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ANALYTICAL CHEMISTRY DIVISION
ANNUAL PROGRESS REPORT
FOR PERIOD ENDING NOVEMBER 15, 1963

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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M. T. Kelley, Director
C. D. Susano, Associate Director

DATE ISSUED

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Summary

PART I. ANALYTICAL RESEARCH

1. Analytical Instrumentation

Several instruments were modified for specialized applications. Detailed design information was provided for the modification of an ORNL model Q-1988 controlled-potential and derivative polarograph for molten-salt voltammetry, and of a model Q-1988A for use at fast scan rates with dropping-mercury electrodes having drop times of ½ sec, or less. A Beckman model B spectrophotometer was modified for continuous recording of the titration of free fluoride ion. The time per analysis was reduced from 75 to 15 min, and the precision of analysis was improved. For a fused salt application, the precision chronopotentiometer was altered to function with system ground isolated from earth ground. Also, an improved constant-current supply was incorporated in the modified instrument.

Progress in controlled-potential coulometry was achieved with the fabrication of two ORNL model Q-2564 high-sensitivity coulometric titrators, and with revision to the method that describes the ORNL model Q-2005 electronic, controlled-potential coulometric titrator. A check-out and test procedure for the Q-2564 is being written.

Development and improvement of apparatus for the remotely controlled analysis of highly radioactive samples, primarily those associated with the MSRE, was continued. The aligning, crushing, and powder-transfer devices are being used in the ORNL High-Radiation-Level Analytical Facility for the remotely controlled preparation of samples obtained from the Volatility Pilot Plant. A hot-cell exhaust filter assembly, which can be removed and replaced by the master-slave manipulators, was designed and installed in the hot cell of the Building 3038 Hot Laboratory.

A dc preamplifier and an ac-to-dc converter, both having high input impedance and providing buffering to the voltage source being measured, were designed for the Non-Linear Systems, Inc., model V35A digital voltmeter. The converter can serve as a standard for ac voltage measurements because of its dc calibration.

The design, construction, and evaluation of the high-sensitivity, direct-reading, linear, recording, conductometric titrator was completed. A proportional temperature controller that provides essentially stepless control of titration cell temperature to within ±0.01°C was designed to supplement the automatic temperature-compensation circuit for high-sensitivity work. The performance of the conductometric titrator on about forty different chemical systems met, or exceeded, design criteria.

The controlled-potential ac polarograph was rebuilt with a new potentiostat having improved performance characteristics. Test runs made with a D.M.E. on solutions that contained 10^{-4} *M* Cd^{2+} in 0.1 *M* KCl show that the instrument achieves excellent rejection of the double-layer charging current. Other tests indicate that excellent resolution of the In^{3+} and Cd^{2+} waves ($\Delta E_{1/2}$ = 38 mv) is obtained.

A model VII high-resolution, flame spectrophotometer, which uses a single multiplier phototube (EMI type 9558QA) to cover the entire wavelength range from 2000 to 8700 A, was designed and put into service for emission photometry. Either instantaneous or integrated flame emission intensities can be recorded for measurement. The unit can also be used with an absorption source assembly for atomic absorption work.

It has been observed that it is necessary to limit the initial current delivered by the potentiostat in the controlled-potential coulometric titrations of any of several ionic species. The reason for a positive bias at high initial current (1 to 2% for uranium) is not known. A study to determine the cause of this error has been initiated.

In controlled-potential coulometry, the reference electrode may be placed arbitrarily in any position in the current density gradient present in the cell. One theory of electrochemical behavior suggests that when the reference electrode is placed in a region of low current density, an error in potential can exist in the reaction zone in the region of high current density. This error, conceivably, could cause the discharge of a second ion, and thereby contribute an error in analysis. A study to determine the importance of reference-electrode placement in controlled-potential coulometry was undertaken. So far, no chemical evidence for the existence of a potential error, even under drastic cell conditions, has been obtained.

An investigation has been completed of the feasibility of polarography for the direct determination of metal complexes in the organic phase following solvent extractions. The ORNL model Q-1988-FES dc polarograph was used to produce controlled-potential regular and first-derivative polarograms of cadmium and uranium in several solvent-extraction systems, including those of the ion-association and chelate types. The average-current and derivative computer circuits were modified to permit the use of a $\frac{1}{2}$-sec, Smoler type, vertical-orifice D.M.E. and the use of scan rates up to 3 v/min. A quantitative method for the determination of microgram quantities of uranium in tri-*n*-octylphosphine oxide extract was developed. Polarography in the organic extracts from solvent extraction offers the following advantages: the substance to be determined can be concentrated selectively, matrix elements that interfere are removed, and a separate stripping step into an aqueous medium is not required. Also, the possibility exists of performing polarographic analysis on species unstable in water.

The compensation of cell resistance by controlled-potential polarography was studied. It was found necessary to place the reference electrode within a distance of 0.1 *r* (where *r* is the radius of the drop) from the mercury drop in order to avoid distorted polarograms in solutions of high specific resistance. An electrode apparatus consisting of a sharpened, Smoler type, vertical-orifice, $\frac{1}{2}$-sec D.M.E. and a reference electrode probe was constructed for this study.

A controlled-potential voltammeter was designed and built for operation in molten-salt (including molten-fluoride) systems. The voltammeter design uses several operational amplifier modules to achieve the functions necessary. The cells, fabricated from graphite or metal, contain a stationary polarized electrode, a counter electrode, and a reference electrode and may have a variable, uncontrolled resistive leakage to earth ground. For the uninsulated cell vessels, system ground must float with respect to earth ground. Performance tests of this voltammeter are in progress. Another controlled-potential instrument that will have chronopotentiometric and stripping-voltammetric functions in addition to the voltammetric function is to be designed.

2. Chemical Analysis of Advanced Reactor Fuels

Studies in this program were concerned mainly with the controlled-potential coulometric titration of uranium in solutions of uranium-bearing fuels and on the determination of various reaction products resulting from the dissolution of uranium carbides and thorium carbides.

A coulometric cell of 15-ml capacity was designed especially for use with the ORNL Q-2564 high-sensitivity, controlled-potential, coulometric titrator; uranium in the amounts of 2.5 and 48 μg in a total volume of 5 ml was determined with a relative standard deviation of 0.8 to 0.2%, respectively.

A controlled-potential, coulometric method for the determination of uranium in sodium fluoride solutions was developed. At the 6-mg level, the relative standard deviation is 0.2%.

Studies on the determination of carbon in aqueous and nitric acid solutions from the dissolution of carbide type fuels were continued. A gas chromatographic measurement of the CO_2 produced by oxidation of the carbon-containing compounds was incorporated into the procedure to effect an improvement in sensitivity of some twentyfold over the manometric measurement of CO_2. The interference of residual oxides of nitrogen is also eliminated by use of the gas chromatographic measurement.

Gas chromatography was used to resolve and determine the products from the reaction of carbide fuels with CCl_4 in the presence of air. With a 15-ft silica-gel column, only Cl_2 and $COCl_2$ were not resolvable from the expected reaction-product mixture of air, CCl_4, CO, CO_2, Cl_2, and $COCl_2$. Silicone-gum-rubber columns of ~15-ft length appear to offer complete resolution of these compounds.

The oxides of nitrogen were determined gas chromatographically on a 3-ft long, 1-in.-ID, silica-gel column programmed from 25 to 300°C. The order of elution under these conditions is NO, N_2O, N_2O_4, and NO_2.

Studies were initiated on the gas chromatographic determination of polynuclear aromatic hydrocarbons such as naphthalene, biphenyl, anthracene, and phenanthrene, which are expected to be formed when uranium carbide is heated in nitric acid and the resulting acids are decarboxylated at elevated temperatures. Silicone SE-30 and SE-52 are promising materials for this problem.

A mixture of di-*sec*-butylphenylphosphonate (2.5 vol %) and diethylbenzene (97.5 vol %) that had been degraded with nitric acid was analyzed gas chromatographically with a Reoplex 40 column at 200°C. The isomers of diethylbenzene were measured on a 200-ft by 0.01-in. capillary column coated with di-*n*-decyl phthalate and operated at 110°C.

3. Analytical Studies of Molten-Salt Systems

Voltammetric studies in molten-fluoride salt systems were continued. The voltammetric behavior of Fe^{2+} in LiF-NaF-KF was determined, and the activation energy for the $Fe^{2+} \rightarrow Fe^0$ reduction was calculated to be 12 kcal/mole. Current-voltage studies were made for zirconium and uranium in LiF-NaF-KF. The zirconium reduction appears to be reversible. Evidence was also noted for the reaction $U^{4+} \rightarrow U^{5+}$ in this melt. A pyrolytic graphite electrode sheathed in boron nitride was developed for use in molten-fluoride systems. Anodic-stripping voltammetry was proved to be feasible for determining trace quantities of iron in molten salts.

Spectrophotometric studies of various molten-salt systems were continued. Molten alkali-metal—alkali-metal-halide systems and the reactions of active metals, such as uranium, with molten-fluoride salts were followed spectrophotometrically.

4. Special Research Problems

The applicability of the pyrolytic graphite indicating electrode in various phases of electroanalytical chemistry was investigated. Potentiometry, voltammetry, amperometry, and coulometry were included in this study. A rotating pyrolytic graphite electrode was fabricated for possible use in molten salts. Coulometry of silver and iron was evaluated by use of the pyrolytic graphite electrode and the high-sensitivity coulometric titrator.

Polarography with the horizontal-orifice Teflon D.M.E. was continued to obtain fundamental polarographic data. The thallium and lead reduction systems were used as references.

Absorption spectrophotometric studies of plutonium in aqueous nitrate systems were subjected to computer resolution to interpret polymer formation as a function of acidity, temperature, and concentration. The radiolysis of chloride solutions was studied to determine the rate of generation of chlorine. Below 1.4 *M* chloride, no chlorine is formed. Radiation and thermal studies were conducted on sodium chloride.

5. Reactor Projects

Studies in process gas chromatography were continued for application in the Gas-Cooled Reactor project. A Beckman model 120A process chromatograph with infrared analyzer was adapted for use in hydrogen autoclave tests to determine methane, nitrogen, carbon monoxide, and carbon dioxide. A Greenbrier model 112 instrument was used to monitor gases (H_2, CO_2, CO, O_2, N_2, CH_4) in a high-temperature steam-graphite loop.

Methods development and evaluation were continued for the analysis of the radioactive MSRE fuel. Methods for zirconium, uranium, fluoride, and chromium were completed. The determination of the reducing power due to U^{3+} in the MSRE fuel was studied. Molten $KHSO_4$-H_3BO_3 is used as a flux to dissolve the fluoride salts except for UF_3, which appears to be insoluble in the melt.

A new facility for analysis of alkali metals was completed. Research and development activities in the analysis of interstitials (oxygen and carbon in particular) in Na, NaK, and K were transferred and implemented in this laboratory.

6. Effects of Radiation on Analytical Methods

Dimethylglyoxime was found to be much less resistant to gamma radiation than is its complex with nickel. The radiation damage to 1×10^{-5} *M* solutions of dimethylglyoxime is of the order of 1×10^{-10} millimole ml^{-1} rad^{-1}. A postirradiation effect was noted when ethyl alcohol was used as the solvent but not with aqueous solutions.

The radiation damage to arsenazo III solutions (in the form of its disodium salt) was determined. In strong acid (9 *N*) the average rate of decomposition is of the order of 2×10^{-6} mole/liter per kilorad of gamma radiation. The damage is less in more dilute acid solutions. Decomposition continues as a postirradiation effect.

Investigations of the effect of gamma radiation on spectrophotometric thiocyanate methods for molybdenum, iron, and uranium were completed. The molybdenum complex is essentially destroyed by radiation doses greater than 1×10^4 rads. The same dose results in an 8 to 22% error for the iron complex. Uranium thiocyanate is affected even less, of the order of 10%.

7. X-Ray and Spectrochemical Analysis

An x-ray fluorescence procedure was devised for determining Gd_2O_3 in Gd_2O_3-Al_2O_3 ceramics. Procedures were worked out to compensate for neighboring absorption edge effects in x-ray absorption edge analysis. A disposable cell was designed for the x-ray absorption edge analysis of radioactive solutions. In atomic absorption analysis, studies were made of the effects of hollow-cathode current and absorption-tube length on absorbance. Tin was detected by this method at the 0.5-μg/ml level. The ammonium phosphomolybdate adsorption–flame photometry method was adapted for the determination of cesium in sea water. Further studies of volatilization losses during the ashing of tissue have confirmed previous results and have failed to show evidence of loss of vanadium. Installation of a punched-tape readout on the Quantometer has reduced analytical time by one-fifth.

8. Mass Spectrometry

A method was devised for determining gas contaminants in quartz capsules that contained UO_2-Al fuel pellets. Space and equipment for the high-alpha, double-magnet mass spectrometry laboratory was put in order. A routine based on a daily isotopic standard was devised and used to analyze about 200 potassium samples. A manual, *Isotopic Mass Spectrometry of the Elements*, is being published.

9. Infrared Spectroscopy

The infrared spectra of radioactive solids were measured by encapsulating the sample in KBr, pressing it at 8 tons for 12 min, and then reencapsulating the pellet with additional KBr.

Waxes were identified that resulted from the hydrolysis of uranium carbides.

Infrared spectra were obtained of the 4-*sec*-butyl-2-(α-methylbenzyl)phenol adducts with cesium to determine the polymeric character of the partially hydrogen-bonded hydroxyl group.

10. Optical and Electron Microscopy

Investigation of methods for the study of radioactive materials by electron microscopy and diffraction continued. An apparatus for the replication of such surfaces was designed. A device for the collection of radioactive particles by electrostatic precipitation was fabricated and put to use. An electron microscope with a resolution of 5 to 10 A is being installed. Research assistance in electron microscopy and thin film work was given to other divisions.

11. Nuclear and Radiochemical Analyses

The decay schemes of Lu^{177m}, Mo^{99}, In^{116}, Cl^{38}, Ba^{131}-Cs^{131}, Te^{129m}, and S^{37} were studied. A 180° Compton-scattered–annihilation gamma-ray sum peak observed in gamma-ray spectrometry was explained. Work has continued on the decay schemes of even isotopes in the osmium region. A gamma spectrometric method for determining Cf^{252} was developed. Work has begun on the determination of fission yields of krypton and xenon nuclides. The half-lives of Sn^{127}, Ba^{133}, and Cs^{137} are being remeasured. Solvent-extraction studies have included cesium and rubidium with 4-*sec*-butyl-2-(α-methylbenzyl)phenol, and cesium and tin with 2-thenoyltrifluoroacetone. Solvent-extraction properties of the sulfur analogs of several organophosphorus compounds were investigated. The chemical effects of isomeric transitions resulting in the separation of the isomers Te^{121}, Te^{129}, and Te^{127} have been elucidated. Efforts to develop a glass-loaded liquid scintillator have continued; a new liquid scintillator for neutron detection and a "balanced quenching" technique for liquid scintillation counting were developed. Improvements and additions to methods and equipment used in low-level analysis for Sr^{90} and other radionuclides were made, optimum methods for low-level counting were outlined, and low-level methods for natural radionuclides were completed.

Use of computer techniques has increased: equilibrium distribution of metal ion complexes was calculated and plotted, a number of applications were made in nuclear analyses, 16 spectra are in the library for electronic resolution of gamma-ray spectra, a computer program for the calculation of various nuclear parameters was developed, and a very important phenomenon – second-order interference in activation analysis – was evaluated by computer techniques. Applications of radioisotopes to analytical chemistry have included publication of a number of papers on the subject, a method for study of wear rates in automotive engines, a method for determining mercury by isotopic exchange and extraction, and a study of radioisotopes in electroanalysis. The photoneutron method for determining beryllium was evaluated and made available for routine work. A number of applied radiochemical studies were made, most of which involved gamma-ray spectrometry. Decay products from fission-produced krypton and xenon isotopes were collected and measured, and mixtures of uranium and fission products were measured. The nuclide Sr^{90} was measured in $SrTiO_3$. The radiochemistry of the pressurized-water in-pile loop of the ORR has received continuing study. A guidebook to activation analysis was written, and the method was applied to a number of specific problems. The fast-neutron cross sections for (*n,p*) reactions on Al^{27} and Ti^{46} were measured. A literature survey of nuclear methods for determining oxygen was published, and a nomograph for use in nuclear analysis is under development. Activation analysis was applied to a number of forensic problems: physical evidence, drugs, heroin, opium, and hair. Allied with these applications have been studies in the determination of trace elements in hair, wool, and other biological materials. Work with the 14-Mev neutron generator has continued. Titanium has been irradiated, oxygen has been determined, and a number of other elements irradiated and studied. Attempts were made to measure and (in one instance) to calculate the neutron spectra from the generator and other neutron sources. A compilation of 14-Mev neutron reactions was prepared; the compilation also includes gamma-ray spectra of the active products.

12. Inorganic Preparations

Numerous preparations of fused salts continued to be made for the Chemistry Division and for the Metals and Ceramics Division. Some problems with the preparation of iodides still persisted.

Preparations with rare-earth metals, as alloys with each other and in ternary oxide compounds with manganese, constituted the chief work for the Physics Division. Some Fe^{57} compounds were also prepared.

Anhydrous $ThCl_4$, $ZrCl_4$, and $AlCl_3$ were either prepared or purified for the Reactor Chemistry Division.

The study of the chemistry of rhenium, in connection with the work of the Chemistry Division, has not led to the discovery of any fluorides of rhenium lower than ReF_4, but several other compounds have been characterized.

The preparation of KCl of very high purity was accomplished for the Solid State Division.

13. Organic Preparations

A number of special organic compounds that are not commercially available were synthesized on request from other research divisions. These compounds were ammonium pyrrolidinedithiocarbamate, 18 new monoacid esters, tetra-*n*-butylammonium tetrabromonickelate(II), and benzyltributylphosphonium tetrachloronickelate(II). Tetrapentylammonium bromide, ethyl cyanide, and phenol were purified for use in special applications.

PART II. ANALYTICAL DEVELOPMENT

14. Methods Development

A polarographic determination of free acid in Tramex process solutions (LiCl matrix) containing aluminum was developed. For a given LiCl concentration, the ratio i_d/C is constant over a hydrogen ion concentration of 1 to 10 *mM*. Aluminum does not interfere.

Lead was determined by atomic absorption spectrometry in prehistoric bones after extracting it with dithizone in hexane from ammoniacal citrate solution.

A rapid method for the determination of Hg^{2+} in nitric acid solutions by titration with thiocyanate solution was applied to calciner waste samples; 150 samples were analyzed in six man-days.

Conductometric titration was evaluated for the detection of the end point in free-acid titrations of Darex solutions (HNO_3-HCl containing many hydrolyzable ions).

The stoichiometry of an erbium manganate sample was established. Efforts to determine the oxidation state of manganese directly were unsuccessful.

A polarographic method was used to determine the extent of nitration of 4-*sec*-butyl-2(α-methylbenzyl)phenol (BAMBP) when contacted with nitric acid. Nonaqueous titrimetry with tetrabutylammonium hydroxide in pyridine was adapted for the determination of phenols in hydrocarbon solutions.

Initial studies were made on the potentiometric titration of technetium with chromous sulfate using the pyrolytic graphite electrode. The reduction of Tc^{7+} to Tc^{3+} was found to be a single-step reaction and reproducible to within 1% for 1 to 6 mg of Tc.

The high-temperature sealed-tube dissolution technique was found to be useful for organic compounds when quantitative retention for such volatile combustion products as halogens, sulfur, phosphorus, and mercury is desired.

Cadmium (0.05 to 0.2%) in HFIR fuel plates (Al, UO_2, B_4C) was determined polarographically, after an ammonium hydroxide precipitation, in 1 *M* NH_4Cl at −0.92 v vs the S.C.E.

