series of 1-inch diameter, highly-polished, stainless steel plates was plated with electrodeposits of thorium, uranium-233, uranium-235, neptunium-237, plutonium-239, plutonium-240, and plutonium-241. For each isotope, two plates, each containing about 100 µg. of the isotope, were prepared. The amount deposited was established by adding a known amount of the isotope to the electrolysis cell and analyzing the electrolyte after completion of the electrolysis. The electrolysis conditions for the four elements are summarized in Table VI-1.

TABLE VI-1. ELECTROLYSIS CONDITIONS FOR PREPARATION OF HEAVY ELEMENT FISSION FOILS

<u>Element Deposited</u>	<u>Electrolyte</u>	<u>Current, Amperes</u>	<u>Time of Electrolysis, Hours</u>	<u>Percent Plated</u>
Thorium	50% Ethanol 45% Acetone 5% 2M HCl	0.15	5.25	90
Uranium	0.15M Ammonium Formate - 0.2M Formic Acid	0.15	5.0	99
Neptunium	Same as Uranium	0.4	5.0	99.9
Plutonium	Same as Uranium	0.15	5.0	90

2.3 Cleaning of Fouled Metal Samples - I. L. Doggett, C. M. Wilcox

Irradiated metal samples fouled with a flocculant material of unknown composition were cleaned using an ultrasonic apparatus (Sonblaster). A dual reservoir system was used to prevent contamination of the ultrasonic apparatus. The outer reservoir was filled with water and the inner removable plastic one contained the sample and the cleaning liquid. Some samples were cleaned remotely, because of the radioactivity level, using water in both reservoirs. Others of a lower radioactivity level were cleaned in a hood behind a lead brick barricade using water in the outer and ethanol in the inner reservoir. Either of these techniques appears to be satisfactory for cleaning objects.

3. WESTINGHOUSE EXPENDED CORE FACILITIES

In the last quarter of calendar year 1963, Westinghouse Expanded Core Facilities began an extensive evaluation of various solution mixtures for descaling (removing the crud from) zirconium-clad fuel elements and requested the services of the Analytical Branch⁽²¹⁾.

During calendar year 1964, a large number of crud solutions were submitted for the analysis of selected elements and radio-nuclides. Also, a number of descaling make-up solutions were submitted for the analysis of their principle constituents. Satisfactory analysis procedures were not available for most of the requested analyses.

3.1 Determination of Chromium, Cobalt, Iron, Manganese, Nickel, and Principal Constituents of Descaling Makeup Solutions - S. S. Yamamura, J. H. Sikes, M. A. Wade

Extensive development studies resulted in the development of suitable procedures for:

1. The digestion and concentration of crud solutions and dissolution of crud solution solids.
2. The determination of chromium, cobalt, iron, manganese, and nickel in crud solutions.
3. The determination of oxalic acid, acidity, potassium permanganate, sodium hydroxide, diammonium citrate, EDTA, and hydrazine in make-up solutions.

Details of the procedures are given in Appendix B, ECF Methods-1, Mod-1.

3.2 Spectrochemical Determination of Nickel in Alkaline Permanganate Solutions - G. W. Dickinson

An emission spectrographic method was developed for analyzing alkaline permanganate solutions for sub-microgram quantities of nickel. One milliliter of filtered solution with vanadium internal standard added is evaporated to dryness. The resulting solids are mixed with graphite, placed in a graphite electrode and excited by the dc arc. Nickel can be determined down to 0.1 µg./10 mg. of solids.

(21) R. C. Shank, et.al., Annual Report of Division Analytical Branch for 1963, IDO-14636, Section III-20, p. 46 and Appendix B, (June, 1964).

3.3 Determination of Mn⁵⁴, Co⁵⁸⁻⁶⁰, and Fe⁵⁹ - M. S. Anderson

A method was developed for the separation of manganese, cobalt, and iron in decontamination solutions from the Expended Core Facility. It was successfully used on oxalic-nitric acid solutions, ethylenediaminetetraacetic acid-hydrazine solutions, and basic permanganate solutions. The elements are separated by anion exchange and determined by gamma ray spectroscopy. Details of the method are given in Appendix C.

4. AEROJET GENERAL NUCLEONICS

4.1 Spectrochemical Determination of Wear Metals in Lubricating Oils - K. R. Arnold

An ASTM suggested method⁽²²⁾ for the determination of wear metals in lubricating oils by the rotating platform electrode technique was investigated. It was found to be ten to thirty times more sensitive than the rotating disk uni-arc methods used previously. A calibration was completed and the method is being used to examine ML-1 lubricating oils.

5. WASTE CALCINING FACILITY

The Analytical Branch has provided a wide variety of services to both the Chemical and Process Development Branch and the Chemical Processing Plant Operations Branch in support of the program for the calcination of radioactive wastes. Analytical data have been used in the development of calcining processes and also in evaluating the performance of the Waste Calcining Facility (WCF).

5.1 Analysis of Calciner Product

5.1.1 Remote Determination of Bulk Density and Particle Size of WCF Product - F. O. Cartan

Procedures and apparatus for the remote determination of bulk density and particle size were developed specifically for WCF product. Bulk density is determined by weighing a sample whose volume is determined "as poured." The particle size is measured with an air elutriator. An empirical equation relating the average particle diameter, the air flow, and the bulk density has been obtained by calibration with known samples. Details of the procedures are reported in Appendix B, Method Calciner Product 2.

(22) Methods for Emission Spectrochemical Analysis, p. 633-638, American Society for Testing Materials, Philadelphia, Pennsylvania (1960).

5.1.2 Remote Analytical Apparatus - F. W. Dykes

The remote analytical apparatus that had been installed last year⁽²³⁾ for the analysis of calciner product operated very satisfactorily during the 10-month hot run of the WCF. The only deficiencies were connected with the remote balance. The chain drive for the balance-pan conveyer broke down several times. A slight instability of the balance was traced to air currents caused by an imperfectly-sealed isolation door.

5.2 Analysis of Off-Gas Samples

5.2.1 Radiochemical Analysis of Off-Gas Filters - A. C. Hill, G. I. Anderson, J. R. Fischer, T. R. Thomas, J. H. Goettsche, D. E. Filion

Radiochemical analysis of off-gas filter samples from the Waste Calcining Facility required adaptation of standard counting techniques. The polyethylene chips used as ruthenium adsorbers were too radioactive to be counted as one unit. The activity was not distributed evenly on the material, therefore the sample had to be divided into sections suitable for counting. As many as thirty sections were required to obtain total ruthenium activity on one adsorber. By obtaining geometries outside of the detection barricade for containers 3" long and 1/2" in diameter, the number of sections for one sample was reduced from thirty to four.

Millipore filters from the waste calcining process gas streams were dissolved in nitric acid and chemically analyzed for radioactive isotopes. Analysis before and after dissolution showed less than ten percent loss of ruthenium during dissolution of the filters. The asbestos filters from this same system were leached with hot nitric acid to remove the activity. The solution was then filtered and analyzed. The asbestos was checked for residual activity which was found to be insignificant compared to the activity in the leach solution.

5.2.2 Analysis of Scrub from WCF Silica Gel Columns for Ruthenium Species - E. M. Fortsch, J. E. Rein

Samples of the scrub solutions from the WCF silica gel columns were examined for ruthenium chemical species identification. Spectrophotometric scans were made from the water cutoff in the near infrared through the nitrate absorbance band at about 320 mμ. A simulated matrix,

(23) R. C. Shank, et. al., Annual Report of Division Analytical Branch for 1963, IDO-14636, Section III-2.1, p. 10 (June 1964).

containing aluminum and mercury nitrates and nitric acid equivalent to the sample, was used for comparison. The only significant spectrum attributable to ruthenium was a continuously rising absorbance starting at about 550 mμ. and blending into the nitrate absorbance at about 320 mμ. This spectrum had no peaks corresponding to the +6, +7, and +8 valence states of ruthenium.

In an attempt to identify the species responsible for the spectrum, a solution of RuCl_3 was added to the simulated matrix and spectrophotometrically examined. The spectrum was similar to that of the samples. Of significance is the fact that when the RuCl_3 was added to the matrix, a color change was observed. This is believed to have been caused by either nitrate complexing or by partial oxidation to Ru(IV) . This finding and the fact that no +6, +7, or +8 species were observed indicate that ruthenium in the sample is in an oxidation state no higher than +4, and probably exists as a nitrate complex.

It is not to be concluded from this study that oxidation states higher than +4 could not have been present on the silica gel columns. In acid medium, especially with traces of a reducing impurity present, RuO_4 is reduced to +4.

5.2.3 Determination of Oxides of Nitrogen in WCF Off-Gas - F. W. Dykes, S. S. Yamamura

Competitive adsorption of oxides of nitrogen on silica gel adsorber beds in the WCF off-gas stream has been postulated as a reason for the erratic release of ruthenium from the beds. To investigate this hypothesis, a method for the determination of total nitrogen oxides in WCF off-gas samples was required. Since the samples contained condensed water in which the oxides are soluble, existing infrared and mass analysis techniques applicable only to the gas phase were not suitable. The development of a chemical procedure was therefore investigated.

The method of Johnson⁽²⁴⁾ appeared suitable for the determination of total nitrogen oxides in WCF off-gas. Johnson used neutralized hydrogen peroxide to convert nitrogen oxides, except N_2O , to nitric acid which then was titrated with sodium hydroxide. Because of its convenient availability in pressurized cylinders, the

(24) C. L. Johnson, Anal. Chem. 24, 1572 (1952).

use of oxygen was thought to be superior to the use of hydrogen peroxide solutions which required special preparation.

The modified procedure using oxygen was tested with standard NO₂ samples prepared by the thermal decomposition of known amounts of lead nitrate. For 7 determinations, the mean recovery was 99.6% and the relative standard deviation was 0.55%, both satisfactory. However, the presence of condensed water vapor in the samples made it impractical to obtain pressure and volume measurements; consequently it was not possible to relate the analytical results to the off-gas stream composition. The only answer obtainable was the total nitrogen oxides in the sample, rather than the percentage concentration of the oxides in the off-gas.

The corrosion-resistant gas pressure gauge of Cartan and Brinkley⁽²⁵⁾ is recommended for pressure measurements of gaseous samples of nitrogen oxides analyzed by this procedure. The corrosive nature of nitrogen oxides prohibits the use of ordinary mercury manometers. Experience at this laboratory indicates also that nitrogen oxides are soluble to some extent in liquids that have been recommended to isolate the mercury column from the sample.

5.3 Calcination of Zirconium Fuel Wastes

The calcination of zirconium fuel wastes involves the addition of calcium nitrate to zirconium waste solutions to complex fluoride, followed by calcination under the established conditions for aluminum fuel wastes. In support of this program, the Analytical Branch was asked to analyze selected flow streams for specified components. In addition to existing routine procedures, some new analytical methods were required.

5.3.1 Dissolution Procedures and Determination of Aluminum, Fluoride, and Calcium - M. A. Wade, S. S. Yamamura, J. H. Sikes

Procedures were needed for the dissolution of product samples and of the calcium fluoride precipitate in the feed samples. The calcined product was fused with a mixture of sodium carbonate and sodium borate, and the melt was dissolved in hydrochloric acid. The addition of calcium nitrate to the zirconium feed caused a delayed precipitation of calcium fluoride. This precipitate was soluble in hot concentrated hydrochloric acid.

(25) R. C. Shank, et. al., Annual Report of Division Analytical Branch for 1963, IDO-14636, Section III-16, pp. 39-41 (June, 1964).

Aluminum was determined by a routine titrimetric procedure based on an acidimetric measurement of hydroxyl ions released from aluminate ions by the addition of fluoride. Samples containing fluoride were first fumed with perchloric acid. Calcium interference was removed by oxalate complexing. Details of the method are reported in Appendix B, Al-1, Mod-6.

Fluoride was determined by an available colorimetric procedure following separation by an improved micro steam-distillation method. Fluoride was separated from metal ions by steam distillation from a phosphoric acid medium using a micro still and an air sweep. Details of the method are given in Appendix B, F-3.

For the analysis of feed samples, calcium was first precipitated as the oxalate and then determined either gravimetrically as the carbonate or titrimetrically with permanganate. Excellent agreement was obtained between the two methods.

5.3.2 Spectrochemical Determination of Calcium and Zirconium - T. R. Lyon, V. R. Olson, W. A. Ryder.

The borax fusion technique for the X-ray spectrographic analysis of powders was investigated for use in determining calcium, zirconium, and aluminum in calcined zirconium wastes. Results showed that calcium and zirconium could be determined with a relative standard deviation of about 2.5%. Aluminum could not be detected in the samples because of its weak characteristic radiation and the large dilution of the sample with the fusion material. Particle size differences among the product, fines, and standards made the direct analysis of pelleted samples unsatisfactory.

Because of the large sample load, product samples and scrub fines samples were analyzed for calcium primarily by X-ray fluorescence. At the outset, a series of product samples was analyzed by both the titrimetric and X-ray fluorescence procedures. The results obtained by the two methods agreed within 10%, the requested level of reliability.

5.4 Pilot Plant Calcination of Second- and Third-Cycle Waste

Sodium nitrate in the second and third cycle waste solutions fuses and cakes the calcine bed so that the required fluidized condition cannot be maintained. Sugar (sucrose) was added to destroy the nitrate. The Analytical Branch made a study of the interference of sugar in the methods used to analyze second- and third-cycle wastes and developed a method

for the analysis of sucrose. Development of a method for the determination of total organic carbon was begun.

The presence of phosphate in second-cycle waste solutions also made it necessary to study the interference of phosphate in the routine analytical methods for the determination of mercury and boron.

5.4.1 Effect of Sucrose on Analytical Methods - D. M. Lund, H. A. Shogren, F. A. Duce, D. N. LeMaire

A study to determine if sugar interfered with the analytical methods used in analyzing second- and third-cycle wastes was conducted by spiking standard samples with sucrose and comparing the analytical results with those obtained from unspiked standards. Methods⁽²⁶⁾ listed below were studied.

1. "The Potentiometric Determination of Free Acid in the Presence of Hydrolyzable Ions," H⁺Pot-4, Mod-5.
2. "Titrimetric Determination of Aluminum," Al-1, Mod-5.
3. "Colorimetric Mercury Determination," Hg-1, Mod-5.
4. "Kjeldahl Determination of Nitrates," NO₃-1, Mod-3
5. "Volumetric Determination of Sulfate," SO₄-2.

Low absorbance values were obtained in the colorimetric mercury method. These were resolved by increasing the nitric acid boil down time until clear solutions were obtained. All other methods were satisfactory without modification.

5.4.2 Determination of Sucrose in CPP Waste Solutions - M. A. Wade

An established procedure⁽²⁷⁾ for the determination of sucrose was adapted successfully. The sucrose is first

(26) M. J. Shepherd, Jr., J. E. Rein, eds, Manual of the Analytical Methods Used by the Control Laboratory at the Chemical Processing Plant. Parts I and II, IDO-14316 (January 1955). Supplement 1 (November 1956). Supplement 2 (March 1957). Supplement 3 (October 1957).

(27) J. H. Lane, L. Eynon, J. Soc. Chem. Ind. 42 463 (1923).

hydrolyzed with dilute hydrochloric acid to the reducing sugars, dextrose and levulose. The sum of dextrose plus levulose then is determined by redox titrimetry using copper(II) in an alkaline tartrate medium.

In perfecting this method for the feed samples, several observations of interest to the calcine process have been noted. First, the sucrose is essentially completely hydrolyzed in the feed to dextrose and levulose. This fact probably explains why the nitrate is destroyed so effectively. Second, there is a slow decomposition of the hydrolyzed sugar in the feed as evidenced by a decrease in the sugar concentration and the appearance of a white precipitate in 2 to 4 days. Third, the addition of the specification level of sucrose to the feed, 238 grams to 1 liter, increases the volume by $11 \pm 1\%$.

5.4.3 Determination of Total Organic Carbon - S. S. Yamamura

A knowledge of the organic content of second-cycle, CPP waste is needed to prepare appropriate synthetic waste solutions for pilot plant studies of the effect of organic substances on the Waste Calcining Facility performance. The development of a method was therefore requested for the determination of total organic carbon, at an estimated concentration of 50 ppm, in the second-cycle waste.

Because only a few samples were to be analyzed, it was hoped that a method reported in the literature could be adapted. Only one method(28), developed at Oak Ridge National Laboratory, seemed feasible. But upon contacting I. B. Rubin(29), developer of the method, it was learned that extensive modifications would be required to handle the second-cycle waste samples. The method involved an ignition to carbon dioxide in a conventional carbon-hydrogen combustion train, freeze-trapping, copper reduction of nitrogen oxides, and gas chromatographic analysis. Mr. Rubin also stated that the method was no longer in use and that the apparatus had been partially dismantled so that a study by ORNL was not practical.

(28) M. T. Kelley, et. al., ORNL-3537, pp. 18-20, 1964.

(29) I. B. Rubin, Private Communication to J. E. Rein, October, 1964.

The time authorized for the development studies was 1 man-month. Therefore, rather than attempting to modify the ORNL method, which was known to require considerable experimentation and calibration, the development of a less-complicated method was decided upon. This new approach consisted of three basic steps:

1. Conversion of the organic carbon to carbon dioxide in a conventional carbon-hydrogen combustion furnace.
2. Separation, if necessary, of the carbon dioxide from the nitrogen oxides resulting from the thermal decomposition of nitrate.
3. Determination of the isolated carbon dioxide by an indirect colorimetric procedure.

The conversion of organic carbon to carbon dioxide was studied only briefly using a dilute aqueous solution of citric acid as the source of organic carbon. The combustion train was of the conventional type and contained, in the direction of the oxygen flow, a source of oxygen, an Ascarite tube to remove carbon dioxide from the oxygen, a sulfuric acid bubbler-tube, flow-rate indicator, a 20-inch x 1-inch i.d. quartz combustion tube with a 12-inch packing of a 2:1 mixture by weight of cupric oxide and lead chromate, and finally, an absorption tube for the carbon dioxide. A Meker burner, moved along by hand, was used as the preburner, and a 12-inch split furnace maintained at 700°C was used as the stationary furnace. In the absence of nitrate, conversion of the citric acid to carbon dioxide was confirmed, but with citric acid samples to which nitrate was added, the conversion of the organic carbon to carbon dioxide was not confirmed. In both cases, the gas from the combustion furnace was adsorbed in ammoniacal ethanol and treated with barium to test for carbonate.

The selective adsorption of nitric acid in a sodium hydrogen phosphate solution at pH 3.5 to 4.0 was investigated for the separation of carbon dioxide from the nitrogen oxides. A scrub column containing hydrogen peroxide in sulfuric acid was used to oxidize the nitrogen oxides to nitric acid. For carbonic acid or carbon dioxide with $pK_{a1} = 6.4$, greater than 99% of the carbonic acid exists as the undissociated acid at pH 3.5 to 4.0. It was hoped, therefore, that the nitric acid would be adsorbed completely and that little or no carbon dioxide would be adsorbed. In actual studies with 125- μ g. portions of carbonate, most of the carbon dioxide was absorbed in the sulfuric acid-hydrogen peroxide-sodium hydrogen phosphate scrub train, as was the nitric acid.

A satisfactory colorimetric procedure was developed for the determination of 35 to 180 $\mu\text{g.}$ of carbon dioxide. The carbon dioxide is precipitated with barium from an ammoniacal, 80% ethanol medium. The barium carbonate is then filtered onto a 0.45- μ membrane filter, washed free of excess barium, and redissolved in dilute hydrochloric acid. Finally, the barium is determined colorimetrically in an ammoniacal medium with Phthalein Complexone(30). The absorbance of the barium-Phthalein Complexone complex is linear with carbon dioxide concentration over the range 35 to 180 $\mu\text{g.}$ Nitrate at levels up to 6 mmoles did not adversely affect the colorimetric measurement procedure.

5.4.4 Phosphate Interference Studies for Boron and Mercury Methods - I. L. Doggett, F. A. Duce, D. M. Lund

A study to determine the effect of phosphate on the "Colorimetric Mercury Determination," Hg-1, Mod-5(31) and the "Titrimetric Boron Determination," B-Macro-1(31) procedures was made. A 20 to 50 mole ratio of phosphate to mercury does not interfere in the Hg-1, Mod-5 Method. Both 3 and 6 mole ratios of phosphate to boron give high results in the B-Macro-1 procedure. An extraction-flame photometric method for boron which tolerates phosphate is recommended for this type of sample.

5.5 Conversion of Calcine to Glass

A substantial reduction in the cost of confinement of radioactive wastes will result if calcined wastes can be converted into glasses. In support of the conversion of calcine to glass program, the Analytical Branch has provided the following services:

1. Development of a dissolution procedure for glass samples.
2. Development of a method to determine the distribution of lead in the glass as a measure of homogeneity.
3. Development of an analytical procedure for the determination of aluminum, a measure of the completeness of fusion.

(30) F. H. Pollard, J. V. Martin, Analyst 81, 348 (1956).

(31) M. J. Shepherd Jr., J. E. Rein, eds, Manual of the Analytical Methods Used by the Control Laboratory at the Chemical Processing Plant. Parts I and II, IDO-14316 (January, 1955). Supplement 1 (November, 1956). Supplement 2 (March, 1957). Supplement 3. (October, 1957).

4. Development of a method for the determination of mercury in the glass.
5. Development of a method for the determination of phosphate in the glass.
6. Analysis of aluminum in water samples from glass solubility studies.

5.5.1 Dissolution of Glasses - F. W. Dykes

The first study was directed to the solubility characteristics of the glass samples. Various samples were completely dissolved by a sodium carbonate fusion followed by hydrochloric acid dissolution of the melt. In addition, hot 6M sodium hydroxide and hot acid solutions including concentrated and 1:2 and 1:4 dilutions of hydrochloric acid, nitric acid, and perchloric acid decomposed the glass samples rapidly. With the acids, a small amount of residue believed to be alumina remained in some cases. This residue was dissolved readily with warm sodium hydroxide. Water and 1M sodium carbonate had no noticeable effect on the glass. With special glass samples containing greater than 25 wt% alumina, the sodium hydroxide and acid solutions were ineffective; however, these samples were dissolved completely by the carbonate fusion procedure.

5.5.2 Determination of the Distribution of Lead in Glass - S. S. Yamamura

The distribution of lead in the glass was selected as an index of sample homogeneity. The glass samples, in the shape of half discs, were sawed into slabs with a cutting wheel; and two widely-spaced slabs were analyzed for lead. After dissolution in hydrochloric acid, the lead was separated as the sulfide and determined titrimetrically with EDTA.

5.5.3 Determination of Completeness of Fusion by Analysis for Aluminum - M. A. Wade, M. E. Kussy

The routine, fluoride-complexing, aluminum procedure (Method, Al-1, Mod-6, Appendix B) was adapted successfully for the determination of aluminum in the glass samples. The interferences of lead and phosphate, major constituents of the sample, were minimized by a combination of oxalate masking for lead and the use of simulated known standards to obtain a correction factor for phosphate.

Because of the observed interference of phosphate in the titrimetric aluminum procedure, the development of an alternate procedure was also attempted. A gravimetric method based on a precipitation of the aluminum as the phosphate proved unsatisfactory, as did a sequential, chelometric titration procedure.

In the chelometric procedure, the sum of lead plus aluminum and lead alone are determined sequentially, and aluminum is obtained by difference. To determine the sum of lead plus aluminum, a measured excess of EDTA is added, and the excess is back titrated with cerium(III) in a pyridine-buffered medium to a xylenol orange indicator end point. Sodium diethyldithiocarbamate then is added to break up the lead-EDTA complex, and the free EDTA equivalent to the lead is titrated with the cerium(III). Though quite satisfactory for synthetic aluminum-lead mixtures, this procedure was found to be unsatisfactory for the analysis of actual glass samples because of phosphate interference.

Two column techniques for phosphate removal were investigated without success. Complete retention of phosphate was not obtained on an anion column of Dowex 2-X8 in the chloride form. When an alumina column known to retain phosphate quantitatively was used, considerable bleeding of the aluminum occurred, and an inconsistent high bias was noted.

5.5.4 Determination of Mercury - F. W. Dykes

Two glass samples prepared with calcined alumina which contained mercury were analyzed for mercury colorimetrically after dissolution in nitric acid under reflux. As a control, two samples of mercury-free glass were spiked with a known amount of mercury and analyzed simultaneously. The recovery of mercury was 101.8% and 103.1%.

5.5.5 Determination of Phosphate - J. H. Sikes

A spectrophotometric procedure reported by R. E. Kitson and M. G. Mellon⁽³²⁾ was used successfully to determine phosphate in the glass samples. Details of the procedure and the results of a comprehensive interference study are given in Appendix B, Method P-Color-2.

(32) R. E. Kitson, M. G. Mellon, Ind. Eng. Chem. Anal. Ed., 16, 379 (1944).

5.5.6 Determination of Aluminum in Water Samples from Glass Solubility Studies - T. R. Lyon, W. A. Ryder

The aluminum concentration was selected as an index of the solubility of the calcine glass in water. Since the aluminum concentration was very low, it was determined spectrographically using a silver spark technique⁽³³⁾.

6. CHEMICAL PROCESS AND DEVELOPMENT BRANCH

6.1 Spectrochemical Determination of Boron in Stainless Steel Solutions - T. R. Lyon

An emission spectrographic method was developed for determining microgram quantities of boron in nitric acid solutions of stainless steels from the electrolytic dissolver process. The iron, nickel, chromium, and manganese were removed from the sample by precipitation with potassium hydroxide. After filtration the filtrate containing the boron was taken to near dryness and the potassium salts formed were removed by a second filtration using an acetone wash. The solids removed in each of the two filtrations were spectrochemically checked for boron, but none was found in either of them. The acetone was evaporated from the final filtrate, cobalt internal standard was added, and the sample was made up to original volume with distilled water. This procedure increased the relative concentration of the boron to the other metals in the samples, making the analysis possible. Boron could not be detected in the untreated samples. The analysis was done by the rotating disc technique.

7. CHEMICAL PROCESSING PLANT OPERATIONS BRANCH

7.1 Determination of Undissolved Solids in WCF Quench Solutions - S. S. Yamamura, M. A. Wade, I. L. Doggett

The amount of undissolved solids in the nitric acid quench solution appeared to suddenly increase when the WCF feed was switched to tank WM-180 from tank WM-183. To aid the identification of the solids, wet chemical analyses for mercury and aluminum were requested. The analyses posed a unique problem of isolating a solids sample of known weight from a Millipore membrane filter. This was accomplished by dissolving the filter in dimethylformamide, settling the solids residue by centrifugation, and filtering the solids on a tared Whatman 540

(33) G. W. Dickinson and G. V. Wheeler, Silver Spark Spectrographic Analysis of High Purity Water, IDO-14591 (July 20, 1962).

filter paper, using acetone for the transfer. These studies showed that the actual amount of insoluble solids on the filter was considerably less than that which had been reported and that the solids were primarily alpha alumina and contained less than three weight percent mercury.

It was found that the membrane filter procedure being used routinely for the solids determination had been giving erroneous, high results. Because of its importance to analysis in general, the filtration studies are reported separately in section III.

8. MATERIALS TESTING REACTOR OPERATIONS BRANCH

8.1 Radiation Damage Check of MTR Pebble Bed Graphite - G. V. Wheeler, B. E. Ginther, W. A. Ryder, F. P. Spessard, V. R. Olsen, L. L. Dickerson

The Materials Testing Reactor graphite pebble bed was sampled at several depths in both VG12 and VG20 positions in December, 1963, to study the extent of radiation damage. For comparison and calibration purposes, a number of previously unirradiated graphite balls were irradiated for one fuel cycle in the MTR 55 "in tank" position. These samples were checked for stored energy, changes in crystal structure, ignition point, hydrocarbon content and weight loss. Several tests were made on annealing rate and control of release rate of stored energy.

The stored energy measurements were made by heating each sample in an oven held at 200°C and recording the sample temperature continuously until it reached equilibrium with the oven. Details of the furnace and the methods for calculating stored energy are given in IDO-16182(34). Changes in crystal structure, particularly C₀ dimension growth, were determined by X-ray diffractometer measurements on powder samples filed from the pebbles before making stored energy measurements. The temperatures for self-sustained combustion were determined by heating each sample with an induction heater while it was suspended on a thermocouple in flowing air. Hydrocarbons present in selected samples were extracted with CCl₄ under reflux in a soxhlet apparatus and their concentrations were determined by infrared absorption.

The energy release rate tests indicated that the release rate was controllable and that additional cooling could prevent large overshoots of temperature, even during the steepest part of the temperature rise.

(34) E. Fast, Graphite Damage as an Index to the Integrated Damaging Neutron Flux, IDO-16182 (September 28, 1954).

8.2 Determination of Chloride in Permanganate Solutions - M. S. Anderson

Radioactive waste storage tank solutions containing large amounts of permanganate were analyzed for chloride. The samples were acidified and heated, and permanganate was reduced to manganese(II) with oxalic acid. After cooling, chloride was determined by a Volhard titration.⁽³⁵⁾

9. HEALTH AND SAFETY BRANCH

9.1 Determination of Tantalum-182 on Contaminated Smears - M. S. Anderson

A method was developed for the determination of tantalum-182 on contaminated smears from the Test Area North. Tantalum was separated from other elements by ion exchange and determined by gamma ray spectroscopy. Details of the method are given in Appendix C, Method Ta-1.

9.2 Spectrochemical Determination of Beryllium and Lead on Air Monitor Filters - K. R. Arnold, B. E. Ginther

An emission spectrographic method for the analysis of beryllium and lead on microsorban air monitor filters was developed. The filter paper is first treated with a few drops of alcohol to make it absorb the molybdenum internal standard solution. The filter is then folded and placed on a 1-1/8 inch diameter silver disc electrode. A few drops of acetone are added which partially dissolve the filter, causing it to contract and stick to the electrode. The electrode is then heated on a hot plate until the filter vaporizes. The residue is analyzed by the rotating platform technique.⁽³⁶⁾ The detection limit is about 1.0 µg. per filter for lead and 0.0005 µg. per filter for beryllium.

10. REACTOR ENGINEERING BRANCH

10.1 Spectrochemical Determination of Tungsten, Silicon, and Copper in Uranium Silicide - T. R. Lyon

An emission spectrographic method was developed for determining silicon, tungsten, and copper in uranium silicide.

(35) M. J. Shepherd Jr., J. E. Rein, eds, Manual of the Analytical Methods Used by the Control Laboratory at the Chemical Processing Plant. Parts I and II, IDO-14316 (January 1955). Supplement 1 (November 1956). Supplement 2 (March 1957). Supplement 3 (October 1957). Method CI-3.

(36) G. V. Wheeler, W. A. Ryder, and K. R. Arnold, Applied Spectroscopy 16, 17 (1962).

The sample was dissolved in 5N HNO_3 . The insoluble portion was filtered off and fused with sodium carbonate. This fused material was recombined with the acid portion, cobalt and molybdenum were added as internal standards, and the sample was analyzed using the rotating disk technique.

10.2 Spectrophotometric Determination of Tantalum in Scandium - M. S. Anderson

A sample of scandium metal was analyzed for tantalum impurity.

Tantalum was measured spectrophotometrically as the pyrogallol complex in ammonium citrate-ammonium oxalate-sulfuric acid medium⁽³⁷⁾. Both the tantalum standard and the scandium sample were converted from HF solutions by evaporation followed by fusion with $\text{K}_2\text{S}_2\text{O}_7$. A scandium precipitate in the sample was removed by filtration just before measuring the absorbance of the tantalum complex.

11. NUCLEAR TECHNOLOGY BRANCH

11.1 Chopper Spectrometry Section

11.1.1 Protactinium-233 Cross Section Sample Analyses - J. H. Sikes, W. A. Ryder, V. R. Olson, E. M. Fortsch, T. R. Thomas, R. A. Nielsen, D. E. Filion

The Chopper Spectrometry Section of the Nuclear Technology Branch, having completed neutron cross section studies on a protactinium-233-thorium dioxide-manganese dioxide sample clad with aluminum, submitted the sample for the determination of manganese, thorium, protactinium-233 and isotopic and total uranium. Uranium-233, daughter of 27.5-day protactinium-233 is the major uranium isotope.