The molar absorptivities of various lanthanides and actinides complexed with disodium arsenazo III were established. Values in excess of 100,000 were observed for Th, U^{4+}, and Zr.

Gas chromatographic analyses were made of Aroclor 1248, a high-boiling organic chloride lubricant, cresols formed by oxidation of gamma-irradiated toluene, and pyrolysis products of biphenyl.

PART III. SERVICE ANALYSES

15. Quality Control

The Statistical Quality Control Program was extended; about 4500 control tests were made. A marked improvement occurred in the quality of all the analytical control work for the year.

16. Low-Level Radiochemical Laboratory

The Low-Level Radiochemical Laboratory performed some 4200 analyses, primarily for the Health Physics Division. The usual types of samples were analyzed.

17. Mass Spectrometric Analysis

The Mass Spectrometry Laboratory reported over 25,000 results on some 3200 samples. Many of these samples were the stable isotopes of 45 elements.

18. Spectrochemical Analyses Laboratory

The Spectrochemical Analyses Laboratory analyzed over 1000 samples, almost half of them for the Isotopes Division. The stable isotopes of some 35 elements were determined. Other samples included beryllium, beryllium oxide, aluminum, and lithium fluoride.

19. Process Analyses

About 159,500 analyses were performed this year, an increase of 6% over last year; the number of persons was increased 1.5%. The increases were due to Transuranium work and the training of new persons for the start-up of this program. Work is continuing on the design of new alpha analytical facilities. A brief statement of new developments in each laboratory follows.

The High-Level Alpha Radiation Laboratory reported 21% more results than were reported last year. Most of this work was done on Transuranium Process development samples. The development of methods for removing actinides from fission products continued. The following instruments were obtained: a spontaneous fission counter, a transistorized 400-channel analyzer, and an automatic alpha proportional counter.

The General Analyses Laboratory developed methods for determining boron in HIFR fuel plates and for measuring the density of pyrolytic carbon coatings. Methods for cyanide and phenol in plant waste water, for hardness of water (<1 ppm), and for the permeability of graphite specimens to various gases were put into use.

The General Hot Analyses Laboratory developed a number of new devices and tested several methods for the remotely controlled analysis of MSRE salts. A gas chromatograph was placed in service for the remotely controlled analysis of radioactive gases. An equilibrium pressure apparatus was installed for determining total gases in solid samples of ThO_2-UO_2. Some equipment was modified for analysis of samples that contain milligram amounts of U^{233}.

The Materials Testing Laboratory continued to analyze fused fluoride salts, granite, gases, and various solutions derived from fuel-reprocessing and waste-disposal studies. A recording DK-2A spectrophotometer and a new Vapor Fractometer with a column-switching reverse-flow accessory were put into operation.

The Radioisotopes-Radiochemistry Laboratory's work load continued at about the same level as last year. The use of computers was extended to include many routine calculations. A paper on the determination of fission yields from $Am^{241,242}$ was presented at the New York meeting of the American Nuclear Society.

The High-Radiation-Level Analytical Facility was used to separate americium and curium from fission products. Total glove-box-type containment of two work cells was completed. Alpha contamination of manipulators and of in-cell equipment has caused operational costs to increase.

Construction of the new High-Level Analytical Laboratory is 75% complete; the laboratory should be in operation by October 1964.

Work is continuing on equipment to be used in both the Transuranium and High-Radiation-Level Analytical Laboratory buildings.

20. Reactor Engineering Service Laboratory

The Reactor Engineering Service Laboratory analyzed more than 2900 samples. Of these, 60% were from the Reactor Division and 30% were from the Reactor Chemistry Division.

PART IV. ORNL MASTER ANALYTICAL MANUAL

21. ORNL Master Analytical Manual

Cumulative indexes for the *ORNL Master Analytical Manual* for the years 1953 (its inception date) through 1962 were prepared by means of an IBM 7090 computer program. The indexes consist of a key word index, permuted from the titles of unclassified methods; a bibliographic index, which is essentially a table of contents to the *Manual* and also provides complete information about each method; an author index; and method-number cross indexes. The indexes have been issued as document TID-7015 (Indexes) and are available from the U.S. Department of Commerce.

The fifth supplement to the reprinted form of the *Manual* was issued. Eighteen new methods and revisions to thirteen methods were issued, and the Table of Contents was revised. The method needs for the Division were determined, particularly with respect to the MSRE and TRU programs, and methods-writing work was planned accordingly.

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Contents

PART I. ANALYTICAL RESEARCH

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PART IV. ORNL MASTER ANALYTICAL MANUAL

Part I. Analytical Research

Research in a variety of fields of analytical chemistry was conducted during the past year for the Reactor, Physical Research, and Isotopes Development Divisions of the Atomic Energy Commission. Research was also conducted for the various research divisions of the Oak Ridge National Laboratory on specific problems related particularly to the programs of the Laboratory.

The progress in these investigations is presented in the following sections.

1. Analytical Instrumentation

M. T. Kelley
D. J. Fisher

MODIFICATION OF THE ORNL MODEL Q-1988 POLAROGRAPH FOR ELECTRONIC SCAN AND USE WITH AN X-Y RECORDER

H. C. Jones

A circuit diagram of the ORNL model Q-1988 polarograph was modified to make the instrument suitable for voltammetry of molten salts. The Instrument Maintenance Shop used the diagram to convert one of the polarographs for this purpose.

The modifications were as follows. Electronic scan rates of 0.05, 0.1, 0.2, 0.5, 1, and 3 v/min were provided, each over a 3-v range. (Scan rates greater than ~5 v/min cause excessive error at the input to the potential-control amplifier. For scan rates faster than ~3 v/min, a fast control amplifier with differential inputs should be used.) Three higher current ranges (1, 3, and 5 ma) were substituted for the 0.1-, 0.3-, and 0.5-μa ranges. Initial-current compensation was provided in three ranges within the overall range from 0 to 100 μa. Electronic linear-residual-current compensation was added. Voltage dividers on the outputs of the scan generator and signal bus deliver signals to the X and Y axes, respectively, of a 1-sec-response X-Y recorder. The fast scan rates necessitate the use of a fast-response recorder. The X-Y recorder is convenient for recording superimposed replicates and has a potential scale that is independent of scan rate and time.

MODIFICATION OF THE ORNL MODEL Q-1988A CONTROLLED-POTENTIAL, DERIVATIVE POLAROGRAPH FOR USE WITH A RAPIDLY DROPPING MERCURY ELECTRODE

W. L. Belew

A circuit diagram of the ORNL model Q-1988A controlled-potential and derivative polarograph was modified to include changes necessary when the polarograph is used with a dropping-mercury electrode (D.M.E.) having a drop time of $\frac{1}{2}$ sec or less. The polarograph with these changes is already described.[1]

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[1] W. L. Belew, D. J. Fisher, and M. T. Kelley, "Controlled-Potential DC Polarography with a Rapidly Dropping Mercury Electrode," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 13.

The changes are as follows. A dual parallel-T filter was added that has two voltage followers and a fundamental section with a rejection frequency of 2 cps. A switch was inserted to reduce a time constant in the derivative circuit by a factor of 10; the fast derivative computer is used with the dual parallel-T filter. The gain of the inverter amplifier was made adjustable to reduce the height of the derivative peak at fast scan rates by factors of 25 and 250. Suitable resistors were added to the scan integrator circuit to provide scan rates of 0.3, 1.5, and 3 v/min. Voltage dividers were added to give outputs for an X-Y recorder with a 1-sec response time. These changes were incorporated by Helen P. Raaen into an existing model of the polarograph.

MODIFICATION OF THE BECKMAN MODEL B SPECTROPHOTOMETER FOR CONTINUOUS RECORDING OF SPECTROPHOTOMETRIC TITRATION CURVES

R. W. Stelzner

A Beckman model B spectrophotometer was modified in a very simple way to record continuously the curve for the titration of fluoride in the presence of large amounts of niobium; the fluoride is titrated with Th^{4+} to the Thoron indicator end point. A shielded cable connected to the junction of 500-ohm R_{25} and 1081-ohm R_{26} (located in the circuit of the 12AU7 vacuum-tube meter) of the spectrophotometer[2] is brought out to the 100-mv Y input of an X-Y recorder. Inasmuch as the titrant is injected at a constant flow rate, the 50-sec/division time base of the recorder is used as the X input; the Y scale is 10 mv/division. The fluoride concentration is calculated from an inflection in the titration curve. Use of the recorder has the advantages that the titration curve is obtained automatically instead of manually, the precision is improved, and the time per analysis is decreased from 75 to 15 min (see "General Analyses Laboratory" in Chap. 19 of this report).

MODIFICATION TO THE PRECISION CHRONOPOTENTIOMETER

W. L. Maddox D. J. Fisher

The precision chronopotentiometer[3] was modified by floating the system ground in order to permit use of the instrument with uninsulated electrolysis cells (see "Controlled-Potential Voltameter" in Chap. 1 of this report). Also, an additional Zener-diode voltage source and a polarity-reversing switch were installed in the constant-current supply. The instrument is being used by Gleb Mamantov[4] in chronopotentiometric studies of fused-salt systems.[5]

REVISION TO THE METHOD FOR THE ORNL MODEL Q-2005 COULOMETRIC TITRATOR

D. J. Fisher H. C. Jones

The method for the ORNL model Q-2005 coulometric titrator[6] was revised to include new check-out, test, and trouble-shooting information gathered from operating experience. Additional specifications were added that define the normal performance of the instrument, and precautions were given about its operation. Check-out and operating instructions were added concerning the high-sensitivity X-50 modification, which is available commercially. The revision, dated July 15, 1963, will be distributed in Supplement 6 of TID-7015.

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[2] *Instruction Manual, Beckman Model B Spectrophotometer and Accessories*, Bulletin 291-A, Fig. 11, "Model B Circuit Diagram," p 19, Beckman Instrument Co., Fullerton, Calif.

[3] W. L. Maddox and D. J. Fisher, "Precision Chronopotentiometer," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, p 4.

[4] Reactor Chemistry Division and University of Tennessee, Knoxville.

[5] Gleb Mamantov, "Electrochemical Studies in Molten Fluorides," presented at the Seventh Annual Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 8–10, 1963.

[6] H. C. Jones, "Automatic Coulometric Titrator, ORNL Model Q-2005, Electronic, Controlled-Potential," Method Nos. 1 003029 and 9 003029 (R. 2-7-62), *ORNL Master Analytical Manual;* TID-7015, suppl 4.

ORNL MODEL Q-2564 HIGH-SENSITIVITY COULOMETRIC TITRATOR

H. C. Jones

The prototype of the ORNL model Q-2564 coulometric titrator is already described.[7] Two of these instruments were fabricated by the Instrumentation and Controls Division. Their electrical performance is being checked, minor revisions are being made to the circuit, and a check-out and test procedure is being written.

REMOTELY OPERATED EQUIPMENT FOR ANALYSIS OF RADIOACTIVE SAMPLES

W. L. Maddox

Remotely Operated Apparatus for Opening and Closing MSRE Sample-Transfer Tubes

Remotely operated apparatus is being developed for opening and closing MSRE sample-transfer tubes.[8] The prototype now has devices that automatically provide overload protection for the gearmotor, turn off the gearmotor, and indicate that the sample-transfer tube has been closed.

Modified Spex Mixer/Mill Clamp

Placement of a copper capsule in the Spex Mixer/Mill clamp is a difficult manipulator operation. To simplify the operation, a "cradle" was added to one jaw of each of the clamps now in use. The capsule is laid in the cradle; thus, both manipulators are left free. Large, knurled, cylindrical knobs, having radial holes drilled at intervals into the periphery to permit insertion of a pry bar, were substituted for the handles and wing nuts that were supplied with the clamps. For remote operation, the knobs are much more convenient than the original equipment.

Vise for Alignment of Copper Capsules for Mixer/Mill

It is necessary to accurately align the halves of the copper capsule used with the Mixer/Mill[9] in order to assemble them remotely. For this purpose, a drill-press vise was fitted with aluminum jaws machined to the radius of the capsule. After the sample is crushed, the vise may be used to grip the capsule while the plug is being removed and a polyethylene storage bottle is screwed onto the outlet.

Powder-Transfer Shaker

It is possible to transfer the powdered sample from the copper capsule to the polyethylene bottle by shaking the capsule, with the bottle attached, in the old-style Mixer/Mill.[10] However, the action of this machine is so violent that destruction of the polyethylene bottle and consequent loss of the sample are very likely. A special shaker was designed to avoid this mishap and to free the procedure from dependence on the design of a particular Mixer/Mill. A Skil model 592, type 6 orbital sander is used as a power unit for the shaker. The sander is attached to a suitable base and is fitted with a clamp that grips both the capsule and the polyethylene bottle. A series resistor limits the speed of the sander.

The powder-transfer shaker can be disassembled remotely into its three modules (sander, sander base, and clamp) and reassembled remotely. The modules are small enough to be removed individually from the hot cell through an access drawer. The design of the shaker is in keeping with the intention to design all equipment planned for remote use in such a way that it can be disassembled and reassembled with master-slave manipulators.

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[7] H. C. Jones, D. J. Fisher, and W. D. Shults, "High-Sensitivity Coulometric Titrator," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 3.

[8] W. L. Maddox, H. C. Jones, and D. J. Fisher, "Remotely Operated Apparatus for Opening MSRE Sample-Transfer Tube," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 10.

[9] W. L. Maddox, H. C. Jones, and D. J. Fisher, "Copper Capsules for Mixer/Mill," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 9.

[10] M. J. Gaitanis, C. E. Lamb, and L. T. Corbin, "A Pulverizer-Mixer for Solidified Molten Salt Reactor Fuel Samples," *Proceedings, 10th Annual Hot Laboratory and Equipment Conference, Washington, D.C., November 1962*, p 333.

The aligning, crushing, and powder-transfer devices described above are being used satisfactorily in the High-Radiation-Level Analytical Facility for the remote preparation of relatively nonhygroscopic, solidified samples from the Volatility Pilot Plant.[11] The usefulness of the equipment for crushing and transferring the hygroscopic MSRE salt mixture is being determined by M. J. Gaitanis,[12] who is experimenting with moisture-free housings for the equipment.

Remotely Replaceable Hot-Cell-Exhaust Filters for the 3038 Hot Laboratory

The exhaust filter originally built into the hot cell of the 3038 Hot Laboratory could be replaced only by opening and entering the cell. A new filter assembly was designed; it consists of three small filters (the type commonly used in room air conditioners) mounted in a Lucite frame. The assembly is located high and to the rear of the cell so that the filters can just be reached by the manipulator hands. They can be removed readily and replaced one at a time with the manipulators and are small enough to be bagged out through an access port at the end of the cell. The installation has operated satisfactorily for about one year.

DC PREAMPLIFIER AND AC CONVERTER FOR THE NON-LINEAR SYSTEMS, INC., MODEL V35A DIGITAL VOLTMETER

R. W. Stelzner

A dc preamplifier and an ac converter, which have operational-amplifier modules (George A. Philbrick Researches, Inc.), were designed for use with the Non-Linear Systems, Inc., model V35A digital voltmeter (DVM). The input impedance of this DVM is 10 megohms for the signal channel and 50 kilohms for the reference channel. During the interval of null-seeking, a voltage pulse is fed back into the circuit being measured and disturbs that circuit. The dc preamplifier buffers the circuit from the DVM and thereby eliminates the annoying voltage pulse.

The preamplifier consists of a GAP/R USA-3-M3 operational amplifier connected so as to have gains of 1.000 for the 10- and 100-v ranges, and 0.100 for the 1000-v range. The input impedance of the preamplifier is 10 megohms on all three ranges but can be increased to 100 megohms by use of a voltage follower at the input of the preamplifier. However, because of the drift characteristics of the K2-XA voltage-follower stage, this increase in input impedance is achieved at the cost of somewhat degraded performance. The output of the chopper-stabilized USA-3-M3 furnishes a low-impedance input signal for the DVM, thus isolating the DVM from the circuit being measured.

The ac converter, which has two unique advantages, is based on the absolute-value circuit[13,14] shown in Fig. 1.1. First, the circuit rectifies the ac signal without loss across the rectifying element. The circuit requires two chopper-stabilized operational amplifiers (USA-3-M3) and the same optional voltage-follower stage used in the dc preamplifier. A root-mean-square value for the ac voltage being measured is obtained by use of the 2.22-megohm resistor in the feedback network of the second amplifier. The input impedance of the ac converter is 1 megohm; the impedance can be increased to 100 megohms by use of the voltage follower. Second, this ac converter can serve as a standard for ac-voltage measurement because of its dc calibration. A Rubicon (or similar) potentiometer can thus become the standard on which ac measurements are based. The output of the second amplifier furnishes a low-impedance dc signal (corresponding to the rms value of the input ac signal) to the DVM, thus also isolating the DVM from the circuit being measured.

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[11] C. E. Lamb, personal communication to W. L. Maddox, Sept. 27, 1963.

[12] General Hot Analyses Laboratory, MSRE Mock-Up Facility.

[13] B. Seddon, *Analog Methods*, Reprint 27, George A. Philbrick Researches, Inc., Boston, Mass., Apr. 5, 1960.

[14] "Precision AC to DC Converter," Application Notes, NOO 3083 (12-22-60), Burr-Brown Research Corp., Tucson, Ariz.

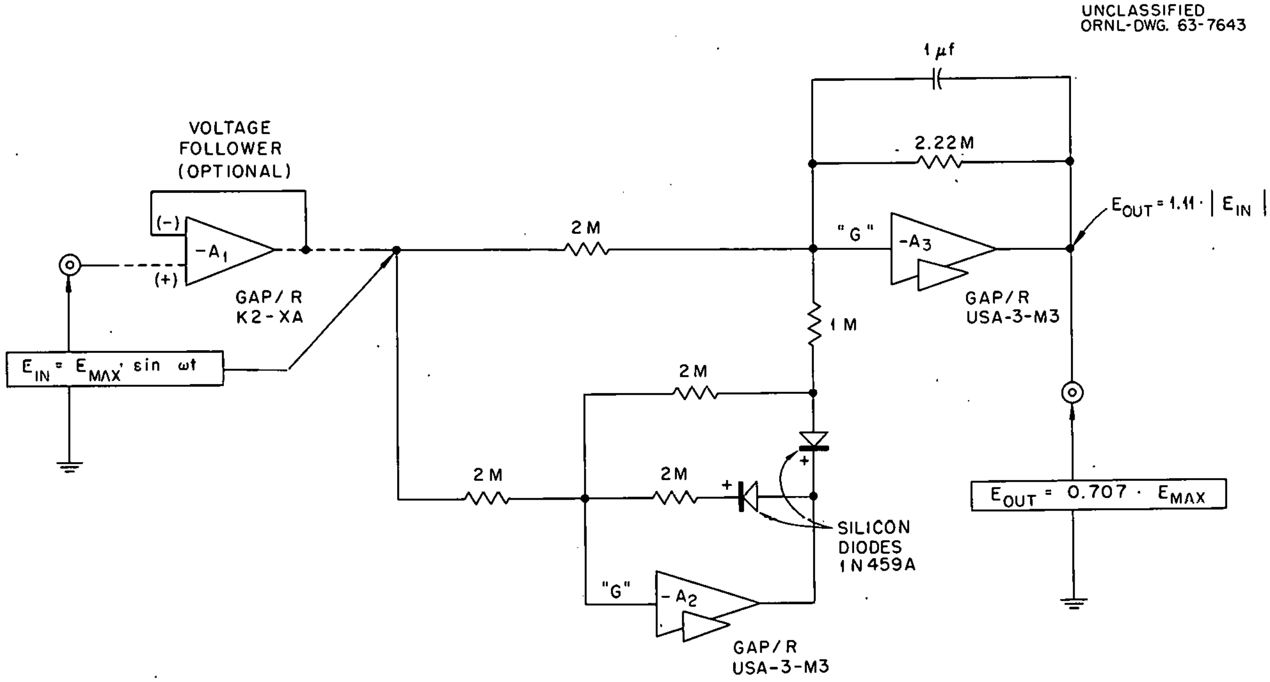

Fig. 1.1. AC to DC Converter (Root-Mean-Square Circuit).