The sample was dissolved in a mixture of hydrochloric, nitric, and hydrofluoric acids. Aliquots of the solution were analyzed for various constituents as follows:

1. Manganese was determined by two methods, X-ray fluorescence and absorption spectrophotometry. It was shown that a precision of about 0.5% could be attained in the X-ray fluorescence method. To minimize any bias in this method, the matrix of the standards used was made as nearly like the samples as could be determined. In the spectrophotometric procedure, periodic acid was used to oxidize the manganese to the +7 permanganate state.

(37) S. Kallman, "Niobium and Tantalum," Treatise on Analytical Chemistry, Part II, Vol. 6 (ed. Kolthoff and Elving) p. 311 Interscience Publishers, New York (1964).

2. Thorium was determined spectrophotometrically as the thorium-thorin complex, without prior separation of the thorium, with a precision of about $\pm 5\%$. Tests on simulated dissolved samples indicated that the X-ray spectrographic analysis of thorium would be difficult because of the interference of the intense L_{α} line of uranium with the weak L_{α} line of thorium.

3. Total and isotopic uranium were determined by isotope dilution mass spectrometry with uranium-238 as the spike isotope.

4. Protactinium-233 was extracted into diisobutylcarbinol and measured by gamma spectrometry.

The analytical results agreed well with the expected values including the protactinium-233 which had decayed through 15 half lives prior to the measurement.

11.2 Reactor Physics Section

11.2.1 Determination of Lead, Thorium, and Uranium in PbO₂-ThO₂ and PbO₂-ThO₂-UO₂ Powder Mixtures - S. S. Yamamura

Upon evaluating the reactivity measurements data for lead dioxide-thorium dioxide and lead dioxide-uranium dioxide-thorium dioxide mixtures, Reactor Physics personnel noted that several of the points were "out of line" and requested an independent determination of the composition of the questionable mixtures which had been prepared originally by intimate mixing of weighed portions of the various oxides. Subsequent analyses showed that in two instances the thorium content differed significantly from the make-up value.

In all cases, the oxide samples ranging from 0.3 to 3.5 grams were dissolved sequentially with hydrochloric acid (to dissolve the PbO₂), nitric acid (to dissolve the uranium oxide), and perchloric acid containing 1 to 2 drops of hydrofluoric acid (to dissolve the thorium dioxide).

The lead in the two types of samples was determined chelometrically after initial separation as the sulfide from acidic medium. The lead sulfide plus filter paper was digested in order with hydrochloric, nitric, and perchloric acids. Finally, the lead was determined by adding a measured excess of EDTA and back titrating with zinc(II) solution to an eriochrome black T end point.

Thorium was determined by reverse EDTA titrimetry at pH 2.8 to 3.0 using a standard thorium solution. Prior to titration, the lead was removed as the sulfide, and the filtrate containing the thorium was evaporated to near dryness.

Uranium was determined by isotope-dilution, mass spectrometry.

11.2.2 Thorium Irradiation Program - S. S. Yamamura

The Reactor Physics Group is conducting a reactivity measurements, neutron irradiation study of thorium. In the preliminary phases of the study, the purity of the thorium metal and the composition and homogeneity of thorium-gold alloys and thorium-boron alloys to be used were of interest. Qualitative emission spectrographic analyses detected beryllium in the thorium rod sample but not in the thorium plate sample that had been rolled from the rod. Also, boron was found in the plate but not in the rod. A chemical determination of beryllium and boron in the thorium rod and plate samples was also requested.

11.2.2.1 Determination of Thorium - M. A. Wade

The thorium rod and plate samples were analyzed by a titrimetric EDTA procedure. The samples were dissolved with nitric and perchloric acids plus a few drops of hydrofluoric acid. A measured excess of EDTA was then added, and the excess was back titrated with standard thorium at pH 2.85 to a xylenol orange end point.

11.2.2.2 Determination of Gold - W. B. Holbrook

Gold was determined by a recently-developed extraction-spectrophotometric procedure,⁽³⁸⁾ the details of which are given in Appendix B, Method Au-Color-1.

11.2.2.3 Determination of Boron - J. H. Sikes

The spectrophotometric procedure of Hayes and Metcalf^(39,40) was adapted for the determination of boron in the thorium samples. A pyrosulfate

(38) W. B. Holbrook, J. E. Rein, Anal. Chem. 36, 2451 (1964).

(39) M. R. Hayes, J. Metcalf, Analyst 87, 956 (1962).

(40) M. R. Hayes, J. Metcalf, AEA Report pG 391 (5), (1962).

fusion under reflux in a quartz apparatus was used to dissolve the thorium samples. The melt was taken up in dilute hydrochloric acid and aliquots of the solution were analyzed.

11.2.2.4 Determination of Beryllium - J. H. Sikes

The thorium rod sample was analyzed for beryllium by a spectrophotometric procedure developed specifically for thorium samples. In the procedure, the sample was dissolved with hydrochloric and perchloric acids, then evaporated to perchloric acid fumes. Dilute hydrofluoric acid was added dropwise to dissolve the residual solids and the sample was again evaporated to perchloric acid fumes to expel the fluoride. Finally, the bulk of the thorium was removed by extraction into hexone as the 8-hydroxyquinolate complex and the beryllium was determined spectrophotometrically with eriochrome cyanine R. In the extraction, complete thorium removal was not attained; thus, comparison standards containing thorium were processed simultaneously with the sample.

Two other techniques were investigated briefly for the separation of thorium from beryllium; a reversed-phase column extraction technique using a stationary bed of Fluoropak coated with 8-hydroxyquinoline in 2-octanone and homogenous precipitation of the thorium with 8-acetoxyquinoline. Neither was satisfactory.

11.2.3 Determination of Low Concentrations of Hydrogen in Zirconium - L. L. Dickerson

The Leco Hydrogen Analyzer was modified to determine hydrogen in the ppm range in zirconium fuel materials for nuclear reactors. The furnace was rebuilt to accept samples as large as metallurgical tensile samples, and the system volume was reduced to give a measurable hydrogen pressure. Difficulty was encountered in obtaining quantitative gas transfer from the furnace to the measuring volume, and three different mercury diffusion pumps were evaluated. A CVC GHG-15 ejector pump was the only one found satisfactory. The modified system will measure 10 ppm of hydrogen in a 2 gram sample of zirconium.

11.3 Reactor Experiments Section

11.3.1 Apparent Crystallite Size - W. A. Ryder

The apparent crystallite size was determined on irradiated and unirradiated graphite by X-ray diffraction, using the Sherrer formula, $L = \frac{K \lambda}{B \cos \theta}$, and established methods.⁽⁴¹⁾

11.3.2 Spectrochemical Determination of Holmium and Thulium in Holmium-Aluminum and Thulium-Aluminum Alloys - T. R. Lyon

An emission spectrographic method was developed for determining holmium and thulium in holmium-aluminum and thulium-aluminum alloys. The concentration of the rare earths was at the 0.1% level.

The samples are dissolved in HCl and the rare earths separated from the aluminum by precipitation with sodium hydroxide in the presence of an indium carrier. The carrier also serves as a control for the recovery. The precipitate is collected on a Microsorban filter paper, and yttrium is added as an internal standard. The filter paper is then ashed on a silver disk electrode and the samples are run using the rotating platform technique.⁽⁴²⁾ This electrode system is free of CN band interference and shows good sensitivity for microgram quantities. It will be investigated as a general method for rare earth determinations.

11.4 Radiation Measurements Section

11.4.1 Phosphors for Alpha Scintillators - T. R. Lyon

The wavelength region of the characteristic emission and the width of the band produced were measured on the emission spectrograph for five phosphors for use in alpha scintillators. Each phosphor was positioned in the optical path of the spectrograph and excited with an ultra-violet source for one-half hour. Wavelengths in the region of 4010A and 4580A were recorded on Eastman 103a-O Spectrum Analysis Plates and those in the regions of 5200A, 5360A, and 5550A were recorded on Eastman 103a-F Spectrum Analysis Plates.

(41) H. P. Klug, I. E. Alexander, X-ray Diffraction Procedures, Chapter 9, Wiley and Sand, New York (1959).

(42) G. V. Wheeler, W. A. Ryder, and K. R. Arnold, Applied Spectroscopy 16, 17 (1962).

12. SAFETY TEST ENGINEERING PROGRAM (STEP)

Analytical services for the Safety Test Engineering Program during 1964 included the analyses of samples from the SNAPTRAN 2/10A-3 reactor and assistance in planning various phases of the LOFT program.

12.1 SNAPTRAN 2/10A-3 - J. G. Scott, W. A. Ryder, R. M. Abernathy, F. O. Cartan, B. R. Hunter

As part of the U. S. AEC's Aerospace Nuclear Safety Program a modified version of the SNAP 2/10A reactor flight package designated the SNAPTRAN 2/10A-3 was destroyed by immersion in water. Samples of the destructive test came from two sources, a sampling grid surrounding the reactor environmental tank and the environmental tank containing the test package.

Various sample collectors were used to catch the material falling onto the grid. Those received for analysis were beryllium filter samples, cyclone samplers, Anderson samplers, fallout plates, water tray samples, high volume air samplers and particle catch cans. All of these samples were analyzed for beryllium and Sr^{89,90}. Samples from the water trays and the particle catch cans were analyzed by gamma spectrum stripping for zirconium-95, iodine-131, ruthenium-103, cesium-137, barium-140, and cerium-141. Certain selected water samples were analyzed for sodium, uranium, zirconium and particle size distribution.

The samples from the environmental tank consisted of environmental water, wafers cut from identifiable fuel pieces, debris from the reactor fuel, and selected reactor vessel components other than fuel. Hydrogen analysis was performed on the samples of zirconium-hydride fuel wafers and fuel debris. The above samples were also analyzed radiochemically and found to contain strontium-89,90, zirconium-95, iodine-131, ruthenium-103, cesium-137, barium-140, and cerium-141. In addition, the fuel wafers were analyzed for zirconium and uranium. A segment of a selected fuel rod was analyzed for krypton-85. A microscopic study for particle size distribution and material identification was made on a sample of reactor fuel debris particles less than $1/4 \mu$ in size. Polaroid microphotographs were taken to assist in the material identification of this sample. Pieces of the fuel, the fuel hydrogen barrier, silvery metallic fragments, green and white ceramic spheres and bits of quartz were found in this sample.

In order to provide STEP personnel with an indication of the power level and the flux profile of the reactor, samples were taken from selected regions of the reactor vessel, the

upper and lower reactor grid plates, and the fuel cladding. These samples were analyzed by gamma spectrometry for cobalt-58 produced by interaction of the fast neutrons and nickel-58. The samples were dissolved in acid and the cobalt was separated by ion exchange. In addition, using radioautographs made of these reactor components, the areas from which the activation samples were taken were scanned by a densitometer and graphed. This was done to enable STEP personnel to make a comparison of the radioautographic technique to the radiochemical technique for determining flux profiles of irradiated materials.

Most of the above determinations were made using established procedures. However, two dissolution techniques and a vacuum extraction technique were especially developed for use on SNAPTRAN samples.

12.1.1 Dissolution of Fallout Plates for Radiostrontium Analysis - M. A. Wade, S. S. Yamamura, M. S. Anderson

In the SNAPTRAN 2/10A-3 experiment, adhesive-coated plastic sheets were distributed in the test area to monitor the fallout of air-borne particles. The plastic fallout plates were examined by gamma spectrometry, then analyzed for radiostrontium and beryllium. The beryllium was determined spectrographically on a portion of the adhesive plate. To determine the radiostrontium, a beta emitter, by radiochemical analysis, a preliminary dissolution of the plastic sheets was necessary.

Two satisfactory methods of dissolution were developed, wet digestion with nitric and perchloric acids and dry ashing followed by acid dissolution of the ash residue. Of these two methods, the faster and safer dry-ashing procedure was selected. The plastic sheet was charred in a platinum dish under a heat lamp until free of fumes, then ignited first with a Meker burner and finally in a muffle furnace at 800°C. The residue, principally the oxides and phosphates of calcium, magnesium, and silicon, was fumed with perchloric and hydrofluoric acids, then dissolved in water using ferric chloride to solubilize the insoluble metal phosphates.

12.1.2 Dissolution of Reactor Component Samples - B. A. Staples, B. R. Hunter

A mixture of hydrofluoric and nitric acids was used to dissolve a large number of stainless steel and Hastaloy SNAP reactor component samples. A polyethylene dissolver-reflux system was designed to perform this operation (Figure VI-1).

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Figure VI-1. POLYETHYLENE DISSOLVER AND REFLUX CONDENSER

A four ounce polyethylene bottle served as the dissolver vessel, and a six inch length of 1/4 inch i.d. polyethylene tubing was used as the condenser. The cooling region of the condenser was lightly packed with Teflon wool to increase the reflux efficiency. The condenser tube was passed thru a 50-ml. lusteroid centrifuge tube cooling jacket. The cooling jacket was packed with dry ice when in use. A hot water bath heated the dissolver.

After the dissolution was completed, the condensate in the reflux condenser was washed back into the dissolver, the dissolver contents were diluted to a known volume in a volumetric flask and the solution was returned to the dissolver bottle for storage. A separate dissolver assembly was made for each sample, thus eliminating cross contamination. The reflux condenser and Teflon packing were discarded after one use, but the lusteroid cooling jacket was reused.

12.1.3 Determination of Hydrogen Content of Finely Divided Fuel Particles - G. D. Workman, R. M. Abernathey

Determinations were made of the hydrogen content of finely divided particles of fuel recovered after the SNAP destruct test. Commercial hydrogen analyzers are designed for gram-size chips; hence, it was necessary to modify the Leco apparatus by adding a quartz cup to position the powder in the furnace. An external magnet was used to move the cup into the furnace after the system was evacuated.

12.2 LOSS OF FLUID TEST (LOFT) - B. R. Hunter, F. O. Cartan

As part of the Atomic Energy Commission's Nuclear Safety Program, an engineering test program was initiated to demonstrate the consequences of a loss of coolant accident for a water-cooled and water-moderated reactor and to investigate the capability of a containment building for retaining fission products. An extensive research program is in progress to study all phases of a loss of coolant accident. The LOFT facility should be ready for initiation of the test program in 1968. It is planned to conduct the loss of coolant test with a radioactive core during the latter part of 1969.

The Analytical Chemistry Branch is participating in an assistance program to LOFT. The assigned areas are:

1. Provide technical consultation.
2. Develop and test analytical chemistry methods necessary for the program.

3. Assist in the evaluation of the various sampling systems.
4. Analyze the samples generated during the program.

Some of the services provided by the Branch are described in this report, and a summary of these follows.

The chemical behavior of fission products released into a reactor containment may be affected by organic vapors already in the atmosphere. A study revealed the flame ionization technique to be the best method to analyze a typical reactor containment atmosphere for organic impurities.

After blowdown, to know when air enters the reactor vessel and if a metal-water reaction is taking place in the reactor vessel, the reactor vessel atmosphere is to be analyzed for oxygen, nitrogen, and hydrogen. Manufacturers of gas analysis equipment are being contacted and the technical journals will be studied to evaluate all possible techniques for these analyses.

Samples of the containment atmosphere will be drawn into evacuated ball samplers through needles penetrating elastomeric plugs. Ideally, particulate matter will be retained on an absolute prefilter, iodine will be adsorbed onto charcoal in a cartridge, and the noble gases will pass into the free space in the sampler. A study revealed that as much as 4% of the iodine passing into a sampler remained on the sample needle as plateout, but this is not an appreciable error. The punctured plugs must seal to prevent the exchange of the atmosphere with the sample and the entrance of water. Tests on rubber serum stoppers showed the leakage was insufficient to cause significant error in the results. In a device simulating the gas sampler, a single experiment revealed that 85% of the xenon sorbed onto charcoal within 20 minutes at room temperature. Boron nitride is being investigated as a possible substitute for charcoal in the gas sampler. Xenon was found not to be adsorbed by boron nitride at -78°C .

Radiochemical methods will be needed to supplement the gamma spectrometric measurements of fission products present on the plateout samplers at selected time intervals after blowdown. A study of the LOFT Curie code supplied the information necessary to determine what chemical separations are necessary to measure the isotopes of biological significance.

The stability of three hydrogen peroxide-based decontamination solutions was measured using a simple, iodometric, titration procedure.

Brief emission and X-ray spectrographic studies were made to determine their feasibility for measuring the total iodine in LOFT experiment samples.

Power reactors are normally stainless steel. For economy, carbon steel is being considered for the LOFT experiment. Fission product adsorption behavior of these two materials was compared. Test specimens, immersed in lithium hydroxide solution, were contaminated with young fission products and counted at selected time intervals. There does not appear to be any great difference between carbon steel and stainless steel in the relative adsorption of young fission products.

The Analytical Branch assisted STEP personnel in reviewing and evaluating the ball sampler and the ventilating air sampling system proposals prepared by Kaiser Engineers.

12.2.1 Analysis of Organic Impurities in the Containment Shell - G. V. Wheeler, L. L. Dickerson, M. A. Wade

Organic impurities normally present in the atmosphere of a reactor containment building may affect the chemical behavior of the fission products released, particularly iodine. A study was made of methods for determining organics in air, and the flame ionization technique was suggested as the most satisfactory. The EBR II containment atmosphere will be analyzed as a typical reactor containment shell to determine the organic impurities that might react with radioiodine. This instrument will also be used to measure organics in the LOFT atmosphere prior to blowdown.

12.2.2 Analysis of Gases in the Reactor Vessel - G. V. Wheeler, L. L. Dickerson

The Spectroscopy Section has been assigned the task of making a preliminary investigation of techniques for analyzing oxygen, nitrogen, and hydrogen in the reactor vessel as a function of time after blowdown. The section has requested information from all known manufacturers of gas analysis instruments. This information and technical journals will be studied to evaluate all possible techniques for these analyses. A continuous measurement of the oxygen and nitrogen content will indicate the time after blowdown at which air begins to enter the reactor vessel. A measurement of the free hydrogen in the reactor vessel after blowdown will indicate if a reaction is taking place between water or steam and fuel components.

12.2.3 Gaseous Fission Product Samplers - F. O. Cartan

One type of apparatus proposed for the remote sampling of the atmosphere in the containment shell is an evacuated metal sphere with a rubber diaphragm on its surface. At the time of sampling, a hypodermic needle will penetrate the diaphragm and the containment atmosphere will flow into the sphere through a filter (if used) and a cartridge of activated charcoal. The assumptions were made that the particulate matter will be retained on the filter, that iodine will be completely adsorbed on the charcoal, and that all the krypton and xenon will pass into the free volume of the sampler. To evaluate this proposed sampler, the following have been or are being studied.

- (1) The plateout of iodine on the needle and filters.
- (2) The leak rate of a perforated rubber diaphragm.
- (3) The sorption of krypton and xenon on activated charcoal.
- (4) The possible substitution of other adsorbents for charcoal.

12.2.3.1 Iodine Plateout Behavior on the Sampling Needle - R. E. Foster

The apparatus used to study iodine plateout on a sampling needle, shown in Figure VI-2, consisted of two sections, an electrically heated release flask and a sampler assembly designed to simulate the action of the LOFT sampler. To prepare a simulated LOFT atmosphere, a solution containing iodine labeled with iodine-131 was evaporated in the release flask. To sample the atmosphere, the needle of the sampler was pushed through the serum stopper into the release flask. When the small stopcock was opened, the iodine-air-water vapor atmosphere was pulled through the needle, through the two charcoal cartridges, and into the evacuated sphere.

A series of releases was performed in which the concentration of iodine in the vapor phase was varied. Following each release and sampling operation, the needle, the two charcoal cartridges, and a decontaminating wash of the cartridge chamber were counted for iodine activity. The use of two cartridges provided a bonus piece of

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1. Heated Release Flask (2000-ml.)
2. Serum Stopper
3. 1 or 1.5" 16-Ga Hypodermic Needle
4. Luerlock Fitting
5. Cartridge Chamber
6. Evacuable Bulb (500-ml.)
7. Perforated Plastic Caps
8. Filter Paper Disk
9. "O"-ring
10. Plastic Tube (1. = dia. = 1")
11. Activated Coconut Charcoal

Figure VI-2. APPARATUS USED TO DETERMINE IODINE PLATEOUT ON SAMPLING NEEDLE

information, an estimate of the iodine collection efficiency of the cartridge.

The measurements are summarized in Table VI-2.

TABLE VI-2. "PLATEOUT" OF IODINE ON SAMPLER NEEDLE

<u>Release</u>	<u>Calculated I₂ Conc. in Release Flask,^a µg/liter</u>	<u>I₂ Plateout on Needle, %</u>	<u>Efficiency of Charcoal Cartridge,^b %</u>
1	50	1.7	99.6
2	50	4.5	O-Ring Seal Leaked
3	500	0.8	99.6
4	0.5	3.9	> 99.0
5	100	1.4	99.6
6	0.0008 ^c	3.8	98.8

^a Assuming half of the fission product iodine of the LOFT core was released into the containment shell, the initial concentration would be approximately 2 µg/liter.

^b₁₀₀ $\frac{\text{I}_2 \text{ activity on first cartridge}}{\text{sum of I}_2 \text{ activity on both cartridges}}$

^c Only tracer I¹³¹ used.

Desorption of iodine from the sampling needle is a possible source of error. During the LOFT sampling operation, a portion of the iodine deposited on the needle by the containment atmosphere or by previous sampling could be desorbed, sucked into the metal sphere sampler, and counted during the subsequent analyses. This desorption was investigated in a separate experiment. A needle was exposed for 3 days to iodine vapor labeled with I¹³¹. The sampler was used to pull an air-steam mixture through the needle, and the resulting activity loss was measured. The needle was exposed to the air-steam mixture three additional times and finally, the air-steam mixture was pulled through the needle for 2 minutes by vacuum. The first exposure to steam removed approximately 10% of the iodine activity. Smaller amounts of

activity were removed with successive exposures, and the fourth exposure removed only 2% of the iodine activity. The prolonged flush with steam removed only 4% of the residual activity.

The following conclusions were drawn:

(1) The amount of iodine plateout on a 16-gauge stainless steel hypodermic needle is as high as 4%. Because the projected uncertainty in the analysis of the iodine content of a LOFT sampler is 10 to 20%, if done by gamma spectrometry, this loss is not serious.

(2) The amount of plateout appears to be dependent on the iodine concentration in the vapor. The percentage adsorbed was greater at the lower iodine concentrations.

(3) The charcoal cartridges were efficient adsorbers of iodine activity.

(4) An appreciable fraction of the unsampled iodine activity was found on the rubber serum stopper during the cleanup of the release flask. This suggests that the outer surface of the rubber diaphragm of the proposed LOFT sampler may collect considerable activity from the LOFT atmosphere. Though not affecting the analysis, this may constitute a radiation hazard.

(5) The desorption of iodine from a contaminated needle decreased with repeated exposures to an air-steam atmosphere. This effect could become important if the iodine concentration in the LOFT atmosphere should decrease sharply, e.g., by a factor of 10, between successive samples.

(6) Ten to 20 seconds were required to establish pressure equilibrium between the sampler and the release flask.

12.2.3.2 Leakage Rate of a Perforated Rubber Diaphragm

A leak in a punctured diaphragm of the gas sampler will permit exchange of the collected gas with the atmosphere and will allow water or condensate to enter.

The type of rubber and the dimensions of the LOFT gas sample diaphragm have not been specified. However, to get an estimate of the magnitude of leakage, soft, red rubber serum stoppers were evaluated. The stoppers were 8-mm. OD, had a 6-mm. hollow plug, and were placed in a short length of glass tubing for the leak tests. The punctures were made with an 0.065-inch OD needle.

Leakage was measured in two ways. The flow of air through a punctured stopper into an evacuated flask was measured by the pressure changes shown on an attached manometer. The pressure changes were very small and the calculated leakage rates were probably not precise. Later measurements were made with a more sensitive helium leak detector.

The gross leakage rates measured with the manometer and evacuated flask were:

<u>Run</u>	<u>Time (days)</u>	<u>Pressure Change (mm. Hg)</u>	<u>Leakage Rate (cc./day)</u>
1	0.85	1.7	1.6
2	14	2.1	0.12

Leakage rates with the helium leak detector were:

<u>Run</u>	<u>Leakage Rate (cc./day)</u>
1	0.6
2	0.3
3	0.005

These leakage rates, although they were not reproducible from stopper to stopper, indicate a rough upper limit of the leak rate of a LOFT gas sampler diaphragm. Leakage of the magnitude observed in these tests should not cause a significant error in the results obtained from the LOFT gas samples. The largest observed leakage rate, which was probably high was 1.6 cc./day at a pressure differential of approximately 640 mm. of mercury. In the LOFT experiment, the pressure differential across the diaphragm will be much less than 640 mm. of mercury

after sampling is complete so that the actual leakage rate will be much less than 1.6 cc./day. The free volume of the sampler is ~500 cc. All gas samples will be analyzed within 40 days after removal and many will be analyzed within a few hours of removal. The bias caused by the leakages should be less than the 5 to 20% error expected for the measurement of the sample activity.

Final estimates of the leakage rate through the punctured gas sampler diaphragm and the effects of steam and radiation on the diaphragm cannot be made until samples of the rubber diaphragms or the prototype samplers become available.

12.2.3.3 Sorption of Xenon on Activated Charcoal

In the proposed sampling program for LOFT, the gas samplers will be dismantled and analyzed after a delay of at least 30 minutes to as much as 40 days after sample collection. During this period, when the sampler will be at ambient temperature, the krypton and xenon may diffuse to and sorb onto the charcoal.

The rate of sorption of xenon onto loosely-packed activated charcoal was measured as a function of time at room temperature in an apparatus which simulated the LOFT sampler. In a single preliminary experiment, the sorption reached equilibrium rapidly with about 85% of the xenon sorbing onto the charcoal in 20 minutes.

Experiments are planned to determine the amount of xenon sorbed onto the charcoal cartridge only during the short period of sampling when the gas is passing through the cartridge. For these experiments, LOFT conditions will be simulated.

12.2.3.4 Sorption of Xenon on Boron Nitride - R. E. Foster

In view of the sorption of xenon that takes place on activated charcoal, boron nitride is being investigated as a possible substitute. Boron nitride has a structure similar to graphite and also has suitable properties of thermal stability and oxidation resistance. It may be that boron nitride could be activated for use as a sorber material for iodine and other fission products.

As a go/no-go type of test, the sorption of xenon onto powdered boron nitride was measured at -78°C . For this test, MTR-irradiated xenon was passed through the material with a helium sweep. There was no significant sorption of the xenon.

12.2.4 Analysis of Plateout Samples - M. S. Anderson

Radiochemical methods are needed to supplement the proposed gamma spectrometric measurements of fission product concentrations on the plateout samples. Consequently it will be necessary to develop methods for the rapid dissolution and analysis of samples containing gross fission products. In order to determine which fission products will be present as a result of the test, the LOFT curie code was studied. From this study the disintegrations per second of each radioactive fission product present at various times after blowdown was determined. Time intervals of 0.278 hours, 1.39 hours, 27.8 hours, 5.79 days, 11.6 days, and 57.9 days were chosen because the disintegration rate is obtainable without interpolation for these times. After determining the amounts of activity of the isotopes present, the gamma spectra of the isotopes will be compared to determine which chemical separations will be necessary to accurately determine those isotopes of biological significance.

12.2.5 Determination of Hydrogen Peroxide in Decontamination Solutions - S. S. Yamamura, J. H. Sikes

Decomposition data were obtained for three hydrogen peroxide-based decontamination solutions proposed for the LOFT studies. The three decontamination solutions were stored at 60°C . in the dark in glass containers. Periodically, samples of each of the solutions were drawn for pH measurements and hydrogen peroxide determinations. A simple iodimetric titration procedure, unaffected by the organic complexing agents of the decontamination solutions, was used for the determination of the hydrogen peroxide. On the basis of 7 determinations at the 0.8-meq. hydrogen peroxide level, the relative standard deviation was 0.1%.

12.2.6 Spectrochemical Determination of Total Iodine - G. W. Dickinson, W. A. Ryder

Brief emission and X-ray spectrochemical studies were made to determine their feasibility for measuring the total iodine in LOFT experiment samples. Emission sensitivity was checked using chloroform and ethanol

solutions and the plasma jet as an excitation source. The minimum amount detectable was 0.5% in either solution.

The X-ray spectrographic study was made using standards prepared by evaporating potassium iodide on filter papers. Using the vacuum spectrograph the minimum detectable amount is about 5 μ g.

12.2.7 Adsorption of Fission Products on Steel Surfaces - R. E. Foster, W. J. Maeck

Power reactor vessels are normally stainless steel. For economy, carbon steel is being considered for the LOFT experiment. The fission product adsorption behavior of these two materials was investigated for lithium hydroxide medium at pH 10 at room temperature, the conditions proposed for the LOFT reactor vessel.

The carbon steels SA-302 grade B and SA-212 grade B, both proposed for the reactor vessel, were compared to 347 stainless steel. Three surface conditions, "as is", "pickled", and "oxidized" were studied for each of the steel types. The adsorption was measured as a function of time.

Aliquots of solutions of young fission products containing a gross gamma activity of 3×10^5 counts/min. were pipetted into Pyrex centrifuge tubes which contained 20 ml. of lithium hydroxide solution and one of the steel specimens. These were thoroughly mixed and allowed to stand for contact times of 10 minutes, 1 hour, and 24 hours. At the end of each of these periods, the tubes were counted for gross gamma activity in a well counter. The specimens then were immediately removed, washed thoroughly with water and counted under identical conditions in clean tubes containing 20 ml. of water. The percentage of total gamma activity adsorbed was calculated by ratios. The 24-hour contact specimens were gamma scanned on a 512-multi-channel analyzer. Based on previous studies⁽⁴³⁾, the experimental errors associated with each determination is ± 28 relative percent.

Considering the surface conditions, there does not appear to be any great difference between carbon steel and stainless steel in the relative adsorption of young fission products from pH 10 lithium hydroxide.

(43) R. E. Foster, W. J. Maeck, J. E. Rein, U. S. Atomic Energy Comm. Rept. IDO-14644, Adsorption of Young Fission Products on Various Surfaces from Neutral and Dilute Acid Media: Application to Water Sample Collection for Step Programs (1964).

12.2.8 Evaluation of Sampling Systems - F. W. Dykes,
F. O. Cartan, B. R. Hunter

The Analytical Branch assisted STEP personnel in reviewing and evaluating the ball sampler and the ventilating air sampling system proposals prepared by Kaiser Engineers.

VII. QUALITY CONTROL

(J. E. Rein, G. J. Curtis)

The comprehensive quality control program on both routine and special methods was continued. The main features of this program are (a) the preparation and supplying of all reagents and standards for the methods, (b) the submission of unknown control samples and the record-keeping of results for transmittal to the statisticians, (c) the submission of controls and the record-keeping for the Training and Testing Program of the Chemical Analysis Section, (d) the maintenance of "bench" standards and control charts, and (e) the surveillance of control data. "Bench" standards of known values are processed prior to samples to prevent the use of faulty apparatus or reagents.

1. BIAS AND PRECISION DATA

Tables of current bias and of precision for routine methods, based on regression equations computed from control data, are now provided by Operations Analysis. These tables, which provide a rapid selection of precision and bias correction for all levels over the range of routine methods, are used by laboratory personnel to report analyses corrected for bias and with precision limits. Table VII-1 is a summary of the precision data for routine methods for 1964.

2. STANDARDS AND REAGENTS

2.1 Routine

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

2.2 Storage of Uranium Standard Solutions

Standard uranium solutions stored in special dispensing bottles⁽⁴⁴⁾ remained stable throughout 1964. This was verified by continuous analyses on both the uranium-233 mass spike solution and the uranium-235 standard solution. Two controls per month were submitted to the mass laboratory. These controls contain uranium solutions which have been pipetted and evaporated to dryness at the time of the initial preparation of the uranium-233 and uranium-235 standard solutions. The addition of the uranium-233 solution to a previously pipetted and dried uranium-235 aliquot checks the stability of the uranium-233, and reversing the procedure checks the stability

(44) R. C. Shank, & staff, Annual Report of Division Analytical Branch for 1962, IDO-14605, Section VII-2.2.1 (April 1963).

TABLE VII-1

PRECISION OF ROUTINE ANALYTICAL METHODS

Methods	Range and Units(a)	Precision(b)
Acid, visual indicator titrimetric	0.5 to 4.5 meq.	0.01 to 0.03 meq.
Acid, oxalate, pH titrimetric	0.5 meq. base to 1.2 meq. acid	0.02 meq., constant
Acid, oxalate, pH titrimetric, remote	0.5 meq. base to 1.2 meq. acid	0.03 meq., constant
Aluminum, fluoride complexing, titrimetric	5 to 11 mg.	0.09 to 0.20 mg.
Beta activity, gross	20 to 175 d/min.	6 to 13 d/min.
Boron, mannitol complexing titrimetric, low level	0.1 to 1.5 mg.	0.04 to 0.07 mg.
Boron, mannitol complexing, titrimetric, high level	0.05 to 5 mg.	0.01 to 0.32 mg.
Cesium-137	4×10^5 to 1.0×10^6 d/m	1.4×10^4 to 3.1×10^5 d/m
Chromium, redox titrimetric	1.6 to 15.6 mg.	0.07 to 0.7 mg.
Chromium, diphenyl-carbazide colorimetric	0.005 to 0.05 mg.	0.0004 to 0.0042 mg.
Fluoride, pyrolysis, Ce(III) titrimetric	6 to 40 mg.	0.5 to 4.7 mg.
Iron, column extraction, EDTA titrimetric	5 to 20 mg.	0.19 mg., constant
Iron, orthophenanthroline colorimetric	1 to 100 μ g.	1.1 to 3.1 μ g.
Iron, column extraction, orthophenanthroline colorimetric	1 to 100 μ g.	1.9 to 0.8 μ g.
Mercury, titrimetric, Hg(II) with KSCN	96 to 300 mg.	0.9 to 8 mg.

PRECISION OF ROUTINE ANALYTICAL METHODS (Continued)

Methods	Range and Units(a)	Precision(b)
Mercury, dithizone colorimetric	50 to 300 µg.	15.3 to 17.5 µg.
Nickel, dimethylglyoxime colorimetric	0.01 to 0.1 mg.	0.006 to 0.002 mg.
Nickel, dimethylglyoxime precipitation, EDTA titrimetric	2 to 28 mg.	0.3 to 0.7 mg.
Nitrate, Devarda reduction, distillation, titrimetric	0.2 to 4.5 milli-moles	0.02 to 0.30 millimole
Phosphate, extraction, colorimetric	10 to 100 µg.	0.9 to 5.4 µg.
Reducing normality, dichromate titrimetric	0.14 to 0.84 meq. Fe(II)	0.010 meq., constant
Specific gravity, Westphal	1.14 to 1.35 specific gravity units	0.002 specific gravity units, constant
Specific gravity, falling drop, remote	1.05 to 1.35 specific gravity units	0.002 to 0.004 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% TBP, constant
Uranium, extraction tetrapropylammonium uranyl trinitrate spectrophotometric	3.5 to 20 mg.	0.1 to 0.6 mg.
Uranium, extraction, tetrapropylammonium uranyl trinitrate spectrophotometric	5 to 38 mg.	0.2 to 0.5 mg.
Uranium, mass isotopic distribution, hand pipetted	1.017% U-234 93.139% U-235 0.180% U-236 5.664% U-238	0.012% 0.060% 0.011% 0.030%

PRECISION OF ROUTINE ANALYTICAL METHODS (Continued)

Methods	Range and Units(a)	Precision(b)
Uranium, isotopic-dilution mass-spectrometric, hand pipetted	1.0 mg.	0.01 mg.
Uranium, mass isotopic distribution, remote pipetted	1.014% U-234 93.127% U-235 0.182% U-236 5.678% U-238	0.009% 0.061% 0.010% 0.033%
Uranium, isotopic-dilution mass-spectrometric, remote pipetted	1.0 mg.	0.016 mg.
Uranium, mass isotopic distribution, high precision	1.0190% U-234 93.1470% U-235 0.1828% U-236 5.6510% U-238	0.0085% 0.0426% 0.0078% 0.0277%
Uranium, isotopic-dilution mass-spectrometric, high precision	1.0 mg.	0.002 mg.
Uranium, extraction, dibenzoylmethane colorimetric	0.01 to 0.1 mg.	0.002 to 0.016 mg.
Uranium, ignition to U_3O_8 , spectrographic impurity correction	220.0 to 230.0 mg.	0.15 mg., constant
Uranium extraction, pellet fluorophotometric	5×10^{-5} to 0.1 mg/ml	2.7×10^{-5} to 2.2×10^{-2} mg/ml
Zirconium, cupferron amperometric	0.01 to 0.1 millimole	0.001 to 0.005 millimole

(a) Amount in aliquot of control taken for analysis.

(b) In terms of standard deviation for a single determination over range of method.

of the uranium-235 solution. An isotopic-dilution, high-precision, mass-spectrometric method (see Table VII-1) is used for these analyses.

2.3 Storage Stability of Liquids

A major problem in analytical chemistry is the storage of standard solutions over extended time periods. Leakage through stoppers, reaction with the vessel surface, and transpiration are factors which cause changes in concentration. An experiment in progress to establish the effects of certain variables is summarized in Table VII-2.

TABLE VII-2

VARIABLES BEING STUDIED FOR LIQUID STORAGE STABILITY

Containers	: borosilicate glass, polyethylene, polypropylene, Teflon
Stoppers	: regular glass, inverted T glass, plastic screw caps, plastic screw caps plus parawax
Aqueous Media	: water; hydrochloric acid, 1M and 12M; hydrofluoric acid, 1M and 12M; nitric acid, 1M and 12M; and sodium hydroxide, 1M and 12M
Organic Media	: ethanol, ethyl ether, hexane, hexone, kerosene

A total of 135 combinations of the above variables is being evaluated. The containers are filled to different levels with the various liquids, and weight changes are being measured at intervals up to a proposed time of one year.

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APPENDIX A
PUBLICATIONS AND PAPERS

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PUBLICATIONS AND PAPERS

1. BOOKS

Booman, G. L., Rein, J. E., Chapter 6, "Expended Reactor Fuels, " Analysis of Essential Nuclear Reactor Materials, C. J. Rodden, ed., Superintendent of Documents, U. S. Government Printing Office, 1964.

2. U. S. ATOMIC ENERGY COMMISSION REPORTS

IDO-14636 R. C. Shank Annual Report of Division Analytical
Branch for 1963

IDO-14649 J. E. Rein Burnup Determination of Nuclear Fuels:
W. J. Maeck 1963 Annual Report

3. JOURNAL ARTICLES

Maeck, W. J., Rein, J. E., "Storage of Radioactive Fission Product Samples," Analytical Chemistry 36, 252 (1964).

Yamamura, S. S., "Determination of Iron(III) by (Ethylenedinitrilo) tetraacetic Acid Replacement Titrimetry Following Selective Separation by Column Extraction," Analytical Chemistry 36, 1858 (1964).

Wade, M. A., Yamamura, S. S., "Column Extraction-Spectrophotometric Determination of Iron," Analytical Chemistry 36, 1861 (1964).

Holbrook, W. B., Rein, J. E., "Extraction and Spectrophotometric Determination of Gold," Analytical Chemistry 36, 2451 (1964).

Yamamura, S. S., "Dangers in the Use of High Purity Spectrographically Analyzed Standards," Analytical Chemistry 36, 2515 (1964).

Dickinson, G. W., Wheeler, G. V., "An Investigation into the Analysis of Nitrogen for Hydrogen by Emission Spectroscopy," Applied Spectroscopy, 18, 152 (1964).

4. PAPERS

Wade, M. A., Yamamura, S. S., "Column Extraction-Spectrophotometric Determination of Iron," 147th National American Chemical Society Meeting, Philadelphia, April, 1964.

Yamamura, S. S., "Determination of Iron(III) by (Ethylenedinitrilo) tetraacetic Acid Replacement Titrimetry Following Selective Separation by Column Extraction," 147th National American Chemical Society Meeting, Philadelphia, April, 1964.

Foster, R. E., "Adsorption of Young Fission Products on Various Surfaces from Neutral and Dilute Acid Media," 19th Annual Northwest Regional American Chemical Society Meeting, Spokane, June, 1964.

Rein, J. E., "Status of Burnup Development Program," Libby-Cockroft Meeting on Ceramic Fuels, Hanford, Washington, May, 1964.

Maeck, W. J., Kussy, M. E., Rein, J. E., "Spectrophotometric Determination of the Lanthanides as Extracted Nitrate Complexes," 148th National American Chemical Society Meeting, Chicago, September, 1964.

Rein, J. E., "Determination of Nuclear Fuel Burnup: Status of Development Program," Eighth Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tennessee, October, 1964.

Maeck, W. J., "Proposed Determination of Nuclear Fuel Burnup Based on the Ratio of Two Stable Fission Products of the Same Element," Eighth Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tennessee, October, 1964.

Maeck, W. J., Kussy, M. E., Rein, J. E., "Separation of Americium from Lower Transuranics: Extraction with Quaternary Ammonium Salts," Eighth Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tennessee, October, 1964.

Ryder, W. A., "Diffraction Analysis of Radioactive Samples," X-ray Analysis Workshop, University of Utah, Salt Lake City, October, 1964.

APPENDIX B

METHODS ADDED TO ICPP ANALYTICAL MANUAL IN 1964

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EXTRACTION, SPECTROPHOTOMETRIC METHOD
SPECIFIC FOR MICROGRAM AMOUNTS OF URANIUM

ABSTRACT

In this method, uranium as the tetrapropylammonium uranyl trinitrate complex is extracted into methyl isobutyl ketone (hexone) from an acid-deficient aluminum nitrate salting solution. An aliquot of the organic phase is scrubbed with an aluminum nitrate solution which contains tartaric acid, oxalic acid, ethylene (dinitrilo) tetraacetic acid (EDTA), and ferrous sulfamate. The chromogenic agent, dibenzoylmethane in an ethanol-pyridine medium, is directly added to the scrubbed organic phase and the absorbance is measured at 415 mμ. The limit of detection is 5×10^{-4} mg. of uranium. Large amounts of thorium interfere and a special procedure is described for thorium-containing samples.

DISCUSSION

The effects of diverse ions in this method have been extensively studied(1). Table I, reproduced from Anal. Chem. 31, 1130 (1959), can serve as a guide.

TABLE I. TOLERANCES OF DIVERSE IONS IN METHOD

Amount of Uranium = 1.05×10^{-4} mmole (25 μg)

Metal Cation	Highest Level Studied with no Interference, mmoles	Anion	Highest Level Studied with no Interference, mmoles
Ag(I)	1.2	Acetate	1.2
B(III)	See Anion		
Ba(II)	0.025	Borate	0.025
Be(II)	1.0	Bromate	0.5
Bi(III)	0.5	Chloride	0.25
Ca(II)	0.75	Citrate	0.25
Cd(II)	0.5	Cyanide	0.25
Ce(III)	0.5	Chromate	0.012
Ce(IV)	0.25 ^a	Formate	1.2
Co(II)	1.2	Fluoride	0.25
Cr(III)	1.5	Ferricyanide	0.25
Cr(VI)	See Anion		
Cu(II)	1.0	Ferrocyanide	0.00025
Fe(III)	0.5	Molybdate	0.025
Hg(I or II)	0.5	Oxalate	0.05
K(I)	0.5	Perchlorate	0.25
Lanthanides(III)	0.5	Persulfate	0.25
		Phosphate	0.25
Mg(II)	0.75	Sulfate	0.25
Mn(II)	0.5	Thiocyanate	0.025
Mo(VI)	See Anion		
Na(I)	1.2	Tungstate	0.0012
Ni(II)	1.0	Vanadate	0.012
Pb(II)	0.25		
Pu(III, IV, or VI)	0.0002		
Sr(II)	0.5		
Th(IV)	0.25 ^a		
V(V)	See Anion		
W(VI)	See Anion		
Zn(II)	1.0		
Zr(IV)	0.25		

^a With special procedure as described.

As stated in the ABSTRACT, large amounts of thorium interfere and a special procedure is included for the thorium-containing samples. Also large amounts of cerium, if in the +4 valence state, interfere. This interference of cerium can be overcome either by using the special procedure described for thorium samples or by prereducing it with such reducing agents as hydrogen peroxide or sodium sulfite.

Uranium must be in the +6 valence state to be quantitatively extracted. A preliminary oxidation with potassium permanganate is included in the procedure which is to be used for all samples in which the uranium is suspected to be present in valence states lower than +6. The stable valence state of uranium in solution is the +6 and most solutions encountered for analysis will not require this oxidation treatment. Lower valence states, especially +4, will exist in solutions that contain either strong reducing agents or complexing agents such as fluoride and oxalate.

APPLICABILITY

With the salting solution composition specified and the volumes of the aqueous and organic phases specified, the maximum volume of sample is 1 ml., the maximum amount of uranium in the sample aliquot is 75 $\mu\text{g.}$, and the maximum amount of acid in the sample aliquot is 16 meq. Larger volumes of samples can be analyzed by evaporating them first. Evaporation also can be used to decrease the acid levels.

This method is not as sensitive as the pellet fluorophotometric method(45) and therefore cannot be used for the routine analysis of low-level uranium plant streams. Because the precision is about five times better than the fluorophotometric method, this method should be used for all other samples which contain sufficiently large concentrations, greater than 1×10^{-3} mg. per ml., of uranium.

SPECIAL SAFETY PRECAUTIONS

Methyl isobutyl ketone (hexone) is flammable.

Pyridine may be slightly toxic if breathed in large concentrations.

(45) Shepherd, M. J., Jr., Rein, J. E., eds. Manual of the Analytical Methods Used by the Control Laboratory at the Chemical Processing Plant. Parts I and II, IDO-14316 (Jan., 1955). Supplement 1 (Nov., 1956). Supplement 2 (March, 1957). Supplement 3 (Oct., 1957), method U-Fluor-1.

APPARATUS AND REAGENTS

A. Apparatus

1. Test tubes, glass 15-x125-mm.
2. Polyethylene stoppers, 11-x17-mm., to fit above test tubes.
3. Extraction apparatus, pin wheel type is recommended.
4. Centrifuge, International Clinical, Model C1, or equivalent.
5. Pipets, volumetric, 2- and 5-ml.
6. Pipets micro, assorted sizes with control syringe.
7. Volumetric flasks, 25-ml.
8. Spectrophotometer, Beckman Model B or DU, or equivalent.
9. Absorption cells, Pyrex, 5-cm., matched or calibrated to ± 0.002 absorbance units.

B. Reagents

NOTE: All reagents are C.P. or Analytical Reagent Grade Stock. Use distilled water for the preparation of all reagents and deionized water throughout the procedure.

1. Potassium permanganate solution, 0.002M. Dissolve 0.316 g KMnO_4 in one liter of water. Store in a dark bottle.
2. Aluminum nitrate salting solution. Slurry 1050 grams of aluminum nitrate nonahydrate with a small amount of water. Add 135 ml. of concentrated ammonium hydroxide, 10 ml. of a 10% solution of tetrapropylammonium hydroxide, and dilute with water to about 950 ml. Stir until dissolved (disregard any fine colloidal suspension), then extract with 250 ml. of hexone in a separatory funnel. Filter the aqueous phase through a large fine-porosity sintered-glass Buchner funnel, add 10 ml. of 10% tetrapropylammonium hydroxide, and dilute to 1 liter with water.
3. Hexone (methyl isobutyl ketone).
4. Scrub solution. Add 940 grams of aluminum nitrate nonahydrate, 33 grams of tartaric acid, 31 grams of oxalic acid, and 64 grams of ethylenediaminetetraacetic acid to 100 ml. of water and 150 ml. of concentrated ammonium hydroxide. Heat mildly and stir until dissolution is complete, cool, filter, and make to 1-liter volume with distilled water. Remove uranium contamination by contacting with methyl isobutyl ketone.

5. Ferrous sulfamate solution. Add ferrous ammonium sulfate to a saturated solution of sulfamic acid until no more dissolves. This reagent is not highly stable. Prepare once a week.
6. Dibenzoylmethane Reagent. Dissolve 0.1140 gram of dibenzoylmethane in 400 ml. of pyridine. Add 25 ml. of ethanol and make to volume in a 500-ml. volumetric flask with pyridine.
7. Special Solutions for Samples which Contain Large Amounts of Thorium [or Cerium(IV)].
 - a. Salting solution. Prepare as described above for Reagent 1 except omit the tetrapropylammonium hydroxide.
 - b. Scrub solution. Dissolve 154 grams of ammonium acetate and 20 grams of the sodium salt of diethyldithiocarbamate in 900 ml. of water. Adjust the pH to 7 with acetic acid, filter, and make to volume in a 1-liter volumetric flask with water.
 - c. Mercuric nitrate solution. Dissolve 0.063 gram of mercuric nitrate in 90 ml. of 1M nitric acid and make to volume in a 100-ml. volumetric flask with 1M nitric acid.

PROCEDURE

A. Matching of Cells

Cells should be matched or correction factors determined to within 0.002 absorbance units. To do this, fill them with hexone and compare in the spectrophotometer at 415 mμ. If cells do not check, they may be cleaned with hexone followed by an acetone rinse.

B. Calibration and Bench Standard

A separate calibration is required for each procedure, E and F. Use 500λ of each of two standards (0.050 and 0.125 mg./ml.). Record the absorbance for each of the standards and divide by the respective milligrams of uranium in the aliquot to obtain the conversion factor. If either the average of the two conversion factors or the difference between them does not agree within limits set by the Quality Control Laboratory, process another pair of standards. Contact your supervisor if agreement is still not obtained.

C. Blank

Substitute 500 λ of 1M nitric acid for the sample and carry through the procedure, (E or F), as applicable.

D. Sample Analysis: (For Samples Void of Thorium)

1. To a test tube, add 1 ml. or less of sample containing from 5×10^{-4} to 0.075 mg. of uranium and less than 16 meq. acid.
 - a. If the uranium is known to be all in the +6 oxidation state, proceed to step 2.
 - b. If uranium in lower oxidation states than +6 is suspected, add 1 drop of concentrated nitric acid, then dropwise add 0.002M potassium permanganate with continuous swirling until the purple color of the permanganate remains for at least 5 seconds. If the total volume exceeds 1.5 ml. (if more than 9 drops of potassium permanganate was added), evaporate without spattering to a volume less than 1 ml. Cool to room temperature.
2. Add 8 ml. of the salting solution (reagent 2).
3. Quantitatively pipet 2.0 ml. of hexone into the tube, stopper with a polyethylene stopper, and extract for 3 minutes.
4. Centrifuge for 1 minute and transfer (with a micropipet) as much of the organic phase as possible to another tube which contains 5.0 ml. of scrub solution (reagent 3).
5. Add 0.25 ml. (5 drops) of the saturated ferrous sulfamate solution, stopper the tube, and scrub for 3 minutes. The ferrous sulfamate cannot be incorporated as part of the scrub solution because the iron(II) will be oxidized to iron(III). This will result in incomplete scrubbing of such elements as plutonium.
6. Centrifuge for 1 minute and transfer (with a micropipet) exactly 1 ml. of the organic phase to a 25-ml. volumetric flask.
7. Add 15 ml. of the dibenzoylmethane-pyridine reagent, mix well, and allow to stand a minimum of 15 minutes. The color is stable for 1 hour.

8. Transfer the solution into a 5-cm. cell and measure the absorbance at 415 mμ. compared to a blank set at 0.000 absorbance.

F. Sample Analysis. (For Samples Containing Thorium or Large Amounts of Cerium).

1. To a test tube, add 1 ml. or less of sample containing from 5×10^{-4} to 0.075 mg. of uranium and less than 16 meq. acid.
 - a. If the uranium is known to be all in the +6 oxidation state, proceed to step 2.
 - b. If uranium in lower oxidation states than +6 is suspected, add 1 drop of concentrated nitric acid, then dropwise add 0.002M potassium permanganate with continuous swirling until the purple color of permanganate remains for at least 5 seconds. If the total volume exceeds 1.5 ml. (if more than 9 drops of potassium permanganate was added), evaporate without spattering to a volume less than 1 ml. Cool to room temperature.
2. Add 8 ml. of the salting solution (reagent 7a).
3. Quantitatively pipet 4.0 ml. of hexone into the tube, stopper, and extract for 3 minutes.
4. Centrifuge for 1 minute and transfer as much of the organic phase as possible to another tube which contains 5.0 ml. of the scrub solution (reagent 7b). Stopper the tube and scrub for 20 minutes.
5. Centrifuge for 1 minute and transfer as much of the organic phase as possible to another tube which contains 5.0 ml. of the salting solution (reagent 7a).
6. Add 500λ of the mercuric nitrate solution, stopper the tube, mix for 10 minutes, and centrifuge for 1 minute.
7. Pipet 2 ml. of the organic phase into a 25-ml. volumetric flask.
8. Add 15 ml. of the dibenzoylmethane-pyridine reagent, mix well, and allow to stand for 15 minutes.
9. Pour the mixture into a 5-cm. cell and read the absorbance at 415 mμ. Compare against a blank set at 0.000 absorbance.

CALCULATIONS

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Absorbance of each of the calibration standards.
B	Conversion factor, obtained by dividing the absorbance reading by the milligrams uranium in the aliquot.
C	Average conversion factor.
D	Sample size, in ml.
E	Absorbance reading of sample.
F	Enrichment factor. See Table I. This factor is based on the use of normal uranium for calibration.
G	Results in mg./ml.

$$G = \frac{E F}{C D}$$

Report results to three significant figures, 0.0697, 0.697, etc.

TABLE II. ENRICHMENT FACTORS

<u>% Enrichment</u>	<u>Factor</u>	<u>% Enrichment</u>	<u>Factor</u>
0.7 (normal)	1.0000	88.1 - 90.0	0.9889
80.0 - 82.0	0.9899	90.1 - 92.0	0.9887
82.1 - 84.0	0.9897	92.1 - 94.0	0.9884
84.1 - 86.0	0.9894	94.1 - 96.0	0.9882
86.1 - 88.0	0.9892	98.1 - 98.0	0.9879
		98.1 - 100.0	0.9877

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GRAVIMETRIC DETERMINATION OF URANIUM

ABSTRACT

A gravimetric method for the determination of uranium is described. Solutions of uranium nitrate are weighed by difference from a Lunge weighing buret into tared platinum crucibles. Hydrofluoric acid is added and the samples are evaporated to dryness and ignited at 900°C. to the black oxide, U_3O_8 . Corrections based on a spectrographic analysis are made for impurity metals.

APPLICABILITY

The method is applicable to any pure aqueous uranium solution containing spectrographically-determinable amounts of nonvolatile impurities.

APPARATUS AND REAGENTS

A. Apparatus

1. Crucibles, platinum, 15-ml.
2. Buret, weighing, Lunge.
3. Heat lamp, infrared.
4. Furnace, muffle.
5. Desiccator.
6. Filtration accelerators, Fisher Scientific Company.

B. Reagents

1. Hydrofluoric acid, 48%, Reagent Grade.

PROCEDURE

1. Ignite the platinum crucible for 10 minutes at 900°C., cool for at least 15 minutes in a desiccator, and weigh. This should be repeated to a constant weight of ± 0.3 mg.
2. Accurately weigh 4 to 6 grams of sample from a Lunge weighing buret into the tared crucible.

3. Add two circles of filtration accelerator and 1 ml. of hydrofluoric acid.
4. Evaporate to dryness under an infrared lamp at a rate to prevent spattering.
5. Ignite in a muffle furnace for 1 hour at 900°C.
6. Cool the crucible for at least 15 minutes in a desiccator.
7. Weigh.
8. Repeat steps 5 through 7 until a constant weight of ± 0.3 mg. is attained.
9. Return the unused portion of the sample from the Lunge weighing buret to the original sample bottle. Rinse the buret with water and save the rinse. Dissolve the U_3O_8 in concentrated nitric acid and add this solution to the rinse solution. Save and concentrate all rinse solutions for salvage.

CALCULATIONS

1. Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Weight of buret plus sample, grams. Also record the buret number.
B	Tare weight of buret after sample withdrawal, grams.
C	Weight of sample, grams. $C = A - B$
D	Weight of crucible + U_3O_8 , grams.
E	Tare weight of crucible, grams.
F	Weight of U_3O_8 , grams. $F = D - E$
G	Uranium gravimetric factor. Obtain from Table I.
H	Purity of uranium. Calculate as shown below.
I	Result, mg of uranium per gram of sample. $I = \frac{F G H 10^3}{C}$

Report results to one decimal place.

2. Calculate the purity of uranium.

- a. Obtain the concentration (ppm) of each impurity from the spectrographic analysis results.
- b. Multiply the concentration of each impurity by 10^{-6} and by the appropriate gravimetric factor obtained from Table II. This gives the decimal fraction of each impurity expressed as U_3O_8 .
- c. Add the decimal fractions of all impurities.
- d. Multiply the total by the appropriate uranium gravimetric factor obtained from Table I. This gives the total decimal fraction of impurities expressed as U.
- e. Subtract the total decimal fraction of impurities expressed as U from 1. This gives the purity of uranium, H.

TABLE I. URANIUM GRAVIMETRIC FACTORS

<u>Enrichment</u>	<u>Gravimetric Factor</u>
82 - 93% U^{235}	0.8465
71 - 82% U^{235}	0.8466
normal U	0.8480

TABLE II. GRAVIMETRIC FACTORS FOR IMPURITIES

<u>Element</u>	<u>Assumed Weighed Form</u>	<u>Gravimetric Factor</u>
Al	Al_2O_3	1.89
Cr	Cr_2O_3	1.46
Cu	CuO	1.25
Fe	Fe_2O_3	1.43
Mn	MnO_2	1.58
Na	Na_2O	1.55
Ni	NiO	1.27
Si	SiO_2	2.14

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1. Shepherd, M. J., Jr., IDO Notebook No. 17, pp. 158-163, 1953.
2. Voss, F. S. and Greene, R. E., K-1040, 1953.
3. Morgan, T. D., Rein, J. E., Private Communication, Sept. 1960.

TITRIMETRIC DETERMINATION OF ALUMINUM

ABSTRACT

The titration of hydroxide ions that are released by the reaction of fluoride on aluminate ions at pH 10.5-10.6 is the basis of this method for the determination of aluminum. The theoretical equation for the reaction is:

In practice, less than four hydroxyl ions are released per aluminate ion, thus, the concentration of the titrant is adjusted to correct the bias. A variety of ions interfere and special treatments are prescribed in the procedure to reduce interferences. These are discussed in detail in the APPLICABILITY section.

APPLICABILITY

The sample aliquot taken for analysis should contain 5 to 11 mg. of aluminum. For best precision, select a sample at the upper limit of the method.

The following is a summary of the effects of diverse ions given by Hays(1) for the direct determination of aluminum without any preliminary treatments:

1. Ions, such as acetate, carbonate, dichromate, and ammonium, which buffer at low pH have no effect.
2. Ions, which form hydroxides or basic anions at pH 10.5 and which release hydroxyl ions upon the addition of fluoride, are potential positive interferences. For example, beryllium, calcium, magnesium, lead, thorium, and zirconium interfere. Uranium(VI) at a 10 to 1 weight ratio to aluminum has no effect, but at 20 to 1, results are 1% high. At 200 to 1, results are 35% high.
3. Ions which precipitate as the hydroxide at pH 10.5 and coprecipitate aluminum cause low results. For example, 1 gram of iron coprecipitates 30 mg. of aluminum.
4. Phosphate, which is an effective buffer at high pH, adversely affects the precision of the method. Accuracy is not significantly affected(46).

(46)Independent studies (3) have shown that phosphate affects the accuracy as well as the precision of the determination. For example, at a 1.7 to 1 phosphate to aluminum molar ratio, the error is -2.7% while at 17 to 1, the error is -7.1% and considerable buffering is encountered.

5. High salt concentration also lessens the precision.

In addition, ions and chelating agents which complex aluminum at pH 10.5 are expected to interfere. Examples are fluoride, citric acid, EDTA, and triethanolamine.

Though many ions interfere, as discussed above, there are a number of treatments that can be used to eliminate or reduce the interference.

Mercury cathode electrolysis, as described under Procedure D, adequately removes Ag, Au, Bi, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, In, Mo, Ni, Pb, Pd, Po, Pt, Re, Rh, Sm, Tl, and Zn.

Uranium can be separated from aluminum by extraction into tributylphosphate-kerosene. Recommended conditions for extraction are 6M nitric acid salting solution and batch contact with an equal volume of 20% tributylphosphate-80% kerosene (AMSCO).

At phosphate to aluminum molar ratios less than about 5 to 1, phosphate bias can be minimized (3) by standardizing the hydrochloric acid titrant against aluminum standards that contain phosphate in amounts similar to that in the samples (Procedure G). At higher phosphate concentrations, preliminary removal of the phosphate by techniques such as ion exchange or analysis by an alternate procedure such as emission spectroscopy or X-ray fluorescence is necessary.

Oxalate can be used effectively (3) to eliminate the interference of the cations, Bi(III), Ca(II), Ce(III,IV), Cu(II), Hg(II), La(III), Mo(VI), Pb(II), Th(IV), V(V), U(VI), and Zr(IV) at equimolar ratios (Procedure F). However, oxalate masking is not effective for the ions, Cd(II), Co(II), Cr(III), Fe(III), Ni(II), and Zn(II) at the 1:1 ratio. The oxalate precipitates of some of the elements such as thorium metathesize at high pH to the hydroxide and interfere by coprecipitating aluminum or releasing hydroxyl ions. The calcium oxalate precipitate formed at pH 5-7 coprecipitates aluminum in this pH region and thus cannot be removed by filtration. In the recommended procedure, F, a filtration is performed at pH 2 to remove those cations which form insoluble oxalates at this acidity.

Volatile interfering ions such as fluoride can be volatilized by fuming the sample with sulfuric or perchloric acid prior to titration. This treatment will also effectively reduce the concentration of volatile common ions and thus reduce the salt concentration of the titration medium. Digestion with nitric and perchloric acids will decompose organic chelating agents such as citric acid and EDTA.

DISCUSSION

With acid-deficient samples such as dibasic aluminum nitrate, the hydroxy aluminum complex is so stable that a drifting end point is obtained. To correct this, a preliminary treatment with nitric acid is included in the recommended procedure.

The temperature of the solution during the titration should be close to room temperature. High temperature adversely affects the precision.

In the recommended titration procedure, the pH is first raised to 12.5 to 13.0 then lowered to pH 10.5 to 10.6. The pH should not be allowed to go below 10.5. At pH's below 10.5, aluminum hydroxide will precipitate, and the hydroxide does not always revert to the aluminate form upon readjustment to pH 10.5. Thus, if the pH falls below 10.5, discard the sample and process a new one.

Procedure H is a special procedure recommended for calcine glass samples containing lead and phosphate (4).

SPECIAL SAFETY PRECAUTIONS

Both the 15M sodium hydroxide and concentrated sulfuric acid can cause serious skin burns. Gloves should be worn when handling these reagents. Wash affected skin with copious quantities of cold water.

APPARATUS AND REAGENTS

A. Apparatus

1. pH meter.
2. Electrode, glass for high pH range.
3. Electrode, calomel.
4. Magnetic stirrer.
5. Magnetic stirring bar, polyethylene coated.
6. Burets, micro, Koch, 5-ml., graduated in 0.01-ml. increments.
7. Pipets, volumetric, assorted sizes.
8. Pipets, micro, assorted sizes with control syringe.