HIGH-SENSITIVITY, DIRECT-READING, LINEAR, RECORDING, CONDUCTOMETRIC TITRATOR WITH AUTOMATIC TEMPERATURE COMPENSATION OR PROPORTIONAL TEMPERATURE CONTROL

T. R. Mueller R. W. Stelzner

The design, construction, and preliminary checkout of the high-sensitivity, direct-reading, linear, recording conductometric titrator have been presented.[15,16] The original circuit has since been modified. The control amplifier was redesigned slightly with the result that noise is reduced and dc stability increased. Also, the initial-conductance-compensation circuit was improved in order to effect compensation with any one of several electrode configurations. For high-sensitivity work, cell temperature must be controlled closely. A proportional temperature controller, described elsewhere,[17] provides control to better than ±0.01°C, which is adequate for titrimetric work.

About 40 different systems were titrated. Acid-base, complexometric, precipitation, redox, and metal ion titrations were made. Some of the acid-base and metal ion titrations were done in the presence of large excesses of foreign electrolytes by use of the initial-conductance-compensation feature of the instrument. The conductometric titration method was evaluated for determining free acid in Darex solutions; this work was done jointly with Lucy E. Scroggie (see "Conductometric Titration of Free Acid in Darex Solutions" in Chap. 14 of this report).

As a service to the Reactor Division, the instrument was used to measure the specific conductances of solutions of NH_4Cl. The samples were submitted because their specific conductances could not be measured accurately with an Industrial Instruments bridge. The values were

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[15] T. R. Mueller and R. W. Stelzner, "Automatic, Recording Conductometric Titrator," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961,* ORNL-3243, p 5.

[16] T. R. Mueller and R. W. Stelzner, "High-Sensitivity, Direct-Reading, Linear, Recording Conductivity Titrator," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962,* ORNL-3397, pp 6 and 7.

[17] T. R. Mueller (see "Arbitrary-Set Proportional Temperature Controller," in chap. 1 of this report).

$\sim$1 ohm^{-1} cm^{-1} and were measured at 5° intervals over the range from 25 to 100°C with compensation for the initial conductances.

The performance of the instrument meets or exceeds design criteria.[15,16] With the exception of the proportional temperature controller, the titrator has been in use 10 hr/day for about a year. Only three components – a vacuum tube, a power supply amplifier, and a multiturn potentiometer – have failed. Failures were not attributable to circuit-design deficiencies. Development work on the titrator is considered to be complete.

D. J. Fisher suggested the method of initial-conductance compensation, the use of operational-amplifier circuitry in the design of the conductometric titrator, and a series of experiments made with various cell geometries. H. C. Jones contributed practical solutions to a number of difficult design problems.

The instrument and the results of the work are described in a paper that will be submitted to *Analytical Chemistry* for publication. The proportional temperature controller circuit will be submitted as an "Aid for the Analyst" in the same journal.

ARBITRARY-SET PROPORTIONAL TEMPERATURE CONTROLLER

T. R. Mueller

During the development of a high-sensitivity conductometric titrator,[16] control of the temperature of the conductivity-cell solution to ±0.01°C was needed. Although the temperature can be so regulated with a good contact thermometer and "on-off" control of the heater, noise is produced on the recorded conductivity curve. With proportional control, excursions about the control point are less abrupt and the recording is smooth.

Commercially available proportional temperature controllers having the required sensitivity are costly. Cheaper units described in the literature have neither the sensitivity nor the long-term drift characteristics required. An arbitrary-set, proportional temperature controller was designed and built as an accessory to the conductometric titrator; the controller may be used with other types of instruments having plus and minus 300-v dc regulated power supplies.

The controller consists of a bridge, amplifier, and control circuit. A low-resistance thermistor (chosen to minimize noise pickup) in one arm of a dc-powered bridge serves as the temperature-sensing element. Imbalance of the bridge is sensed by a high-gain, chopper-stabilized amplifier, the output of which drives a silicon-controlled-rectifier (SCR) circuit. The SCR circuit is identical with one described in the General Electric Company SCR manual[18] except that the manually operated variable resistor is replaced by a transistor.

The regulating capabilities of the controller appear to be well within the design goal of ±0.01°C. Short-term regulation and stability were checked by using the unit to regulate the temperature of 300 ml of 0.3 *M* KCl–1 × 10^{-4} *M* HCl solution during the conductometric titration of the HCl with a solution of NaOH.

The cell was cooled by a cold finger set at a temperature 2°C below the control temperature and was heated with an external 100-w projection lamp. Noise associated with "on-off" temperature control was absent from the recorded conductivity curve. Cell temperature measurements made with a second thermistor indicate that the short-term (15 min) regulation is within ±0.002°C. Electrical regulation and drift of the controller itself correspond to ±0.005°C or less per day. The long-term temperature-regulating capability of the instrument is being determined. The design of the controller will be submitted to *Analytical Chemistry* for publication as an "Aid for the Analyst."

CONTROLLED-POTENTIAL AC POLAROGRAPHY

R. W. Stelzner

The controlled-potential ac polarograph was rebuilt to incorporate a computer-type adder circuit[19] in the potentiostat. Use of a George A.

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[18] F. W. Gutzwiller (ed.), *Silicon Controlled Rectifier Manual*, 2d ed., p 116, General Electric Co., Auburn, N.Y., 1961.

[19] R. W. Stelzner, "AC Controlled-Potential Polarography," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 10.

Philbrick Researches, Inc., type P2 chopper-stabilized amplifier as a voltage follower reduced the drain of current through the reference electrode and, in conjunction with the adder circuit, provided a realtively fast (no error up to 200 cps) potentiostat having a circuit-ground reference for all input voltages (initial potential, ac, and scan). For phase-selective, fundamental, ac polarography, an operational amplifier tuned to the first-harmonic frequency of the alternating voltage is used in the current amplifier section of the polarograph. The output of the current amplifier is phase-selectively rectified by a shunt-connected chopper, and the pulsating dc current is smoothed out by a first-order lag circuit. The drop-frequency component (f = 0.2 cps) is removed by a tuned, quadruple, parallel-T filter. Final presentation is on a Moseley 2D-2 X-Y recorder.

The polarograph was operated at a frequency of 42 cps with an amplitude of 7.1 mv rms for test runs made on 1×10^{-4} M Cd^{2+} in 0.1 M KCl. At this concentration of reducible ion, rejection of the double-layer charging current was very satisfactory.

Evaluation of resolution, by use of Cd^{2+} and In^{3+} in 0.1 M KCl (ΔE = 38 mv) and a scan rate of 50 mv/min, indicated a very favorable comparison with resolutions produced by the ORNL model Q-1988A dc polarograph.

The evaluation of this high-accuracy, high-sensitivity, controlled-potential ac and dc polarograph will be continued. The effects of frequency and amplitude on the sensitivity and resolution achieved with it will be studied in particular. Inasmuch as this polarograph is readily adapted to the determination of the higher harmonic components of the ac polarographic current, it is planned also to investigate second-harmonic ac polarography as an alternative technique to phase-selective fundamental ac polarography.

The assistance of J. K. Frischmann[20] in this work is acknowledged.

MODEL VII FLAME SPECTROPHOTOMETER

H. C. Jones D. J. Fisher M. T. Kelley

The model V high-resolution flame spectrophotometer was discussed previously.[21,22] The model VII, which in many respects is identical with the model V, is at present intended only for flame emission work. Reliable, high-quality, commercial power supplies and operational amplifiers reduce the cost and simplify its construction and maintenance.

To allow for insertion of a light-beam-chopper disk and a motor, a Jarrell-Ash 82-500 flame attachment is separated ~7 in. from a Jarrell-Ash 82-000 scanning spectrometer, which has a linear reciprocal dispersion of 16 A/mm. Chopping provides zero stability, even with infrared-sensitive phototubes, which have a variable, high, and temperature-dependent dark current. With an absorption source unit, chopping makes possible measurements by the atomic absorption method, even for elements with flame emission intensities that are not negligible with respect to the intensity of the line source. A 3-in.-focal-length quartz lens focuses the light beam on the entrance slit of the spectrometer. For spectrally uncomplicated samples, wide slits can be used to increase the photoelectric sensitivity. Even with 500-μ slits, the spectral band pass is only 8 A.

Use of the model VII flame spectrophotometer as an atomic absorption device would require a suitable stable light source, relocation of the chopper disk, and substitution of a burner giving a longer light-path length than is provided by the standard Beckman oxyhydrogen burner. The necessary changes for absorption work will be made when and if the General Analyses Laboratory has need for the absorption function.

At present, an EMI/US 9558QA multiplier phototube is used to span the wavelength range from 2000 to 8700 A. A combination of phototubes,

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[20] Technical assistant from Michigan State University, East Lansing.

[21] H. C. Jones, D. J. Fisher, and M. T. Kelley, "High-Resolution, High-Sensitivity, Scanning, Recording Flame Spectrophotometer," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, pp 5–6.

[22] H. C. Jones, D. J. Fisher, and M. T. Kelley, "High-Resolution, High-Sensitivity, Scanning, Recording Flame Spectrophotometer," *Analytical Chemistry in Nuclear Reactor Technology, Fifth Conference, Gatlinburg, Tenn.*, Oct. 10–12, 1961, TID-7629, pp 31–41.

such as the EMI/US 6256B and the International Telephone and Telegraph Company FW-118, could be used to span the same range, possibly with greater sensitivity. A John Fluke model 412A power supply provides the high voltage necessary for the multiplier phototubes.

In the first amplifier stage, which is a directly coupled current amplifier, a 2-megohm resistor in parallel with a 510-pf capacitor is used as a feedback network instead of the three resistors used in the current amplifier of the model V spectrophotometer. The gain of this stage at the chopper frequency (320 cps) is reduced to $\frac{2}{3}$ that of the current amplifier in the model V. The two tuned voltage amplifiers are the same type as those used in the model V; all three are GAP/R K2-XA operational amplifiers.

The synchronous rectifier system used in the model V was discarded in favor of an amplifying, precision, half-wave rectifier circuit based on principles described by Seddon[23] and by the Burr-Brown Research Corporation.[24] This circuit uses a GAP/R USA-3 amplifier to compensate for the forward voltage drop across the diode junction. Elimination of the synchronous rectifier and its drive system simplifies the construction and adjustment of the model VII.

Either of two modes of flame-emission measurement can be used. In the first, the emission is recorded as a function of time by means of a chopper-stabilized voltage amplifier, which is provided with variable damping and with a zero-set control for flame-background compensation. This amplifier is connected as an inverting amplifier with a gain of 1 and variable damping. The damping is provided by switching capacitors in the feedback network of the amplifier. The *RC* time constants available are about 0.1, 0.2, 0.4, 0.8, 1.6, and 3.2 sec. The output of the inverting amplifier is fed through a voltage divider to a 1-sec-pen-response recorder. This variable damping permits relatively fast wavelength scanning of signals that do not require excessive damping. Background compensation (zero adjustment) is provided by feeding current from a Zener-diode-regulated power supply to the input of the inverting dc amplifier. Approximately four times full scale on the recorder is provided by the zero adjustment.

In the second way of measuring the flame emission, the time integral of the output of the rectifier circuit is taken by another USA-3 connected as a time integrator. The fixed integration period, determined by a Haydon 1-rpm timer, is ~45 sec. Three integration rates are provided. The instantaneous output of the inverting amplifier is recorded during the integrator timing period. The timer automatically switches the recorder to read the output of the integrator for about 5 sec after the integration period. It then switches the recorder back to the output of the inverting amplifier. Monitoring during integration assures that no artifacts occurred during the integration and therefore that integration over a fixed time interval is valid. When work is being done at very high sensitivity, causing the noise due to flame fluctuations to be high relative to the average value of the signal, the integrator is a more convenient means of averaging the signal than is visual measurement.

The performance of the model VII should be equivalent to that of the model V. By means of calibration curves prepared with the model VII instrument, the General Analyses Laboratory has determined Mg, K, Na, Ca, Li, Sr, Ba, Rb, and Cs; Sn and Cd have been determined by standard addition. The instrument has high resolution and is stable and very sensitive.

STUDIES OF INITIAL CURRENTS IN CONTROLLED-POTENTIAL COULOMETRY

R. W. Stelzner

In the controlled-potential coulometric determination of uranium with the ORNL model Q-2005 automatic, electronic, controlled-potential coulometric titrator[25] and with a titration cell of standard design, high results are obtained if the initial current exceeds 65 ma.[26] This effect is

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[23] B. Seddon, *Analog Methods*, Reprint 27, George A. Philbrick Researches, Inc., Boston, Mass., Apr. 5, 1960.

[24] "Precision AC to DC Converter," Application Notes, NOO 3083 (12-22-60), Burr-Brown Research Corp., Tucson, Ariz.

[25] M. T. Kelley, H. C. Jones, and D. J. Fisher, "Electronic Controlled-Potential Coulometric Titrator," *Anal. Chem.* 31, 488, 956 (1959).

[26] W. R. Laing, personal communication to R. W. Stelzner, October 1963.

also observed to various degrees for other substances. The current of the potentiostatic circuit can be limited either by means of a resistor in series with the counter electrode, a deliberate design feature in the Q-2005, or by starting the analysis at a low potential and increasing the control voltage at a rate such that, in the case of uranium, the cell current does not exceed 65 ma until the desired control potential (−0.345 v vs the S.C.E.) is reached. When either of these current-limiting procedures is used, the analytical results are within the quality control limits of ±2*S*, *S* = 0.1%, where *S* is the relative standard deviation. If the analysis for uranium is begun at −0.345 v vs the S.C.E. with insufficient limiting of the current by means of a resistor, the results show a positive bias of 1 to 2%.

The reason for the positive bias under these conditions is not readily apparent. It has been attributed to: the slow response of the potentiostatic circuit of the Q-2005 titrator, oxygen leaking into the cell from the isolated anode compartment, faulty performance of the analog integrator circuit, and discharge of hydrogen ion. Of these possibilities, all except the last have been checked.

By means of an oscilloscope, the potentiostatic circuit of the coulometric titrator was checked extensively during the course of titrations; not one instance of loss of control was observed. For a period at the start of an electrolysis, the correct potential is not applied because the potentiostat cannot furnish the current demanded by the cell reaction. However, the direction of the error (duration <1 sec) is such that a more cathodic reaction would not take place.

Leakage of oxygen into the cell from the anode compartment would cause a positive bias. To check this possibility, hydrazine sulfate, which is oxidized to nitrogen, was substituted for sulfuric acid in the anode compartment. A positive error of 1 to 2% was still present; consequently, oxygen leakage as a source of error was discounted.

The analog integrating circuit was checked by successively integrating both small and large step currents. Some discrepancies between integral calibrations occurred but were not of sufficient magnitude to account for the positive bias.

As yet, no experiment has been devised to check the possibility that discharge of hydrogen ion causes the positive bias. It is planned to continue this investigation to determine the cause for the positive bias at high initial currents.

REFERENCE ELECTRODE PLACEMENT IN CONTROLLED-POTENTIAL COULOMETRY

R. W. Stelzner M. T. Kelley D. J. Fisher

In controlled-potential coulometry with a three-electrode electrochemical cell, the reference electrode may be placed arbitrarily in the current-density gradient present in the cell. If the position of the reference electrode is between the controlled and counter electrodes, the cell region is one of high current density, and the action is such as to limit the initial cell current. If the position is remote from the counter electrode, the region is one of low current density, and the initial cell current is limited by the current capacity of the potentiostat or by the reaction or material transport rate.

One theory of the dynamic behavior in an electrochemical cell under controlled-potential conditions suggests that when the reference electrode is in a low-current-density region, an error in potential can exist in the reaction zone in the region of high current density. The error would be such that the potential difference which constitutes the thermodynamic driving force, and thereby determines the possible electrochemical reactions occurring, would be greater than the control voltage set into the potentiostat. (It is assumed that the potentiostat is exactly balancing its input voltages, unless current limiting results in the application of a limited potential.) It is conceivable that the potential at the counter electrode could be such as to permit the discharge of a second ion in the region of high current density; yet, the potentiostat is maintaining exact control in the region where the reference electrode is placed, which is of low current density. Inasmuch as the basic idea of separation of ionic species by limited or controlled-potential electrolysis is challenged by this theory, a study of the problem of placement of the reference electrode was undertaken.

Probe measurements made with a Luggin-Haber capillary disclosed that potential differences as high as 400 mv exist between reference electrodes located in regions of high and low current density when a total cell current of 100 ma flows. The potential difference relative to a reference electrode in a low-current-density region decreases from 400 to 0 mv as the capillary probe is moved from the surface of the counter electrode to the surface of the controlled electrode. No reversal in the sign of this potential difference is observed. The polarity and the reduction in value suggest that this potential difference is due to *IR* drop in the bulk resistance of the solution. The size of the miniature probe tip is still large relative to the dimensions of the reaction zone. It was concluded that probe measurements would furnish no evidence of potential error at the reaction zone; consequently, an experiment that would provide chemical evidence for or against potential error in the reaction zone was devised.

The postulated potential error would be most severe when the reference electrode is in a low-current-density region, the more easily reduced ion has a low exchange current, and the total cell current is a maximum. If, under these conditions, two ions with discharge potentials separated by the classical value for quantitative analysis (200 mv) are electrolyzed at the discharge potential of the more readily reducible of the species, subsequent chemical analysis for the other ion would indicate the presence or absence of potential error. The ions Cu^{2+} and UO_3^{2+} are an almost ideal system for such a study. In acid medium, their discharge potentials are separated by about 200 mv. Any UO_2^{2+} (the second ion) that might be reduced to UO_2^{+} because of potential errors during the electrolysis for Cu^{2+} would produce an equivalent amount of U^{4+} in the coupled disproportionation reaction in the strongly acid medium. The U^{4+} will remain since the overall reaction is irreversible. Because uranium can be determined with high precision (S = 0.1%), conclusions drawn from the results of analyses will be highly reliable. However, Cu^{2+} has a rather high exchange current.

The experiment was to conduct the controlled-potential electrolysis for Cu^{2+} at high current levels and then to determine whether any UO_2^{2+} had been reduced. Any decrease in UO_2^{2+} concentration would be indirect, but nevertheless positive, evidence for the postulated error. The ORNL model Q-2005 titrator was used for this work.

The cell devised for this study is shown in Fig. 1.2. The cell uses mechanical stirring and countercurrent flow of both solution and mercury to achieve high electrolysis currents. A helium lift was selected for pumping because, in addition to furnishing a satisfactory flow rate (400 ml/min) and not bringing metal in contact with the aqueous solution, it sparged the solution and maintained an inert atmosphere in the cell. Mercury was pumped through the cell by gravity feed at a rate of 2 ml/min. A plot of cell current vs time is shown in Fig. 1.3. The results of the experiment are summarized in Table 1.1. They permit the conclusion that if an error in the potential in the reaction zone exists at all, its effect, even under exaggerated conditions and cell geometry, is very small.

This conclusion was strengthened by running the same experiment at a potential difference of -0.050 v vs the S.C.E., that is, 50 mv more negative than that of the first experiment. In this case, some UO_2^{2+} was reduced (~1%); however, there was no significant difference in the UO_2^{2+} loss when the reference electrode was located in high- and low-current-density regions. This result indicates that, in the experiment run at 0.00 v vs the S.C.E., if an error of 50 mv had existed, a readily measured amount of UO_2^{2+} would have been lost.