9. Beakers, Griffin, 50-ml.
10. Beakers, quartz, 100-ml.
11. Hot plate.
12. Eberbach Dynacath Mercury Cathode Apparatus.
13. Stirring rods, glass, 4-mm.
14. Centrifuge, clinical type.
15. Tubes, centrifuge, 15-ml., graduated, calibrated with water from a 15-ml. pipet.
16. Millipore filter apparatus, 1-in. diameter, with 1-in., 0.45- μ Gelman or Millipore membrane filters.
17. Fisher filtrator or equivalent for direct vacuum filtrations into the titration beaker.

B. Reagents

NOTE: All reagents are made from C.P. or Analytical Reagent Grade stock. Use distilled water throughout.

1. Hydrochloric acid, standard, $0.3840 \pm 0.0005M$.
2. Hydrochloric acid, 1 to 1. Mix equal volumes of concentrated acid and water.
3. Sodium hydroxide solution, $15M$.
4. Potassium fluoride solution. Dissolve 60 grams of potassium fluoride, $KF \cdot 2H_2O$, in 40 ml. of distilled water and adjust to a pH of 11.5 at room temperature with silica-free $1M$ potassium hydroxide solution. Prepare a fresh solution daily. Upon standing the solution acquires buffer properties and the pH drops. Store the solution in polyethylene containers.
5. Sulfuric acid, concentrated.
6. Sulfuric acid, $0.05M$.
7. Potassium oxalate, $2M$.
8. Nitric acid, concentrated.
9. Hydrochloric acid, concentrated.
10. Hydrochloric acid, $0.01M$.
11. Standard buffer solution at pH 10.
12. Saturated potassium oxalate solution.

PROCEDURE

A. Blank

For all types of samples except calcine glass samples (Procedure H), process the blank by the same procedure used for samples, substituting distilled water for the sample.

B. Bench Standard

Run a single determination of the aluminum bench standard according to the procedure used for the samples. Limits will be specified by the Quality Control Laboratory.

C. Preliminary Treatment for Samples Containing Fluoride

1. Quantitatively pipet an aliquot of sample which contains 5 to 11 mg. of aluminum into a 100-ml. quartz beaker.
2. Cautiously add 1 ml. of concentrated sulfuric acid.
3. Fume to dryness on a hot plate set at medium heat.
4. While the sample is fuming, standardize the pH meter with a pH 10 buffer solution.
5. Cool and add 20 ml. of distilled water, washing down the sides of the dish thoroughly.
6. Add about 1 ml. of 15M sodium hydroxide.
7. Heat to assure solution of the aluminum. Remove from the hot plate just before the boiling point is reached to prevent splattering.
8. Cool to room temperature.
9. Proceed to step 4, part G.

D. Preliminary Treatment for Samples Containing Large Amounts of Iron, Nickel, Chromium, Mercury, and Other Elements Deposit-able at a Mercury Cathode

NOTE: The mercury level in the cells should be kept at the bottom of the outlet tube.

1. Rinse the cell and electrodes with 100 ml. of water.
2. Raise the electrodes and drain the water into a waste beaker.

3. Place a 100-ml. beaker on the rubber stopper of the cell outlet, and using vacuum, remove as much water as possible.
4. Close the stopcocks.
5. Pipet an aliquot of the sample which contains from 5 to 11 mg. of aluminum into the cell.
6. Add 20 ml. of 0.05M sulfuric acid.
7. Turn on the cooling water at the water tap. There is no need to change the water dial on the instrument.
8. Set the cell selector switch.
9. Turn on the power switch and adjust the current to 5 amperes.
10. Electrolyze for 15 minutes. This is adequate for up to 50 mg. of reducible metal ions.
11. Adjust the current to zero and turn off the power switch.
12. Allow the solution to stand for about 1 minute.
13. Raise the electrodes out of the solution and drain the solution into a 100-ml. beaker which has been placed on the rubber stopper.
14. Use vacuum to remove as much solution as possible.
15. Lower the electrodes completely and rinse the cell and electrode with 25 ml. of water.
16. Rinse the electrode and drain the solution into the beaker using vacuum.
17. Continue with the analysis at step 4, part G.

E. Preliminary Treatment for Acid-Deficient Samples.

1. Quantitatively pipet an aliquot of sample which contains 5 to 11 mg. of aluminum into a 50-ml. beaker.
2. Add 1 ml. of concentrated nitric acid and mix by swirling.
3. Heat for 5 minutes in a boiling water bath.
4. Proceed to step 3, part G.

F. Oxalate Pretreatment for Samples Containing Calcium, Cerium(III, IV), Lanthanides, Thorium, Uranium(IV,VI), Vanadium(V), and Zirconium

NOTE: As discussed in the APPLICABILITY section, oxalate will also effectively mask equimolar amounts of the ions, Bi(III), Cu(II), Hg(II), Mo(VI), and Pb(II). However, these ions can also be removed by mercury cathode electrolysis, Procedure D.

1. Pipet an aliquot of the sample containing 5 to 11 mg. of aluminum and not more than equimolar amounts of the above mentioned cations into a 30- or 50-ml. beaker.
2. Add 1 ml. of concentrated hydrochloric acid, and heat to near-boiling. This will effectively destroy the stable hydroxy-aluminum complexes.
3. Add 5 ml. of the saturated potassium oxalate solution and stir.
4. With the aid of a Fisher filtrator, filter the sample through a 1-inch, 0.45- μ Millipore or Gelman membrane filter and wash through with 0.01M hydrochloric acid. Quantitative transfer of the aluminum is essential.
5. Continue with step 4 of Procedure G.

G. Titrimetric Procedure for Interference-Free Samples and Samples Treated According to Previous Sections

NOTE: Best results are obtained when the final volume for the titration is less than 50 ml. Considerable drifting in the meter occurs with larger volumes. This may be alleviated with an additional 2 or 4 ml. of the potassium fluoride reagent. If drifting still occurs, wait 30 seconds after titrating to the required pH. Continue this procedure until the drifting stops.

1. Standardize the pH meter with a pH 10 buffer solution.
2. Quantitatively pipet an aliquot of the sample which contains 5 to 11 mg. of aluminum into a 50-ml. beaker.
3. Dilute to 20 ml. with distilled water.
4. Place the stirring bar in the beaker and place the beaker on the stirrer.
5. Position the electrodes and buret tip in the beaker.
6. Adjust the stirrer to a medium speed.

7. If the pH of the solution is not 12.5 to 13.0, add 15M sodium hydroxide solution dropwise until this pH range is reached, but do not exceed pH 13. An excess results in large concentrations of sodium chloride which will decrease the sensitivity at the end point.
8. Add 1 to 1 hydrochloric acid dropwise until the pH is near 12, then add standard 0.384N hydrochloric acid from the buret until a pH of 10.5 to 10.6 has been reached. The pH should not be allowed to go below 10.5. Aluminum hydroxide will precipitate and the hydroxide may not redissolve upon readjustment to pH 10.5 - 10.6. If the pH falls below 10.5 discard the sample and process a new one.
9. Record the exact pH of step 8.
10. Pipet 2.0 ml. of the potassium fluoride reagent into the beaker.
11. Titrate with standard 0.384N hydrochloric acid until the exact pH previously recorded is reached.

NOTE: When the sample contains calcium, add the potassium fluoride reagent immediately after pH adjustment to 10.5, then titrate immediately.
12. Record the volume of hydrochloric acid titrant and determine the aluminum concentration as described under CALCULATIONS, part A.

II. Special Procedure for Calcine Glass Samples Containing Lead and Phosphate

NOTE: The majority of the glass samples will have the approximate composition, 25 wt.% Al_2O_3 , 18.5 wt.% Na_2O , 40.5 wt.% P_2O_5 , and 16 wt.% PbO . In some cases, a higher charge of Al_2O_3 is contemplated and in such cases, the concentration of the other oxides will be proportionately lower.

1. Standardization of the Hydrochloric Acid Titrant.

Standardize the hydrochloric acid titrant against 8.00-mg. portions of aluminum spiked with lead and phosphate in amounts comparable to that present in the samples. For glass samples of the composition shown above, the Pb:Al mole ratio is 0.2 and the phosphate:Al mole ratio is 1.44. Proceed according to the following procedure for the analysis of the samples beginning at step c. Run at least 2 titrations.

2. Analysis of Calcine Glass Samples.

- a. Weigh a suitable sample into a 50-ml. centrifuge tube and dissolve it with hot concentrated nitric or hydrochloric acid and water. If phosphate is to be determined also, use nitric acid. A small, usually insignificant amount of residue may remain undissolved. If complete dissolution is desired, isolate the residue, dissolve in sodium hydroxide, acidify, then recombine with the bulk of the sample. Dilute with water to an appropriate volume.

With samples of the excess alumina type (the glass sample will be white in appearance -- a noticeable conglomerate of relatively distinct alumina particles), sodium carbonate fusion is necessary. Weigh the crushed sample into a platinum crucible and fuse with 20 times its weight of sodium carbonate. Dissolve the melt with nitric or hydrochloric acid and dilute to a suitable volume with water.

- b. Pipet an aliquot of the dissolved sample into a 50-ml. beaker. The aliquot taken should contain 5 to 11 mg. of aluminum.
- c. Add 5 ml. of the saturated potassium oxalate solution and dilute to approximately 20 ml. with water.
- d. Position the electrodes in the beaker and add 15M sodium hydroxide dropwise until the pH reaches 12.5 to 13.0.
- e. Add 1:1 hydrochloric acid dropwise to pH 12, then add the standardized hydrochloric acid titrant from the buret just to pH 10.5.
- f. Pipet 2.0 ml. of the potassium fluoride reagent.
- g. Titrate with the standardized hydrochloric acid titrant to pH 10.5.
- h. Determine the aluminum concentration as described under CALCULATIONS, part B.

CALCULATIONS

A. For Analyses Performed According to Procedure G.

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Volume of sample, in ml.
B	Exact pH reached.
C	Volume of hydrochloric acid required for sample, in ml.
D	Volume of acid required for blank, in ml.
E	Result: Molarity of aluminum.

$$E = \frac{C-D}{10A}$$

Report results to three significant figures.

B. For Analyses Performed According to Procedure H.

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Volume of hydrochloric used to titrate the 8.00-mg. aluminum standards.
B	Calibration Factor
	$B = \frac{8.00}{A}, B' = \frac{8.00}{A}$
C	Average calibration factor
	$C = 0.5 (B + B')$
D	Weight of sample in grams.
E	Sample dilution, ml.
F	Sample aliquot analyzed, ml.
G	Volume of hydrochloric acid used to titrate the sample aliquot, in ml.
H	Result, mg. aluminum per gram of sample.

$$H = \frac{CEG}{DF}$$

Report the results to 3 significant figures.

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SPECTROPHOTOMETRIC DETERMINATION OF GOLD

ABSTRACT

A spectrophotometric method is described for the determination of gold. It is based on the orange-yellow bromaurate-TOPO (tri-octylphosphine oxide) complex formed upon extraction of the gold from a hydrobromic acid solution into chloroform containing TOPO. Absorbance of the organic phase is measured at 395 m μ ., the wave length of maximum absorbance for the complex formed. The method is rapid and highly specific.

APPLICABILITY

The method will tolerate large amounts of numerous cations and inorganic anions. When aqua regia is used for the dissolution of metal samples, care should be used to assure that the concentration of nitric acid after dilution to volume does not exceed 0.6M. As the ratio of hydrochloric acid to nitric acid decreases, the tolerance to nitric acid increases.

Free bromine greatly affects the sensitivity of this method; therefore it is necessary to distill reagent grade hydrobromic acid in the presence of metallic silver to remove the free bromine. Bromine is then added to the distilled solution in an amount necessary for maximum sensitivity.

Reagent or Spec Grade chloroform contains ethyl alcohol as a preservative. Its presence creates an actinically induced reduction process causing slow fading of the complex color. It is therefore necessary to redistill the chloroform, taking not greater than an 80% cut from the still, to remove the ethanol and possible degradation products.

If the presence of tin is expected in samples, it is necessary to use hydrogen peroxide to insure that all tin(II) is oxidized to tin(IV). Hydrobromic acid is then used to remove excess peroxide, and boiling removes the resulting bromine. Aqua regia will not completely oxidize the tin.

The sample aliquot taken for analysis should contain from 20 to 100 μ g. of gold. This will give the absorbancy range of linear response and of highest accuracy. The maximum volume of sample is 3.0 ml.

The following table gives the tolerance limits of all cations and anions investigated. Limits are given in mole ratios of the ion to gold. This table is given as a guide for the preparation of samples for analysis.

TABLE I
TABLE OF TOLERANCE LIMITS (MOLE RATIO TO GOLD)

<u>Metal Ions</u>					
Ag(I) ^a	100	Ir(IV)	1	Sc(III)	1000
Al(III)	6100	La(III)	1000	Se(VI)	2500
As(V)	10,000	Mg(II)	9400	Sn(II)	1
Ba(II)	10,000	Mn(II)	10,000	Sn(IV)	500
Be(II)	1,000	Mo(VI)	200	Ta(V)	1000
Bi(III)	300	Na(I)	10,000		
Cd(II)	10,000	Nb(V)	50	Te(IV)	1000
Ce(III)	1,000	Ni(II)	10,000	Th(IV) ^a	2500
Co(II)	10,000	Os(IV)	250	Ti(III)	4
Cr(III)	8,900	Ph(II)	1,000	Ti(IV) ^a	200
Cu(II)	3,300	Pd(II)	400	V(V)	200
Dy(III)	1,000	Pt(IV)	200	V(IV)	2000
Fe(III)	1,400	Rh(III)	400	W(VI)	150
Ga(III)	1,400	Ru(III)	500	Zn(II)	5000
Hg(II)	1,500	Sb(III)	500	Zr(IV) ^a	300

^a Slowly form precipitates

Anions

Chloride	40,000
Fluoride	29,000
Nitrate	26,000
Phosphate	25,000
Sulfate	30,000

APPARATUS AND REAGENTS

A. Apparatus

1. Spectrophotometer, Beckman Model B or DU.
2. Aminco absorption cells, 5-cm. optical path.
3. Distillation flasks, 500-ml. and 1000-ml.
4. Heating mantles, for 500-ml. and 1000-ml. distillation flasks.
5. Condensers, helix type equipped with diamond spray baffles.
6. Volumetric flasks, assorted sizes.
7. Pipets, volumetric, assorted sizes.
8. Pipets, micro, assorted sizes, and syringe.

9. Separatory funnels, 60-ml., pear-shaped, Teflon stopcocks.
10. Test tubes, glass, 16-x 125-mm., screwtop, Teflon-lined caps.
11. Stoppers, hollow polyethylene, size S-1.

B. Reagents

NOTE: All reagents are made from C. P. or Analytical Reagent stock. Use distilled water for the preparation of all reagents and throughout the procedure.

1. Standard gold stock solution, 1.000 mg. of gold per ml. Dissolve 1.0000 gram of gold metal in hot hydrochloric acid, adding nitric acid dropwise until the dissolution is complete. Evaporate the solution to near dryness and then add 50 ml. of concentrated hydrochloric acid and dilute to 1 liter with water.
2. Gold calibration standard I, 80.0 μg . of gold per ml. Dilute 4.00 ml. of standard gold stock solution to 50 ml. with 0.6M hydrochloric acid.
3. Gold calibration standard II, 40.0 μg . of gold per ml. Dilute 2.00 ml. of standard gold stock solution to 50 ml. with 0.6M hydrochloric acid.
4. Bromine water, 0.1%. Dissolve 0.100 ml. of bromine in water and dilute to 100 ml. Dissolution is slow but do not heat.
5. Hydrobromic acid solution, 1.75M. Distill 100 ml. of hydrobromic acid from a distillation flask containing silver metal turnings. Do not begin the collection of distillate until the solution in the distillation flask is nearly colorless. Add the freshly distilled hydrobromic acid to a 500-ml. volumetric flask, containing about 250 ml. of water and 2.00 ml. of 0.1% bromine water, and dilute to 500 ml. Prepare fresh daily.
6. TOPO-chloroform solution, 0.01M. Distill 500 ml. of chloroform, from a distillation flask containing 700 ml. of chloroform, into a 500-ml. volumetric flask containing 1.9333 grams of trioctylphosphine oxide. Do not collect the first 50 ml. of distilled chloroform. Discard the remaining chloroform after each distillation. Prepare fresh daily.

7. Phosphoric acid solution, concentrated.
8. Sodium sulfate, anhydrous powder.

PROCEDURE

Special Precautions: Stopper all vessels containing chloroform immediately after transfers. The vapors are poisonous, especially in contact with a flame when phosgene is formed.

A. Blank

Process a reagent blank with each series of samples and calibration standards.

B. Calibration and Bench Standard

Process a pair of calibration standards with each series of samples. The calibration standards are analyzed in the same manner as the unknowns, using 1.00-ml. aliquots of each.

Divide the absorbances by the micrograms of gold to obtain the conversion factors. The difference between the two conversion factors should not exceed the limits set by the Quality Control Laboratory. Also, the average conversion factor should agree with the established conversion factor within the specified limits. If either or both of the specifications are not met, process another pair of calibration standards. Consult your supervisor if difficulties still are experienced.

C. Samples

NOTE: It is recommended that a blank and a set of calibration standards be analyzed with six or less samples as a series.

1. Pipet 15.0 ml. of 1.75M hydrobromic acid solution into a 60-ml. separatory funnel.
2. Add 10 drops of concentrated phosphoric acid solution and swirl to mix.
3. Add an aliquot, of the unknown sample solution, containing from 20 to 100 $\mu\text{g.}$ of gold. The aliquot volume cannot exceed 3.0 ml. Swirl to mix.
4. Add 15.0 ml. of the 0.01M TOPO-chloroform solution and stopper the separatory funnel with a polyethylene stopper.

5. Shake vigorously for 1 minute and allow the phases to separate for 5 minutes.
6. Transfer the organic phase to a screw-top test tube containing about 1 gram of anhydrous sodium sulfate.
7. Shake vigorously and then centrifuge for 1 minute.

NOTE: This step will remove the water from the organic phase and a clear solution will result. If the solution is not clear either insufficient shaking or sodium sulfate is the cause.

8. Read the absorbance of the samples at 395 mμ. in 5-cm. cells against the reagent blank.

NOTE: Time is critical after the initial contact of the organic solution with the aqueous solution. The samples should be read between 15 and 30 minutes after contact. Precision and accuracy can be maintained by careful repetition of time.

9. Record the absorbance of the calibration standards and the samples on the worksheet and calculate the gold concentration of the samples according to the section pertaining to calculations.

CALCULATIONS

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Micrograms gold in the calibration standards.
B	Absorbance of the standards.
C	Conversion factors: $C = B/A$ $C' = B'/A'$
D	Average conversion factor: $D = 0.5(C + C')$
E	Volume of sample in ml.
F	Sample absorbance.
G	Result, μg. Au per ml. of sample solution
	$G = \frac{F}{DE}$

Report the results to three significant figures, such as: 7.21, 72.1, and 721 μg. per ml.

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2. White, J. C., Ross, W. J., "Separations by Solvent Extraction with Tri-n-octylphosphine Oxide," NAS-NS-3102 (February, 1961).
3. Holbrook, W. G., Rein, J. E., Anal. Chem. 36, 2451 (1964).

REMOTE DETERMINATION OF BULK DENSITY
AND PARTICLE SIZE OF WCF PRODUCT

ABSTRACT

Methods are described for the remote measurement of bulk density and average particle size of the WCF product.

APPLICABILITY

The procedures and apparatus described were developed specifically for the WCF calciner product. An 8-cc. sample is sufficient for both measurements. The procedures are applicable to samples with particle sizes between 0.3 mm. and 1.0 mm. and bulk densities between 1.5 and 0.8. The methods are, in principle, applicable to other sizes and densities; although such materials have not been tested.

DISCUSSION

The bulk density procedure is similar to the procedure used for cold samples (47). A weighed sample is poured through a funnel into a 10-ml. graduate and the volume is determined "as poured".

The particle size is measured with an air elutriator. A stepwise increasing flow of air passing up through a column of solids removes first the fines and, progressively, the larger particles. The solids collect in a graduated collection tube at the bottom of a cyclone-like air-solids separator. The air flow at which one half of the solids is transferred is determined by a graphical method. This flow is a function of the particle shape and density, as well as the particle size. For typical calciner product, however, the particle shape is independent of its size and density, and the particle density is proportional to the bulk density. An empirical equation relating the average particle diameter, the air flow, and the bulk density has been obtained by calibration with known samples.

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- (47) Shepherd, M. J., Jr., Rein, J. E., eds. Manual of the Analytical Methods Used by the Control Laboratory at the Chemical Processing Plant. Parts I and II, IDO-14316 (Jan., 1955). Supplement 1 (Nov., 1956). Supplement 2 (March, 1957). Supplement 3 (Oct., 1957) method Calciner Product-1.

SPECIAL SAFETY PRECAUTIONS

The calciner product is highly beta-gamma radioactive. Observe all Health Physics regulations.

APPARATUS

A. Apparatus Outside the RAF Box Shield

1. Controlled air supply. A pressure regulator (30 psig.), a control valve, and a flowmeter at the left of the viewing window.
2. Electric stop clock, mounted at the right of the viewing window.

B. Apparatus Inside the RAF Box

1. Elutriation apparatus. An elutriation tube, an air-solids separator, an air filter, and a solids collection tube.
2. Remote analytical balance.
3. Graduate, 10-ml.
4. Plastic funnel.
5. Wooden sample block.
6. Aluminum opening tube.
7. Air operated clamp compressor.
8. Suction line and trap (for collection of spilled solids).

C. Probability Paper, 2-cycle Log (K and E 358-24).

PROCEDURE

Prepare a worksheet using the example supplied with this procedure as a model.

A. Bulk Density

1. Insert the aluminum opening tube into the sample bottle. Weigh the tube and bottle. Record the weight (W_1) on the worksheet.

2. Place the small plastic funnel in the 10-ml. graduate. Turn the graduate so that the graduations are visible. Pour approximately 8 cc. of the sample into the graduate, being careful not to jar it. (Note 1) Estimate the volume of sample in the graduate to the nearest 0.1 ml. (When estimating the volume, remember that you are looking down at the solids. The top surface of the solids is usually better illuminated than the sides. Read the level of the sample with the graduations at the side of the tube or use the 1-ml. graduation rings to estimate the level.) Record the volume on the worksheet (V_1).
3. Weigh the sample bottle and tube. Record the weight (W_2) on the worksheet.

B. Average Particle Size

1. Remove the lead weighted plug from the sample entry port. Place the small funnel in the port and pour the contents of the graduate through it into the elutriator tube. Remove the funnel and replace the plug. (Note 2)
2. Verify that the pressure gauge at the left of the viewing window reads 30 psig. Release the air trapped in the regulator by opening the control valve until the trapped air flow stops. (No sample particle should be carried over.)
3. Slowly open the control valve until the sample just begins to enter the separator, then increase the flow until the bottom of the flowmeter ball rests at the next unit calibration.
4. Wait 3 minutes, then record the flowmeter reading (bottom of the ball) and the volume of solids in the collection tube.
5. Increase the airflow until the bottom of the flowmeter ball rests one unit higher. Again wait 3 minutes and read and record the flowmeter reading and the volume of solids in the collection tube.
6. Repeat step 5 until less than 0.5 cc. of sample remains. Increase the airflow to carry over the last solids. Record the total volume in the collection tube.
7. Remove the collection tube clamp using the air operated clamp compressor. While holding the tube with one manipulator, slide the supporting sponge to one side with the other manipulator. Remove the tube.

8. Insert the plastic funnel into the sample bottle through the opening tube and pour the solids from the collection tube back into the sample bottle. (Note 3)
9. Reinstall the collection tube on the separator by reversing the removal steps. Be sure the graduations are visible before reclamping. Remove the funnel and the opening tube from the sample bottle.

C. Calculations

1. Calculate the bulk density of the solids using the relation:

$$\text{Bulk Density} = \frac{W_1 - W_2}{V_1}$$

Record the calculated bulk density on the worksheet.

2. Compute and record the percentage of solids carried over at each flowmeter reading.
3. Plot the percentage carried over as a function of the flowmeter reading on a sheet of 2-cycle log probability paper. Draw a smooth curve through the points between 20 and 80%. The flowmeter reading at which 50% of the solids were transferred is proportional to the Mass Mean Air Velocity. Record the flowmeter reading as MMAV on the worksheet.
4. Calculate the Mass Median Particle Diameter (MMPD) by:

$$\text{MMPD} = a - (b)(\text{MMAV})(\text{Bulk Density}) + c(\text{MMAV})^2$$

where a, b, and c are constants determined by calibration with known samples. Record the calculated MMPD. Attach the graph to the worksheet.

NOTES

1. Spilled calciner product should be promptly picked up with the suction line to prevent the spread of contamination.
2. The filter on the solids-air separator should be replaced if the lead weighted plug will not remain seated in its entrance port at high air flows. Periodic replacement may be needed to reduce the background radiation level.
3. The samples for the nitrate and alpha alumina determination should be taken before the solids are returned to the sample bottle.

ANALYTICAL PROCEDURES FOR WESTINGHOUSE ECF SAMPLES

DETERMINATION OF CHROMIUM, COBALT, IRON, MANGANESE,
NICKEL, AND PRINCIPAL CONSTITUENTS OF DESCALING MAKE-UP SOLUTIONSABSTRACT

This is a collection of methods for the analysis of Westinghouse ECF fuel descaling (crud) solutions. Included are procedures for the pretreatment of samples (section A), and procedures for the determination of chromium, cobalt, iron, manganese, nickel, and principal components of ECF descaling make-up solutions (sections B, C, D, E, F, and G, respectively).

INTRODUCTION

Westinghouse NRF is evaluating various processes for descaling irradiated zirconium-clad fuel elements. The nature of the treatments and the estimated compositions of the resulting sample solutions are described in Table I.

TABLE I
FUEL ELEMENT DESCALING PROCESSES AND APPROXIMATE
COMPOSITIONS OF THE DESCALED SAMPLE SOLUTIONS

Descaling Treatment	Remarks	Approximate Sample Composition ^a
1. Supersonic agitation of the fuel elements in water.	Normally, only the solids are to be analyzed. In some cases, when total solids are low, the solids are dissolved with a NaHSO ₄ fusion and combined with the filtrate.	(a) Combined solution H ₂ SO ₄ , 0.5M HNO ₃ , 0.5M metal ions Na ₂ SO ₄ -NaHSO ₄ , ~3g/l. (b) Solution of the solids Na ₂ SO ₄ -NaHSO ₄ , ~3g/100 ml. metal ions
2. Sequential treatment with (a) 20 mg./ml. oxalic acid (b) 0.5M HNO ₃	Loosened but undissolved crud is usually present in both solutions. The crud is filtered off, fused with NaHSO ₄ and re-dissolved in the parent solution. Equal volumes of the two solutions are then combined.	Oxalic acid, 10 mg./ml. HNO ₃ , 0.3M H ₂ SO ₄ , 0.1M metal ions Na ₂ SO ₄ -NaHSO ₄ , ~3g/l.

TABLE I (Continued)

<u>Descaling Treatment</u>	<u>Remarks</u>	<u>Approximate Sample Compositions^a</u>
3. Contact with an ammoniacal solution of EDTA (0.25M) and N_2H_4 (0.5M)	The samples tend to be low (2 to 20 $\mu\text{g./ml.}$) in iron.	EDTA, 0.25M N_2H_4 , 0.5M NH_4^+ , 0.5M metal ions Na_2SO_4 - $NaHSO_4$, ~3g/l.
4. Sequential treatment with (a) 12 mg./ml. $KMnO_4$ - 6 mg./ml. NaOH (AP) (b) 30 mg./ml. $(NH_4)_2H$ - citrate (AC)	Each solution will be submitted separately for analysis.	(a) $KMnO_4$, 12 mg./ml. NaOH, 6 mg./ml. Cr and Fe (low) (b) $(NH_4)_2H$ citrate, 30 mg./ml. $KMnO_4$, 0.5 mg./ml. NaOH, low metal ions Na_2SO_4 - $NaHSO_4$, ~3g/l.
5. Immersion in concentrated HCl	Crud dissolves completely. On this basis, the samples will tend to be high in iron.	HCl, high metal ions

^a When complete dissolution of crud is obtained, the iron concentration will range from 2 to 200 $\mu\text{g./ml.}$ with most samples expected to range from 50 to 100 $\mu\text{g./ml.}$ With the exception of solution 4a, the concentration of the accompanying metal ions: Co, Cr, Mn, Ni, and Zr will be proportionate to the iron as shown below.

<u>Metal</u>	<u>Relative Percent</u>
Fe	90
Co	0.5
Cr	3
Mn	1
Ni	5
Zr	1

The methods described in the following sections were developed specifically for the analyses of samples of the compositions shown in Table I. As stated in the footnote of Table I, iron is the principle metal component and the accompanying metal ions: Co, Cr, Mn, Ni, and Zr are proportionate to the iron. Thus, the determination of iron should be concluded first to facilitate subsequent determinations for the minor constituents.

Though investigated, no satisfactory procedure is available for the spectrophotometric determination of zirconium. Zirconium, therefore, should be determined spectrographically.

As described in Table I, a number of the samples contain organic chelating agents which interfere in the colorimetric procedures for chromium, cobalt, manganese, and nickel. Also, the concentrations of the metal ions are generally low. Digestion procedures are therefore included in the various procedures to destroy the interfering organic reagents and to concentrate the samples to within the range of the colorimetric procedures. Two digestion procedures are used, digestion with nitric, perchloric, and sulfuric acids, and digestion with sulfuric acid and hydrogen peroxide. Both procedures can be used for the determination of cobalt, manganese, and nickel. For the chromium determination, the latter must be used.

Based on the results of the analyses of samples received to date, the metal ion concentration of a large proportion of the samples is extremely low even after concentration. Thus, clean all equipment carefully and use distilled water whenever possible.

PROCEDURES

Presented in separate sections below are the following procedures:

- A. Pretreatment of Samples
- B. Determination of Chromium
- C. Determination of Cobalt
- D. Determination of Iron
- E. Determination of Manganese
- F. Determination of Nickel
- G. Determination of Principal Components of ECF Descaling Make-up Solutions.

A. Pretreatment of Samples

The pretreatment procedures for ECF crud samples are summarized in Table II.