From these experiments, it was concluded that the electrical potential difference established in

Table 1.1. Results of Controlled-Potential Experiment with Cu^{2+} and UO_2^{2+} (See Fig. 1.3)

Position of reference electrode, low-current-density region

Supporting electrolyte, 1 *M* H_2SO_4

Control voltage, 0.00 v vs the S.C.E.

Reducible Ion	Concentration of Reducible Ion (mg/ml)		
	Sample 1	Sample 2	Sample 3
Cu^{2+}	0.991	0.394	0.279
UO_2^{2+} (as U)	10.79	10.80	10.79

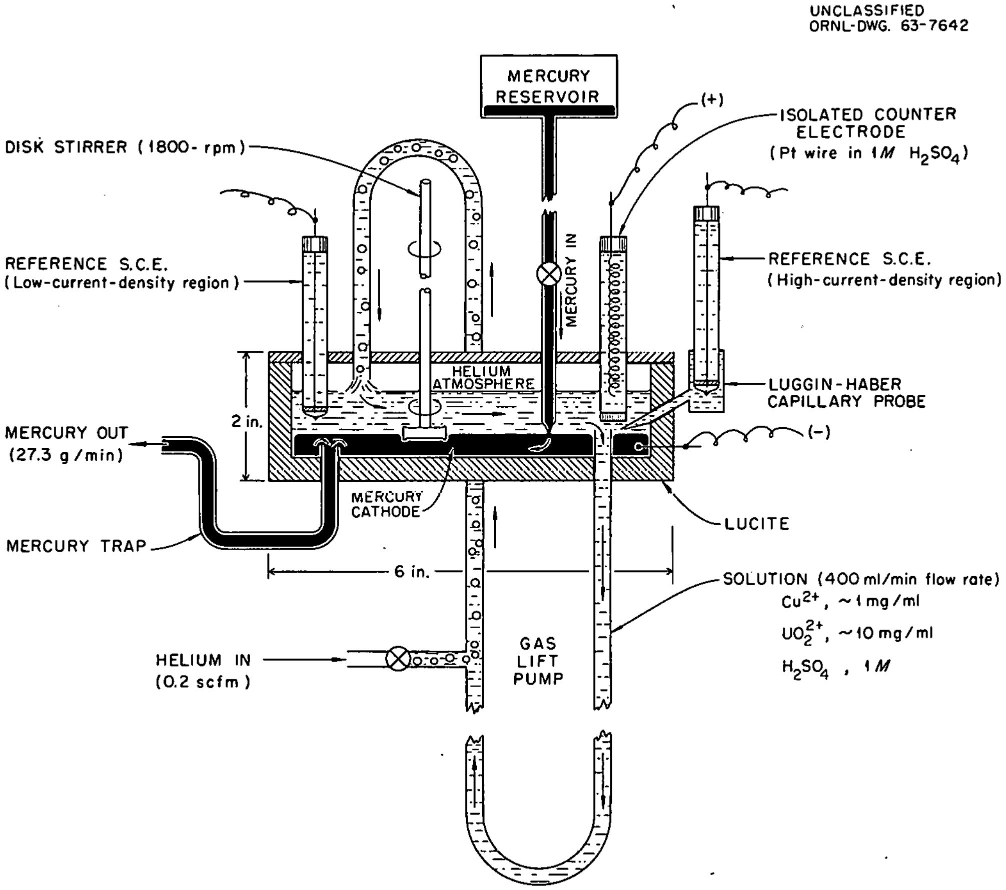
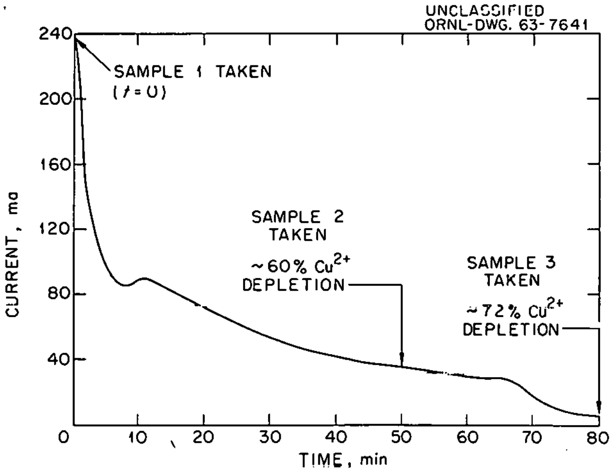


Fig. 1.2. Counter-Current, Flowing-Stream Coulometric Cell Used in the Study of Reference Electrode Placement.

Fig. 1.3. Current-Time Profile for Cu^{2+}-UO_2^{2+} Controlled-Potential Experiment with Reference Electrode in Low-Current-Density Region. (See Table 1.1.)



the reaction zone by the potentiostat may act in much the same way that a chemical depolarizer acts in controlled-current electrolysis. No evidence was found for the existence of the postulated potential error associated with placement of the reference electrode, but evidence was not obtained which proves unequivocally that this error is nonexistent. This series of experiments will be continued under even more exaggerated cell geometry and, perhaps, with a better chemical system, to determine whether any chemical evidence for error in controlled-potential coulometry can be found.

CONTROLLED-POTENTIAL AND DERIVATIVE POLAROGRAPHY: APPLICATION TO THE DETERMINATION OF METAL COMPLEXES IN ORGANIC EXTRACTS

W. L. Belew J. A. Dean[27]
D. J. Fisher M. T. Kelley

A study was made of the suitability of polarography for the direct determination of metal complexes in the organic phase following solvent extraction. By comparison with polarography in aqueous media, polarography in the organic extracts from solvent extractions offers the following advantages. The substance to be determined can be concentrated several fold during the extraction step, thus increasing the sensitivity of the method. Matrix elements that interfere are removed. A separate stripping step is not required. Also, the possibility exists of performing polarographic analysis in an organic solvent with species that are not stable in aqueous solutions.

Several solvent-extraction systems were investigated with complexes of cadmium or uranium as the reducible ions. Regular and first-derivative polarograms were obtained for both ion-association and chelate-type extraction systems. In general, chelate systems are less suitable for polarographic analysis than ion-association systems, since the reduction potentials of the chelating agents are usually such as to cause interference in the determination of the metal complexes. Several types of solvents were used; the effect of solvent type on the reducibility of the metal complex was determined. The effect of the specific resistance of the solution on the form of the polarograms was investigated by using solvents of different dielectric constants and by varying the concentration of the supporting electrolyte. Since the extracts are equilibrated with water, they are not anhydrous.

Instrumentation

Polarograms were obtained with the Q-1988-FES polarograph, which is the Q-1988-ES polarograph[28,29] modified to permit use of a $\frac{1}{2}$-sec Smoler vertical-orifice D.M.E.,[30] and were recorded with a 1-sec-response X-Y recorder. Where the form of the polarographic wave was of interest, a 0.3-v/min scan rate was used so that time lags in the fast current-averaging and derivative computers are negligible. In order to increase the sensitivity for derivative polarography, scan rates as fast as 3 v/min were used to record derivative polarograms for quantitative analysis. The controlled-potential feature of the polarograph allows polarograms to be recorded for high-specific-resistance solutions without adverse effect from bulk *IR* drop in the solution or from the resistance of the reference electrode. Since essentially no current is drawn through the reference electrode, a small Beckman aqueous S.C.E. with a fiber tip was used throughout the investigation. The junction potentials are not known, but they evidently are either reproducible or negligible. The half-wave potentials of the waves were reproduced within a few millivolts with no difficulty. The resistance of the reference electrode in the organic media was 10 to 40 kilohms.

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[27] University of Tennessee, Knoxville.

[28] M. T. Kelley, H. C. Jones, and D. J. Fisher, "Controlled-Potential and Derivative Polarograph," *Anal. Chem.* 31, 1475 (1959).

[29] M. T. Kelley, D. J. Fisher, and H. C. Jones, "Controlled-Potential Polarograph Polarizing Unit with Electronic Scan and Linear Residual Current Compensation," *Anal. Chem.* 33, 1262 (1960).

[30] W. L. Belew, D. J. Fisher, and M. T. Kelley, "Controlled-Potential DC Polarography with a Rapidly Dropping Mercury Electrode," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 13.

Organic Extracts That Contained Cadmium(II)

Tetrabutylammonium iodide was used as both the extractant and supporting electrolyte to extract Cd^{2+} from 1 M HCl into each of these solvents: isoamyl alcohol, ethylene chloride, and 2,2′-dichlorodiethyl ether. With isoamyl alcohol, the organic phase has a specific resistance of 1500 ohm-cm, and the polarograms are reproducible. The slopes of the polarograms correspond to a two-electron reduction, which indicates that the uncompensated resistance[31] is small. The half-wave potential is -0.73 v vs an aqueous S.C.E. With both ethylene chloride and 2,2′-dichlorodiethyl ether, no polarographic wave is obtained for cadmium, although the specific resistance is lower than the specific resistance of the isoamyl alcohol solution. In each case, when an alcohol is added to the extract, a cadmium wave appears at the expected half-wave potential (~ -0.7 v). The diffusion current is fully developed when the solvent contains ~15 v/v % ethyl alcohol. It is assumed that an alcohol in association with the cadmium complex makes possible the electron-transfer step.

Organic Extracts That Contained Uranium(VI)

Polarograms of U^{6+} were made in the organic phase from three extraction systems. In each case, $LiClO_4$ was added when additional supporting electrolyte was needed. The chelate complex was extracted with thenoyltrifluoroacetone in isoamyl alcohol. Polarograms of the organic phase were made directly after the $LiClO_4$ was added. The waves are drawn out, and the half-wave potential is about -0.25 v vs an aqueous S.C.E. The system does not appear to be useful analytically because the waves are small and difficult to reproduce.

Two ion-association systems were studied: tri-*n*-octylphosphine oxide in cyclohexane, and tetrapropylammonium nitrate separately in isoamyl alcohol, 2-octanol, 2,2′-dichlorodiethyl ether, amyl acetate, and ethylene chloride. With the tri-*n*-octylphosphine oxide system, it is necessary to dilute the cyclohexane with a solvent of higher dielectric constant in order to dissolve a supporting electrolyte and to reduce the specific resistance. Excellent polarograms are obtained for a 50 v/v % ethyl alcohol–cyclohexane solution that was 0.1 M in $LiClO_4$. In the tetrapropylammonium nitrate system, the uranium was extracted from an aqueous phase that contained 2.4 M $Al(NO_3)_3$ as a salting agent. When isoamyl alcohol, ethylene chloride, or 2,2′-dichlorodiethyl ether is the solvent, polarograms are obtained directly in the organic phase without solvent dilution or the addition of electrolyte. With isoamyl alcohol, the specific resistance of the solution was 3000 ohm-cm, and a small amount of uncompensated resistance[31] was indicated by the slope of the polarogram. When either amyl acetate or 2-octanol is the solvent, no polarograms are obtained directly in the organic phase, because sufficient supporting electrolyte is not soluble in these solvents and the resulting solution has a very high specific resistance. To lower the specific resistance, ethyl alcohol that contains $LiClO_4$ may be added to the organic phase after the extraction. Polarograms are then obtained with half-wave potentials of -0.33 v vs an aqueous S.C.E.

A quantitative method was developed for U^{6+}. The U^{6+} is extracted into 0.1 M tri-*n*-octylphosphine oxide in cyclohexane. This extraction system was investigated thoroughly by White and Ross[32] and shown to be efficient for extracting U^{6+} at microgram levels. Following equilibration and phase separation, the organic phase is diluted with an equal volume of 0.2 M $LiClO_4$ in ethyl alcohol. The specific resistance of the resulting solution is 1500 ohm-cm. Well-defined polarograms are obtained; the half-wave potential of the reduction is -0.34 v vs an aqueous S.C.E. The relations between concentration and diffusion current and between concentration and first-derivative peak height are linear over the range of uranium concentration from 5×10^{-6} to 1×10^{-4} M. At higher concentrations, the diffusion currents are smaller than would be predicted from a linear relation between concentration and diffusion current. It is assumed that the small diffusion currents are due to migration-current effects resulting

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[31] W. L. Belew *et al.* (see "Cell-Resistance Compensation in Controlled-Potential Polarography" in chap. 1 of this report).

[32] J. C. White and W. J. Ross, *Separations by Solvent Extraction with Tri-n-octylphosphine Oxide, NAS-NS-*3102 (Feb. 8, 1961).

from an insufficient amount of effective supporting electrolyte.

The results of this work have been described in detail.[33] It is anticipated that the work will be submitted for publication in a journal.

COMPENSATION OF CELL RESISTANCE IN CONTROLLED-POTENTIAL POLAROGRAPHY

W. L. Belew M. T. Kelley
D. J. Fisher J. A. Dean[34]

In high-specific-resistance solutions at usual polarographic current levels or in low-specific-resistance solutions at very high currents, a significant portion of the cell resistance remains uncompensated in polarograms made with a potential-control circuit (potentiostat) unless the tip of the reference electrode is placed very close to the surface of the mercury drop of the D.M.E. This effect is not due to malfunctioning of the potentiostat. The potentiostat controls the cell potential in accordance with the potential seen by the tip of the reference electrode. The ORNL model Q-1988-FES controlled-potential and derivative dc polarograph, which is a modified Q-1988-ES polarograph,[30] has been used to evaluate the resistance compensation that is attainable in a polarographic cell by means of controlled-potential electrolysis. The Q-1988-ES polarograph and the operation of the potential control circuit have been described.[35]

Laitinen and others[28,36–41] have suggested that the resistance of a polarographic cell consists of two components, internal resistance (R_i) and external resistance (R_e), which are illustrated in Fig. 1.4. The R_e is that resistance in the bulk of the solution between the anode and the region of high current density at the surface of the mercury drop. At the surface of the mercury drop, the current lines extend radially into the solution. The R_i is the resistance in the thin layer of solution at the surface of the mercury drop where the current density is high compared with that in the rest of the cell. McKinney and Schaap[37] have shown that R_i is not compensated in controlled-potential polarography unless the tip of the reference electrode is placed very near the surface of the mercury drop and inside the high-current-density region at the surface of the drop; the uncorrected IR drop at the interface has also been mentioned elsewhere.[28]

With the usual levels of polarographic current, the value of R_i is negligible in solutions of low specific resistance; however, in solutions of high specific resistance, R_i can become a significant portion of the total cell resistance. Ilkovič[38,39] derived equations for R_i. The average value of R_i (i.e., $\overline{R}_i$) is greater than the minimum value, which occurs at maximum drop size, by a factor of $^4\!/_3$ (ref 38) and is expressed by the equation

$$\overline{R}_i = \frac{\rho}{3\pi r_{\max}} . \qquad (1.1)$$

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[33] W. L. Belew, "Application of Controlled-Potential and Derivative Polarography to the Determination of Metal Complexes in Organic Extracts and Compensation of Polarographic Cell Resistance in High Specific Resistance Solutions," Master's Thesis, Department of Chemistry, University of Tennessee (to be published).

[34] University of Tennessee, Knoxville.

[35] M. T. Kelley *et al.*, "Controlled-Potential and Derivative Polarography," pp 158–82 in *Advances in Polarography* (ed. by I. S. Longmuir), vol 1, Pergamon, Oxford, 1960.

[36] I. M. Kolthoff, J. C. Marshall, and S. L. Gupta, "The Effect of Cell Resistance on Acute Polarographic Maxima," *J. Electroanal. Chem.* 3, 209 (1962).

[37] P. S. McKinney and W. B. Schaap, "Resistance Compensation in Electrolytic Cells," presented at the 145th American Chemical Society Meeting, New York, Sept. 9–13, 1963.

[38] D. Ilkovič, "Polarographic Studies with the Dropping Mercury Kathode. – Part XXVIII. – The Evolution of Hydrogen from Neutral and Alkaline Solutions," *Collection Czechoslov. Chem. Communs.* 4, 480 (1932).

[39] D. Ilkovič, "Polarographic Studies with the Dropping Mercury Electrode. – Part III. – The Cause of Maxima on Current-Voltage Curves," *Collection Czechslov. Chem. Communs.* 8, 13 (1936).

[40] R. Brdicka, "Polarographic Studies with the Dropping Mercury Electrode. – Part IV. – The Influence of Circuit Resistance on Maxima of Current-Voltage Curves," *Collection Czechoslov. Chem. Communs.* 8, 419 (1936).

[41] J. Devay, "Messung und Naherungsweise Berechnung des Inneren Widerstandes der Polarographischen Zelle," *Acta Chim. Acad. Sci. Hung.* 35, 255 (1963).

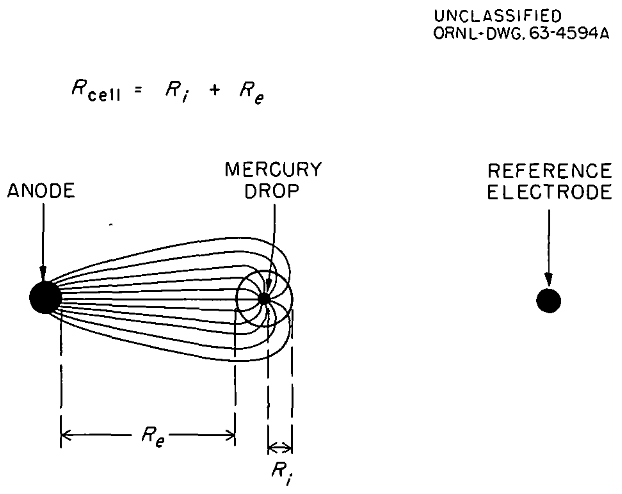

Fig. 1.4. Components of Cell Resistance.

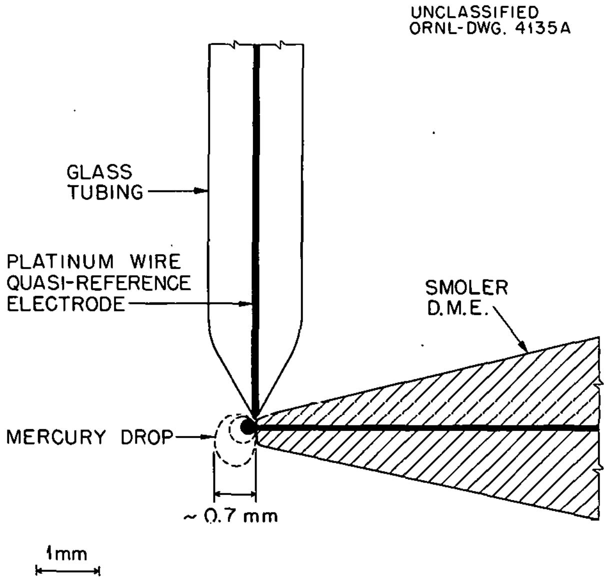

Fig. 1.5. Position of Reference Electrode for Compensation of Internal Resistance (R_i).

The value of $\bar{R}_i$ depends only on the maximum radius of the mercury drop, r_{max}, and on the specific resistance of the solution, ρ. A value of $\bar{R}_i$ calculated by this formula will be smaller than the value that actually exists under experimental conditions with a D.M.E. because the effective area of the drop is necessarily smaller as a result of shielding by the glass capillary.[36,41] For a Smoler $\frac{1}{2}$-sec D.M.E. with the tip of the reference electrode located 10 r or more away from the center of the drop, the value of $\bar{R}_i$ calculated from Eq. (1.1) is $\sim 3\ \rho$.