TABLE II. PRETREATMENT PROCEDURES FOR ECF CRUD SAMPLES

Sample Type and Analytical Sample Code	Recommended Pretreatment Procedure	Remarks
I. Water (W)	<ol style="list-style-type: none"> 1. Measure the sample volume. 2. Filter the crud on a tared 0.45-μ, 47-mm membrane filter, air dry, and weigh. NOTE: When washing the precipitate, remove the "chimney" reservoir and wash the periphery of the filter paper. 3. Char the filter, then dissolve the crud by fusion with NaHSO_4. Use a minimum amount of NaHSO_4. Generally, 2 to 3 grams will be sufficient. 4. Dissolve the melt in water and dilute to a small known volume. 	Normally, there is no request for analyses on the filtrate. Recombine the dissolved crud with the filtrate only when so advised. The requestor has asked that this be done only when the crud level has been very low. Therefore, when the crud level is low, contact the requestor. $\text{K}_2\text{S}_2\text{O}_7$ fusion should not be used because K interferes with the Mn determination.
II. Oxalic-Nitric (ON)	<ol style="list-style-type: none"> 1. Measure the volume of the oxalic (O) and nitric (N) solutions separately. 2. Filter each through a 0.45-μ membrane filter. 	<p>$\text{K}_2\text{S}_2\text{O}_7$ fusion should not be used because K interferes with the Mn detn.</p> <p>Occasionally, samples arrive already combined and are so specified. If so, proceed with the analyses.</p>

TABLE II (Continued)

Sample Type and Analytical Sample Code	Recommended Pretreatment Procedure	Remarks
III. EDTA-N ₂ H ₄ -NH ₄ OH (HV)	3. Char the filter, then dissolve the crud from each solution by fusion with MINIMUM NaHSO ₄ . Take up the melt in its respective filtrate.	K ₂ S ₂ O ₇ should not be used because K interferes in the Mn determination.
	4. Combine equal volumes of both solutions.	
	1. Filter the residue on a 0.45-μ, 47-mm membrane filter.	
	2. Char the filter, then dissolve the crud by fusion with MINIMUM NaHSO ₄ .	
IV. Alkaline Permanganate (AP) Ammonium Citrate (AC)	3. Take up the melt in the original filtrate.	NOTES: 1. Occasionally, some AP samples have been acidic rather than alkaline. In such a case, copious amounts of MnO ₂ residue are present, and in fact, all of the KMnO ₄ has precipitated as MnO ₂ in some cases. Make a note of this and inform the requestor and the Spectroscopy Section.
	1. The following is a schematic diagram of the procedure for AP samples. (See NOTE 1):	

Table II (Continued)

Sample Type and Analytical Sample Code	Recommended Pretreatment Procedure	Remarks
<p style="text-align: center;"><u>Sample</u></p> <p style="text-align: center;">↓ Measure volume.</p> <p style="text-align: center;">↓ Filter the crud on a 0.45-μ, 47-mm membrane filter.</p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> <p>↓</p> <p>Filtrate</p> <p>(Save for chemical, spectrographic, and radiochemical analyses)</p> </div> <div style="text-align: center;"> <p>↓</p> <p>Solid Residue</p> <p>Dissolve with HCl + H₂O₂ (See NOTE 2).</p> <p>If dissolution is incomplete, filter the residue on a membrane filter.</p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> <p>↓</p> <p>Filtrate</p> <p>Dilute to 100 ml. and send 10 ml. to the Spectroscopy Section for Cr analysis</p> </div> <div style="text-align: center;"> <p>↓</p> <p>Residue</p> <p>Char the paper and dissolve the solids with a NaHSO₄ fusion.</p> <p>Dissolve the melt in water and dilute to 100 ml. (See NOTE 3). Discard 10 ml. and combine the balance with the balance of the filtrate.</p> </div> </div> </div> <p style="text-align: center;">↓</p> <p style="text-align: center;">Combined Solution</p> <p>(Save for radiochemical and chemical analyses)</p> </div>		
		<p>2. In about 8 of 10 cases complete dissolution is obtained. If so, dilute to 100 ml. with water. Send a portion of the solution to the Spectroscopy Section and save the balance for radiochemical and chemical analyses.</p> <p>3. The filtrate and the dissolved residue should not be combined because the high Na₂SO₄ concentration interferes in the spectrographic analyses. No Cr has ever been detected in the residue.</p>

2. AC procedure:

- a. Filter the residue on a 0.45-μ, 47-mm membrane filter.
- b. Char the filter and dissolve the residue by fusion with MINIMUM NaHSO₄.
- c. Take up the melt in the original filtrate.

B. Determination of Chromium

B:1 Discussion

This procedure for the determination of chromium is a modification of the routine chromium procedure, Method Cr-4, Mod-1. It is a spectrophotometric method based on the formation of a red-violet chromium(III)-diphenylcarbazone complex produced by the reaction of chromium(VI) with diphenylcarbazide.

The major modifications are as follows:

1. In the usual procedure, sulfuric acid, nitric acid, and hydrogen peroxide are added to the sample and the sample is evaporated to sulfur trioxide fumes. These steps have been omitted.
2. Ammonium hexanitratocerate is used instead of ammonium persulfate for the oxidation of chromium(III) to chromium(VI) (1). The excess cerium(IV) is reduced with sodium azide.
3. The range of the method is 0.5 to 6 $\mu\text{g.}$ of chromium. Cells of 5.0-cm. length are used throughout.
4. For greater sensitivity, samples are diluted to 25 ml. instead of 50 ml. as prescribed in the normal procedure.
5. In many of the steps, the volume of reagent added has been reduced.

According to Sandell (3) the tolerance limit for iron, the principal component of crud samples, is about 200:1 mole ratio to chromium; however, recent studies indicate that the practical tolerance limit is about 50:1.

B:2 Apparatus and Reagents

B:2.1 Apparatus

NOTE: All glassware including new glassware must be cleaned before use. The following treatment has been found to be satisfactory: Pour a few ml. of a 1:1 mixture of nitric acid and hydrochloric acid into the glassware, boil for 5 minutes, then rinse well with water.

1. Spectrophotometer, Beckman Model DK or Cary Model 14.
2. Absorption cells, 5-cm.
3. Volumetric flasks, 25-ml.
4. Pipets, micro, assorted sizes.
5. Pipets, volumetric, macro, assorted sizes.
6. Pipets, Mohr, 5- or 10-ml.
7. Erlenmeyer flasks, 250-ml. and 125-ml.
8. Hot plate, oscillating.
9. Hot plate, Chromalox.
10. Transite board.
11. Reflux head for 250-ml. and 125-ml. Erlenmeyer flasks, obtained from G. Frederick Smith Chemical Co., Columbus, Ohio.
12. Tongs.
13. Test tube holders.
14. Ice bath.

B:2.2 Reagents

NOTE: All reagents are made from C.P or Analytical Reagent Grade stock. Use distilled water for all reagents and throughout the procedure.

1. Standard chromium stock solution, 0.5 mg. of chromium per ml. Dissolve 1.4144 grams of potassium dichromate in water and dilute to 1 liter.
2. Chromium calibration standard I, 4.00 μ g. of chromium per ml. Dilute 4.00 ml. of the chromium stock solution to 500 ml. with water.
3. Chromium calibration standard II, 2.00 μ g. of chromium per ml. Dilute 4.00 ml. of the chromium stock solution to 1 liter with water.
4. Ammonium hexanitratocerate reagent, 0.2M. Dissolve 2.75 grams of ammonium hexanitratocerate (obtainable from G. Frederick Smith Chemical Co., Columbus, Ohio) in 100 ml. of 0.5M sulfuric acid and dilute to 250 ml. with water.
5. Diphenylcarbazide solution, 0.25 percent. Dissolve 0.25 grams of diphenylcarbazide in 5 ml. of glacial acetic acid and dilute to 100 ml. with 95 percent ethanol. Prepare fresh daily.

6. Sulfuric acid solution, 5M.
7. Hydrogen peroxide, 30 percent. Keep in refrigerator when not in use.
8. Sodium azide solution, 0.1M. Dissolve 0.65 gram of sodium azide in water. If a clear solution is not obtained, filter through a 0.45- μ membrane filter. Dilute to 100 ml. with water.

B:3 Blank

Process a reagent blank with each series of samples and calibration standards according to the procedure used for the analysis of the sample(s).

B:4 Calibration and Bench Standard

Process a pair of calibration standards with each series of samples.

Pipet 1.00-ml. portions of the two standards (4 μ g. and 2 μ g. per ml.) into two 25-ml. volumetric flasks. Add 1.0 ml. of 5M sulfuric acid and 0.5 ml. of 30 percent hydrogen peroxide and evaporate to the appearance of sulfur trioxide fumes. Cool, rinse down the flask with 5 ml. of water, and continue as described in B:5 beginning at step 2.

Divide the absorbances by the micrograms of chromium to obtain the conversion factors. The difference between the two conversion factors should not exceed limits set by the Quality Control Laboratory. Also, the average conversion factor should agree with the established conversion factor within the specified limits. If either or both of the specifications are not met, process another pair of calibration standards. Consult your supervisor if difficulties still are experienced.

B:5 Predigestion and Concentration of ON, HV, and AC Samples

1. Pipet an aliquot (consult the following table for sample volume limits) containing 0.5 to 6 μ g of chromium. For aliquots less than 10 ml., use a 25-ml. volumetric flask. For aliquots larger than 10 ml., use a 250-ml. Erlenmeyer flask.

<u>Sample Type</u>	<u>Permissible Aliquot</u>
EDTA-N ₂ H ₄ -NH ₄ OH (HV)	50 ml.
(NH ₄) ₂ Citrate (AC)	50
Oxalic acid-HNO ₃ (ON)	100

2. Add 0.5 ml. of 30% hydrogen peroxide.
3. Add 1 ml. of 5M sulfuric acid for each 10 ml. of sample. For samples that are less than 10 ml., add 1 ml.
4. Evaporate to strong sulfuric acid fumes or until sample turns black.
5. Cool slightly, then add 30% hydrogen peroxide dropwise to destroy the charred organic material.
6. Evaporate again to sulfur trioxide fumes or until the sample turns black, then add more 30% hydrogen peroxide. Repeat steps 4 and 5 until all the organic matter is destroyed. If much sulfuric acid is volatilized in the process, it may be necessary to add additional sulfuric acid. The absence of organic matter is indicated by the absence of charring on strong fuming.
7. Evaporate to near dryness on a hot plate. In the case of samples containing appreciable amounts of molten ammonium salts, evaporate until copious sulfur trioxide fumes are no longer being evolved.
8. Cool. Add 1 ml. of 5M sulfuric acid and about 3 ml. of water and heat gently to dissolve the solids. If the sample is in an Erlenmeyer flask, transfer the sample quantitatively to a 25-ml. volumetric flask with small water rinses. The total volume of the sample should not exceed 15 ml. after the transfer.
9. Continue with the determination of chromium according to B:7.

B:6 Predigestion and Concentration of Water Samples

1. Pipet an aliquot of the sample containing 0.5 to 6 µg. of chromium into an Erlenmeyer flask (samples larger than 10 ml.) or a 25-ml. volumetric flask (samples 10 ml. or less).

2. Add 1 ml. of 5M sulfuric acid and 0.5 ml. of 30% hydrogen peroxide.
3. Evaporate to the appearance of sulfuric acid fumes.
4. Cool, then add 3 to 4 ml. of water. Heat gently to dissolve any solids. If the sample is in an Erlenmeyer flask, transfer the sample to a 25-ml. volumetric flask with small, water rinses. The total volume after transfer should not exceed 15 ml.
5. Continue according to B:7.

B:7 Color Development and Measurement

1. To the digested sample from B:5, step 8 or B:6, step 4, add the 0.2M ammonium hexanitratocerate solution dropwise until a permanent distinct yellow color of the cerium(IV) ion appears. If the sample contains a large amount of manganese, add the ammonium hexanitratocerate solution to the appearance of the permanganate color.
2. Heat the sample for 15 minutes on a Chromalox hot plate set at low. Use a Transite board on the hot plate to prevent overheating.
3. Remove the sample from the hot plate and cool it in an ice bath to 25°C. or less.
4. Add 0.1M sodium azide with swirling until the yellow color and/or the permanganate color is decolorized. If the sample is brown after the addition of sodium azide, discard the sample and process a new one. The brown color indicates that the digestion was incomplete.
5. Dilute to about 22 ml. with water and cool to room temperature.
6. Add 1 ml. of the 0.25% diphenylcarbazide solution, dilute to volume and mix thoroughly. Full color development is obtained immediately and the color is stable for 1 hour.
7. Measure the absorbance of the sample against the reagent blank at 540 mμ. in 5-cm. cells. Use a Beckman DK-2 or a Cary Model 14 spectrophotometer.

8. Record the data on the worksheet and compute the chromium concentration as described in B:8.

B:8 Calculations

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Micrograms chromium in the calibration standards.
B	Absorbance of the standards.
C	Conversion factor: $C' = B'/A', C'' = B''/A''$ Average conversion factor $C = 0.5 (C' + C'')$
D	Volume of sample in ml. (from step 1 of section <u>B:5</u> or section <u>B:6</u> .)
E	Digested sample dilution in ml.
F	Volume of digested sample used in ml.
G	Sample absorbance.
H	Result, $\mu\text{g. Cr per ml.}$ of the original sample. $H = \frac{EG}{CDF}$

Report the results to three significant figures for values greater than 1 and to the nearest 0.001 $\mu\text{g.}$ for values less than 1, for example: 16.7, 1.67, 0.167 and 0.017 $\mu\text{g. per ml.}$

B:9 References

1. Fortsch, E. M., Private Communication, Dec., 1964.
2. Holbrook, W. B., IDO Notebook No. U-47, 1957.
3. Sandell, E. B., "Colorimetric Determination of Traces of Metals", 2nd Ed., pp. 260-264, Interscience, New York, 1950.

C. Determination of Cobalt

C:1 Discussion

A solvent extraction-spectrophotometric procedure is described for the determination of microgram amounts of cobalt. The pink cobalt-2-nitroso-1-naphthol complex is formed in an acetate buffered medium at pH 5.5. A reaction time of thirty minutes is required for complete color formation. Concentrated hydrochloric acid then is added to break the complexes formed between the reagent and other metal ions such as iron, and the cobalt complex is extracted into a 3:1 mixture of carbon tetrachloride and xylene. Excess reagent is stripped from the organic phase with dilute sodium hydroxide and the absorbance of the cobalt complex is read in a 5-cm. cell at 525 m μ .

The lower limit of detection is about 0.25 microgram of cobalt, but for accuracy 1 to 7 micrograms should be taken for analysis.

C:2 Apparatus and Reagents

C:2.1 Apparatus

1. pH meter, Leeds & Northrup.
2. L & N miniature probe electrodes, modified.
Extend the calomel reference electrode as follows:
Sever the electrode below the bulbous reservoir and seal a two-inch Pyrex extension between the two ends. Extend the glass electrode with a two-inch straight piece of polyethylene tubing. Heat and straighten the glass electrode before attaching the polyethylene tubing. Stretch the electrode spring shield to accomodate the modified electrode.
3. Spectrophotometer, Beckman Model B, DU, or DK with matched 5.0-cm. cells of 7-ml. capacity.
4. Culture tubes, 50-ml., with Teflon-lined screw caps.
5. Test tube racks.
6. Pipets, volumetric, macro and micro, assorted sizes.
7. Erlenmeyer flasks, 250-ml.
8. Reflux head for 250-ml. Erlenmeyer flasks.
9. Hot plate, oscillating.
10. Medicine droppers.
11. Hengar granules (boiling chips).
12. Centrifuge tubes, 50-ml.

13. Beakers, assorted sizes.
14. Ice bath.
15. Speedy-vap cover glasses to fit beakers.

C:2.2 Reagents

1. 2-nitroso-1-naphthol, 0.5%. Purify the commercial reagent. Dissolve 2 grams of 2-nitroso-1-naphthol in 75 ml. of acetone. Transfer to a 500-ml. separatory funnel and add 300 ml. of xylene. Extract four times with 100-ml. portions of 0.5M sodium hydroxide. Combine the basic extracts in a clean 1-liter beaker. Discard the organic phase. Precipitate the reagent by adding concentrated hydrochloric acid to the combined basic extracts. Let the solution stand for 30 minutes, then filter off the solid reagent and air dry.

Dissolve 1.00 gram of the purified 2-nitroso-1-naphthol in 20 ml. of 0.5M sodium hydroxide and dilute to 200 ml. with water.

2. Hydrochloric acid, concentrated.
3. Sodium hydroxide, 0.5M.
4. Ammonium hydroxide, concentrated.
5. 2,4-dinitrophenol pH indicator. Dissolve 50 mg. in 100 ml. of water.
6. Sodium sulfate, anhydrous powder.
7. Acetic acid, glacial.
8. Sodium citrate, 0.5M.
9. Cobalt stock solution, 1.00 µg. cobalt per ml. Dissolve 1.0000 gram of cobalt metal in 35 ml. of nitric acid and dilute to 1 liter.
10. Cobalt calibration standard I, 5 µg. cobalt per ml. Dilute 5.00 ml. of the cobalt stock solution to 1 liter with 0.5M nitric acid.
11. Cobalt calibration standard II, 10 µg. cobalt per ml. Dilute 10.00 ml. of the cobalt stock solution to 1 liter with 0.5M nitric acid.
12. Carbon tetrachloride-xylene solvent. Mix 750 ml. of carbon tetrachloride with 250 ml. of xylene. Store in a brown glass bottle.
13. Perchloric acid, concentrated.
14. Sulfuric acid, concentrated.
15. Nitric acid, concentrated.
16. Triacid digestion mixture, 1:2:5 sulfuric acid, perchloric acid, and nitric acid. Prepare as needed.

C:3 Blank

Run a blank with each set of samples.

C:4 Calibration and Bench Standard

Process a pair of calibration standards with each series of samples. Use 500 λ of each of the two cobalt calibration standards I and II and process these according to D:5. Divide the absorbance by the micrograms of cobalt to obtain the conversion factors. The difference between the two factors should not exceed limits set by the Quality Control Laboratory. Also, the average conversion factor should agree with the established factor within the specified limits. If either or both of the specifications are not met, process another pair of calibration standards. Consult your supervisor if difficulties still are experienced.

C:5 Predigestion and Concentration of Oxalic-Nitric (ON) and EDTA-N₂H₄-NH₄OH (HV) Samples.

NOTE: The concentration of ammonium citrate (AC) samples, which require no digestion is described in section C:6.

1. Pipet an aliquot of the samples containing 0.5 to .7 μ g. of cobalt into a 250-ml. Erlenmeyer flask. Generally, 50-100 ml. of sample will be required. Practical sample volume limits are 100 ml. for both ON and HV samples.
2. Add a Hengar granule boiling chip and place a reflux head on the flask.
3. Evaporate to about 10 ml. on an oscillating hot plate.
4. Add a 1:2:5 mixture of sulfuric acid, perchloric acid, and nitric acid slowly, a small portion at a time. If necessary, cool the Erlenmeyer flask in an ice water bath to control the reaction. Generally, 8 ml. of the mixture will be required for each 20 ml. of sample.
5. When the required acid mixture has been added and the reaction subsides, return the flask to the hot plate and evaporate the sample to about 2 or 3 ml.
6. Cool. Transfer quantitatively with small water rinses to a 50-ml. centrifuge tube.
7. Fume down to about 1 ml. over a Meker burner. Swirl the flask continuously to avoid baking the sample. If a brown color indicative of undigested organic compounds persists, cool the flask, add 1 ml. of con-

centrated nitric acid and reheat. Continue the nitric acid treatment until the brown color no longer appears on strong fuming.

8. Evaporate the sample to near dryness. Do not bake the sample. With large HV samples, large amounts of ammonium sulfate are formed during the digestion. In such cases in which the ammonium sulfate melt may be as much as 2 ml., evaporate the sample until copious evolution of sulfuric acid fumes ceases.
9. Cool. Add 3 ml. of water and heat gently to dissolve the solids. Transfer the sample to a 50-ml. culture tube with small water rinses. The total sample volume after transfer should be 10-ml. or less.
10. Continue with the determination as described in C:7.

C:6 Concentration of AC and Water (W) Samples

NOTE: No digestion is necessary for AC samples.

1. Pipet a sample containing 0.5 to 7 μg . of cobalt into a 150-ml. beaker (for samples larger than 10 ml.) or a culture tube (for samples 10 ml. or less). Generally, 25- to 50-ml. portions of the AC sample and 5- to 25-ml. portions of the water samples will be adequate.
2. Add a Hengar granule boiling chip and evaporate the sample to 3 or 4 ml. on a hot plate set at medium. Use a Speedy-vap cover glass on the beaker to minimize contamination.
3. If the sample is in a beaker, transfer the sample quantitatively to a 50-ml. culture tube with small water rinses. Keep the volume of the sample after transfer at 10 ml. or less.
4. Continue according to C:7.

C:7 Color Development and Color Measurement

1. To the sample in the culture tube from C:5 or C:6, add 1 ml. of glacial acetic acid.
2. Add 1 ml. of 0.5M sodium citrate to complex the iron.
3. Add 2 drops of the 2,4-dinitrophenol pH indicator. Some samples, especially the AC samples are often colored. If so, the indicator color change will not be noticeable. Delete the indicator and continue with step 5.

4. Add concentrated ammonium hydroxide dropwise until the solution turns yellow (pH about 3.5) and then add 1 ml. more. COOL.
5. Using the pH meter, adjust the pH to 5.5 ± 0.1 by adding concentrated ammonium hydroxide dropwise.
6. Add 0.5 ml. of the 0.5 percent 2-nitroso-1-naphthol reagent.

NOTE: It has been found that the addition of the 2-nitroso-1-naphthol reagent PRIOR to pH adjustment leads to very low results.

7. Let the solution stand for at least 30 minutes for color development.
8. Add 10 ml. of concentrated hydrochloric acid to break the complexes formed between the reagent and metal ions such as iron and chromium. COOL.
9. Add 10.00 ml. of the carbon tetrachloride-xylene mixed solvent, screw the cap on tightly, and shake vigorously for 2 minutes.
10. Remove and discard the upper aqueous phase. Use a 500- λ micro pipet attached to a vacuum wash train to draw off the aqueous solution.
11. Using a wash bottle, wash down the walls of the tube with 10 ml. of water. Remove the water washings.
12. Add 15 ml. of 0.5M sodium hydroxide to extract excess 2-nitroso-1-naphthol from the organic phase. Shake vigorously for 1 minute. Remove the aqueous phase.
13. Wash two times with about 10 ml. of water and discard the washings. (Do not shake, merely wash down the sides of the tube.)
14. Wash a third time with 10 ml. of water. This time shake vigorously for about 10 seconds.
15. Centrifuge for 1 minute and remove the aqueous phase.
16. Using a 10-ml. pipet, transfer the organic phase to a 5-cm. cell.

17. Read the absorbance at 525 mμ. against a reagent blank.
18. Record the data on the worksheet and compute the cobalt concentration as described under calculations.

C:8 Calculations

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Micrograms of cobalt in the calibration standards
B	Absorbance of the calibration standards
C	Conversion factors
	$C = \frac{B}{A}, C' = \frac{B'}{A'}$
D	Average conversion factor
	$D = 0.5 (C + C')$
E	Sample volume, in ml.
F	Sample absorbance
G	Result, μg. of cobalt per ml. of sample
	$G = \frac{F}{DE}$

Report the results to the nearest 0.001 μg. for values less than 1 μg. per ml. and to 3 significant figures for values greater than 1 μg. per ml. as: 1.11, 0.111, 0.011 and 0.001 μg. per ml.

C:9 References

1. Claasen, A., Daamen, A., Anal. Chim. Acta 12, 547 (1955).
2. Sandell, E. B., Colorimetric Determination of Traces of Metals, Vol. III, p. 420, Interscience, New York, 1959.
3. Speer, R. L., Private Communication, Dec. 1964.
4. Wade, M. A., IDO Notebook U-870, pp. 68-100, 1964.

D. Determination of Iron

D:1 Discussion

Two procedures for the determination of iron are presented in this section, both based on the formation of the red iron(II)-1,10-phenanthroline complex.

In the first procedure (section D:5) directly applicable for the determination of iron in all ECF samples except KMnO_4 -NaOH samples, the iron(II)-1,10-phenanthroline colored complex is developed in an EDTA-citrate medium buffered at pH 5 to 6.5 with pyridine and measured at 507 m μ . All solutions are heated at $60 \pm 5^\circ\text{C}$. for 25 minutes, then cooled and allowed to stand for not less than 25 minutes at room temperature for full color development. The diverse cations expected to be present in the crud samples do not interfere. Samples of the KMnO_4 -NaOH type (sample 4a, Table I) cannot be analyzed by the direct procedure and must be analyzed by the column extraction-colorimetric measurement procedure described in subsection D:6.

In both procedures, the sample aliquot taken for analysis must contain between 2 and 100 μg . of iron. Without any prior digestion and concentration, the maximum aliquot that can be taken is 10 ml. and accordingly, the lower limit is 0.2 μg . Fe per ml. in the original sample solution. With prior digestion and concentration, the lower limit can be extended to as low as 0.01 μg . Fe per ml.

Once formed, the iron(II)-1,10-phenanthroline complex is stable for months (2). Thus, samples may be measured after several hours or, if necessary, after 1 day.

D:2 Apparatus and Reagents

D:2.1 Apparatus

1. Spectrophotometer, Beckman Model B, DU, or DK, or Cary Model 14.
2. Absorption cells, 1.0-cm. and 5.0-cm.
3. Pipets, volumetric, macro and micro, assorted sizes.
4. Pipets, Mohr, 5- and 10-ml.
5. Flasks, volumetric, assorted sizes.
6. Beakers, assorted sizes.
7. Petrie dish, large.

8. Hot plate-magnetic stirrer combination such as a Stir-Plate or Thermo-Stir hot plate.
9. Polyethylene wash bottles.
10. Water bath, at 60°C.
11. Ion exchange columns, 7.2-mm. i.d. x 15-cm. with a 30-mm. o.d. x 6-cm. reservoir, a Teflon-plugged stopcock, and a glass wool plug to support the column packing.
12. Glass stirring rods, 6-mm. o.d.
13. Speedy-vap cover glasses to cover beakers.

D:2.2 Reagents

1. Standard iron stock solution, 1.000 mg. Fe per ml. Dissolve 7.0250 grams of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 100 ml. of 0.05M hydrochloric acid and dilute to 1 liter with water.
2. Iron calibration standard I, 40.0 μg . Fe per ml. Dilute 10.00 ml. of the iron stock solution to 250 ml. with 0.005M hydrochloric acid.
3. Iron calibration standard II, 60.0 μg . Fe per ml. Dilute 15.00 ml. of the iron stock solution to 250-ml. with 0.005M hydrochloric acid.
4. Iron calibration standard III, 6.00 μg . Fe per ml. Dilute 3.00 ml. of the iron stock solution to 500 ml. with 0.005M hydrochloric acid.
5. Iron calibration standard IV, 12.0 μg . Fe per ml. Dilute 3.00 ml. of the iron stock solution to 250-ml. with 0.005M hydrochloric acid.
6. 1,10-Phenanthroline reagent, 0.05M. Dissolve 4.96 grams of 1,10-phenanthroline monohydrate in 500 ml. of 2-propanol.
7. Hydroxylamine hydrochloride solution, 2M. Dissolve 70 grams of hydroxylamine hydrochloride in 500 ml. of water.
8. EDTA-citrate reagent. Dissolve 93 grams of disodium EDTA dihydrate and 113 grams diammonium citrate in water and dilute to 1 liter.
9. Pyridine.
10. Hydrochloric acid, concentrated and 7M.
11. Oxalic acid, saturated aqueous solution.
12. Hydroquinone, 0.1M aqueous solution. Dissolve 2.20 grams of the reagent in 200 ml. of water. Prepare a new solution when significant discoloration occurs.
13. 2-Propanol.
14. Hydrogen peroxide, 30 percent.

15. 2-Octanone.
16. Fluoropak, 20 to 70 mesh. Fluoropak is available from Wilkens Instrument and Research, Inc., Box 313, Walnut Creek, California.

D:3 Blank

Run a blank with each series of samples according to D:5 or D:6.

D:4 Calibration and Bench Standard

In the usual colorimetric procedure, two calibration standards are processed with a series of samples. In this procedure, the number of calibration standards has been increased to four to cover a broader range and thus, to minimize the number of repeat analyses that are required because of improper sample aliquots. Two of the calibration standards are designed for the low (1 to 20 $\mu\text{g. Fe}$) range. The other two standards are designed for the high (15 to 100 $\mu\text{g. Fe}$) range.

Run a separate calibration for each series of samples. Use 1.00-ml. portions of each of the four standards and process these according to D:5 or D:6 depending on the method used for the samples. Use 1.0-cm. cells for standards I and II (40 and 60 $\mu\text{g. Fe}$ per ml., respectively) and 5.00-cm. cells for standards III and IV (6 and 12 $\mu\text{g. Fe}$ per ml., respectively). Divide the absorbances by the micrograms of iron to obtain the conversion factors. The difference between the two conversion factors for each of the two groups should not exceed limits set by the Quality Control Laboratory. Also, the average of the two conversion factors should agree with the established conversion factor for each group within the specified limits. If either or both of the specifications are not met, reprocess the pair or pairs of calibrations standards. Contact your supervisor if difficulties still are experienced.

D:5 Direct Procedure

NOTE: This procedure is applicable to the determination of iron in the various types of crud samples with the exception of the KMnO_4 -NaOH samples. Refer to Procedure D:6 for the analysis of KMnO_4 -NaOH samples.

1. Pipet a sample (10 ml. or less) containing 2 to 100 $\mu\text{g.}$ of iron into a 25-ml. volumetric flask.

2. Using a Mohr pipet, add 0.5 ml. of concentrated hydrochloric acid.
3. Add 5 ml. of the EDTA-citrate reagent.
4. Using a Mohr pipet, add
 - a. 1 ml. of 2M hydroxylamine hydrochloride.
 - b. 2 ml. of 0.05M 1,10-phenanthroline.
5. Swirl to mix, then add 3 ml. of pyridine.
6. Dilute to volume with water, stopper, and mix well.
7. Heat the sample in a water bath, maintained at $60 \pm 5^{\circ}\text{C}$., for 25 minutes.

NOTE: A simple, satisfactory water bath can be set up by placing a large Petrie dish containing water on a combination stirrer-hot plate set at an appropriate temperature setting. Add cold water or boiling water if rapid temperature adjustment is desired.

8. Cool to room temperature in a dish of cold water. Let stand for at least 25 minutes.
9. Measure the absorbance against the reagent blank in 5.0-cm. or 1.0-cm. cells. Select the appropriate cell for the absorbance measurements by visually comparing the intensity of the samples with the intensity of the four calibration standards. Make all 5.0-cm. cell measurements first to enable subsequent 1.0-cm. cell measurements to be made on the same solution if necessary.
10. Record the absorbances of the calibration standards and samples on the worksheet and compute the iron concentration as described in section D:7.

D:6 Determination of Iron in KMnO_4 -NaOH Samples

D:6.1 Column Preparation

1. Half fill a 600-ml. beaker with 20 to 70-mesh Fluoropak.
2. Slurry with 2-octanone.
3. Filter on a large Buchner funnel and draw air through the 2-octanone-saturated Fluoropak for 10 to 15 minutes. Store in a screw-capped wide mouth jar.

4. Transfer about 15 ml. of the 7M hydrochloric acid to the ion exchange column.
5. Transfer the treated Fluoropak to the column reservoir and slurry the Fluoropak with the 7M hydrochloric acid using a 6-mm. glass stirring rod. Open the stopcock and as the Fluoropak settles, tamp gently. AVOID EXCESSIVE PRESSURE. Prepare a bed 5-inches high. Do not allow the column to run dry.

D:6.2 Column Extraction-Spectrophotometric Measurement Procedure

1. Pipet a sample (10-ml. or less) containing 2 to 100 µg. of iron into a 50-ml. beaker.
2. Cover the beaker with a Speedyvap cover glass and add 2 ml. of concentrated hydrochloric acid.
3. Add saturated oxalic acid 0.5 ml. at a time until the permanganate solution is decolorized.
4. Evaporate to near dryness.
5. Cool. Dissolve the residue with 7M hydrochloric acid and transfer the sample with 7M hydrochloric acid rinses to the column prepared according to D:6.1.

NOTE: Commerical hydrochloric acid contains small amounts of iron. Run a blank with each series of samples using identical amounts of all reagents.

6. Add 2 drops of 30 percent hydrogen peroxide, then mix the contents of the reservoir with a stream of 7M hydrochloric acid delivered from a wash bottle.
7. Pass the sample through the column at the rate of 3 to 5 ml. per minute. Collect the column effluent in a 250-ml. beaker or Erlenmeyer flask.
8. Wash the column well using 25 ml. of 7M hydrochloric acid added in 5-ml. increments. Drain the wash solution until the acid level is at the top of the Fluoropak bed.
9. Strip the iron and 2-octanone with 15 to 18 ml. of 2-propanol added in small portions. Collect the column effluent in a 25-ml. volumetric flask containing 0.5 ml. of 0.1M hydroquinone.