To compensate for significant $\bar{R}_i$ in controlled-potential polarography, the tip of the reference electrode must be inside the region of high current density at the drop surface. To accomplish this with a D.M.E., it is necessary to have a micro reference-electrode probe that can be placed very close to the surface of the growing mercury drop without shielding the drop from the cell solution. An apparatus was built that includes a sharpened, Smoler, vertical-orifice, $\frac{1}{2}$-sec D.M.E. and a platinum quasi-reference electrode[42] (Fig. 1.5). It is planned to also use a Luggin-Haber reference-electrode probe in place of the quasi-reference electrode. Use of the Smoler electrode is advantageous because the principal direction of drop growth is downward; therefore, it is possible to approach the drop from the top to within $\sim 0.1\ r$ without appreciably disturbing the drop time or mercury flow rate. The platinum quasi-reference electrode is mounted on a micrometer screw to obtain data as a function of distance from the D.M.E. Table 1.2 presents data obtained with this apparatus for a series of uranium polarograms. As the reference-electrode probe was moved away from the D.M.E., the resistance increased very rapidly until a distance of 1 r was reached. The total cell resistance was 100 kilohms, more than half of which appeared to be within 1 r of the surface of the mercury drop. At probe-to-D.M.E. distances greater than 4 r, the amount of uncompensated internal resistance remained constant at $\sim$70 kilohms.

With a potentiostatic circuit and an electrode apparatus of this type (Fig. 1.5), polarograms were made of solutions that had specific resistances as high as 25 kilohms-cm. At normal polarographic currents ($\lesssim 10\ \mu a$), the distortion of polarograms due to cell resistance was negligible.

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[42] M. T. Kelley *et al.*, "Controlled-Potential and Derivative Polarography," pp 175 and 181 in *Advances in Polarography* (ed. by I. S. Longmuir), vol 1, Pergamon, Oxford, 1960.

Table 1.2. Relation Between Uncompensated Resistance and Distance of Reference Electrode from Mercury Drop

Test solution, 1×10^{-3} *M* U^{6+}–1×10^{-3} *M* $LiClO_4$ in cyclohexane–ethyl alcohol (50 vol %)

Cell resistance, 100 kilohms

Specific resistance of test solution, 15,000 ohm-cm

D^a (r^b)	R^c (ohms)
0.1	0
0.4	26,000
0.7	37,000
1.0	52,000
2.5	63,000
3.9	70,000

[a] *D* = distance from the mercury drop to the reference probe in units of *r*.

[b] *r* = maximum radius of the mercury drop.

[c] *R* = uncompensated resistance introduced by moving reference probe away from the mercury drop.

CONTROLLED-POTENTIAL VOLTAMMETER

D. J. Fisher W. L. Maddox
M. T. Kelley R. W. Stelzner

A controlled-potential voltammeter was designed and built for use by groups in the Reactor Chemistry and Analytical Chemistry Divisions for voltammetry in molten-salt systems, including molten-fluoride systems.[43] The design criteria for the instrument are the specific requirements of this application; however, the instrument presumably can also be used in other electrochemical applications. The voltammeter consists of several operational-amplifier systems and has test, operate, and cell-open functions.

The features of the molten-salt application, as described by Gleb Mamantov,[43] are as follows. The electroanalytical cell contains stationary (solid) polarized, counter, and reference electrodes; the latter is initially the quasi-reference electrode.[42] The cell vessel is fabricated from graphite or metal. At a future date, the cell vessel may be a metal process line. Some cell vessels are connected either directly or through variable, uncontrolled leakage resistances to earth ground. Others are provided with an insulating sleeve. In the case of uninsulated vessels, system ground must float with respect to earth ground. For safety, all chassis are connected to earth ground. For applications not requiring a floating system ground, a switch is provided to connect system ground to earth ground. Other specifications include:

Current ranges: from 0–1 μa to 0–5 ma full-scale

Maximum current output of potentiostat: >5 ma

Scan rates: 0.2 to 20 v/min of ±0.5% long-term reproducibility

Scan range: ±3 v

Initial potential range: ±3 v

Recording devices: 1-sec-response, 11 × 17 in. X-Y recorder or oscilloscope provided with a camera

The instrument operates in the following way. The Y axis of the recording device is driven by a chopper-stabilized current amplifier that holds the polarized electrode at system ground potential. The output of the current amplifier is 1 v per 100 μa of cell current. The X axis of the recording device is driven by the potential of the polarized electrode with respect to that of the reference electrode. The potential-control amplifier consists of a truly differential-input, stabilized, operational amplifier that drives a current-booster amplifier. One input of the potential-control amplifier is the potential of the reference electrode with respect to that of the polarized electrode; the other input is the sum of the initial potential and the scan voltage with respect to system ground. The system used to generate the initial potential and the scan voltage is a fast integrator with initial conditions; a differential-input operational amplifier is used in this system. The power supply for the operational amplifiers does not have a special power transformer; therefore,

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[43] G. Mamantov, "Electrochemical Studies in Molten Fluorides," presented at the Seventh Annual Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 8–10, 1963.

with a floating ground system, an excessive amount of line-frequency ac voltage would be fed through the interwinding capacitances and would appear on the cell electrodes. This voltage is not present on the cell electrodes because this pickup is compensated by means of an ordinary line-isolation transformer and a "hum-bucker" circuit across the power transformer primary.

The prototype of this controlled-potential voltammeter was fabricated, and its performance is being tested. Another controlled-potential instrument will be designed; it will have chronopotentiometric and stripping-voltammetric functions in addition to the voltammetric function.

2. Chemical Analysis of Advanced Reactor Fuels

J. C. White

A. S. Meyer P. F. Thomason

DETERMINATION OF MICROGRAM AMOUNTS OF URANIUM(VI) WITH A HIGH-SENSITIVITY, CONTROLLED-POTENTIAL COULOMETRIC TITRATOR

J. M. Dale

The coulometric titration of U^{6+} at the microgram level was studied with the prototype ORNL model Q-2564 high-sensitivity, controlled-potential coulometric titrator.[1] This study was conducted to determine the accuracy and precision attainable with the lowest range of the titrator. The design of the coulometric cell and the method of preparing the standard solution of U^{6+} were evaluated, and sources of error in the procedure were considered and eliminated, if possible.

Because the amount of U^{6+} to be titrated was small, the volume of the test solution was also maintained as small as possible. For this purpose, a small titration cell was constructed from a 15-ml weighing bottle fitted with a tapered Teflon cap. Porous Vycor tubes ($\frac{1}{4}$-in. OD) inserted through the cap were used as bridges to the reference cell and anode. The cap also had entries for the stirrer, mercury-cathode contact, and purging-gas (Ar, 0.0001% O_2) tube. The geometry of the cell permitted the use of 2 ml of mercury as the cathode and 2 ml of test solution, which were stirred with an 1800-rpm synchronous motor. The stirring action caused a small amount of the solution to be entrapped under the mercury. This difficulty was eliminated by making a small indentation in the center of the bottom of the coulometric cell.

Also, it was necessary to prepare special standard solutions and to weigh the test portions of the standard solution. Standard solutions of ~50-μg/ml U^{6+} concentration in 0.5 *M* H_2SO_4 were prepared from 99.9% uranium metal and were stored in polyethylene bottles. The total uncertainty in the amount of uranium in a 1000-μl test portion of the standard solution was calculated to be less than ±0.1%. This calculation included the uncertainties in the weighing of the uranium metal, dilution, measurement of the density of the solution, and final weighing of the test portion. As the test portion became smaller, the uncertainty in the amount of uranium taken increased progressively because of the increase in the uncertainty of the final weighing step. However, the uncertainty was still less than ±0.4% for a 50-μl test portion that contained ~2 μg of uranium.

A positive error in the analyses existed. The error was traced to the diffusion or leakage of air into the system through the purge-gas line and was corrected by using metal tubing from the cylinder

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[1] H. C. Jones, D. J. Fisher, and W. D. Shults, "High-Sensitivity Coulometric Titrator," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 3.

of argon to the coulometric cell with no purification of the gas. It was then possible to attain reproducible background currents of 0.5 μa compared with 1.0 to 1.5 μa in previous analyses.

Table 2.1 shows the results of the analyses of test portions of different size. In addition to a blank correction, which included a "charging" current, a correction for faradaic background was made.[2] To eliminate operator error in making the faradaic correction, the automatic titration cutoff of the instrument was set at 0.5 μa, and the total reduction time was recorded. The results indicate that the "kinetic" and "induced" background currents are not significant in the $U^{6+} \longrightarrow U^{4+}$ reduction at the microgram level.[2]

To minimize the tendency toward the occurrence of the reaction

$$2M + O_2 + 2H_2SO_4 \rightleftharpoons 2MSO_4 + 2H_2O\ , \quad (2.1)$$

where M represents mercury or impurities in the mercury, the sample was purged with argon for 5 min prior to the addition of mercury to the cell. This practice consistently gave lower readout potentials for the prereduction step. The reduction times for the analyses summarized in Table 2.1 were 10 min or less, not including the purge time or prereduction time.

The results of this study are to be included in an open-literature article that will describe the high-sensitivity coulometric titrator and its performance.

Table 2.1. Results of Controlled-Potential Coulometric Titration of Microgram Quantities of U^{6+} in 0.5 M H_2SO_4

Prereduction potential: 0 v vs the S.C.E.
Reduction potential: −0.25 v vs the S.C.E.
Blank correction: 0.25 ±0.01 μg

Number of Determinations	U^{6+} (μg) Taken	U^{6+} (μg) Found	Error (%)	Relative Standard Deviation (%)
11	18.32	18.34	<0.1	0.2
10	2.48	2.47	<0.5	0.8

CONTROLLED-POTENTIAL COULOMETRIC TITRATION OF URANIUM(VI) IN AQUEOUS SOLUTIONS OF SODIUM FLUORIDE

W. R. Mountcastle[3]   Louise B. Dunlap
P. F. Thomason

A method was developed for the controlled-potential coulometric titration of U^{6+} in aqueous solutions of sodium fluoride. The U^{6+} is coulometrically reduced to U^{4+} at −1.00 v vs the S.C.E. in neutral or slightly acid 0.75 M NaF. At the 6-mg level, the relative standard deviation is ∼0.2%, and the error is +0.2 to +0.3%. Reasonable amounts of Cr^{3+}, Cu^{2+}, Mo^{6+}, and Zr^{4+} do not interfere. Iron(III) and Al^{3+} present in mole ratios to U^{6+} as large as 1:1 and 5:1, respectively, can be tolerated. This method was applied satisfactorily to a number of synthetic reactor dissolver solutions. A paper describing this work is to be submitted to *Analytical Chemistry*.

DETERMINATION OF CARBON IN AQUEOUS AND NITRIC ACID SOLUTIONS

I. B. Rubin

Studies on the determination of carbon in aqueous and nitric acid solutions were continued.[4] The optimum atmosphere for the combustion of carbon compounds and the effects of temperature of the copper reductor on carbon dioxide and nitrogen dioxide were determined. The apparatus was modified so that carbon dioxide can be measured gas chromatographically rather than manometrically. Conditions were established for the chromatographic separation of carbon dioxide from nitrous oxide and for the gas chromatographic determination of the carbon dioxide.

In the determination of carbon, various atmospheres are used for the combustion of samples. Combustion of carbon compounds in a stream of pure oxygen resulted in a higher conversion to carbon dioxide than did combustion in a stream of helium, *in vacuo*, or in a stream of oxygen with WO_3 as an accelerator. The carbon was in aqueous

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[2] L. Meites and S. A. Moros, "Background Corrections in Controlled-Potential Coulometric Analysis," *Anal. Chem.* 31, 23 (1959).

[3] Temporary summer employee from Birmingham-Southern College, Birmingham, Ala.

[4] I. B. Rubin and A. S. Meyer, "Determination of Carbon in Aqueous and Nitric Acid Solutions," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 41.

solution as sucrose. In each case, the combustion gases were passed over hot cupric oxide.

During the earlier studies in which nitric acid was added to the solutions of the carbon compounds,[4] the combustion gases were collected and then passed over copper that was heated to about 825°C. Results were often erratic; therefore, the effect of the temperature of the copper on the reduction of nitrogen oxides was studied over the range from 625 to 1025°C. Gas chromatographic analysis of the gases resulting from the combustion of nitric acid, after they were passed over hot copper, indicated that the components were NO, N_2O, and CO_2. The proportions of the components in the mixture were dependent on the temperature of the copper. Quantitative results were not obtained. Table 2.2 illustrates how the oxides of nitrogen are reduced as the temperature increases. The gases pass almost instantaneously through the tube that contains copper. The quantity of carbon dioxide remained essentially constant, which indicates that the amount of nitric acid taken would create a substantial blank. Apparently, the temperature does not affect the recovery of carbon dioxide, although a similar test made with sucrose in water indicated a decrease in the recovery of carbon dioxide as the temperature increased. This study will be continued.

Table 2.2. Effect of Temperature of Copper on the Reduction of Nitrogen Oxides

Column: Burrell high-activity silica gel (3 ft)
Temperature: 28°C
Flow of helium: 30 ml/min
Sample: distilled 16 *M* HNO_3 (0.20 ml)

T (°C)	Attenuation Range		
	NO[a]	N_2O[b]	CO_2[c]
625[d]	512 (off scale)	64	16
825	32	16	8
925	8	1	8
1025	1		8

[a] Elution time was 1.8 to 2.2 min.

[b] Elution time was 13 to 15 min.

[c] Elution time was 16 to 17 min.

[d] Droplets of blue liquid, probably N_2O_3, in trap. CO_2 peak partially obscured by N_2O peak. N_2O probably added to height of CO_2 peak.

In the manometric measurement of the gaseous products of combustion, there is no way to distinguish carbon dioxide from the residual oxides of nitrogen; therefore, the apparatus was modified so that the combustion gases could be analyzed by gas chromatography. A portion of the gas-measuring system was replaced with a detachable trap, which also serves as a sample loop for the gas chromatograph. An attempt was made to separate nitrous oxide and carbon dioxide so that the copper reductor would not have to be operated at 1025°C. These two gases have been separated by Szulczewski and Higuchi[5] and by Marvillet and Tranchant;[6] however, the analytically useful separation takes ~30 min, which is considered to be too long. The following types of columns were tested in an effort to reduce this separation time: silica gel of various lengths and grades, activated charcoal of various types, activated alumina, several organic columns, and combinations of some of these. No conditions were found that gave substantial improvements over those previously cited.[5,6] Since nitrous oxide can be eliminated by reduction with hot copper, this was done.

The following conditions were established for determining carbon dioxide. The chromatographic column consisted of a 3-ft length of $\frac{1}{4}$-in.-OD copper tubing filled with Burrell, 30/65-mesh, high-activity silica gel. The Greenbrier Chromo-Lab 950 gas chromatograph was used. The oven temperature was held at 60°C, and the helium carrier flow was 60 ml/min. Under these conditions, the elution time was 2.3 to 2.6 min, depending on the sample size. The bridge current was set at 18 ma. In the range of sample size from 4 to 100 μl (at STP), the relative standard deviation for a series of standards was 7% and in the range of sample size from 100 to 700 μl, the deviation was 4%. The sensitivity is such that 1 μl of gas would cause ~15% of full-scale deflection on a 0–1 mv recorder.

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[5] D. H. Szulczewski and T. Higuchi, "Gas Chromatographic Separation of Some Permanent Gases on Silica Gel at Reduced Temperatures," *Anal. Chem.* 29, 1541 (1957).

[6] L. Marvillet and J. Tranchant, "Qualitative and Quantitative Analysis, by Gas-Solid Chromatography, of Mixtures Containing Nitrogen Oxides," pp 321–30 in *Gas Chromatography* (ed. by R. P. W. Scott), Butterworths, Washington, D. C., 1960.

A sample that contains as much as 1500 μl (at STP) of carbon dioxide can be analyzed. Since 1 μl of carbon dioxide is equivalent to about 0.5 μg of carbon, the gas chromatographic determination of carbon is probably 20 times more sensitive than the manometric determination.[4]

GAS CHROMATOGRAPHIC STUDY OF THE REACTION PRODUCTS FROM THE PROCESSING OF CARBIDE-CONTAINING NUCLEAR FUELS

A. D. Horton

A method proposed by the Chemical Technology Division for processing carbide-containing nuclear fuels[7] requires reacting the fuel with carbon tetrachloride in the presence of air. The expected reaction products include excess air, excess CCl_4, CO, CO_2, Cl_2, and $COCl_2$. The process will be monitored by gas chromatography. The instrument now in use contains a 15-ft silica-gel column. An investigation was made to determine whether the expected products can be separated by this column. It was learned that the column resolves all the components in the mixture except Cl_2 and $COCl_2$.

An 8-ft silicone-gum-rubber column (25 wt % on C-22 firebrick), when operated at room temperature, will resolve all components except air and CO. A 15-ft column of the same type is expected to resolve all the components.

The Chemical Technology Division will try the existing silica-gel column before proceeding further.

GAS CHROMATOGRAPHIC DETERMINATION OF THE OXIDES OF NITROGEN

A. D. Horton A. S. Meyer
J. L. Botts

A sampling manifold for corrosive gases[8] was used to measure as much as 10 ml of a sample that contained NO, N_2O, and the equilibrium mixture $N_2O_4 \rightleftharpoons 2NO_2$. These compounds are resolved on a 1-m-long by 0.5-cm-ID Pyrex column that contains 20/30-mesh, dry silica gel (Fig. 2.1). The helium flow is 60 cc/min, and the column is temperature-programmed from 25 to 300°C. The order of elution appears to be NO, N_2O, N_2O_4, and NO_2. The sequence of the last two peaks is indicated by the disappearance of the third peak (N_2O_4) in accordance with the mass-action effect on the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ as the sample pressure is reduced. Emmett[9] has suggested that the equilibration rate of the $N_2O_4 \rightleftharpoons 2NO_2$ equilbrium is

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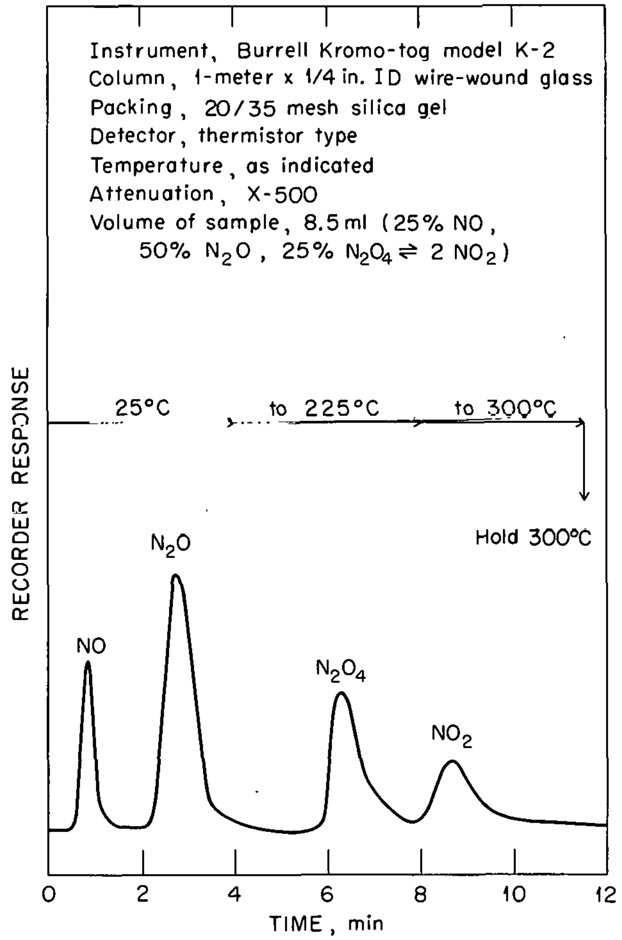

Fig. 2.1. Results of the Gas Chromatographic Determination of the Oxides of Nitrogen.

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[7] F. G. Kitts, Chemical Technology Division, private communication to A. D. Horton, Aug. 12, 1963.

[8] A. D. Horton, "Gas Chromatographic Determination of the Oxides and Chlorides of Nitrogen," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 48.