10. Add 2 ml. of the 0.03M 1,10-phenanthroline in propanol reagent, mix, then add 3 ml. of pyridine. Cool to room temperature and dilute to volume with 2-propanol. Mix well.
11. Measure the absorbance after 15 minutes in 1.0- or 5.0-cm. cells against the blank.
12. Record the absorbances of the calibration standards and the samples on the worksheet and compute the iron concentration as described in section D:7.

D:7 Calculations

Record the data on the worksheet as follows:

Column	Unit to Record
A	Micrograms iron in the calibration standards.
B	Absorbance of the calibration standards.
C	Conversion factors: $C_1 = \frac{B_1}{A_1}, \quad C_1' = \frac{B_1'}{A_1'}$ $C_2 = \frac{B_2}{A_2}, \quad C_2' = \frac{B_2'}{A_2'}$
D	Average conversion factors: $D_1 = 0.5 (C_1 + C_1')$ $D_2 = 0.5 (C_2 + C_2')$
E	Sample size, in ml.
F	Dilution factor, if used.
G	Sample absorbance.
H	Result, $\mu\text{g.}$ iron per ml. of sample $H = \frac{FG}{DE}$

Report the results to three significant figures for values greater than 1 $\mu\text{g.}$ per ml. and to the nearest 0.01 $\mu\text{g.}$ per ml. for values less than 1 $\mu\text{g.}$ per ml. For example: 606, 60.6, 6.06, and 0.61 $\mu\text{g.}$ per ml.

D:8 References

1. Sandell, E. B., Colorimetric Determination of Traces of Metals, 3rd Ed., pp. 537-572, Interscience, New York, 1959.
2. Snell, F. D., Snell, C. T., Colorimetric Methods of Analysis, Vol. II, pp. 314-318, Van Nostrand, New York, 1949.
3. Vydra, F., Kopanica, M., Chemist Analyst 52, 88 (1963).
4. Wade, M. A., Yamamura, S. S., Anal. Chem. 36, 1861 (1964).
5. Yamamura, S. S., IDO Notebook U-850, pp. 38-52, 1964.

Determination of Manganese

E:1 Discussion

This procedure for the determination of manganese is based on the oxidation of manganese(II) to permanganate with periodic acid and measurement at 524 m μ . The oxidation is carried out in a sulfuric acid medium containing phosphoric acid to complex iron which otherwise prevents complete color development.

The molar absorptivity of the permanganate ion is not very great. Thus, samples are diluted to 10.00 ml. and measured in special 5.0-cm. cells with a capacity of only about 7.5 ml. The sample taken for the final color measurement should contain between 1 and 25 μ g. of manganese.

One serious problem is the formation of insoluble, white, phosphoric acid polymers during the initial evaporation of the samples to sulfuric acid fumes. The best remedy for this problem is to avoid the polymer formation by using a small flame and constant swirling.

E:2 Apparatus and Reagents

E:2.1 Apparatus

1. Spectrophotometer, Beckman Model B, DU, or DK, or Cary Model 14.
2. Absorption cells, Aminco, 5.0-cm. with 7.5 ml. capacity.
3. Volumetric flasks, 10-ml.
4. Pipets, volumetric, macro and micro, assorted sizes.
5. Pipets, Mohr, assorted sizes.
6. Dropping bottles
7. Test tube holders.
8. Support rack or block for 50-ml. centrifuge tubes.
9. Meker burner.
10. Hot plate.
11. Beakers, 400-ml. and 100-ml.
12. Fisher filtrator.
13. Millipore filter apparatus, 1-inch diameter. To facilitate filtrations, attach 5 inches of 6-mm. Pyrex tubing to the filter base.
14. Membrane filter paper, 0.45- or 0.30- μ . pore size.
15. Centrifuge tubes, 50-ml.

E:2.1 Reagents

1. Manganese stock solution, 1.00 mg. Mn per ml. Dissolve 3.0770 grams of manganous sulfate in water and dilute to 1 liter with water.
2. Manganese calibration standard, 20 μ g. Mn per ml. Dilute 10.00 ml. of the stock solution to 500 ml. with water.
3. Sulfuric acid, concentrated.
4. Phosphoric acid, 85 percent.
5. Periodic acid solution, 0.5M. Dissolve 11.4 grams of periodic acid (H_5IO_6) in water and dilute to 100 ml. with water.
6. Treated water. Add 2 ml. of sulfuric acid and 0.5 gram of periodic acid to 1 liter of water and boil for 10 minutes. Cool. Store in a polyethylene bottle.
7. Boiling chips such as Hengar granules.
8. Nitric acid, concentrated.
9. Perchloric acid, concentrated.
10. Triacid digestion mixture. Prepare 1:2:5 sulfuric acid:perchloric acid:nitric acid as needed.

E:3 Preparation of the Calibration Curve

Prepare a calibration curve with each series of samples. Use 0.00, 0.25-, 0.50-, 0.75-, and 1.00-ml. portions of the 20 μ g. per ml. calibration standard and process these according to E:6. Prepare the calibration curve by plotting absorbances on the vertical Y axis vs. micrograms manganese on the horizontal X axis and drawing a straight line through the points.

E:4 Predigestion and Concentration of Oxalic-Nitric (ON), EDTA-Hydrazine (HV), and Ammonium Citrate (AC) Samples

1. Pipet a sample containing between 1 and 25 μ g. of manganese into a 50-ml. centrifuge tube. With very large samples, it will be necessary to pipet the samples in 25-ml. portions and to evaporate each portion before admitting the next portion. Use Hengar granule boiling chips during the evaporation to prevent bumping. Sample volume limits are 100 ml. for ON and AC samples and 50 ml. for HV samples.
2. When the required volume of sample has been pipetted into the centrifuge tube, place the tube in a 600-ml. beaker, and evaporate the sample to about 10-15 ml. on a hot plate.

3. Slowly add a 1:2:5 mixture of sulfuric, perchloric and nitric acids. Cool the centrifuge tube as needed in an ice water bath to control the reaction. Use 8 ml. of the acid mixture for each 20 ml. of sample.
4. When the required volume of the acid mixture has been added and the vigorous reaction ceases, evaporate the sample to about 1 ml.
5. If the sample darkens, add 1 ml. of perchloric acid and 2 ml. of nitric acid and evaporate again to about 1 ml.
6. Repeat 5 until the sample no longer darkens on strong fuming.
7. Evaporate the sample to about 0.5 ml. over a low blue flame of a Meker burner. The sulfuric acid should be refluxing near the top of the centrifuge tube.
8. Cool. Continue according to E:6.

E:5 Concentration of Water Samples

1. Pipet a sample containing between 1 and 25 μg . of manganese into a 50-ml. centrifuge tube.
2. Add a Hengar granule boiling chip and 1 ml. of sulfuric acid.
3. Evaporate the sample to about 0.5 ml.
4. Cool. Continue according to E:6.

E:6 Color Development and Measurement

1. Add 10 drops of 85% phosphoric acid and continue the evaporation over a flame to fumes of sulfuric acid. SWIRL THE SAMPLE CONTINUOUSLY TO PREVENT THE FORMATION OF INSOLUBLE PHOSPHORIC ACID POLYMERS. Swirl the solution sufficiently to wet the bottom half of the centrifuge tube.
2. Cool to about $80 \pm 10^\circ\text{C}$. (at this temperature, the tube feels just a little too hot to hold with your bare hand).
3. Add 10 drops of 0.5M periodic acid solution to oxidize the manganese.

4. Rinse down the sides of the centrifuge tube with 3 to 4 ml. of the treated water. Let stand 10 minutes for color development.
5. Cool to room temperature, then transfer quantitatively to a 10-ml. volumetric flask with treated water rinses. Dilute to volume with the treated water and mix well.
6. Read the absorbance within 1 hour in 5.0-cm. cells at 524 mμ. against the reagent blank.

NOTE: DO NOT USE ORGANIC SOLVENTS TO DRY THE CELLS. Solvents such as acetone or alcohols will reduce the permanganate. Rinse the cells with the treated water and flip dry.

7. Determine the manganese concentration from the calibration curve and complete the calculation as described in section E:7.

E:7 Calculations

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Micrograms manganese in the calibration standards.
B	Absorbances of standards.
C	Sample volume, in ml.
D	Dilution factor, if used.
E	Sample absorbance
F	Micrograms manganese in the sample taken for color measurement (from curve).
G	Result, micrograms manganese per ml. of the original sample.

$$G = \frac{DF}{C}$$

Report the results to 3 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. For example: 2.56, 0.256, 0.026, and 0.003 μg. Mn per ml.

E:8 Reference

1. Snell and Snell, Colorimetric Methods of Analysis, 3rd Ed., pp. 390-395, Van Nostrand, New York, 1949.

F. Determination of Nickel

F:1 Discussion

This procedure for the determination of nickel, specially adapted for the determination of nickel in crud solutions, is a modification of the routine colorimetric nickel procedure, Method Ni-1, Mod-1. The color is developed, as in the usual procedure, with dimethylglyoxime in ammonium carbonate medium containing persulfate. Tartaric acid masking is not employed. Instead, interfering metal ions, principally iron, are precipitated with sodium hydroxide, then removed by filtration prior to the addition of the dimethylglyoxime reagent. In all cases the iron level is adjusted to $250 \pm 50 \mu\text{g}$ before the precipitation. Below this level the iron is not precipitated completely and above this level, nickel is coprecipitated.

The nickel-dimethylglyoxime complex is measured at 465 m μ in 5-cm. cells. For added sensitivity, all solutions are diluted to 25 ml. instead of 50 ml. as in the usual procedure.

Some of the important phases of this method need emphasis. The pH must be controlled at 11.5. Below this, a different complex with different optical properties is formed. A high concentration of carbonate is necessary to complex nickel and other cations, preventing their precipitation at the high pH used. Samples that are highly acidic should be evaporated initially to minimize the expulsion of carbonate as carbon dioxide. The sample aliquot taken for analysis should contain between 0.5 and 10 μg . of nickel.

F:2 Apparatus and Reagents

F:2.1 Apparatus

1. Spectrophotometer, Beckman Model B, DU, or DK, or Cary Model 14.
2. Absorption cells, 5-cm.
3. Volumetric flasks, 25-ml.
4. Pipets, volumetric, macro and micro, assorted sizes.
5. Hot plate.
6. Centrifuge tubes, 50-ml.
7. Fisher filtrator.
8. Millipore filter apparatus, 1-inch diameter size. Attach 5 inches of 6-mm. Pyrex tubing to the filter base to facilitate direct filtrations into 25-ml. volumetric flasks.

9. Membrane filter paper, 0.30- or 0.45- μ pore size.
10. pH meter, Leeds and Northrup with miniature probe glass and calomel electrodes.
11. Ice bath.

F:2.2 Reagents

NOTE: Use distilled water and C.P. or Analytical Reagent Grade reagents throughout.

1. Ammonium carbonate solution, 20%. Dissolve 20 grams of ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, in distilled water and make up to 1 liter. Filter to remove extraneous particles.
2. Dimethylglyoxime solution, 1%. Dissolve 5 grams of dimethylglyoxime, $(\text{CH}_3\text{CNOH})_2$, in 500 ml. of 95% ethanol.
3. Standard nickel solution, 1.000 mg. Ni per ml. Dissolve 1.000 gram of pure nickel metal in 10 ml. of concentrated nitric acid and dilute to 1 liter with water.
4. Nickel calibration standard I, 8 μg . Ni per ml. Dilute 4.00 ml. of the 1.000 mg. per ml. stock solution to 500 ml. with water.
5. Nickel calibration standard II, 4 μg . Ni per ml. Dilute 4.00 ml. of the stock solution to 1 liter with water.
6. Sodium hydroxide solution, 19M and 9M. Remove insoluble sodium carbonate.
7. Potassium persulfate, 5%. Dissolve 50 grams of potassium persulfate in water and dilute to 1 liter.
8. Hengar granules (boiling chips).
9. Iron solution, 1.0 mg. per ml. Dissolve 0.50 gram of iron metal in nitric acid and dilute to 500 ml. with water.
10. Hydrochloric acid, concentrated.
11. Perchloric acid, concentrated.
12. Sulfuric acid, concentrated.
13. Nitric acid, concentrated.
14. Triacid digestion mixture. Prepare the triacid mixture as needed in the ratio, 1 sulfuric acid, 2 perchloric acid, and 5 nitric acid.

F:3 Reagent Blank

Process a reagent blank with each series of standards and samples.

F:4 Calibration and Bench Standard

A separate calibration is required for each series of samples. Use 1.00 ml. of each of the calibration standards and process these according to F:7 beginning at step 3. Divide the absorbances by the micrograms of nickel to obtain the conversion factors. The difference between the two conversion factors should not exceed limits set by the Quality Control Laboratory. Also, the average of the two conversion factors should agree with the established factor within the limits specified. If either or both specifications are not met, process another pair of standards. Contact your supervisor if difficulties still are experienced.

F:5 Predigestion and Concentration of Oxalic-Nitric (ON), EDTA-Hydrazine (HV) and Ammonium Citrate (AC) Samples

1. Pipet a sample containing between 0.5 and 10 μg . of nickel into a 50-ml. centrifuge tube (for samples 25 ml. or less) or a 250-ml. Erlenmeyer flask (for samples larger than 25 ml.) Sample volume limits are 50 ml. for HV samples and 100 ml. for ON and AC samples.
2. Add a Hengar granule boiling chip and evaporate to about 10 ml. on a hot plate.
3. If the sample is in an Erlenmeyer flask, cool, transfer the sample quantitatively with small water rinses to a 50-ml. centrifuge tube, then evaporate to about 10 ml.
4. Slowly add a 1:2:5 mixture of sulfuric, perchloric, and nitric acids. Cool the centrifuge tube in an ice bath as needed to control the reaction. Use 8 ml. of the acid mixture for each 20 ml. of sample.
5. When the required volume of acid has been added and the vigorous reaction ceases, evaporate the sample to sulfuric acid fumes.
6. If the sample darkens in step 5, add 1 ml. of perchloric acid and 2 ml. of nitric acid and evaporate again to sulfuric acid fumes. Repeat the perchloric acid-nitric acid treatment until the sample no longer darkens on strong fuming.
7. Evaporate the sample to near dryness. With HV samples, large amounts of ammonium sulfate will be present after the digestion. The melt may be as much as 2 ml. In such cases, evaporate until copious evolution of sulfuric acid fumes ceases.

8. Cool. Add 1 ml. of hydrochloric acid and 3 ml. of water. Heat gently to dissolve the solids, then evaporate to about 2 ml.
9. Continue according to F:7.

F:6 Concentration of Water Samples

1. Pipet a sample containing between 0.5 and 10 μg . of nickel into a 50-ml. centrifuge tube.
2. Add 1 ml. of sulfuric acid and 1 Hengar granule boiling chip and evaporate to near dryness.
3. Cool. Add 1 ml. of hydrochloric acid and 3 ml. of water. Heat gently to dissolve the solids, then evaporate to about 2 ml.
4. Continue according to F:7.

F:7 Color Development and Measurement

1. Adjust the iron content of the sample to $250 \pm 50 \mu\text{g}$. by adding an appropriate volume of 1.0 mg. per ml. iron solution.

NOTE: On all ECF samples, the determination of iron is performed first. Use the results for iron to determine the proper amount of iron needed. Add 250 μg . of iron when running the calibration standards.

2. Add 0.5 ml. of the 20% ammonium carbonate reagent, then add 19M sodium hydroxide dropwise until the carbon dioxide evolution ceases. Do not add too much sodium hydroxide. If the solution turns yellow, too much has been added. Discard the sample and start over.
3. Add 4.5 ml. of the 20% ammonium carbonate solution.
4. Add 5 ml. of the 5% potassium persulfate reagent.
5. Add a Kel-F- or Teflon-coated stirring bar and while stirring continuously, adjust the pH to 11.5 with 9M sodium hydroxide.
6. Let stand for at least 10 minutes to settle the ferric hydroxide.

7. Filter off the ferric hydroxide on a 0.45- or 0.30- μ membrane filter paper. Catch the filtrate and water washings in a 25-ml. volumetric flask.
8. Add 0.50 ml. of the dimethylglyoxime reagent, dilute to volume with water, and mix well.
9. Read the absorbance after 20 minutes in a 5.0-cm. cell at 465 m μ against the reagent blank.

NOTE: If the filtrate from step 7 appears pale yellow before the addition of the dimethylglyoxime reagent, add the dimethylglyoxime reagent and measure the absorbance after exactly 20 minutes. If the filtrate from step 7 is intensely yellow, discard the solution and reprocess the sample.

10. Record the absorbances of the calibration standards and the sample(s) on the worksheet and calculate the nickel concentration as described in F:8.

F:8 Calculations

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Micrograms nickel in the calibration standards.
B	Absorbance of standards.
C	Conversion factor $C = B/A, \quad C' = B'/A'$
D	Average conversion factor $D = 0.5(C + C')$
E	Sample volume in ml.
F	Dilution factor, if used.
G	Result, micrograms of nickel per ml. of sample.

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

Report results to 3 significant figures for values greater than 1 $\mu\text{g. per ml.}$ and to the nearest 0.001 $\mu\text{g.}$ for values less than 1 $\mu\text{g. per ml.}$ For example: 10.6, 1.06, 0.106, and 0.011 $\mu\text{g. Ni per ml.}$

F:9 References

1. ORNL Master Analytical Manual, U. S. Atomic Energy Commission, C. F. No. 53-1-235, Method 9 00715410-19, 1956.
2. Yamamura, S. S., IDO Notebook U-850, pp. 35-70, 1964.

G. Determination of Principal Components of ECF Descaling Make-Up Solutions

G:1 Discussion

On previous samples occasional wide variations in the make-up compositions of ECF descaling solutions have been noted. For example, the EDTA concentration of the 0.25M EDTA - 0.5M N_2H_4 - 0.5M NH_4OH (HV) samples has varied from 0.00M to 0.28M.

To guard against faulty make-up, Westinghouse has decided to submit the various descaling solutions for verification of make-up compositions. As shown in Table III, this will be done by determining principal components of the descaling solutions with the methods indicated. Details of the analytical methods are presented in subsections G:2 through G:5.

TABLE III. SELECTED METHODS FOR CHECKING THE MAKE-UP OF ECF DESCALING SOLUTIONS

Descaling Solution	Component(s) Selected For Measurement	Method
I. Water	none	---
II. A. 20 g/l Oxalic acid	$H_2C_2O_4$	Titration with $KMnO_4$.
B. 0.5M HNO_3	Acidity	H-Vol-1.
III. 0.25M EDTA-0.5M N_2H_4 - 0.5M NH_4OH	1. EDTA	Titration with Ce(III).
	2. N_2H_4	Titration with I_2 .
IV. A. 12 g/l $KMnO_4$ -0.15M NaOH	1. $KMnO_4$	Titration with EDTA after reduction with $NH_2OH \cdot HCl$.
	2. NaOH	Titration with std. H_2SO_4 to potentiometric end point.
B. 30 g/l $(NH_4)_2H$ -Citrate	$(NH_4)_2H$ Citrate	Titration with std. NaOH after reaction with copper(II).
V. HCl	none	---

G:2 Determination of Oxalic Acid

G:2.1 Discussion

The determination is based on the reaction:

where: 1 mole of KMnO_4 = 2.5 moles of $\text{H}_2\text{C}_2\text{O}_4$

$$\text{Equivalent weight} = \frac{\text{KMnO}_4}{5} = \frac{\text{H}_2\text{C}_2\text{O}_4}{2}$$

For best results, the titration should be carried out in a 0.4M sulfuric acid solution heated initially to between 80 and 90°C. The temperature of the solution should be above 60°C. at the end point.

Potassium permanganate is a powerful oxidant and will oxidize lint, filter paper, and other organic substances. Therefore, use lint-free glassware and avoid the introduction of tissue paper when pipetting the sample. Do not use polyethylene wash bottles for dispensing permanganate solutions.

G:2.2 Apparatus and Reagents

1. Apparatus

- a. Buret, 25- or 50-ml.
- b. Erlenmeyer flasks, 125- or 250-ml.
- c. Magnetic stirrer and stirring bars.
- d. Hot plate.
- e. Pipets, assorted sizes.
- f. Graduated cylinder, 50-ml.

2. Reagents

- a. Sodium oxalate standard solution, 0.1000M (0.2000N). Dissolve 13.401 grams of sodium oxalate in water and dilute to 1 liter with water.
- b. Potassium permanganate solution, 0.040M (0.20N). Dissolve 6.32 ± 0.01 grams of potassium permanganate in 1 liter of water. Let stand for 2 days. Filter through a medium porosity sintered glass crucible or funnel or through a glass fiber filter paper, No. 934-AH, manufactured by Hurlbut

Paper Co. Store in a dark bottle in a cool, dark place. CAUTION: Do not use a screwcap with an aluminum liner. A screw-cap with a Teflon liner is recommended. Standardize the permanganate solution against 20-ml. portions of the standard sodium oxalate solution according to G:2.3.

- c. Sulfuric acid solution, 2M. Cautiously add 110 ml. of concentrated sulfuric acid to 500 ml. of water. Cool and dilute to 1 liter with water.

G:2.3 Procedure

1. Pipet a sample containing between 10 and 20 mg. (0.11 to 0.22 mmole) of oxalic acid into a 125-ml. Erlenmeyer flask.

NOTE: A 20 mg./ml. oxalic acid solution is 0.22M.

2. Add 15 ml. of 2M sulfuric acid and dilute to 75 ml. with water.
3. Heat on a hot plate to $85 \pm 5^\circ\text{C}$.
4. Titrate the hot solution with potassium permanganate to a permanent pink end point, using magnetic stirring.

NOTE: The reaction of permanganate with oxalate is very slow at the start of the titration. The reaction becomes rapid as the manganese(II) concentration increases.

G:2.4 Calculations

1. Standardization of potassium permanganate.

$$\text{KMnO}_4 \text{ Normality} = \frac{(20.00)(0.2000N)}{\text{Vol. of KMnO}_4}$$

$$\text{KMnO}_4 \text{ Molarity} = (\text{KMnO}_4 \text{ Normality})(0.2)$$

2. Samples

$$\text{H}_2\text{C}_2\text{O}_4 \text{ Molarity} = 2.5 \frac{(\text{Vol. KMnO}_4)(\text{KMnO}_4 \text{ Molarity})}{(\text{Samp. Vol. in ml.})}$$

$$\text{Result, mg. H}_2\text{C}_2\text{O}_4/\text{ml.} = 90.04 (\text{H}_2\text{C}_2\text{O}_4 \text{ Molarity})$$

G:3 Determination of KMnO_4 and NaOH in KMnO_4 - NaOH Solutions

G:3.1 Discussion

Potassium permanganate is determined titrimetrically after reduction to manganese(II) in acidic medium with hydroxylamine hydrochloride. A replacement titration technique with $\text{NaCeEDTA} \cdot 8\text{H}_2\text{O}$ is used which provides a simple procedure with a sharp end point.

Sodium hydroxide is determined by direct titration with standard sulfuric acid to a potentiometric end point.

G:3.2 Apparatus and Reagents

G:3.2.1 Apparatus

- a. Buret, micro, 10-ml.
- b. Beakers, assorted sizes.
- c. Pipets, macro and micro, assorted sizes.
- d. Magnetic stirrer and stirring bars.
- e. pH meter with a glass-calomel electrode system.

G:3.2.2 Reagents

- a. EDTA, 0.05M. A 0.05M EDTA solution (18.62 grams $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ per liter) standardized against a zinc solution will be provided by the Quality Control Laboratory.
- b. Sulfuric acid solution, 0.10N. Dilute 2.78 ml. of 95% sulfuric acid to 1 liter with water. Standardize against standard sodium hydroxide or tris-(hydroxymethyl)amino methane (THAM).
- c. Hydroxylamine hydrochloride, 1M. Dissolve 35 grams of hydroxylamine hydrochloride in water and dilute to 500 ml. For convenience, dispense from a dropping bottle.
- d. $\text{NaCeEDTA} \cdot 8\text{H}_2\text{O}$. The salt, prepared as described in method Fe-4, will be provided by the Quality Control Laboratory.
- e. Xylenol orange, 0.2%. Dissolve 0.20 gram of xylenol orange in 100 ml. of water.

- f. Pyridine. For convenience, store in a dropping bottle.
- g. Sulfuric acid, concentrated. For convenience, store in a dropping bottle.

G:3.3 Procedures

G:3.3.1 Determination of KMnO_4 .

- a. Pipet a sample containing between 11 and 22 mg. (0.2 to 0.4 mmole) of manganese into a 150-ml. beaker.
NOTE: A 12 mg./ml. KMnO_4 solution is 0.076M or 4.17mg. Mn/ml.
- b. Add 5 drops of concentrated sulfuric acid, then 1M hydroxylamine hydrochloride until the sample turns colorless. Generally, 3 ml. of the hydroxylamine hydrochloride solution is sufficient for complete reduction of the permanganate.
- c. Dilute to 100 ml. with distilled water and add 0.5 gram (1 scoopful) of the $\text{NaCeEDTA} \cdot 8\text{H}_2\text{O}$ salt.
- d. Stir, then add 5 drops of 0.2% xylene orange and 1 ml. of pyridine.
- e. Titrate with standard EDTA to a change from reddish-purple to yellow. Titrate to the complete disappearance of the red.

G:3.3.2 Determination of NaOH.

- a. Pipet a sample containing between 0.2 and 0.8 meq. of sodium hydroxide into a 150-ml. beaker.
- b. Dilute with distilled water to about 100 ml.
- c. Titrate with standard 0.1N sulfuric acid. Determine the end point potentiometrically as described in Method C1-4, page 3.

G:3.4 Calculations

G:3.4.1 Determination of KMnO_4 .

$$\text{KMnO}_4 \text{ Molarity} = \frac{(\text{Vol. EDTA})(\text{EDTA Molarity})}{\text{Sample Vol. in ml.}}$$

$$\text{Result, mg. KMnO}_4/\text{ml.} = 158.03 (\text{KMnO}_4 \text{ Molarity})$$

G:3.4.2 Determination of NaOH

$$\text{NaOH Molarity (Normality)} = \frac{(\text{Vol. H}_2\text{SO}_4)(\text{H}_2\text{SO}_4 \text{ Normality})}{\text{Sample Vol. in ml.}}$$

G:4 Determination of $(\text{NH}_4)_2\text{HCitrate}$

G:4.1 Discussion

$(\text{NH}_4)_2\text{HCitrate}$ (AC) reacts with copper(II) to form a 1:1 copper(II)-citrate complex and two equivalents of hydrogen ions per mole of AC.

Thus, a measurement of the acid released in the chelate formation provides a simple method for the determination of AC where:

$$\text{AC} = 0.5 (\text{Meq. H}^+)$$

Presumably, because of the presence of ammonia which complexes copper, a 2.75 to 1 copper to AC molar ratio is necessary for the complete release of the hydrogen ions. At copper to AC ratios above 3 to 1, a significant positive bias is observed. The bias, which increases with increasing copper concentration, is believed to be caused by the reaction:

In the recommended procedure, 60 to 100 mg. of AC is specified for the determination. Over this range, the bias varies from 0% at the 100-mg. level to about +1.7% at the 60-mg. level.

G:4.2 Apparatus and Reagents

G:4.2.1 Apparatus

- a. pH meter with glass-calomel electrode system.
- b. Buret, micro, 10-ml.
- c. Magnetic stirrer and stirring bars.
- d. Beakers, assorted sizes.
- e. Pipets, assorted sizes.
- f. Dropping bottles.

G:4.2.2 Chemicals

- a. Sodium hydroxide solution, 0.1N. A 0.1000N solution standardized against potassium acid phthalate will be supplied by the Quality Control Laboratory.
- b. Copper(II) nitrate solution, 0.25M. Dissolve 60.4 grams of cupric nitrate trihydrate in water and dilute to 1 liter.
- c. Hydrochloric acid, 0.1N.
- d. Citrate (AC) bench standard, 0.0750M (0.1500N). Dissolve 8.4821 grams of $(\text{NH}_4)_2\text{HCitrate}$ in water and dilute to 500 ml.

G:4.3 Bench Standard

Before analyzing samples, run a single determination on the bench standard. Process 5.00 ml. of the AC bench standard according to G:4.4. The result obtained should be within the range: 0.0720M to 0.0780M.

G:4.4 Procedure

1. Pipet 5 ml. of the 0.25M copper nitrate solution into a 150-ml. beaker.
2. Dilute to about 100 ml. with distilled water. Insert the pH meter electrodes and adjust the pH to exactly 5.1 with the 0.1N sodium hydroxide titrant. If necessary, 0.1N hydrochloric acid may be used also.

3. Pipet a sample containing between 60 and 100 mg. (0.265 to 0.44 mmole) of AC into the beaker. (The pH will drop because of the release of H^+ ions.)

NOTE: A 30 gram per liter AC solution is 0.133M.

4. Titrate with 0.1000N sodium hydroxide back to pH 5.1. (Be sure to refill the buret or read the buret before titrating.)

G:4.5 Calculations

$$AC \text{ Normality} = \frac{0.1000(\text{Vol. NaOH})}{\text{Sample Vol. in ml.}}$$

$$AC \text{ Molarity} = 0.5 (\text{AC Normality})$$

$$\text{Result, mg. AC per ml.} = 226.2 (\text{AC Molarity})$$

G:5 Determination of EDTA and Hydrazine

- G:5.1 The hydrazine-versene (HV) descaling solution has the composition:

0.25M EDTA (added as the tetrabasic acid),
0.5M N_2H_4 , and 0.5M NH_4OH .

The EDTA is determined by direct titration with cerium(III) to a visual indicator end point.

N_2H_4 is determined iodimetrically. The iodine titration is performed in a bicarbonate medium at pH 7.2 under a protective blanket of nitrogen.

G:5.2 Apparatus and Reagents

G:5.2.1 Apparatus

- a. pH meter with a miniature probe glass-calomel electrode system.
- b. Buret, 10-ml.
- c. Beakers, 150-ml.
- d. Dropping bottles.
- e. Erlenmeyer flasks, 125-ml.

G:5.2.2 Reagents

- a. Cerium(III) solution, 0.05M. Prepare a 0.050M solution using 21.71 grams of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ per liter of solution. Standardize against 5.00 ml. of standard 0.05M EDTA according to C-1.
- b. Xylenol orange, 0.2%. Dissolve 0.20 gram of xylenol orange in 100 ml. of water.
- c. Pyridine.
- d. Hydrochloric acid, concentrated and 1M.
- e. Standard hydrazine sulfate solution, 0.0500M. Dissolve 3.2530 grams of hydrazine sulfate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$) in water and dilute to 500 ml.
- f. Iodine solution, 0.10N. Dissolve 12.5 grams of iodine and 40 grams of potassium iodide in water and dilute to 1 liter with water. Standardize the iodine solution by titrating 4.00 ml. of the standard hydrazine sulfate solution according to C-2.
- g. Starch solution, 1%. Prepare a 1% starch solution using a hot 1:1 glycerol-water mixture.
- h. Nitrogen gas.

G:5.3 Procedures

G:5.3.1 Determination of EDTA

- a. Pipet a sample containing 0.20 to 0.40 mmole of EDTA into a 150-ml. beaker.
- b. Dilute to 100 ml. with water and acidify (phenolphthalein indicator may be used) with concentrated hydrochloric acid. Add 5 drops of concentrated hydrochloric acid in excess.
- c. Add 5 drops of 0.2% xylenol orange indicator solution and 1 ml. of pyridine.
- d. Titrate with the standard cerium(III) solution to a change from yellow to reddish-purple.

G:5.3.2 Determination of Hydrazine

- a. Pipet a sample containing between 0.10 and 0.20 mmole of hydrazine into a 125-ml. Erlenmeyer flask. Dilute to about 60 ml. with water.
- b. Direct a stream of nitrogen gas into the flask.

- c. Add 1 gram of sodium bicarbonate, stir to dissolve, then adjust the pH to 7.2 using 1M hydrochloric acid and/or 1M sodium hydroxide.
- d. Add 1 ml. of the 1% starch indicator solution and titrate with the iodine solution to the appearance of a blue color.

G:5.4 Calculations

G:5.4.1 Determination of EDTA

$$\text{EDTA Molarity} = \frac{(\text{Vol. Ce})(\text{Ce Molarity})}{\text{Sample Vol. in ml.}}$$

G:5.4.2 Determination of Hydrazine

NOTE: 1 mole of $\text{N}_2\text{H}_4 \approx 2$ moles of $\text{I}_2^\circ \approx 4$ equivalents

$$\text{N}_2\text{H}_4 \text{ Molarity} = 0.25 \frac{(\text{Vol. I}_2^\circ)(\text{I}_2^\circ \text{ Normality})}{\text{Sample Vol.}}$$

G:6 Reference

Yamamura, S. S., IDO Notebook U-850, pp. 57-65.

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MACRO FLUORIDE DETERMINATION

ABSTRACT

An indirect complexometric method is described for the determination of macro amounts of fluoride. After preseparation by pyrolysis, the fluoride is quantitatively precipitated (as cerium trifluoride) at pH 1.85 with a measured excess of cerium(III) nitrate. The excess cerium is then measured by titrating a portion of the supernatant solution with ethylenediaminetetraacetic acid (EDTA) in a pyridine-buffered medium to a xylenol orange indicator end point. The amount of cerium precipitated serves as a measure of the fluoride.

APPLICABILITY

The method is applicable to samples containing more than 2.0 mg. of fluoride per ml. ($>0.1M$). Between 6 and 40 mg. of fluoride should be taken. Nitric, perchloric, and hydrochloric acids do not interfere, but sulfate and phosphate must be absent. Metal ions are quantitatively removed during pyrolysis. When samples contain hydrochloric or hydrobromic acids, EDTA-reactive metals which volatilize as halides, such as germanium, tin, and antimony, will interfere.

Plant samples which have been analyzed successfully include:

1. Nitric acid solutions containing zirconium, aluminum, and other metals.
2. Fluoboric acid samples (no pyrolysis is necessary in the absence of metal ions). Large amounts of boric acid cause results to be slightly low.
3. Nitric acid solutions containing beryllium and other metals.
4. Ammonium bifluoride solutions. No pyrolysis is necessary in the absence of metal ions.

In all cases, 1 ml. of saturated aluminum nitrate is added to the sample in the platinum boat to assure a quantitative, controlled release of fluoride.

APPARATUS AND REAGENTS

A. Apparatus

1. pH meter, Leeds and Northrup, with miniature probe electrodes.
2. Pyrolysis furnace connected through a Variac resistor.
3. Thermocouple to measure the temperature of the furnace.
4. Air flow meter. Pyrex float, "TRU-TAPER" tube size 6-15-2.
5. Dilute sodium hydroxide scrubber. Phenolphthalein indicator added to this scrubber will indicate when the solution becomes acidic.
6. Platinum boats.
7. Spatula.
8. Centrifuge tubes, 50 ml.
9. Centrifuge tubes, 50 ml, modified for use as pyrolyte collection tubes. Make four deep indentations half-way up each tube.
10. Lab jacks.
11. Teflon sheet. From a Teflon sheet cut a circle large enough to cover the top of a 50-ml. centrifuge tube. Cut a hole in the center of the circle so that the exit tube of the pyrolysis tube can pass through it.
12. Wash bottle with a long hypodermic needle attached.
13. Magnetic stirrer and stirring bars.
14. Ice bath.
15. Pipets, macro, assorted sizes.
16. Pipets, micro, assorted sizes.
17. Buret, micro, 10-ml.
18. Graduated cylinder, pharmaceutical, 30-ml.
19. Beakers, assorted sizes.

20. Flasks, volumetric, 50-ml.
21. Water bath, heated to boiling on a hotplate.
22. Centrifuge, clinical type.
23. Pyrolysis tube. The tube is a 17.25-inch x 30-mm. O.D. standard-wall quartz tube fitted with a 29/42 ♀ female joint and 5.5 inches of 6-mm. O.D. standard-wall quartz tubing bent at a right angle as shown in Figure 1. The dimensions of the exit tube are of critical importance.
24. Quartz 29/42 ♂ male joint with quartz tubing connected to air hose.

Figure 1. Pyrolysis Tube

B. Reagents

1. EDTA, 0.05M. Dissolve 37.2 ± 0.1 grams of disodium ethylenediaminetetraacetate, dihydrate in water and dilute to 2 liters. Standardize against standard 0.05M zinc according to Procedure A.
2. Zinc standard solution, 0.0500M. Dissolve 4.0690 grams of pure zinc oxide in 15 ml. of concentrated hydrochloric acid. Dilute to 1 liter with 0.05M hydrochloric acid.
3. Cerium nitrate solution, 0.075M. Dissolve 65.14 grams of cerous nitrate, hexahydrate in 1.5 liters of 0.01M nitric acid. Filter through a 0.45μ Millipore filter and dilute to 2 liters with 0.01M nitric acid. Standardize against the EDTA solution according to Procedure B.

4. Chloroacetic acid, 1M. Dissolve 47.3 grams of chloroacetic acid in water and dilute to 500 ml.
5. Phenolphthalein, 0.05%.
6. Sodium hydroxide, 9 ± 1 M. Prepare approximately 14M carbonate-free sodium hydroxide by dissolving 400 grams of sodium hydroxide pellets in 600 ml. of water. Filter through a large, fine-porosity, sintered glass Buchner funnel. Dilute 200 ml. of the filtered solution to 300 ml. with water. Store in a polyethylene bottle.
7. Fluoride standard, 24 mg. of F^- per ml. Dissolve 53.0492 grams of sodium fluoride in water and dilute to 1 liter.
8. Nitric acid, concentrated and 2M.
9. Ammonium hydroxide, concentrated and 2M.
10. Tungstic anhydride (WO_3), purified.
11. Xylenol orange indicator, 0.2% (w/v). Dissolve 0.20 gram of xylenol orange indicator in 100 ml. of water.
12. Eriochrome black T, 0.2%. Dissolve 0.2 gram of eriochrome black T in 100 ml. of triethanolamine (2, 2', 2''-nitrilotriethanol).
13. Pyridine, reagent grade.
14. Saturated aluminum nitrate. Prepare in 0.1M nitric acid.
15. Nitric acid, ~ 0.01 M, $pH = 1.85 \pm 0.1$. Adjust 0.01M HNO_3 with dilute nitric acid or ammonium hydroxide to $pH 1.85 \pm 0.1$.

PROCEDURE

A. Standardization of EDTA.

1. Pipet 5.00-ml. portions of the standard zinc solution into 100- or 150-ml. beakers.
2. Add 75 ml. of water and 1 medicine dropper full (about 1-ml.) of concentrated ammonium hydroxide.
3. Add 2 drops of eriochrome black T indicator.

4. Titrate slowly with the EDTA solution to a clear blue color.
5. Molarity of EDTA =
$$\frac{(\text{ml. Zn})(\text{Molarity of Zn})}{\text{ml. EDTA}}$$

B. Standardization of Cerium

1. Pipet 5.00-ml. portions of the cerium nitrate solution into 100- or 150-ml. beakers.
2. Add 75 ml. of water, 2 drops of xylenol orange indicator, and 10 drops of pyridine.
3. Titrate slowly with EDTA to the complete disappearance of the violet cerium(III)-xylenol orange complex. The final end point color change is orange to yellow.
4. Molarity of cerium =
$$\frac{(\text{ml. EDTA})(\text{Molarity of EDTA})}{(\text{ml. Ce})}$$

C. Bench Standard

Analyze 1 ml. of the bench standard according to D and E.

NOTE: When samples do not require pyrolysis, analyze the bench standard by pipetting 1 ml. of the standard fluoride solution into a 50-ml. centrifuge tube containing 4 ml. of 9M sodium hydroxide and 20 ml. of water. Analyze according to Procedure E.

D. Pyrolysis Procedure

1. Check to see if the furnace and its accessory equipment are in operating condition. Assemble as shown in Figure 2. Set air flow at 2 cm. This is equivalent to about 2.5 liters per minute.

2. a. Liquid Samples

Pack the platinum boat nearly $\frac{3}{4}$ full with WO_3 . Make a tiny furrow by running the edge of the spatula down the middle of the packed WO_3 bed. Pipet the sample, 3-ml. or less containing 6 to 40 mg. of fluoride, evenly along the entire length of the boat. Pipet 1 ml. of saturated aluminum nitrate also delivered along the length of the boat. Cover with additional WO_3 and pack down well.

b. Solid Samples

Grind samples thoroughly in a mortar to ensure homogeneity. Weigh a sample containing 6 to 40 mg. of fluoride and mix intimately with the WO_3 accelerator. Transfer the sample quantitatively to the platinum boat using small portions of WO_3 to aid the transfer. Deliver 1 ml. of saturated aluminum nitrate along the length of the boat, cover with additional WO_3 , and pack down firmly.

3. Pipet 4 ml. of the 9M sodium hydroxide solution into the specially-indented centrifuge tube and add 15 ml. of water. Support the tube on a lab jack and immerse the pyrolysis exit tube to the bottom of the caustic solution.

NOTE: To avoid partial loss of sample by spattering, cover the centrifuge tube with a small sheet of Teflon.

4. Place the boat in the pyrolysis tube in a 200°C. or less furnace. Connect the air supply as shown in Figure 2 and heat rapidly to 950°C. Maintain at this temperature for an additional 5 to 10 minutes. Total pyrolysis time is 35 to 45 minutes.
5. Turn off the power. With the air purge left on, lower the collecting tube and rinse the inside of the exit tube with water directed from a wash bottle through a long hypodermic needle inserted into the exit tube. Finally, rinse down the outside walls of the exit tube.
6. Lift the top cover of the furnace to facilitate cooling. Continue according to E.

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Figure 2. Assembled Pyrolysis Apparatus

E. Analysis of Pyrolate

1. Place the centrifuge tube containing the pyrolate into an ice bath and insert the pH meter electrodes into the pyrolate.
2. Adjust the pH to 7-8 using concentrated nitric acid. Allow to cool to room temperature. Add 2 drops of 1M chloroacetic acid.
3. Adjust to pH 3.5 ± 0.5 with either nitric acid or ammonium hydroxide.
4. Pipet exactly 10 ml. of the cerium solution. Adjust the pH to 1.85 ± 0.1 and rinse the electrodes with 0.01M nitric acid (pH 1.85 ± 0.1).
5. Transfer to a 50-ml. volumetric flask using 0.01M nitric acid (pH = 1.85 ± 0.1). Do not dilute to volume.
6. Stopper loosely and place in a boiling water bath until the precipitate settles and the supernatant solution is clear. Usually about 20 minutes will be required. Remove and cool to room temperature by immersion in cold water.
7. Dilute to volume with 0.01M nitric acid (pH = 1.85 ± 0.1) and mix well.
8. Transfer 35 ml. of the solution to a 50-ml. centrifuge tube and centrifuge.
9. Carefully pipet 25 ml. of the supernatant solution into a 150-ml. beaker. Add 50-ml. of water, 10 drops of pyridine, and 2 drops of xylenol orange indicator.
10. Using vigorous magnetic stirring, titrate with 0.05M EDTA to a yellow end point.

NOTE: If the end point is overrun, quickly pipet an additional 5- or 10-ml. aliquot of the sample into the beaker and continue the titration. Correct back to 25 ml.

CALCULATIONS

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Sample volume in ml. or sample weight in grams.
B	Volume of EDTA used, in ml.
C	Molarity of EDTA.
D	Millimoles cerium used. $D = 10$ (molarity of Ce).
E	Milligrams fluoride in sample. $E = 57(D-2BC)$.
F	Result, milligrams fluoride per ml. (per gram) of sample. $F = \frac{E}{A}$

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MICRODISTILLATION-COLORIMETRIC FLUORIDE DETERMINATION

ABSTRACT

A sensitive, highly specific procedure is described for the determination of 2.5 to 25 μg . of fluoride. Fluoride is separated from fluoride-complexing metal ions by steam distillation from a phosphoric acid medium. The fluoride then is determined in the distillate by a direct colorimetric procedure based on the reaction of the red lanthanum(III)-Alizarin Complexone (La-AC) chelate with fluoride to form a blue double-complex. A comprehensive discussion of the effects of diverse ions is presented under APPLICABILITY

APPLICABILITY

This procedure is applicable to the determination of fluoride in aqueous samples containing high concentrations of diverse ions. A comprehensive study was made of the effects of various ions on the procedure. As shown by the data summarized in Figure 1, few ions interfere.

At a 500:1 diverse ion to fluoride molar ratio, Al(III), Cd(II), Ce(III), and Mn(II) cause a 5 to 10% negative bias. However, these metals do not interfere at the 100:1 ratio.

Borate and silicate interfere seriously even at the 100:1 diverse ion to fluoride molar ratio by retarding the distillation of fluoride. This interference can be overcome if 60 ml. of distillate are collected instead of 20 ml. as described in the procedure. However, the distillate must be evaporated in a polyethylene beaker to less than 25 ml. before the La-AC color reagent is added.

For samples that contain little or no metal ions or complexing anions, direct colorimetric measurement of the fluoride is possible with no distillation necessary. The effect of various diverse ions on the La-AC colorimetric fluoride procedure is summarized in Table I. In general, metal ions that complex fluoride interfere. Iron(III) in equimolar amounts is without effect, but at this same level aluminum(III) and zirconium(IV) interfere seriously. Sulfate and silicate interfere slightly at 77 to 1 molar ratio, but phosphate at 2 to 1 and sulfite at 380 to 1 interfere seriously. The monovalent anions bromide, chloride, nitrate, and perchlorate at 3800 to 1 have no effect. Nitrite is reduced with hydroxylamine hydrochloride in the procedure and thus does not interfere at the 1500 to 1 molar ratio.

Fig. 1. Tolerance Level of Diverse Ions in the
Distillation-Colorimetric Measurement Procedure

Li *	Be II 500	ELEMENT VALENCE STATE TOLERANCE (ION TO FLUORIDE) MOLE RATIO										B II INTERFERES SEE TEXT	C	N III 1,000 V 1,000	O	F
Na *	Mg II 500											Al III 100	Si IV INTERFERES SEE TEXT	P V 70,000	S VI 18,000	Cl -1 1,000
K *	Ca II 100	Sc III 500	Ti	V V 500	Cr III 500 IV 1,000	Mn II 100	Fe III 1,000	Co II 500	Ni II 500	Cu II 500	Zn II 500	Ga III 500	Ge	As III 500	Se VI 300	Br -1 1,000
Rb *	Sr II 500	Y III 100	Zr IV 500	Nb V 500	Mo VI 17,500	Tc	Ru III 50	Rh	Pd	Ag I 1,000	Cd II 100	In III 500	Sn II 500	Sb	Te	I -1 1,000
Cs *	Ba	Lc III 500	Hf	Ta	W VI 500	Re	Os	Ir	Pt	Au	Hg II 500	Tl	Pb II 500	Bi III 500	Po	At
Fr *	Ra	Ac														
			Ce III 100	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb III 500	Lu
			Th IV 500	Pa	U VI 500	Np	Pu	Am	Cm	Bk	Cf					

*NO INTERFERENCE EXPECTED

*NO INTERFERENCE EXPECTED

TABLE I. THE EFFECT OF DIVERSE IONS ON THE DIRECT LANTHANUM-ALIZARIN COMPLEXONE COLORIMETRIC PROCEDURE^a

<u>Ion Added</u>	<u>Diverse Ion To Fluoride Molar Ratio</u>	<u>Fluoride Found, %</u>
Bicarbonate	2310	100.0
Borate	500	100.3
Bromide	4600	98.3
Chloride	7700	98.6
Nitrate	3850	98.3
Nitrite	1540	99.7
Perchlorate	3850	100.0
Phosphate	2	87.5
Silicate	38	99.4
	77	94.9
Sulfate	77	95.4
	380	Interferes
Sulfite	380	Interferes
Aluminum(III)	1	Interferes
Barium(II)	770	99.7
Calcium(II)	770	100.8
Iron(III)	1	99.7
Magnesium(II)	190	100.6
Zirconium(IV)	1	Interferes

^a All samples contained 25 μ g of fluoride. Each value is the average of two or more determinations.

DISCUSSION

Phosphoric acid is used in the distillation because it forms strong complexes with such fluoride-complexing metal ions as aluminum(III), iron(III), zirconium(IV) and the rare earths, thus releasing fluoride for distillation as fluosilicic acid. As mentioned under APPLICABILITY, phosphate interferes seriously in the colorimetric procedure. The microdistillation apparatus illustrated in Figure 2 contains a perchloric acid trap to minimize the carry-over of phosphate. It is important that the rate of addition of water and the flow rate of the air be maintained at the levels specified in the procedure. Higher rates may cause such vigorous bumping that phosphate will be forced over.

Silicate causes a negative interference in the color procedure. Thus it is important that sodium hydroxide used in the procedure be stored in and dispensed with polyethylene ware.

Nitrate is reduced by cerium(III) or manganese(II) to nitrite during distillation from phosphoric acid. The nitrite, which interferes seriously in the color procedure, must be reduced with hydroxylamine hydrochloride prior to color development.

The absorbance of the blue, La-AC fluoride complex is proportional to the fluoride concentration over the range 2.5 to 25 μg . The colored complex is developed in a 20%(v/v) acetone-water or acetonitrile-water medium buffered with acetic acid and sodium acetate at pH 4.35 ± 0.05 . Under these conditions, full color development is obtained in 20 minutes and the colored complex is stable for 24 hours.

Although the calibration curve obtained by plotting absorbance vs. fluoride concentration is linear as noted above, there is a small, constant negative intercept characteristic of the La-AC fluoride system. A small correction for this negative intercept is included in the calculations.

APPARATUS AND REAGENTS

A. Apparatus

1. Spectrophotometer, Beckman DU or DK or Cary Model 14.
2. Absorption cells, Corex, 1-cm. matched set.
3. Volumetric flask, 50-ml.
4. Pipets, volumetric, macro and micro, assorted sizes.

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Fig. 2. Microdistillation Apparatus

5. Distillation apparatus (see Figure 2).
6. Heating mantles, beaker type, 800-ml. size.
7. Glycerine bath, 800 ml. beaker containing glycerine.
8. Lab Jacks
9. Collection tubes. 50-ml. polyethylene graduated cylinders.
10. Dropping bottles, polyethylene construction.
11. Pipets, volumetric, assorted sizes, polyethylene.

B. Reagents

NOTE: Use distilled water and C.P. or Analytical Reagent Grade chemicals throughout.

1. Fluoride stock solution, 1.00 mg. per ml. Dissolve 1.1050 gram of sodium fluoride in water and dilute to 500 ml. with water. Store in a polyethylene bottle.
2. Fluoride calibration standard I, 20.00 μ g. per ml. Dilute 10.00 ml. of the fluoride stock solution to 500 ml. with water. Store in a polyethylene bottle.
3. Fluoride calibration standard II, 10.00 μ g. per ml. Dilute 5.00 ml. of the stock solution to 500 ml. with water. Store in a polyethylene bottle.
4. Lanthanum nitrate stock solution, 0.0167M. Dissolve 3.616 grams of lanthanum nitrate hexahydrate in water and dilute to 500 ml.
5. Alizarin Complexone stock solution, 0.0167M. Suspend 0.643 gram of the reagent (obtainable from Burdick and Jackson Laboratories, Muskegon, Michigan) in 50 ml. of water. Dissolve with 0.25 ml. of concentrated ammonium hydroxide. Add 0.25 ml. of glacial acetic acid and dilute to 100 ml. This solution is stable for 2 weeks.
6. pH 4 buffer solution. Dissolve 60 grams of sodium acetate trihydrate in 500 ml. of water. Add 115 ml. of glacial acetic acid and dilute to 1 liter with water.
7. Composite fluoride reagent. Mix in order and with swirling, 330 ml. of acetone or acetonitrile, 68 ml. of the buffer solution, 10.00 ml. of the Alizarin Complexone stock

solution, 10.00 ml. of the lanthanum stock solution, and 75 ml. of water. Warm to room temperature and dilute to 500 ml. with water. This reagent, stored in a polyethylene bottle, is stable for 5 days. PREPARE A FRESH SOLUTION AFTER 5 DAYS.

8. Hydrochloric acid, concentrated, and 1M.
9. Sodium hydroxide, carbonate-free, 1M and 0.5M.
10. Hydroxylamine hydrochloride solution, 2M. Dissolve 70 grams of the salt in 500 ml. of water.
11. Phosphoric acid. Heat 1 liter of phosphoric acid to 160°C. in a 3-liter round bottom flask and bubble steam through the hot acid for 4 hours.
12. Perchloric acid. One liter of perchloric acid is purified in the same manner as the phosphoric acid.
13. Sodium hydroxide, 0.5M and 2M. Prepare aqueous solutions and store in polyethylene bottles.
14. Hydrochloric acid, 1M and 0.5M.
15. Phenolphthalein, 0.2%.

PROCEDURE

A. Blank

Process a blank with each series of samples. Substitute water for the sample aliquot and process according to the same procedure used for the sample.

- B. Run a separate calibration with each series of samples. Use 1.00-ml. of each of the two fluoride calibration standards, 10.00 and 20.00 µg. F/ml., respectively, and process these according to the procedure used for the analysis of the samples. Add 0.007 absorbance units to the absorbance of each of the standards. Divide the corrected absorbances by the micrograms of fluoride to obtain the calibration factor. The difference between the two factors should not exceed limits set by the Quality Control Laboratory. Also, the average of the two factors should agree with the established conversion factor within the specified limits. If either or both of the specifications are not met, reprocess the pair of calibration standards. Contact your supervisor if difficulties still are experienced.

C. Microdistillation of Fluoride

1. Clean the distillation flask and bubbler tube by immersing in hot concentrated sulfuric acid followed by thorough washing with distilled water.
2. Transfer 4 ml. of 0.5M sodium hydroxide to the collection tube with a polyethylene pipet.
3. Add 1 ml. of concentrated perchloric acid to the trap through the arm of the distillation flask.
4. Assemble the apparatus with the condenser delivery tube extending below the surface of the sodium hydroxide in the collection tube.
5. Remove the bubbler tube and add an aliquot of the sample (5-ml. or less) containing 2.5 to 25 $\mu\text{g.}$ of fluoride and less than 1.75 mmoles of distillable anions to the distillation tube. The distillable inorganic anions include the halides, nitrate, and nitrite.
6. Replace the bubbler tube and add 3.0 ml. of phosphoric acid.
7. Adjust the air flow rate so that 2 to 3 bubbles per second emerge from the perchloric acid trap.
8. Raise the glycerine heating bath and adjust the temperature to $165 \pm 5^\circ\text{C.}$
9. Maintain the temperature at 165°C and admit water from the reservoir at a rate of 7 to 10 drops per minute.
10. Collect 20 ml. of distillate.
11. Remove the collection tube and wash down the condenser with 1 to 3 ml. of water. Combine the washings with the distillate.
12. Continue according to D beginning at step 2.

D. Colorimetric Fluoride Measurement

1. Pipet an aliquot of the sample (25 ml. or less) containing between 2.5 and 25 $\mu\text{g.}$ of fluoride to a 50-ml. volumetric flask. The sample must be free of interfering ions and contain less than 3.0 mmoles of the ions chloride, nitrate, and perchlorate.

2. Add 1 drop of 0.2% phenolphthalein and 1 ml. of 2M hydroxylamine hydrochloride.
3. Add 1M hydrochloric acid dropwise till colorless, then add 1 drop more. Let stand 3 to 5 minutes with occasional mixing.
4. Add 2M sodium hydroxide dropwise from a polyethylene pipet until basic, then add 0.5M hydrochloric acid until the solution just turns acidic.
5. Add 15 ml. of the composite fluoride reagent and transfer the solution to a 50-ml. volumetric flask.

NOTE: For samples analyzed directly (without distillation), the transfer is not necessary.

6. After 20 minutes, measure the absorbance against the reagent blank in a 1.0-cm. cell at 617 mμ.
7. Calculate the concentration of fluoride as described below.

CALCULATIONS

<u>Column</u>	<u>Unit to Record</u>
A	Micrograms fluoride in the calibration standards.
B	Absorbance of standards.
C	Corrected absorbances $C = B + 0.007$ $C' = B' + 0.007$
D	Calibration factors $D = C/A$ $D' = C'/A'$
E	Average calibration factor $E = 0.5 (D + D')$
F	Sample volume in ml.
G	Sample absorbance.
H	Result, μg. F ⁻ per ml. $H = \frac{G + 0.007}{EF'}$

Report results to 3 significant figures.

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DETERMINATION OF TOTAL HALOGENS IN ORGANIC MATERIALS

ABSTRACT

The sample is decomposed and the halogens are oxidized to the free state by successive oxidations with fuming sulfuric acid, potassium persulfate, and chromic acid or potassium permanganate. The free halogens are distilled into an absorber in which they are reduced to the halides with sodium arsenite. The halides are precipitated with a measured excess of silver nitrate, filtered, washed, dried, and weighed. The excess silver nitrate in the filtrate and washings is titrated with potassium thiocyanate.

APPLICABILITY

This procedure was developed for the analysis of halogens in marking materials, and is applicable to most organic materials. The lower limit of detection is 2 mg of chlorine, 0.2 mg of bromine, and 2 μ g of iodine.

SAFETY PRECAUTIONS

Fuming sulfuric acid is extremely hazardous. Always wear rubber gloves when using it. Rubber gloves are also advisable when handling potassium persulfate in concentrated sulfuric acid.

The distillation should be performed in a hood. Air flow must be carefully regulated during the distillation to prevent the absorber solution from backing up to the condenser.

APPARATUS AND REAGENTS

A. Apparatus

1. Special distilling apparatus

- a. Distillation flask, 250 ml round-bottomed flask with dropping funnel.
- b. Condenser, water cooled, 28 inches long.
- c. Adapter with air inlet through a stopcock.
- d. Connecting tube, glass tubing attached to bubbler assembly of gas scrubber cylinder.
- e. Absorption flask, gas scrubber cylinder.

NOTE: All parts of the distilling apparatus which come in contact with the halogens must be made of glass.

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Figure 1. Distillation Apparatus

2. Heating mantle.
3. Variac resistor.
4. Glass beads.
5. Graduated cylinders.
6. Pipets, 100 ml.
7. Beakers, 600 ml.
8. Suction flask, 1000 ml.
9. Fritted glass crucible, fine porosity, 30 ml. capacity.
10. Stirring bars, Teflon coated bar magnets.
11. Buret, 25 ml, graduated in 0.1 ml. divisions.
12. Buret, 10 ml, graduated in 0.02 ml. divisions.

B. Reagents

NOTE: All reagents used are C.P. or Analytical Reagent grade stock. Use distilled water for the preparation of all reagents.

1. 10% sodium hydroxide-1% As_2O_3 . Dissolve 100 g sodium hydroxide and 10 g As_2O_3 in water and dilute to one liter with water. Store in a polyethylene bottle.
2. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.
3. Sulfuric acid, fuming.
4. $\text{K}_2\text{S}_2\text{O}_8$.
5. Sulfuric acid, concentrated.
6. Chromic acid, CrO_3 .
7. KMnO_4 solution. Dissolve 100 g KMnO_4 in 1 liter of water.
8. Methyl orange indicator. Dissolve 0.1 g of methyl orange in 100 ml of water.
9. HNO_3 , 6N. Dilute 400 ml of concentrated nitric acid to 1 liter with water.
10. Nitric acid, concentrated.
11. Acetone

12. Standard AgNO_3 , 0.01715N. This reagent comes ready for use.
13. HNO_3 , 1N. Dilute 67 ml of concentrated HNO_3 to 1 liter with water.
14. Ferric ammonium sulfate, saturated. Dissolve 124 g of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in 100 ml of water.
15. Ammonium thiocyanate solution, standard 0.1N. Dissolve 7.6 g NH_4SCN in 1 liter of water. Standardize by titrating against the standard silver nitrate.

PROCEDURE

A. Distillation

1. Pipet 100 ml of 10% NaOH - 1% As_2O_3 and 100 ml of distilled water into the absorption flask. Swirl to mix.
2. Accurately weigh about 1 g of sample into the distillation flask. Add 0.5 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and three glass beads.
3. Assemble the distillation apparatus as shown in Figure 1. Grease all joints with silicone grease, and secure them with rubber bands around the glass hooks.
4. Turn on the water flow to the condenser. Maintain as high a flow rate as is practical. This water should drain to the Service Waste. Close the stopcock regulating the air flow.
5. Carefully and slowly add 20 ml of fuming sulfuric acid through the dropping funnel. Turn on the air flow so that a slow but steady bubbling occurs in the absorption flask. Heat the distillation flask with an electric heating mantle regulated by a variac resistor. Boil gently for 30 minutes, using a variac setting of about 70.
6. Slowly and carefully add a suspension of 10.0 g $\text{K}_2\text{S}_2\text{O}_8$ in 20 ml of concentrated sulfuric acid. The air flow may have to be stopped to allow the suspension to enter the distillation flask, but care must be taken to prevent the absorption solution from being drawn back to the condenser.

7. Rinse all the $K_2S_2O_8$ into the distillation flask with an additional 15 ml of concentrated H_2SO_4 . Turn on the air flow. Increase the variac setting to about 110. Maintain vigorous boiling, but do not heat enough that SO_3 fumes pass through the condenser. Continue the boiling for 30 minutes or until the green color of copper sulfate is pronounced. If all the organic material has not decomposed after 30 minutes, add a suspension of 5 g CrO_3 in 15 ml concentrated H_2SO_4 and continue boiling until all the organic material is decomposed.
8. Slowly and cautiously add 50 ml of distilled water to the boiling mixture. Regulate the air flow as needed to allow the water to enter the distillation flask. Maintain vigorous boiling.
9. Turn off the water flow to the condenser, and drain all the water from it.
10. If no CrO_3 was added, add $KMnO_4$ solution to the distillation flask until the purple color is permanent and continue boiling for 5 minutes. If CrO_3 was added, this step is not necessary.
11. Disconnect the connecting tube and the adapter. Turn off the variac and the air flow. When the distillation flask and condenser have cooled, disconnect and clean them. If a residue of MnO_2 is present, use H_2SO_4 and H_2O_2 to dissolve it.

B. Determination of total halogens.

1. Use gentle air pressure applied to the gas outlet of the absorption flask to force absorption solution almost to the top of the connecting tube. Allow the solution to drain back into the absorber. Transfer the absorption solution quantitatively to a 600 ml beaker, using water rinses.
2. Add 5 drops of methyl orange indicator. Add 40 ml of 6N HNO_3 . Add 6N HNO_3 dropwise until the color changes from yellow to pink.
3. From this point on, keep the solution and halide precipitate away from strong light. Add 25.0 ml of standard $AgNO_3$ and 5 ml of concentrated HNO_3 . Heat to boiling to coagulate the precipitate. Cool.

4. Filter the solution through a tared fine porosity fritted glass crucible into a 1 liter suction flask. Rinse the beaker with 1N HNO_3 and then with distilled water, quantitatively transferring the precipitate to the crucible. Rinse the crucible with acetone, and dry it to constant weight at 105°C .
5. Quantitatively transfer the filtrate and washings to a 600 ml beaker. Add 5 ml of saturated ferric ammonium sulfate solution. Titrate to the orange endpoint with standardized ammonium thiocyanate from a microburet.