[9] P. Emmett, Johns Hopkins University, Baltimore, Md., private communication to A. S. Meyer, Sept. 16, 1963.

too rapid to permit the resolution of these gases as separate peaks and that the apparent elution of two peaks results from the cooling effect of the endothermic dissociation of an equilibrium concentration of N_2O_4 at the surface of the detector thermistor. The temperature of the gases in the detector is 50°C and the estimated thermistor temperature is about 75°C. Possibly, as the peak maximum of the eluted $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium mixture in the helium carrier is approached, the cooling effect of the dissociation of the equilibrium concentration of N_2O_4 outweighs the reduction of thermal conductivity brought about by the NO_2 to yield a W-shaped peak similar to that observed in the gas chromatographic determination of large quantities of hydrogen when helium is used as the carrier.

This theory does not apply when the rate of temperature programming is changed to cause the $2NO_2 \rightleftharpoons N_2O_4$ fraction to emerge from the column as a single peak or when the $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium mixture is passed through a charcoal column[10] or a Teflon column. By use of these columns, only one peak is obtained for the $2NO_2 \rightleftharpoons N_2O_4$ fraction. The carrier and the detector are the same.

When the sampling manifold has been used for several days, the corrosive gases cause the Viton O-rings to stick to the glass wall of the stopcocks. This problem can probably be corrected by applying a light spray of Fluoroglide, a Teflon spray available from Chemplast, Inc., Newark, N.J.

In anticipation of the demand for the analysis of samples that contain corrosive gases, the development of a corrosion-resistant gas chromatograph was started.

GAS CHROMATOGRAPHIC DETERMINATION OF THE HYDROLYSIS PRODUCTS OF URANIUM CARBIDES AND THORIUM CARBIDES

A. D. Horton J. L. Botts

Experimental work was completed on the gas chromatographic analysis of the gaseous phase of the hydrolysis products of uranium carbides and thorium carbides. The results of this experimental work are being published.[11]

GAS CHROMATOGRAPHIC DETERMINATION OF THE NITRIC ACID OXIDATION PRODUCTS OF URANIUM CARBIDES AND THORIUM CARBIDES

A. D. Horton

A preliminary investigation was made of the gas chromatographic determination of possible products formed when uranium carbides and thorium carbides are heated in nitric acid and the resulting organic acids are decarboxylated by heating with anhydrous $CuSO_4$ and quinoline at 265°C. The products are not expected to contain nitrates but may contain naphthalene, biphenyl, anthracene, and phenanthrene.[12]

All the components listed, except anthracene and phenanthrene, are resolved on a 10-ft-long by $\frac{1}{4}$-in.-OD column that contains 40/50-mesh glass beads coated with 0.15 wt % silicone 550. The operating conditions are: helium flow, 60 cc/min; column temperature, isothermal at 100°C for 9 min and then programmed to 175°C at 8 to 10°C/min. Naphthalene is eluted first, followed by quinoline, biphenyl, and – at the end of the program – anthracene and phenanthrene as a single peak (Fig. 2.2). The column bleeds slightly at a temperature above 150°C; however, this can be avoided by using silicone SE-30 or SE-52 as the coating for the glass beads. It is proposed to obtain an SE-52-coated capillary column to enhance the resolution of such a mixture.

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[10] R. M. Bethea and F. S. Adams, Jr., "Vapor-Phase Butane Nitration Product Analysis by Parallel Column Gas Chromatography," *J. Chromatog.* 10, 1 (1963).

[11] A. D. Horton and J. L. Botts, "Gas Chromatography as Applied to Nuclear Technology. II. Gas Chromatographic Determination of the Hydrolysis Products of Uranium Carbides and Thorium Carbides," *Nucl. Sci. Eng.* (to be published).

[12] L. M. Ferris, Chemical Technology Division, private communication to A. D. Horton, Sept. 6, 1963.

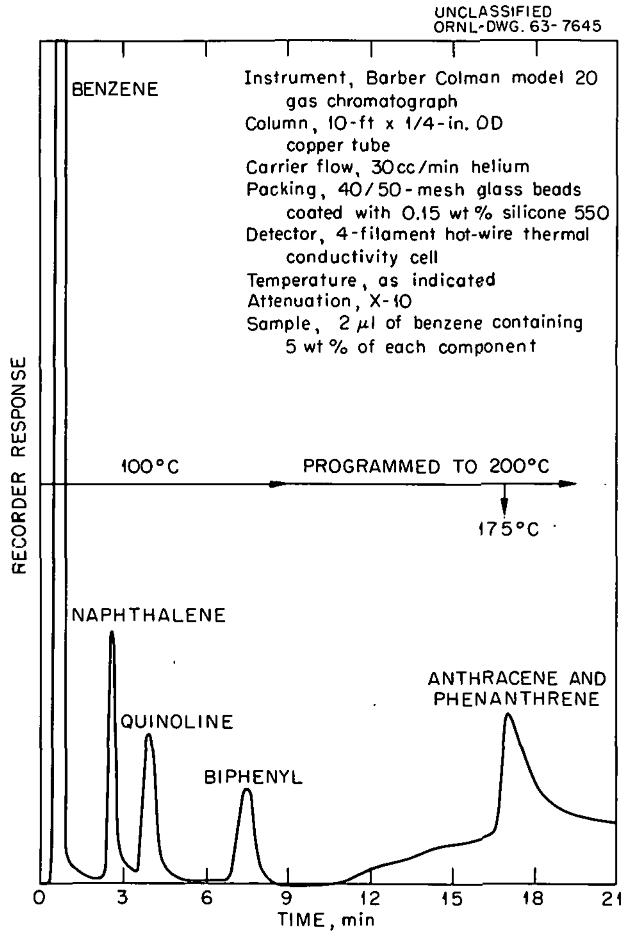

Fig. 2.2. Results of the Gas Chromatographic Determination of Some Polynuclear Aromatics.

GAS CHROMATOGRAPHIC ANALYSIS OF NITRIC ACID–DEGRADED DI-*sec*-BUTYLPHENYLPHOSPHONATE–DIETHYLBENZENE

A. D. Horton

In connection with the Kilorod program, a gas chromatographic method was developed for the analysis of nitric acid–degraded di-*sec*-butylphenylphosphonate (I) (2.5 vol %)–diethylbenzene (II) (97.5 vol %). The degradation products are quantitatively determined but not identified. The concentrations of I, II, and the degradation products of the solution are determined with a Reoplex 400 column[13] (20 wt % on 60/80-mesh Chromosorb W), operated at 206°C and a helium flow of 60 cc/min. The percentages of the isomers of II are measured with a 200-ft-long by 0.01-in.-ID capillary coated with di-*n*-decyl phthalate and operated at 110°C and 30 psig argon pressure. A radium-argon ionization detector is used to monitor the column eluate. Table 2.3 shows the analytical data obtained from the previously mentioned analyses.

Table 2.3. Results of the Gas Chromatographic Analysis of Nitric Acid–Degraded Di-*sec*-butylphenylphosphonate (I) (2.5 vol %)–Diethylbenzene (II) (97.5 vol %)

Sample	Component (vol %)						
	I	II	Isomers of II[a]			Degradation Products	Impurities
			o	*m*	*p*		
1	3.5	95.9	4.4	61.9	26.7	0.6	7.0
2	3.3	96.2	6.3	62.2	25.4	0.5	6.1
3	3.0	97.0				<0.01	<0.01
4	3.0	96.9				0.1	

[a] Manufacturer's specifications (vol %): *o*, 5; *m*, 61; *p*, 26; impurities, 8.

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[13] R. Feinland, J. Sass, and S. A. Buckler, "Determination of Trialkylphosphines and Their Oxidation Products by Gas Liquid Chromatography," *Anal. Chem.* 35, 920 (1963).

To determine the reactions that occur in the degradation, C. A. Blake[14] treated a sample of II with boiling concentrated nitric acid and fractionated the product on an Auto-Prep preparative gas chromatograph. The fraction that contained only II and lower-boiling components was analyzed gas chromatographically. The results (vol %) were: *o*, 13.2; *m*, 56.6; *p*, 28.6; and impurities, 1.6. Compared with the manufacturer's specifications (*o*, 10; *m*, 50; *p*, 36; and impurities, 4), the results indicate a marked degradation of the para isomer of II.

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[14] Chemical Technology Division.

3. Analytical Studies of Molten-Salt Systems

J. C. White

VOLTAMMETRIC STUDIES IN MOLTEN-FLUORIDE SALT SYSTEMS

D. L. Manning

The apparatus designed and fabricated for conducting voltammetric investigations in molten-fluoride salt systems was described previously.[1]

Voltammetry of Iron(II) in Molten LiF-NaF-KF

The voltammetry of Fe^{2+} in molten LiF-NaF-KF (46.5-11.5-42.0 mole %) was studied over the temperature range from 470 to 545°C. Since Fe^{2+} is a corrosion product associated with reactor fuels of the molten-salt type, it is of interest from the standpoint of applying electroanalytical methods to the analysis of molten-salt systems. The current-voltage curves were recorded at a scan rate of 100 mv/min by means of the ORNL model Q-1988 controlled-potential polarograph and a stationary platinum microelectrode coupled with a platinum quasi-reference electrode. A third platinum electrode, which was isolated, was the counter electrode. At the relatively slow scan rate used, the curves were the characteristic S-shape. Two waves exist: an anodic wave – which is believed to correspond to the $Fe^{2+} \rightarrow Fe^{3+}$ oxidation – with a half-wave potential of about +0.1 v, and a cathodic wave with a half-wave potential of about –0.5 v vs the platinum quasi-reference electrode. The latter wave represents the reduction $Fe^{2+} \rightarrow Fe^{0}$. The electrode reactions appear to proceed reversibly under the prevailing conditions. The limiting current (wave height) of the cathodic wave is proportional to the concentration of Fe^{2+} in the melt. An activation energy of about 12 kcal/mole was calculated for the $Fe^{2+} \rightarrow Fe^{0}$ reduction. A paper on this work was published.[2]

Current-Voltage Curves for Zirconium(IV) and Uranium(IV) in Molten LiF-NaF-KF

A cathodic wave for the reduction of Zr^{4+} (as ZrF_4) and an anodic wave for the oxidation of U^{4+} (as UF_4) in molten LiF-NaF-KF (46.5-11.5-42.0 mole %) at 500°C were observed.

The reduction of Zr^{4+} at both platinum and tungsten microelectrodes occurs at a half-wave potential of about –1.4 v vs the platinum quasi-reference electrode. Generally, the waves were better defined at a tungsten indicator electrode. That the Zr^{4+} undergoes a four-electron change

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[1] D. L. Manning, "Analysis of Molten Salts by Electrochemical Methods. Voltammetry of Molten Fluoride Salts," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 25.

[2] D. L. Manning, "Voltammetry of Iron in Molten Lithium Fluoride–Sodium Fluoride–Potassium Fluoride," *J. Electroanal. Chem.* **6**, 227 (1963).

was indicated from reverse scans in which reasonably well defined stripping curves were obtained in all cases. On reverse scans, the current passed through zero at about −1.25 v; however, the stripping curve exhibited no hesitancy in passing through zero current, a fact which suggests that the electrode process is essentially reversible.

For the U^{4+} wave, which has a half-wave potential of about +0.5 v, the slope of a plot of log $[(i_1 - i)/i]$ vs E indicates a one-electron change,[3] which suggests that the oxidation $U^{4+} \rightarrow U^{5+}$ occurs under the prevailing conditions.

In general, the correlation between limiting current (wave height) and concentration of electroactive species was poor. This poor correlation may be due in part to the surface condition of the electrode, as well as to traces of oxide impurities in the melt, which impurities could cause partial precipitation of UO_2 and ZrO_2.

A paper that describes this work was accepted for publication in the *Journal of Electroanalytical Chemistry*.

Rapid-Scan Voltammetry of Iron(II) at a Pyrolytic Graphite Indicator Electrode

In an effort to find more inert electrodes for electrochemical measurements in molten fluorides, a pyrolytic graphite electrode was fabricated and tested. Miller[4] has shown that a pyrolytic graphite electrode prepared from commercially available plates, when properly oriented and sheathed in epoxy resin, presents a strictly impervious surface to aqueous solutions. It should behave in the same way in high-temperature melts if the exposed layered edges of the c planes are electrically insulated. For this purpose, hot-pressed boron nitride was chosen. A typical electrode is shown in Fig. 3.1. The boron nitride insulating sheath (¼-in. diam × 1-in. length) is press-fitted around the graphite with as close tolerances as is possible by machining techniques. With this arrangement, it appears thus far that only the impervious surface of the graphite is exposed to the melt. Yim and Feinleib[5] demonstrated the compatibility of boron nitride with molten fluorides. Boron nitride is a nonconducting material at temperatures used in this study. Laitinen and Rhodes,[6] using a specially prepared pyrolytic graphite electrode, demonstrated its usefulness in molten LiCl-KCl.

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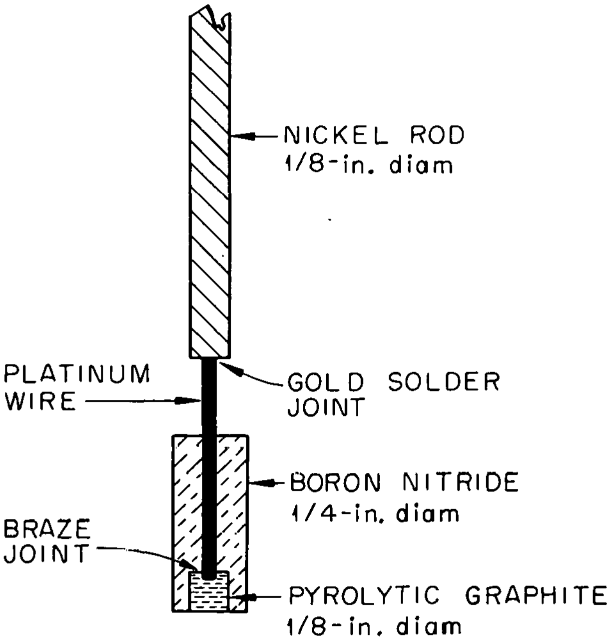

Fig. 3.1. Pyrolytic Graphite Electrode for Molten-Fluoride Environment.

An ORNL model Q-1988 controlled-potential polarograph was modified by D. J. Fisher[7] and H. C. Jones[7] to measure cell currents as large as 5 ma and to provide voltage scan rates as fast as 10 v/min. The advantage of rapid-scan voltammetry as applied to high-temperature melts is that conditions can be achieved whereby the transport process to the electrode is more nearly diffusion-controlled.

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[3] I. M. Kolthoff and J. J. Lingane, *Polarography*, vol 1, pp 205–9, Interscience, New York, 1952.

[4] F. J. Miller and H. E. Zittel, "Fabrication and Use of a Pyrolytic Graphite Electrode for Voltammetry in Aqueous Solutions," *Anal. Chem.* 35, 1866 (1963).

[5] E. W. Yim and M. Feinleib, "Electrical Conductivity of Molten Fluorides," *J. Electrochem. Soc.* 104, 622 (1957).

[6] H. A. Laitinen and D. R. Rhodes, "The Electrochemistry of V_2O_5 in LiCl-KCl Eutectic Melt," *J. Electrochem. Soc.* 109, 413 (1962).

[7] Analytical Instrumentation Group.

The effect of scan rate on the shape of the current-voltage curves for the reduction $Fe^{2+} \rightarrow Fe^0$ was ascertained. In the scan-rate range from 50 to 500 mv/min, the curves are S-shaped. From 500 mv/min to 10 v/min, peak-shaped curves are obtained. The occurrence of the peak is in agreement with the theory for diffusion-controlled processes of continuously changing potential. The relationship between peak current and scan rate at 500°C is given by the equation

$$i_p = 2.29 \times 10^5 (n^{3/2} C A D^{1/2} v^{1/2}) , \qquad (3.1)$$

where i_p is the peak current, n the electron change, C the concentration of electroactive species, A the electrode area, D the diffusion coefficient of the electroactive species, and v the rate of voltage scan. A plot of i_p vs $v^{1/2}$ is a straight line; from the slope of the line, a value of D of $\sim 1 \times 10^{-6}$ cm^2/sec was calculated. This value is believed to be one of the first reported for the diffusion coefficient of Fe^{2+} in molten-fluoride salt systems at 500°C.

An article that describes this work was submitted for publication in the *Journal of Electroanalytical Chemistry*.

Anodic-Stripping Voltammetry

Anodic-stripping voltammetry is a method in which a metal is deposited on an indicator electrode and is then anodically removed under controlled conditions. This technique was studied with Fe^{2+} at a concentration of 265 ppm in molten LiF-NaF-KF (46.5-11.5-42.0 mole %) at 500°C. Preliminary tests showed that this technique may prove valuable for determining trace quantities of metal impurities in molten-salt systems.

By control of such variables as electrode area, potential of the electrode during the plating cycle, plating time, and rate of voltage scan for the dissolution process, the area under the stripping curve is related to the concentration of the metal ion in the melt. The method is at least ten times more sensitive than conventional voltammetry.

Stripping curves for Fe^{2+} were recorded at a pyrolytic graphite electrode encased in boron nitride and also at tungsten, platinum, and silver indicator electrodes. The curves, which are peak-shaped, are generally well defined. The half-peak potential is about −0.5 v vs the platinum quasi-reference electrode.

There was evidence of alloy formation when the iron was deposited on a platinum electrode. For short plating times (~1 min), the deposited iron did not strip off the electrode at −0.5 v but instead was observed at about +0.1 v. For longer plating times, however, the characteristic curve at −0.5 v appeared, and the area under the curve at +0.1 v did not change appreciably with longer plating periods. It appears, therefore, that the first layers of iron that deposit form an alloy with the platinum. Following a probable surface-saturation effect on the electrode, additional iron is then deposited as pure iron. Of the electrodes tested, platinum appears to be the least suitable for determining iron in molten-fluoride salts by anodic-stripping techniques.

Future work will include a study of the electrochemical behavior of nickel, chromium, and other electroactive species likely to be present in molten-salt-type reactor fuels.

In cooperation with the Reactor Chemistry Division, it is planned to test various metal–metal oxide couples and possibly metal–metal halide couples in an effort to develop a true reference electrode for molten-fluoride environments.

SPECTROPHOTOMETRIC STUDIES OF MOLTEN-SALT SYSTEMS

J. P. Young

Spectrophotometric studies of various molten-salt systems were continued. Of interest have been the study of the reactions of active metals, such as uranium, with various molten salts and the application of ligand-field theory to the interpretation of the spectra of the 3*d*-transition-metal ions dissolved in fluoride salts. The absorption spectra of some solutions of alkali metals in molten alkali-metal halides have been determined. The techniques and apparatus used in these studies and some of the recent experimental results were discussed.[8]

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[8] J. P. Young, "Spectrophotometric Studies of Molten Fluoride Salts," presented at the Seventh Annual Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 8–10, 1963.

All-Metal High-Temperature Cell Assembly

The new high-temperature cell assembly (Fig. 3.2) mentioned previously[9] was fabricated from nickel metal and is in use. As originally designed, the assembly was to have coiled-tungsten-wire heaters situated outside the vacuum-tight sample chamber but inside the insulating chamber. The heated portion of the assembly was to be insulated by a vacuum. The coiled tungsten wires were unsatisfactory for long-term service, probably because of embrittlement of the metal during fabrication and installation, and have been replaced by platinum-wire heaters of special design. Because of the change in heaters, it has also been necessary to use fibrous insulation, at atmospheric pressure, around the heated part of the assembly. The new cell assembly has been operated successfully at temperatures as high as 800°C; ~400 w is required to attain this temperature.

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[9] J. P. Young, "Spectrophotometric Studies of Molten-Salt Systems," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, pp 32–36.