CALCULATIONS

<u>Column</u>	<u>Unit to Record</u>
A	Weight of sample taken, g
B	Weight of silver halide precipitate, g
C	Normality of AgNO_3
D	Volume of AgNO_3 , liters
E	Normality of NH_4CNS
F	Volume of NH_4CNS , liters
107.9	Equivalent weight of silver
G	% halogens

$$G = \frac{B \left[\frac{B}{C \left(D - \frac{E F}{C} \right)} - 107.9 \right] 100}{A \left[\frac{B}{C \left(D - \frac{E F}{C} \right)} \right]}$$

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SPECTROPHOTOMETRIC DETERMINATION OF MILLIGRAM LEVELS
OF PHOSPHOROUS AS MOLYBDIVANADOPHOSPHORIC ACIDABSTRACT

An intense yellow coloration forms upon the addition of an excess of molybdate to an acidified solution mixture of vanadate and phosphorous as orthophosphate. This is the basis of a simple colorimetric procedure described for the determination of milligram amounts of phosphate. An extensive discussion of the effects of diverse ions and of color development conditions are included in the APPLICABILITY and DISCUSSION sections, respectively.

APPLICABILITY

This procedure for milligram amounts of phosphate, based on a method by Kitson and Mellon(1) is especially suited for aluminum-based samples such as the calcine glass samples for which it was originally tested. However, because only a few ions interfere seriously, this method is applicable also to a wide variety of samples. The effects of diverse metal ions and anions are shown in Tables I and II, respectively. Included in Tables I and II is a column of remarks to guide the analyst in the analysis of samples with interfering or potentially interfering substances.

The linear range of the method is 1 to 40 ppm of phosphorous. With the prescribed dilution to 100 ml, this corresponds to a range of 0.1 to 4 mg. of phosphorous or 0.3 to 12 mg. of phosphate.

DISCUSSION

According to Kitson and Mellon(1) the following conditions must be controlled for complete, reproducible color development:

Acidity. The optimum acidity of the reaction medium is about 0.5N. The permissible variation from this acidity depends on the acid used. With nitric acid, the acid recommended for this procedure and most generally used, full color development is obtained in the range of 0.2N^A. With hydrochloric acid, perchloric acid, and sulfuric acid, the minimum acidity is 0.2N also, but for these acids, the maximum permissible acidity is 1N, 0.7N, and 0.9N respectively.

TABLE I. EFFECTS OF DIVERSE METAL IONS

Phosphate Added, Mg.	Ion Added	Ion to Phosphate Molar Ratio ^a	Absorbance ^b	Remarks
10.00	None	-	0.586	Based on 10 det'ns., the std. dev. is 0.0031 absorbance unit and the 95% confidence limits are 0.586 ± 0.007 absorbance unit for a single det'n. and 0.586 ± 0.005 for the average of 2 det'n.
8.00	None	-	0.475	Based on 35 det'ns., the std. dev. is 0.0015 absorbance unit and the 95% C.L. are 0.475 ± 0.003 absorbance unit for a single det'n. and 0.475 ± 0.002 absorbance unit for the average of 2 det'ns.
10.00	Al(III)	80	0.587	
8.00	Bi(III)	2.0 5.0	0.472(2) Precipitates	Bi(III) interferes seriously at Bi(III) to phosphate molar ratios exceeding 2:1.
10.00	Ca(II)	80	0.587	
10.00	Cd(II)	80	0.589	
10.00	Ce(III)	80	0.590	
8.00	Co(II)	20	0.476(2)	Co(II) absorbs at the working wavelength. Run reagent blank, sample blank (sample without vanadate and molybdate color reagents), and sample and measure the absorbance of each vs. water. Apply reagent and sample blank corrections to the sample.
8.00	Cr(III)	5 10 60 100	0.460(2) 0.456(2) 0.465 0.475	Cr(III) absorbs at the working wavelength. Apply sample blank correction, as for Co(II). The reason for the interference decrease with increasing Cr(III) to phosphate ratio is not known.

TABLE I. EFFECTS OF DIVERSE METAL IONS (Continued)

Phosphate Added, Mg.	Ion Added	Ion to Phosphate Molar Ratio ^a	Absorbance ^b	Remarks
10.00	Cu(II)	80	0.589	Cu(II) does not absorb at the working wavelength.
10.00	Fe(III)	40	0.588	Fe(III) absorbs slightly at the working wavelength. For example, at the 80:1 ratio [8.4 mmole Fe(III)], the sample blank absorbance vs. water is 0.003.
		80	0.568	
10.00	Hg(II)	40	0.589	Measure within 10 minutes after color development to avoid the formation of a precipitate.
		80	0.587	
10.00	K(I)	80	0.583	
10.00	Mg(II)	80	0.589	
10.00	Mn(II)	80	0.589	Mn(II) absorbs slightly at the working wavelength. Apply sample blank correction as for Co(II).
10.00	Mn(VII)	12	0.587	Reduce Mn(VII) to Mn(II) with NaNO ₂ .
10.00	Ni(II)	80	0.591	Ni(II) absorbs at the working wavelength. Apply sample blank correction as for Co(II).
10.00	Pb(II)	10	0.593	Measure within 5 minutes after color development to avoid the formation of lead molybdate precipitate.
		20	0.600(3)	
10.00	Sr(II)	80	0.590	
8.00	Th(IV)	0.1	0.468(2)	Serious interference.

TABLE I. EFFECTS OF DIVERSE METAL IONS (Continued)

Phosphate Added, Mg.	Ion Added	Ion to Phosphate Molar Ratio ^a	Absorbance ^b	Remarks
10.00	U(VI)	80	0.584	U(VI) absorbs at the working wavelength. Apply sample blank correction as for Co(II).
8.00	W(VI)	0.5	0.458(2)	Serious interference.
8.00	Zr(IV)	0.05	0.451(2)	Serious interference. Interference can be minimized by the addition of 10 ml. of 0.25M NaF-0.1M Al(NO ₃) ₃ .

^a 10.00 mg. PO₄⁻³ = 0.1053 mmole; 8.00 mg. PO₄⁻³ = 0.0842 mmole.

^b Single det'n except where noted otherwise by the numbers in parenthesis.

TABLE II. EFFECTS OF DIVERSE ANIONS

Ion Added	Ion to Phosphate Molar Ratio	Absorbance ^a	Remarks
Chloride (as NaCl)	50	0.585(2)	Though stated by Kitson and Mellon(1) to be a serious interference at greater than a 2.5:1 $\text{Cl}^-/\text{PO}_4^{3-}$ weight ratio, independent studies (2) show that chloride does not interfere at the 100:1 molar ratio. In fact, color development is rapid and complete in 0.5M HCl.
Chloride (as HCl)	100	0.584(2)	
Citrate	7	0.581	At high levels, citrate bleaches the color. Moderate amounts of citrate can be destroyed by digesting with nitric acid (5 ml.) and perchloric acid (1 ml.).
	12	0.538	
Fluoride (as HF)	5	0.583	Fluoride interferes at greater than 25:1 mole ratios; however, the fluoride can be masked effectively* with 5 mmoles of $\text{Al}(\text{NO}_3)_3$.
	25	0.579	
	60	Interferes	
	60*	0.588(2)	
Nitrate (as NaNO_3)	100	0.586(2)	
Nitrate (as HNO_3)	93	0.584	
	186	0.576	
Nitrite (as NaNO_2)	60	0.584	
	120	0.570(2)	
Oxalate	5	0.583	Moderate amounts of oxalate can be destroyed by digesting with nitric acid (5 ml.) and perchloric acid (1 ml.).
	7	0.581	
	12	0.528	
Perchlorate (as HClO_4)	138	0.582	
	276	0.578	

TABLE II. EFFECTS OF DIVERSE ANIONS

Ion Added	Ion to Phosphate Molar Ratio	Absorbance ^a	Remarks ^b
Silicate	20	0.591	At greater than 20:1 mole ratios, silicate introduces a positive bias.
	40	0.601	
	80	0.633	
Sulfate (as H ₂ SO ₄)	120	0.578(2)	At greater than 20:1 mole ratios, silicate introduces a positive bias.
	240	0.535(2)	
Tartrate	24	0.581	Moderate amounts of tartrate can be destroyed by digestion with nitric acid (5 ml.) and perchloric acid (1 ml.).
	48	0.554	

^a Phosphate maintained at 10.00 mg. (0.1053 mmole). Single determination except when noted otherwise by the numbers in parenthesis.

^b Based on 10 det'ns. at the 10.00 mg. level, the std. dev is 0.0031 absorbance unit and the 95% confidence limits are 0.586 ± 0.007 absorbance unit for a single det'n. and 0.586 ± 0.005 absorbance unit for the average of 2 det'ns.

Vanadate and molybdate level. An excess of vanadate and molybdate is necessary.

Order of reagent addition. The order of reagent addition is: acid, vanadate, then molybdate. This order should be maintained to avoid complications(1).

Phosphate concentration. The linear range of the method is 1 to 40 ppm of phosphorous corresponding to 0.3 to 12 mg. of phosphate per 100 ml. of solution.

Color development time. Generally, the color development is complete in 3 to 10 minutes. The resulting color is stable for at least 1 week.

APPARATUS AND REAGENTS

A. Apparatus

1. Spectrophotometer, Beckman, Model B or Model DU, or Cary, Model 14 with 1-cm. Corex cells.
2. Volumetric flasks, 100-ml.
3. Pipets, volumetric, assorted sizes.
4. Pipets, micro, assorted sizes with syringe.

B. Reagents

1. Phosphate calibration and bench standard I, 2.00 mg. phosphate per ml. Dissolve 1.3906 grams of diammonium hydrogen phosphate in water and dilute to 500 ml.
2. Phosphate calibration and bench standard II, 1.50 mg. phosphate per ml. Dissolve 1.0430 grams of diammonium hydrogen phosphate in water and dilute to 500 ml.
3. Ammonium molybdate reagent, 5% (w/v). Dissolve 25 grams of ammonium molybdate, $(\text{NH}_4)_7\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, in warm water and dilute to 500 ml. with water.
4. Ammonium vanadate, 0.25% (w/v). Dissolve 2.50 grams of ammonium vanadate, NH_4VO_3 , in 500 ml. of boiling water. Cool slightly, add 20 ml. of concentrated nitric acid, cool to room temperature then dilute to 1 liter with water.
5. Nitric acid, 5M. Dilute 160 ml. of concentrated nitric acid to 500 ml. with water.

PROCEDURE

A. Blank

Run a reagent blank with each set of standards and samples.

B. Sample Blank

When samples contain metal ions that absorb at the working wavelength of 270 mμ, process a sample blank with the samples. The sample blank contains the sample aliquot identical to that used for the analysis, and all the reagents except the ammonium molybdate and the ammonium vanadate.

C. Calibration and Bench Standard

Process a pair of calibration standards with each series of samples. Use 4.00-ml. portions of the two calibration standards and process these according to D. Divide the absorbance by the milligrams of phosphate in the standards to obtain the conversion factor. The difference between the two factors should not exceed limits set by the Quality Control laboratory. Also, the average of the two factors should agree with the established conversion factor within the specified limits. If either or both of the specifications are not met, reprocess the pair of calibration standards. Consult your supervisor if difficulties still are experienced.

D. Recommended Procedure

1. Pipet a sample containing 1 to 10 mg. of phosphate into a 100-ml. volumetric flask.
2. Add 10 ml. of 5M nitric acid. Swirl to mix.
3. Add 10 ml. of 0.25% (w/v) ammonium vanadate. Swirl to mix.
4. Add 10 ml. of 5% (w/v) ammonium molybdate, dilute to volume with water, and mix well.
5. Let stand 5 minutes, then measure the absorbance of the sample against the reagent blank at 470 mμ in 1-cm. cells.

NOTES: (a) With samples containing metal ions that absorb at 470 mμ, measure the absorbances of the sample, the sample blank, and the reagent blank against water. Then, subtract the total absorbance of the reagent blank plus the sample blank from the sample absorbance to obtain the net absorbance of the sample.

- (b) When samples contain lead(II) or mercury(II), develop the color only a few samples at a time and measure the sample absorbance immediately after 3 minutes to avoid the interference due to the formation of a precipitate.

6. Record the data on the worksheet and compute the results as described under CALCULATIONS.

CALCULATIONS

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit of Record</u>
A	Mg. phosphate in calibration standards.
B	Absorbance of standards.
C	Conversion factor. $C' = \frac{B'}{A'}$ $C'' = \frac{B''}{A''}$
D	Average conversion factor $D = 0.5(C' + C'')$
E	Sample volume in ml.
F	Sample absorbance.
G	Results, mg. phosphate per ml. $G = \frac{F}{DE}$

Report results to three significant figures as 111, 11.1, and 1.11 mg. phosphate per ml.

REFERENCES

1. Kitson, R. E., Mellon, R. G., Ind. Eng. Chem., Anal. Ed. 16, 379 (1944).
2. Yamamura, S. S., IDO Notebook U-850, pp. 111-150.

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GRAVIMETRIC DETERMINATION OF SILICON

ABSTRACT

A method is described for the determination of silicon in various types of samples. Metal samples usually are dissolved in nitric acid or in aqua regia. Perchloric acid is added, the sample is heated to fumes of perchloric acid, filtered immediately, and the residue is ignited and weighed. The residue then is fumed with hydrofluoric acid, ignited, and weighed. The loss in weight represents silicon dioxide.

APPLICABILITY

This procedure is applicable to a wide variety of samples including carbon and high-silicon steels, high-chromium steels, alloy cast iron, nickel, chromium-nickel, chromium-vanadium, and similar alloy steels.

Tungsten, as tungstic acid, also is volatilized to cause high results.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, 400-ml.
2. Speedivap watchglasses, 4-inch. diameter.
3. Platinum crucibles and covers.
4. Hot plate.
5. Muffle furnace.
6. Meker burner.
7. Buchner funnel, size No. 1.
8. Vacuum flasks, 500-ml.
9. Sand bath.
10. Filter paper, Whatman 42, 11-cm. diameter.
11. Rubber policemen.
12. Wash bottles, glass, 500-ml.

B. Reagents

1. Nitric acid, concentrated and 6M.
2. Hydrochloric acid, concentrated, 6M, and 0.6M.
3. Hydrofluoric acid, 28M (48%).
4. Perchloric acid, concentrated (70-72%).
5. Sulfuric acid, 9M.

SPECIAL PRECAUTIONS

A. Safety

1. Perform all digestions with perchloric acid in the special hood designated for that purpose.
2. Extreme care should be followed when adding concentrated acids to the solution and also when adding water to concentrated acid solutions. In all cases the sample should be cooled before the additions.
3. Care should be taken and rubber gloves worn when handling hydrofluoric acid.

B. Procedure

1. The filter paper must be thoroughly washed in section D, step 11. Perchloric acid held in the silicic acid or on the filter paper will cause spattering and loss of material upon ignition.
2. If more than 0.5 gram of silica is obtained in section D, step 23; repeat steps 16 through 24.

PROCEDURE

A. Bench Standard

Run a single determination on the bench standard. Limits will be specified by the Quality Control Laboratory. The bench standard will be a NBS certified sample.

B. Sampling

1. Select the sample size as follows:

<u>Estimated % Si</u>	<u>Sample Size</u>
< 0.5	5 grams
0.5-5.0	2.5 grams
> 5	1 gram

2. Accurately weigh to ± 0.5 mg.

C. Dissolution

1. Carbon and High-Silicon steels.

- Transfer the sample to a 400-ml. beaker.
- Add 40 ml. of 6M nitric acid.
- Cover with a watchglass and heat cautiously until solution is complete.
- Continue according to section D.

2. High-Silicon Alloys

- Transfer the sample to a 400-ml. beaker.
- Add 40 ml. of 6M hydrochloric acid.
- Cover with a watchglass and heat cautiously until solution is complete.
- Oxidize carefully with 40 ml. of 6M nitric acid.
- Continue according to section D.

3. High-Chromium Steels (Stainless Steels).

- Transfer the sample to a 400-ml. beaker.
- Add 50 ml. of concentrated nitric acid.
- Carefully add 50 ml. of concentrated hydrochloric acid. Keep beaker cool. Use ice bath if necessary.
- Cover with a watchglass.
- Do not heat until the initial reaction subsides. After the reaction subsides, carefully heat until the sample is in solution.
- Continue according to section D.

D. Silicon Dioxide Separation

1. Cool to below boiling, then remove the cover.
2. Cautiously add 50 ml. of concentrated perchloric acid.
3. Evaporate to dense white fumes of perchloric acid.
4. Cover the beaker with a watchglass and continue to heat at such a rate that perchloric acid refluxes on the side of the beaker for 15 to 20 minutes.
5. Remove from the hot plate.
6. Add 125 ml. of distilled hot water.
7. Stir until salts are in solution, heating gently, if necessary. Do not boil.
8. Crush any lumps of silica with a glass stirring rod.
9. Filter immediately, using a Buchner funnel and Whatman 42 filter paper.
10. Transfer all the residue to the filter paper, scrubbing the beaker thoroughly with a rubber policeman.
11. Wash the paper and residue alternately with hot 0.6M hydrochloric acid and hot water until iron salts have been removed. The washing of the paper must be thorough, for residual perchloric acid held in the silicic acid will cause spattering and loss of material upon subsequent ignition. This usually requires at least six washings with 5- to 10-ml. portions of each wash liquid.
12. Transfer the paper and residue to a platinum crucible.
13. Ash carefully.
14. Ignite for 30 minutes at 1100°C.
15. Cool in a desiccator and weigh.
16. Moisten the silica with water.
17. Add 6 drops of 9M sulfuric acid.
18. Add 5 to 10 ml. of 28M hydrofluoric acid.
19. Evaporate, carefully in a sand bath, to dense white fumes of sulfur trioxide.

20. Carefully add 2 to 3 ml. more of hydrofluoric acid.
21. Evaporate to dryness and carefully heat to dryness.
22. Ignite at 1000°C.
23. Cool in a desiccator and weigh. The loss in weight represents silica.
24. If the weight of silica is more than 0.5 gram, repeat steps 16 through 24.

CALCULATIONS

Record the data on the worksheet as follows:

<u>Column</u>	<u>Unit to Record</u>
A	Weight of sample, in grams.
B	Weight of crucible plus residue, in grams.
C	Weight of crucible plus residue after HF treatment, in grams.
D	Weight loss (equal to weight of silica), in grams. $D = B - C$
E	Result, weight percent silicon $E = \frac{46.75 D}{A}$

Report results to three significant figures.

REFERENCE

1. American Society for Testing Materials "ASTM Methods for Chemical Analysis of Metals," p. 121-122, 1961.

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APPENDIX C
RADIOCHEMICAL METHODS DEVELOPED IN 1964

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DETERMINATION OF RADIOACTIVE
MANGANESE, ZIRCONIUM-NIOBIUM, COBALT, AND IRON

ABSTRACT

Manganese, zirconium-niobium, cobalt, and iron are separated by anion exchange and determined by gamma ray spectrometry. Differences in the distribution coefficients of the chloride complexes of manganese, cobalt, and iron make their separation by ion exchange possible. Ion exchange behavior of zirconium-niobium is controlled by the fluoride complexes.

APPLICABILITY

This method was developed for the separation of manganese, cobalt, and iron in decontamination solutions from the Expended Core Facility. It was successfully used on oxalic-nitric acid solutions, ethylenediaminetetraacetic acid-hydrazine solutions, and basic permanganate solutions. Large amounts of manganese do not interfere. The presence of large amounts of zirconium, cobalt, or iron will not interfere if a sufficiently large column of ion exchange resin is used. Basic permanganate solutions must be acidified and the permanganate reduced prior to the ion exchange separation. Sample volumes should be 5 ml or less if the volume of the manganese fraction is to be 50 ml.

The presence of large amounts of Cr^{51} will seriously interfere in the determination of Mn^{54} , but will not affect the determination of ZrNb^{95} , $\text{Co}^{58,60}$, or Fe^{59} .

SAFETY PRECAUTIONS

Ordinary procedures for the prevention of excessive exposure to radiation should be observed. Because of the high concentration of hydrochloric acid, the ion exchange separation should be performed in a hood.

APPARATUS AND REAGENTS

A. Apparatus

1. Ion exchange columns. A ten-inch length of 11-mm polyethylene tubing with a Teflon wool plug in one end makes a satisfactory ion exchange column. If the zirconium-niobium separation is not needed and the hydrofluoric acid is not added to the 9M hydrochloric acid, a ten-inch length of 9-mm glass tubing with a drawn tip, plugged with glass wool, may be used.

2. Pipets, assorted sizes.
3. Beakers, assorted sizes.
4. Medicine droppers.
5. Glass stirring rods.
6. Volumetric flasks, 50 ml.
7. Counting tubes. Polystyrene vials, 50 ml capacity.

B. Reagents.

1. Ion exchange resin. Dowex 1-X8, 100-200 mesh.
2. Manganese carrier, 1 mg Mn/ml. Dissolve 3.6 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 750 ml of concentrated hydrochloric acid and dilute to 1 liter with water.
3. Zirconium carrier, 10 mg Zr/ml. Dissolve 29.3 g $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 100 ml of concentrated hydrochloric acid and 900 ml of water.
4. Cobalt carrier, 10 mg Co/ml. Dissolve 40.4 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 1 liter of water.
5. Iron carrier, 10 mg Fe/ml. Dissolve 54.3 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 750 ml of concentrated hydrochloric acid and 250 ml of water.
6. Hydrochloric acid, concentrated.
7. Hydrofluoric acid, 0.4M. Dilute 15 ml concentrated hydrofluoric acid to 1 liter with water.
8. Hydrochloric acid, 9M. Dilute 750 ml of concentrated hydrochloric acid to 1 liter with water.
9. Hydrochloric acid, 9M, hydrofluoric acid, 0.004M. Mix 750 ml of concentrated hydrochloric acid and 3 drops of concentrated hydrofluoric acid. Dilute to 1 liter with water.
10. Hydrochloric acid, 9M, hydrofluoric acid, 0.18M. Mix 750 ml of concentrated hydrochloric acid and 7 ml of concentrated hydrofluoric acid. Dilute to 1 liter with water.
11. Hydrochloric acid, 4M. Dilute 333 ml of concentrated hydrochloric acid to 1 liter with water.
12. Hydrogen peroxide, H_2O_2 , 30%.

PROCEDURE

A. Preparation of ion exchange columns.

1. Soak the resin in a beaker with 9M HCl-0.004M HF. If a zirconium separation is not desired, use 9M HCl only.
2. Wet the polyethylene tubing and Teflon wool plug with 9M HCl-0.004M HF. If a zirconium separation is not desired, use glass tubing and glass wool and wet it with 9M HCl.

3. Pour the slurry of resin into the tubing. Allow the excess acid to drain out of the column. The resin in the column should be six to eight inches long.

B. Preparation of sorption solution.

1. Mix the following in a small beaker.
 - a. 5 ml of sample, or less.
 - b. Concentrated HCl, three times the sample volume.
 - c. 1 ml of Mn carrier. Omit this for basic permanganate samples.
 - d. 1 drop of Zr carrier. Omit this if a Zr separation is not desired.
 - e. 1 drop of 0.4M HF for each ml of sample. Omit this if a Zr separation is not desired.
 - f. 1 drop of Co carrier.
 - g. 1 drop of Fe carrier.
 - h. 1 drop of 30% H_2O_2 .
2. Basic permanganate samples should be heated, and additional H_2O_2 added until the purple color is gone and the sample is clear.
3. A white precipitate will be observed at this point in samples containing ethylenediaminetetraacetic acid. It may be ignored, but will require extra space at the top of the resin column.

C. Ion exchange separation.

1. Place a 50 ml volumetric flask under the resin column. If the Mn^{54} activity is not too great, a counting tube may be used instead of the volumetric flask.
2. Pour the sorption solution, a little at a time, onto the top of the resin column. Rinse with 9M HCl-0.004M HF until 50 ml have been collected in the flask or counting tube. If a zirconium separation is not desired, use 9M HCl. This fraction contains the Mn^{54} .
3. Omit this step if a zirconium separation is not desired. Place a 50 ml counting tube under the resin column. Rinse the column with 9M HCl-0.18M HF until the tube is full. This fraction contains $ZrNb^{95}$.
4. Place a volumetric flask or counting tube under the resin column. Rinse the column with 4M HCl until the flask or counting tube is full. This fraction contains Co^{58} and Co^{60} .

5. Place a volumetric flask or counting tube under the resin column. Rinse the column with water until the flask or counting tube is full. This fraction contains Fe^{59} .
 6. Place used ion exchange columns in plastic bags and discard to hot waste.
- D. Determination of Mn^{54} , ZrNb^{95} , Co^{58} , Co^{60} , and Fe^{59} .
1. Count each fraction or a dilution from it in the well crystal, using the 512-channel analyzer. Subtract the background on the instrument.
 2. Determine the factor for the reciprocal of the combined detection efficiency, peak to total ratio, and absorbance for each isotope being determined. This factor can be obtained from the standard curve for the particular well crystal in which the activity was counted.
 3. Determine the Mn^{54} in the manganese fraction. Integrate the peak at 0.84 MeV. Use a branching ratio of 0.99.
 4. Determine the ZrNb^{95} in the zirconium fraction. Integrate the peak at 0.76 MeV. Use a branching ratio of 0.99.
 5. Determine the Co^{60} in the cobalt fraction. Integrate the peak at 1.32 MeV. Use a branching ratio of 1.00.
 6. Determine the Co^{58} in the cobalt fraction. Remove the contribution of Co^{60} by gamma subtraction. Integrate the peak at 0.805 MeV. Use a branching ratio of 1.00.
 7. Determine the Fe^{59} in the iron fraction. Integrate the peak at 1.29 MeV. Use a branching ratio of 0.44.

CALCULATIONS

<u>Record</u>	<u>Unit to Record</u>
A	Sample volume, in milliliters
B	Dilution factor
C	Counts in the integrated peak
D	Counting time, in minutes

<u>Column</u>	<u>Unit to Record</u>
E	Branching ratio of particular isotope
F	Factor for the reciprocal of the combined detection efficiency, peak to total ratio, and absorbance.
G	Disintegrations per minute per milliliter.

$$G = \frac{C F B}{A D E}$$

REFERENCES

1. Kraus and Nelson, "Anion Exchange Studies of the Fission Products", P/837 (USA) Session No. 9B. 1.
2. Kraus and Moore, J. Am. Chem. Soc. 73, 9(1951).
3. Rein, J. E., Personal Communication. Rein-44-63A-N.

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DETERMINATION OF Ta¹⁸² BY ION EXCHANGEABSTRACT

Tantalum is separated from the other elements by ion exchange and determined by gamma ray spectroscopy. The ion exchange separation is made possible by the formation of chloro-fluoro complexes of tantalum. Tantalum is eluted by increasing the fluoride concentration and decreasing the acid concentration so that F⁻ replaces the tantalum complex on the resin.

APPLICABILITY

This method was developed for the determination of Ta¹⁸² on contaminated smears. A method for dissolving the smears is given. No interferences in the determination of Ta¹⁸² are known, therefore the method is considered applicable to all types of samples.

SAFETY PRECAUTIONS

Rubber gloves should be worn when HF or NH₄F is being handled.

APPARATUS AND REAGENTS

A. Apparatus

1. Beakers, 150 ml.
2. Volumetric flasks, 10 ml.
3. Funnels, 1 inch.
4. Ion exchange columns. A ten-inch length of 11-mm polyethylene tubing with a Teflon wool plug in one end makes a satisfactory column.
5. Beakers, polyethylene, assorted sizes.
6. Stirring rods, polyethylene.
7. Pipets, assorted sizes.
8. Counting tubes, polystyrene vials, 50 ml capacity.

B. Reagents

NOTE: All reagents used are C.P. or Analytical Reagent grade stock. Use distilled water for the preparation of all reagents. All reagents containing fluoride should be stored in polyethylene bottles.

1. Nitric acid, concentrated.
2. Sulfuric acid, concentrated.
3. Hydrogen peroxide, 30%.
4. Ion exchange resin. Dowex 1-X8, 100-200 mesh.
5. TaCl_5 . (Ta_2O_5 is an acceptable substitute.)
6. Hydrofluoric acid, 27M. Concentrated.
7. Hydrochloric acid, 2M. Dilute 167 ml of concentrated hydrochloric acid to 1 liter with water.
8. Iron carrier, 10 mg Fe/ml. Dissolve 54.3 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 100 ml of concentrated hydrochloric acid and 900 ml of water.
9. 1M hydrofluoric acid - 0.25M hydrochloric acid. Dilute 37 ml of concentrated hydrofluoric acid and 21 ml of concentrated hydrochloric acid to 1 liter with water.
10. 10% Hydrofluoric acid - 60% hydrochloric acid. Dilute 100 ml of concentrated hydrofluoric acid and 600 ml of concentrated hydrochloric acid to 1 liter with water.
11. 14% NH_4Cl - 4% hydrofluoric acid. Dissolve 140 g NH_4Cl in 800 ml of water. Add 40 ml concentrated hydrofluoric acid, and dilute to 1 liter with water.
12. 14% NH_4Cl - 4% NH_4F . Dissolve 140 g NH_4Cl in 800 ml of water. Add 40 ml concentrated hydrofluoric acid and 72 ml concentrated NH_4OH . Dilute to 1 liter with water.

PROCEDURE

A. Dissolution of smears.

1. Place the smear in a 150 ml beaker. Add about 5 mg TaCl_5 or Ta_2O_5 . Add concentrated nitric acid.

2. Heat gently on a hotplate until the smear is decomposed.
3. Cool. Carefully add 10 ml of concentrated H_2SO_4 . If charring occurs because the paper was not completely decomposed, carefully add 30% H_2O_2 a drop at a time until the carbon is dissolved.
4. Heat gently on a hotplate until fumes of SO_3 are observed. Continue heating until the volume is about 5 ml.
5. Cool. With the aid of a 1-inch funnel, transfer to a 10 ml volumetric flask. Rinse the beaker with small amounts of concentrated H_2SO_4 several times. Make to volume with concentrated H_2SO_4 .

B. Preparation of ion exchange columns.

1. Soak the resin in a polyethylene beaker with 1M HF - 0.25M HCl.
2. Wet the polyethylene tubing and Teflon wool plug with 1M HF - 0.25M HCl.
3. Pour the slurry of resin into the tubing. Allow the excess acid to drain out of the column. The resin in the column should be about six inches long.

C. Preparation of sorption solution. Mix the following in a polyethylene beaker.

1. About 5 mg TaCl_5 or Ta_2O_5 dissolved in 4 drops of 27M HF.
2. 1 ml of sample. Larger aliquots of sample may be used if the final concentration of the sorption solution is kept 1M in HF and 0.25M in HCl.
3. 1 ml of iron carrier.
4. 12 drops of 2M HCl.
5. 2 ml of water.

D. Ion exchange separation.

1. Pass the sorption solution through the column. Rinse the column with 50 ml of 1M HF - 0.25M HCl.
2. Rinse the column with 20 ml of 10% HF - 60% HCl.

3. Rinse the column with 20 ml of 14% NH_4Cl - 4% HF .
4. Place a counting tube under the resin column. Elute the tantalum with 20 ml of 14% NH_4Cl - 4% NH_4F . Finish filling the counting tube with water, stopper with a plastic cap, and mix.
5. Place used ion exchange columns in plastic bags and discard to hot waste.

E. Determination of Ta^{182}

1. Count the Ta^{182} in the well crystal, using the 512-channel analyzer. Subtract the background on the instrument.
2. Determine the factor for the reciprocal of the combined detection efficiency, peak to total ratio, and absorbance. This factor can be obtained from the standard curve for the particular well crystal in which the activity was counted.
3. Integrate the peak at 0.100 MeV. Use 0.56 for the branching ratio.

CALCULATIONS

<u>Column</u>	<u>Unit to Record</u>
A	Sample aliquot volume, in ml
B	Total sample volume, in ml
C	Counts in the integrated peak
D	Counting time, in minutes
E	Branching ratio
F	Factor for the reciprocal of the combined detection efficiency, peak to total ratio, and absorbance.
G	Disintegrations per minute per sample

$$G = \frac{C F B}{A D E}$$

REFERENCE

Kallman, "Niobium and Tantalum", Treatise on Analytical Chemistry (ed. Kolthoff and Elving), Part II, volume 6, pp. 252-255, Interscience Publishers, New York, (1964).

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