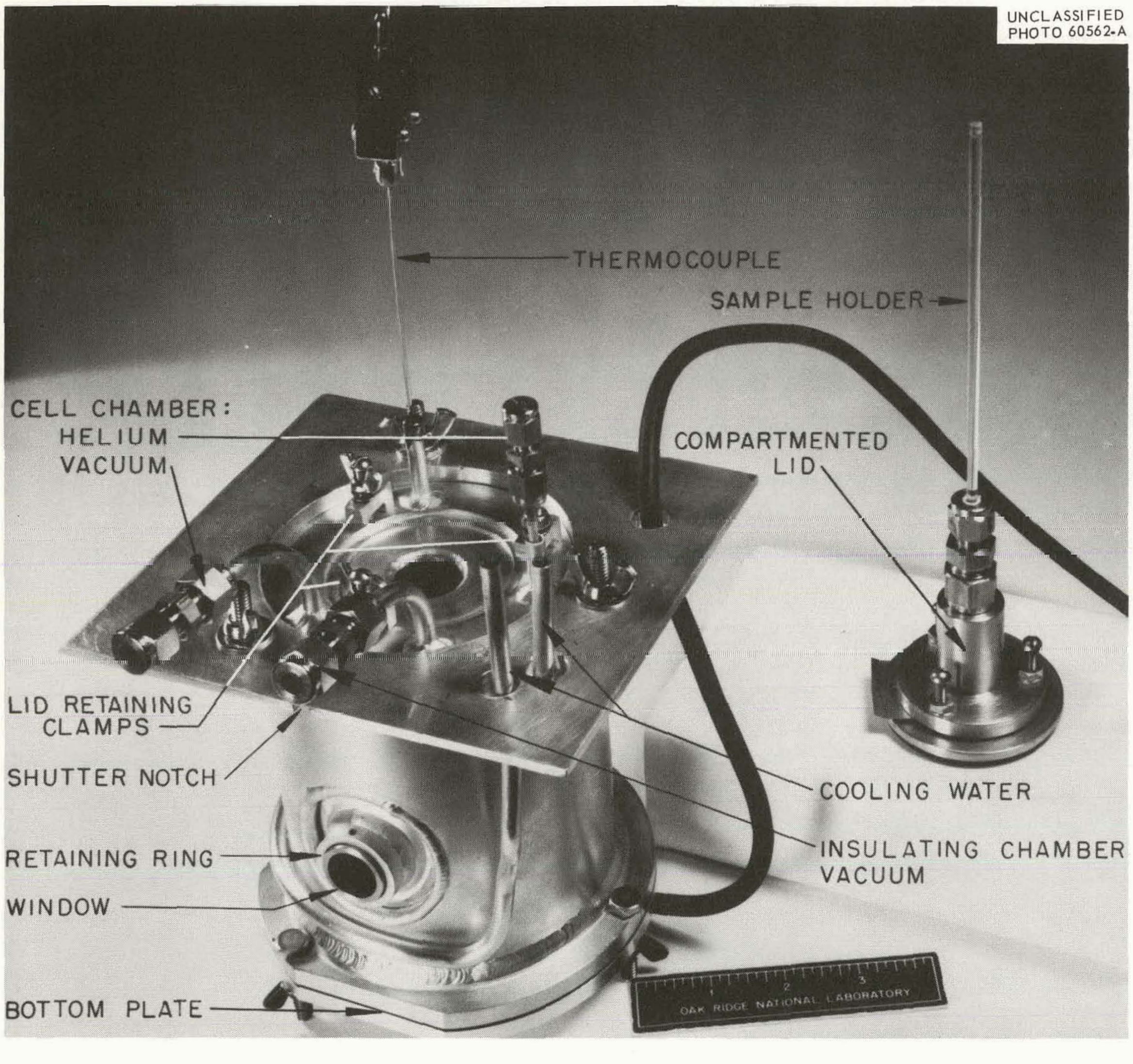

Fig. 3.2. High-Temperature Cell Assembly Made from Nickel.

Captive-Liquid Cells

The initial evaluation of the newly developed captive-liquid cells[9] was completed. The cells were described orally.[10] Also, an article about them was accepted by *Analytical Chemistry*. Such cells, made from platinum, copper, and molybdenum, have been used for confining corrosive liquids for spectral study. From the evaluation of spectra of praseodymium fluoride in LiF-NaF-KF (46.5-11.5-42.0 mole %) at 540°C, a relative standard deviation of 2% was found for the absorbance of the 444-mμ peak of Pr^{3+}. From the absorbance of this peak and the molar absorptivity for Pr^{3+} in LiF-NaF-KF at 540°C,[11] which was obtained from earlier pendent-drop data, the effective path length of molten LiF-NaF-KF at 540°C in a 0.635-cm-OD captive-liquid cell was calculated to be 0.77 cm; the absolute standard deviation was 0.02 cm. In similar cells, aqueous solutions at 25°C have an effective path length of 0.68 cm (absolute standard deviation, 0.02 cm).[9] The effects of density and surface tension on the path lengths of liquids contained in these cells will be determined for other molten-salt systems at various temperatures. It is hoped that the data can be used to establish an empirical relationship among density, surface tension, and path length of any salt system.

Reaction of Uranium and Other Active Metals with Molten LiF-NaF-KF

The reaction of uranium metal with molten LiF-NaF-KF (46.5-11.5-42.0 mole %) to form an unstable solution of U^{3+} has been mentioned, and a preliminary spectrum of U^{3+} in this solvent was shown.[9] This study was continued and extended to include spectrophotometric studies of the reactions of a number of active metals with molten alkali-metal halides. The general equation for these reactions is

$$MX + \frac{1}{n}R^0 \rightarrow \frac{1}{n}RX_n + M^0\uparrow, \qquad (3.2)$$

where MX is an alkali-metal halide, R^0 an active metal, and n the valence of R in RX_n. These reactions proceed by the volatilization of the alkali metals that are formed and by the oxidation of the active metal. The alkali-metal vapors are identified by their characteristic resonance absorption spectra. The systems studied, together with the free energy change (ΔF) per atom of alkali metal produced for the reactions at 1000°K, are summarized in Table 3.1. The ΔF values, extrapolated to 1000°K, were calculated from the free energies of formation given by Glassner[12] for the reactants and products in their proper physical state. The reactions in the fluoride system were studied experimentally at 800°K; those in the chloride system, at 700°K.

In view of the spectrophotometric observation of the reaction of U^0 and UF_3 with LiF-NaF-KF, the following reactions can be written:

$$\tfrac{1}{3}U^0 + MF \rightarrow \tfrac{1}{3}UF_3 + M^0\ , \qquad (3.3)$$

$$UF_3 + MF \rightarrow UF_4 + M^0\ , \qquad (3.3a)$$

$$4UF_3 \rightarrow U^0 + 3UF_4\ . \qquad (3.3b)$$

It has not been possible to determine spectrophotometrically which of the reactions, 3.3*a* or 3.3*b*, occurs; possibly both occur. The overall effect of these reactions, however, is that lower-valent uranium will be oxidized to U^{4+} in molten LiF-NaF-KF under the experimental conditions of this study.

Although U^{3+} is not stable in LiF-NaF-KF, it was possible to obtain its spectrum and, by quenching the melts at appropriate times, to estimate the molar absorptivities of the various absorption peaks. These results are shown in Fig. 3.3. The molar absorptivity of the strongest peak in the near-infrared spectrum is ~40 liters $mole^{-1}$ cm^{-1},

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[10] J. P. Young, "Windowless Spectrophotometric Cell for Use with Corrosive Liquids," presented at the 145th American Chemical Society Meeting, New York, Sept. 8–13, 1963.

[11] J. P. Young and J. C. White, "Absorption Spectra of Molten Fluoride Salts," *Anal. Chem.* 32, 1658 (1960).

[12] A. Glassner, "The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K," ANL-5750 (1957).

Table 3.1. Summary of Studies of the Reduction of Molten Alkali-Metal Halides by Active Metals

Reaction: $MX + \frac{1}{n}R^0 \rightarrow \frac{1}{n}RX_n + M^0\uparrow$

Solvent	R^0	R^{n+} Formed	Source of Observed Resonance Absorption	ΔF per atom of M^0 at 1000°K (kcal)		
				K	Na	Li
LiF-NaF-KF (46.5-11.5-42.0 mole %) at 800°K	Fe	None	*a*	44	47	56
	Cr	Cr^{2+}, Cr^{3+}	*a*	38	41	50
	Zr	Zr^{4+}	K, Na	17	20	29
	U	U^{3+}	K, Na	16	19	28
	(UF_3)	U^{4+}	K, Na	20	23	32
	Mg	Mg^{2+}	K, Na	−3	0	9
	Y	Y^{3+}	K, Na	−2	1	10
	Li	Li^{+}	K, Na	−12	−9	
LiCl-KCl (59-41 mole %) at 700°K	U	None	*a*	30	25	26
	Mg	None	*a*	25	20	21
	Ca	Ca^{2+}	K (Na impurity)	5	0	1

[a] No resonance absorption observed.

whereas that for the strongest peak in the visible region is ~500 liters mole^{-1} cm^{-1}.

A paper in which the results of these studies were discussed was presented.[13]

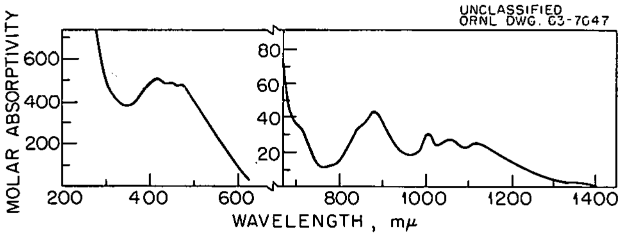

Fig. 3.3. Spectrum of U^{3+} in Molten LiF-NaF-KF (46.5-11.5-42.0 mole %) at 525°C.

Studies of Molten Alkali-Metal–Alkali-Metal-Halide Systems

Alkali metals are generated by the reaction of active metals with LiF-NaF-KF (46.5-11.5-42.0 mole %) and are believed to form colored solutions with their respective molten halides. It was therefore of interest to prepare these solutions and to obtain their spectra in order to determine whether any of the U^{3+} peaks or absorption peaks of other metal ions were, in fact, due to alkali metals. Since molten-fluoride salts are studied spectrophotometrically in windowless containers, Na or K cannot be added directly to the solution because they would immediately distill out of the melt. However, a solution believed to be K and/or Na in LiF-NaF-KF was prepared by reacting an excess of Mg or Y with the solvent at 525°C. Over the wavelength range from 250 mμ to 2 μ, the resultant blue solution exhibits one broad absorption band with maximum at 615 mμ. The resonance

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[13] J. P. Young, "Spectrophotometric Observations of the Reaction of Molten LiF-NaF-KF with Several Active Metals," presented at the 145th American Chemical Society Meeting, New York, Sept. 8–13, 1963.

absorption spectra of Na and K are seen in the gas phase surrounding the solution. Since Li is not as volatile as Na or K, solutions of Li in LiF-NaF-KF can be made by direct additions of this metal to the melt. However, the ΔF values given in Table 3.1 indicate that Li is unstable in such a system and is therefore oxidized by the other alkali-metal halides. A blue solution, which has a spectrum similar to that obtained from the reaction of Mg or Y with the melt, again results.

It is also possible to prepare solutions of Li in molten LiCl. Such solutions are very corrosive and react with transparent materials used for spectrophotometric cells, but are inert to molybdenum metal. A spectral study of Li in LiCl was made at 650°C, the sample being held in a molybdenum captive-liquid cell. Although lithium metal distills out of the solution at this temperature, it was possible to obtain spectra. The Li-LiCl solutions were magenta and exhibited a single broad absorption with a maximum at 550 mμ. A note pertaining to this study was accepted by the *Journal of Physical Chemistry.*

Further absorption spectral studies of molten alkali-metal–alkali-metal-halide systems are planned. In collaboration with persons in the Chemistry Division, a sealed crystalline Al_2O_3 cell is being designed. This cell should be useful for the spectrophotometric study of alkali-metal–alkali-metal-halide solutions except those that contain Li or fluoride. If the cell proves satisfactory, a similar cell will be fabricated from crystalline MgO for use with the fluoride systems.

Coordination of Dissolved Ionic Species in Fluoride Melts

Although the application of ligand-field theory to the interpretation of absorption spectra is not specifically a problem in analytical chemistry, the results of such considerations are of definite value in both a physical and an analytical sense. In attempts to identify new or unstable valence states of transition-metal ions by absorption spectroscopy, reasonable estimates of both position and intensity of expected absorption peaks can be made. Likewise, the interpretation of spectra of transition-metal ions of known valence states yields information about the coordination of these ions in melts of interest and thereby provides an insight into their behavior in solution.

The spectrum of Ni^{2+} (as NiF_2) in LiF-NaF-KF (46.5-11.5-42.0 mole %) at 525°C was studied in detail over the concentration range from 0.2 to 1.0 w/w % Ni^{2+}. Table 3.2 gives the results of this study.

The peak at 1550 mμ is broad and very weak; it permits only an approximation of its absorption maximum and the molar absorptivity. The peak at 540 mμ is a weak shoulder on the side of the strong peak at 434 mμ. The probable assignment of this shoulder is that of a spin-forbidden transition, as shown in Table 3.2. A fit of the experimental transition energies to theoretical energy levels is very satisfactory for an octahedral configuration of Ni^{2+} which, in the melt, has a cubic ligand-field parameter (D_q) of –650 cm^{-1} and

Table 3.2. Absorption Spectral Data for NiF_2 in LiF-NaF-KF (46.5-11.5-42.0 mole %) at 525°C

Wavelength of Absorption Peaks		Molar Absorptivity	Transition
(mμ)	(cm^{-1})	(liters mole^{-1} cm^{-1})	
434	23,000	12	$^3A_{2g}(F) \rightarrow {^3T_{1g}}(P)$
~540	~18,500		$^3A_{2g}(F) \rightarrow {^1T_{2g}}(D)$
910	11,100	2.0	$^3A_{2g}(F) \rightarrow {^3T_{1g}}(F)$
~1550	~6,500	~0.8	$^3A_{2g}(F) \rightarrow {^3T_{2g}}(F)$

Racah's interelectronic repulsion parameter (*B*) of 950 cm^{-1}. Work of this nature has not been undertaken previously in molten-fluoride salts. This study of Ni^{2+} was done jointly with G. P. Smith,[14] who made the calculations. A paper on the subject was accepted by the *Journal of Chemical Physics*.

Spectral absorption data are now being obtained for Fe^{2+}, Cr^{2+}, and Cr^{3+} in molten LiF-NaF-KF and will be obtained in molten LiF-BeF_2-ZrF_4 for interpretation. Iron(II) in LiF-NaF-KF exhibits a strong peak at 970 mμ with a molar absorptivity of ~4.0 at 525°C; there is also some evidence of a very weak peak at 1900 mμ. A preliminary interpretation of this spectrum is that most of the Fe^{2+} is octahedrally coordinated in the alkali-fluoride eutectic, but the existence of the peak at 1900 mμ indicates that a small fraction of the Fe^{2+} is tetrahedrally coordinated. Work on this problem will continue.

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[14] Metals and Ceramics Division.

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4. Special Research Problems

J. C. White
P. F. Thomason

PYROLYTIC GRAPHITE ELECTRODE

F. J. Miller

Possibilities for the use of the pyrolytic graphite electrode in various phases of electroanalytical chemistry have been investigated and are discussed below.

Potentiometry

A pyrolytic graphite electrode was furnished to Anne A. Terry[1] and P. F. Thomason to be evaluated as an indicator electrode for the potentiometric titration of Tc^{7+} with Cr^{2+}. Their work indicates that the electrode is superior to a noble-metal electrode for this application.

A pyrolytic graphite electrode was supplied to the General Analysis Group for use in the potentiometric titration of U^{4+} with Ce^{4+}. The suitability of the electrode for this purpose has not yet been determined.

Voltammetry

The initial article on the fabrication of the pyrolytic graphite electrode and its use in aqueous voltammetry has been published.[2]

The difficulty of voltammetry in the anodic region with a platinum electrode prompted the study of the pyrolytic graphite electrode in this region. The voltammetry of Ce^{4+}, Mn^{7+}, Cr^{6+}, and V^{5+} was studied. The $E_{1/2}$'s of these ions range from +1.15 to +0.44 v vs the S.C.E. The $Ce^{4+} \rightarrow Ce^{3+}$ reaction at the pyrolytic graphite electrode is reversible. The electrode was not damaged after protracted use at the high positive potential necessary to the $Ce^{4+} \rightarrow Ce^{3+}$ reduction. The working range of the electrode can be extended to +1.8 v vs the S.C.E. in sulfuric acid solution. Voltammetry of Mn^{7+} was successful only insofar as delineating the salient features of the reduction wave. Only with a new or thoroughly cleaned electrode is an excellent wave obtained. Repetitive results could not be obtained, presumably because of the formation of

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[1] Research participant from Texas Woman's University, Denton.

[2] F. J. Miller and H. E. Zittel, "Fabrication and Use of the Pyrolytic Graphite Electrode in Aqueous Voltammetry," *Anal. Chem.* **35**, 1866 (1963).

MnO_2 and its subsequent adsorption on the electrode. The voltammetric determinations of V^{5+} and Cr^{6+} were not successful.

An article that describes these voltammetric studies in the anodic region has been accepted by the *Journal of Electroanalytical Chemistry.*

Amperometry

The pyrolytic graphite electrode may be most useful as an indicator electrode in amperometric titrations. To demonstrate this possibility, various amperometric studies were made.

The determination of U^{4+} in nuclear fuels is of interest. A study has shown that U^{4+}, in phosphoric acid solution, can be determined by amperometric titration with a sulfuric acid solution of Ce^{4+}. Over the U^{4+} concentration range from 0.05 to 11 μg/ml, the maximum relative error of the method is ±1.12%. Applied potentials in the range from +1.0 to 0.0 v vs the S.C.E. can be used; the more positive potentials are preferred. The electrode shows no damage as a result of repeated usage with Ce^{4+} solutions in a region of high positive potential. It is not necessary to treat the electrode prior to or during a series of titrations.

The results of the study are given in an article accepted for publication in *Analytical Chemistry.*

In a similar manner, Fe^{2+} was titrated with Ce^{4+}. The precision and accuracy of a series of titrations are comparable with those obtained in the titrations of U^{4+}. Solutions that were 2×10^{-6} *M* in Fe^{2+} were titrated successfully. A report on this work is being written.

At ORNL, the determination of low concentrations of Cl^- is a recurring problem. The amperometric method is significantly more sensitive than the potentiometric titration and equally precise. The amperometric method consists in titrating with Ag^+ the solution of Cl^- in 50 v/v % ethyl alcohol; an ice bath is used. The end point is ascertained by monitoring the diffusion current of the Ag^+ as it appears in solution. Further experiments will be made to determine the sensitivity of the pyrolytic graphite electrode for amperometric titrations.

Coulometry

Coulometry is of great value, especially in the analysis of radioactive substances. Its success is due to excellent instrumentation, which makes possible the precise control of electrode potential, and to the large electrode area that is provided by a stirred mercury electrode. The solid pyrolytic electrode cannot compete with the mercury electrode from the standpoint of area. A large electrode area is essential for driving an electrode reaction very nearly to completion within a reasonable time. A different technique is therefore needed for coulometry with a solid electrode. Accordingly, a rotating-disk, pyrolytic graphite electrode was constructed and is being used. This electrode is much more sensitive than the stationary electrode. However, the current obtained is still too small to effect completion of the electrode reaction. The time required would be so long that the value of the procedure would be doubtful.

The following method of McNevin and Baker[3] can be used. The current i generated during the time t of electrolysis is recorded, log i vs t is plotted, and the total coulombs required for the complete reaction is calculated from the log i intercept at $t = 0$ and from the slope of the line. The electrolysis need be run only until the slope of the line becomes constant. This method depends on the i-vs-t curve following an exponential function. If the curve is strictly exponential, the total coulombs required for the reaction can also be determined by using standard curve-fitting techniques to obtain the parameters of the equation and then calculating the area under the curve.

The coulometry of Ce^{4+} is being investigated to determine the usefulness of this method. The high-sensitivity coulometric titrator was modified according to directions given by H. C. Jones[4] to record an i-vs-t curve. Mathematical analysis of a curve for the reduction of Ce^{4+} (a solution 1.088×10^{-2} *M* in Ce^{4+} and 1 *M* in H_2SO_4) at an electrode rotated at 1800 rpm shows that the curve can be fitted to an equation of the form

$$i = ae^{-nt} \, , \tag{4.1}$$

where a and n are appropriate constants. In the particular case, the equation becomes

$$i = 3.537e^{-0.00017t} \, . \tag{4.2}$$

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[3] W. M. MacNevin and B. B. Baker, "Primary Coulometric Determination of Iron(II) and Arsenic(III)," *Anal. Chem.* **24**, 986 (1952).

[4] Analytical Instrumentation Group.

The equation fits the curve very well except for a small wedge-shaped portion at the start of the electrolysis. The area under the curve is calculated from the equation

$$A = a/n\,. \tag{4.3}$$

The area may then be divided by the faraday to obtain the chemical equivalent.

In the particular case chosen, the milliequivalent calculated from the equation of the curve was 0.2144. Calculations made by plotting log i vs t, graphically determining i, and then substituting i in the equation

$$A = i/(2.303k)\,, \tag{4.4}$$

where k is the slope of the line, gave the result 0.213 meq. The known amount determined by taking a fixed volume of a standardized solution was 0.217 meq.

This study is being continued to determine the significance of the wedge-shaped portion of the curve, precision, accuracy, sensitivity, and minimum time required for electrolysis.

Miscellaneous Uses

Assistance was given to D. L. Manning in devising a pyrolytic graphite electrode for use in molten-salt voltammetry. Although a pyrolytic graphite electrode had been used by Laitinen[5] in molten salts, the design of his electrode did not provide constant area and would necessitate tedious measurements to determine the depth of immersion and the consequent working area. The electrode designed and being used by Manning is planar and therefore has constant area.

A rotating-disk electrode of pyrolytic graphite was supplied to J. M. Dale for use in anodic-stripping voltammetry.

ROTATING PYROLYTIC GRAPHITE ELECTRODE

J. M. Dale

A pyrolytic graphite electrode that can be rotated in an electrolytic cell was fabricated. The characteristics of the electrode in aqueous solution are being determined preliminary to the possible use of such a rotating electrode in molten salts.

To determine the suitability of the electrode for coulometric titrations, separate solutions of Ag^+ and Fe^{3+} were studied qualitatively with the high-sensitivity coulometric titrator. Silver was plated in a reasonable length of time, whereas the reduction of Fe^{3+} was very slow. When the polarity of the electrode was reversed, silver stripped off; however, the stripping was quantitative only at the lower range of usability of the instrument. It was therefore decided to use the controlled-potential polarograph to study the characteristics of the electrode. Plating and stripping cycles were made with 10 ml of $\sim 10^{-5}$ M solutions of Ag^+ in 0.1 M $HClO_4$. The silver was plated during a 20-sec voltage sweep from +0.7 to −0.3 v vs the S.C.E. The voltage scan was reversed immediately, and the silver was stripped off. From the area under the stripping curve, the amount of silver involved was estimated to be ~ 0.3 μg (i.e., < 0.01 μeq). The peak current was about 70 μa. The stripping peak current for the rotating electrode was about eight or nine times greater than that observed for a still solution. Also, sufficient silver was plated in 3 or 4 min from a 10^{-7} M solution of Ag^+ to give a well-defined stripping curve.

The anodic wave of Fe^{2+} was studied; the test solution was 2×10^{-5} M Fe^{2+} in 1 M H_2SO_4–1 M H_3PO_4. At a scan rate of 0.3 v/min, the peak current was ~ 225 μa.

Because of the relatively large currents involved and the time of electrolysis, an appreciable amount of the ions present was being reduced or oxidized at the electrode. For this reason a new cell was designed to make possible the use of a total volume of 100 ml.

The reduction of Fe^{3+} in 1 M KCl–0.1 M HCl was the first studied with this new cell. The cathodic wave began at about +0.3 v vs the S.C.E.; however, the limiting current was still increasing slightly at −0.5 v. The most nearly

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[5] H. A. Laitinen and D. R. Rhodes, "The Electrochemistry of V_2O_5 in LiCl-KCl Eutectic Melt," *J. Electrochem.* **109**, 413 (1962).

linear relation between concentration and limiting current was obtained at −0.5 v. The waves were very reproducible but were long and drawn out. The ratio of the limiting current to concentration was constant for the three voltage scan rates used (0.5, 1, and 3 v/min).

Table 4.1 gives the results for the reduction of Ag^+ in 1 *M* KNO_3 for a total volume of 100 ml at a scan rate of 0.3 v/min. The ratios of limiting current i_l to concentration C^0 shown are the averages of several runs on the same solution. Because the ratio i_l/C^0 was about 10% higher for the above conditions than that obtained for a 10-ml cell using 0.1 *M* HNO_3 as a supporting electrolyte, it was of interest to study the $Ag^+ \rightarrow Ag^0$ reduction in 1 *M* KNO_3 with the 10-ml cell. In this case each reduction was made on a separate aliquot, and the precision was determined at three concentrations (Table 4.1).

Graphic integration of the term it, where i is the current at any time t, showed that, at each concentration, 4.4% of the total amount of silver present in the 10-ml samples was reduced up to the potential at which the limiting current was read. However, the limiting current did not decrease as the scan continued to more negative potentials, which might be expected if the bulk concentration of the solution were changing. Also, if the total amount of Ag^+ present in the cell were a controlling factor, then the ratio i_l/C^0 should be larger for the 100-ml sample than for the 10-ml sample. That this is not the case is evident from Table 4.1. However, there may be a cancellation of effects between the total amount of Ag^+ present and the movement of the solution in each case. The reason for the differences between the two sets of $E_{1/2}$'s is also not immediately apparent.

The theoretical expression for the limiting current at a rotating-disk electrode is given by the equation

$$i_l = nFAC^0 \frac{D^{2/3}\omega^{1/2}}{1.62\nu^{1/6}}, \qquad (4.5)$$

where ω is the angular velocity of the electrode and ν is the kinematic viscosity of the solution. The kinematic viscosity was obtained from handbook values of the absolute viscosity and density of a 1 *M* KNO_3 solution. From the results in Table 4.1, the diffusion coefficient for Ag^+ was calculated to be 1.37×10^{-5} cm²/sec. This value

Table 4.1. Reduction of Ag^+ in 1 *M* KNO_3 at a Rotating Pyrolytic Graphite Electrode

Instrument: ORNL model Q-1988A controlled-potential polarograph
with rapid-scan circuitry
Electrode area: 1.16 cm²
Rotation: 1800 rpm
Scan rate: 0.3 v/min

Ag^+ Concentration (*M*)	100-ml Cell		10-ml Cell		
	$E_{1/2}$ (v vs the S.C.E.)	i_l/C^0 (μa μmole^{-1} liter)	$E_{1/2}$ (v vs the S.C.E.)	i_l/C^0 (μa μmole^{-1} liter)	Relative Standard Deviation (%)
$\times 10^{-5}$					
2.02	0.17	1.19	0.04	1.22	1.50
4.04	0.20	1.17	0.08	1.22	
6.06	0.21	1.17	0.14	1.21	0.61
8.08	0.21	1.15	0.16	1.21	
10.10	0.21	1.16	0.18	1.21	0.98

Table 4.2. Comparison of the Reduction of Ag^+ at a Stationary and a Rotating Pyrolytic Graphite Electrode

Instrument: ORNL model Q-1988A controlled-potential polarograph
with rapid-scan circuitry
Electrode area: 1.16 cm^2
Solution volume: 10 ml
Supporting electrolyte: 1 *M* KNO_3
Scan rate: as shown

Ag^+ Concentration (*M*)	i_p/C^0 for Stationary Electrode (μa μmole^{-1} liter)			i_l/C^0 for Rotating Electrode[a] (μa μmole^{-1} liter)
	3 v/min	1.5 v/min	0.3 v/min	0.3 v/min
$\times 10^{-5}$				
4.04	0.38	0.27	0.13	1.22
6.06	0.33	0.23	0.10	1.21
8.08	0.31	0.22	0.10	1.21
10.10	0.27	0.20	0.09	1.21

[a] Electrode rotating at 1800 rpm.

compares favorably with the value 1.65×10^{-5} cm^2/sec for Ag^+ at infinite dilution.[6]

From the expression

$$\delta = \frac{1.62 D^{1/3} \nu^{1/6}}{\omega^{1/2}} \qquad (4.6)$$

the thickness of the diffusion layer was calculated to be 0.013 mm.

It was of interest to compare the current-potential characteristics of Ag^+ in still solutions with those in stirred solutions. Data were obtained under the conditions defined above except that the electrode was not rotated. The current-potential curves from still solutions exhibited the expected peak shape, whereas those for the stirred solution were S-shaped.

The theoretical expression for the peak current at 25°C for the reversible deposition of an insoluble substance in still solution is

$$i_p = 3.67 \times 10^5 \left(n^{3/2} A C^0 D^{1/2} v^{1/2}\right) , \qquad (4.7)$$

where v is the voltage scan rate. The ratios of i_p to C^0 are given in Table 4.2 for different concentrations of Ag^+. The ratios for the rotating electrode are also given for comparison.

Table 4.3. $i_p/v^{1/2}$ Values for the Reduction of Ag^+ at a Pyrolytic Graphite Electrode in Still Solution

Instrument: ORNL model Q-1988A controlled-potential polarograph with rapid-scan circuitry
Electrode area: 1.16 cm^2
Solution volume: 10 ml
Supporting electrolyte: 1 *M* KNO_3
Scan rate: as shown

Ag^+ Concentration (*M*)	$i_p/v^{1/2}$ [μa/(v/min)$^{1/2}$]		
	3 v/min	1.5 v/min	0.3 v/min
$\times 10^{-5}$			
4.04	9.4	9.0	8.9
6.06	11.2	11.2	11.5
8.08	14.3	14.8	14.5
10.10	16.8	16.1	15.9

Equation (4.7) also shows that at constant concentration the ratio $i_p/v^{1/2}$ should be constant. These results are given in Table 4.3.

The average diffusion coefficient obtained from Eq. (4.7) for still solutions is 1.19×10^{-5} cm^2/sec as compared with 1.37×10^{-5} cm^2/sec obtained from Eq. (4.5) for the rotating-disk electrode.

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[6] I. M. Kolthoff and J. J. Lingane, *Polarography*, 2d ed., vol 1, p 411, Interscience, New York, 1952.

POLAROGRAPHY IN HYDROFLUORIC ACID AND OTHER GLASS-CORRODING MEDIA

Helen P. Raaen

Polarography with the horizontal-orifice Teflon D.M.E.[7] was continued. From experimentation, the electrode is shown to be perfectly satisfactory for obtaining all qualitative and quantitative polarographic data one might wish to take. Data obtained with it for redox systems in glass-corroding media can be compared directly with data taken by means of a glass D.M.E. for systems in media that do not corrode glass. A Smoler type vertical-orifice Teflon D.M.E. was fabricated and its evaluation begun. This recent work is discussed below.

Evaluation of the Teflon D.M.E. for Use in Obtaining Fundamental Polarographic Data

It is essential to know how polarographic data taken with the Teflon D.M.E. in glass-corroding media are related to such data obtained with a glass D.M.E. in media that do not corrode glass. To determine this relation, polarographic data were taken with a Teflon D.M.E. for the $Tl^+ \rightarrow Tl^0$ and the $Pb^{2+} \rightarrow Pb^0$ reductions, which are references in polarographic work. A D.M.E. having a 72-μ-diam Teflon segment and a 70-μ-diam glass segment was used. The diameter of the Teflon D.M.E. is typical of Sargent 2–5 sec polarographic capillaries. The reference electrode was an S.C.E. connected to the test solution through a KCl solution and an NaF–agar-agar bridge. The Q-1988A polarograph was used in its three-electrode function, the third electrode being graphite ($\frac{1}{16}$-in.-diam drawing lead). Platinum contacts were eliminated from the system to avoid the catalytic effect of platinum in acid solution.

The studies included the following: determining drop time t vs $E_{d.e.}$ curves (equivalent to electrocapillary curves) for the supporting electrolytes; recording regular, average-currents, and first-derivative polarograms for the supporting electrolytes and for solutions of the reducible ions in concentrations C ranging from 2×10^{-5} to 1×10^{-3} M; determining the relation between C and wave height and between C and derivative peak height; establishing the electron change n for the reduction and the half-wave potential $E_{1/2}$ at which it occurs; ascertaining diffusion control of the wave height and peak height by determining whether the ratios $i_d/h^{1/2}$ and peak height/$h^{1/2}$ (where h is mercury pressure) are constant; calculating the diffusion coefficient D of the reducible ion from the Ilkovič equation by means of measurements of i_d, n, C, m (rate of flow of mercury) at $E_{1/2}$, and t at $E_{1/2}$; and checking the reversibility of the reaction by plotting $\log [(i/(i_d - i)]$ vs $E_{d.e.}$ and by calculating the slope of the plot. Also, the precision of the recording of polarograms was measured.

The $Pb^{2+} \rightarrow Pb^0$ Reduction. – The $Pb^{2+} \rightarrow Pb^0$ reduction was studied with $PbCl_2$ in 1 M HCl in the absence of a maximum suppressor.

The results were as follows. The t-vs-$E_{d.e.}$ plots and the regular, average-currents, and first-derivative polarograms were of the same form as those obtained with a glass D.M.E. The precision of the polarograms was comparable with that obtained with a glass D.M.E. Both the C vs wave height and the C vs peak height relations were linear, and curves obtained as a result of the rectilinear plots of the data both passed through the origin. From measurements of peak width at half-peak height, the n for the $Pb^{2+} \rightarrow Pb$ reduction was determined to be 2 (1.98, the average of 12 measurements). The $E_{1/2}$ at 25.0°C was -0.457 v vs the S.C.E.; values reported in the literature for Pb^{2+} in 1 M HCl and presumably taken under a variety of conditions include -0.435, -0.44 (0.01% gelatin present), and -0.49. The ratios $i_d/h^{1/2}$ and peak height/$h^{1/2}$ were constant over a range of h values, thus indicating diffusion control of the wave height and peak height. By means of the instrumentation for the automatic measurement of m and t, it was possible to determine these values at $E_{1/2}$ and thereby to calculate that D for Pb^{2+} in 1 M HCl at ~25°C is 1.27×10^{-5} cm^2/sec. The D value calculated from the equivalent conductance of Pb^{2+} in aqueous solution at infinite dilution and 25°C is reported to be 0.98×10^{-5} cm^2/sec.[8] The data gave a linear plot of $\log [i/(i_d - i)]$ vs $E_{d.e.}$ with a slope of 0.034,

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[7] Helen P. Raaen, "Teflon Dropping Mercury Electrode for Polarography in Hydrofluoric Acid and Other Glass-Corroding Media," *Anal. Chem.* **34**, 1714 (1962).

[8] I. M. Kolthoff and J. J. Lingane, *Polarography*, 2d ed., vol 1, p 52, Interscience, New York, 1952.

which is consistent with the facts that the reaction is reversible and the theoretical value of the slope is 0.0295.

For a glass D.M.E., it is known that as the voltage scan rate is decreased, the $E_{1/2}$ value becomes more positive and the accuracy of the n value, calculated from the width of the first-derivative peak at half-peak height, increases. These effects of scan rate are the same with the Teflon D.M.E.

The $Tl^+ \rightarrow Tl^0$ Reduction. – The $Tl^+ \rightarrow Tl^0$ reduction was studied both with TlCl in 0.1 *M* KCl–1 × 10^{-3} *M* HCl and with $TlNO_3$ in 1 *M* HCl.

As for the $Pb^{2+} \rightarrow Pb^0$ reduction, so for the $Tl^+ \rightarrow Tl^0$ reduction in 0.1 *M* KCl–1 × 10^{-3} *M* HCl, the fundamental polarographic data and relations determined with the Teflon D.M.E. were consistent with the known polarographic characteristics of the reduction. The $E_{1/2}$ at 25.0°C was about −0.458 v vs the S.C.E.; a value of −0.460 for Tl^+ in 0.1 *M* KCl and in 0.1 *M* HCl is reported in the literature. The n value calculated from the first-derivative peak was 1. The slope of the plot of log $[i/(i_d - i)]$ was 0.0574 compared with the theoretical value 0.0591 for a one-electron reduction. The value for D calculated from the polarograph data was 2.40×10^{-5} cm^2/sec; the D value calculated from the equivalent conductance of Tl^+ in aqueous solution at infinite dilution and 25°C is reported to be 2.00×10^{-5} cm^2/sec.[8]

On the other hand, the study of the $Tl^+ \rightarrow Tl^0$ reduction with $TlNO_3$ in 1 *M* HCl indicated that the thallium was possibly present in more than one valence state. Because of the low solubility of Tl^+ in 1 *M* HCl, the solution had been prepared by mechanical stirring overnight and became warm. It is likely that some of the Tl^+ was oxidized. The C vs peak height relation was not entirely linear. The n value calculated from widths of first-derivative peaks at half-peak height was greater than 1; the derivative polarograms showed evidence of two peaks.

Because of the excellence of the results obtained in the evaluation of the Teflon D.M.E. with the $Pb^{2+} \rightarrow Pb^0$ and $Tl^+ \rightarrow Tl^0$ reductions, no other reference reductions will be studied. Articles describing this work will be prepared for publication in the open literature.

Vertical-Orifice, Rapid Teflon D.M.E.

A Smoler type vertical-orifice glass D.M.E., which is a rapidly dropping D.M.E., is being studied by W. L. Belew.[9] It has the considerable advantage that polarographic data can be taken with it very quickly. Also, it behaves reproducibly, and the polarograms obtained show no maximum of the second kind.

It was decided to determine whether a similar capillary could be made of Teflon. If so, it would thereby be possible to rapidly take polarographic data in hydrofluoric acid and other glass-corroding media, a possibility much desired in view of the large amount of work that is to be done with the Teflon D.M.E. Such a Teflon capillary (Fig. 4.1) was made by the ORNL Fabrication Shops, without particular attention being given to refinement of technique and perfection of geometry of the orifice; the orifice was slightly oval (270 × 300 μ). When this capillary was used with a 100-μ-diam glass controlling capillary, a drop time as short as 0.3 sec was achieved.

On the basis of the performance of this first vertical-orifice Teflon capillary, the supplementary circuitry necessary to the use of a rapidly dropping D.M.E. was built into the Q-1988A polarograph. Members of the Analytical Instrumentation Group advised regarding this work (see "Modification of the ORNL Model Q-1988A Controlled-Potential, Derivative Polarograph for use with a Rapidly Dropping Mercury Electrode," in Chap. 1 of this report). A 0.5-sec quadruple, parallel-T, RC filter was added to average the current oscillations for D.M.E.'s of 0.5-sec maximum drop time. Resistors were added to the scan-integrator circuit to provide additional scan rates of 0.3, 1.5, and 3 v/min. Also, circuitry was added to make possible the recording of the output on an X-Y recorder, with the possibility of recording on a Brown recorder being retained. With the X-Y recorder, data can be taken more rapidly, and polarograms obtained under different conditions (different scan rates are of particular interest) can be superimposed on the same scale. An Electro Instruments, Inc., model 500 X-Y recorder was purchased and modified slightly as required for use with the Q-1988A

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[9] W. L. Belew, D. J. Fisher, and M. T. Kelley, "Vertical-Orifice Capillaries" and "Controlled-Potential DC Polarography with a Rapidly Dropping Mercury Electrode," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3397, pp 12–14.

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ORNL-DWG. 63-7648

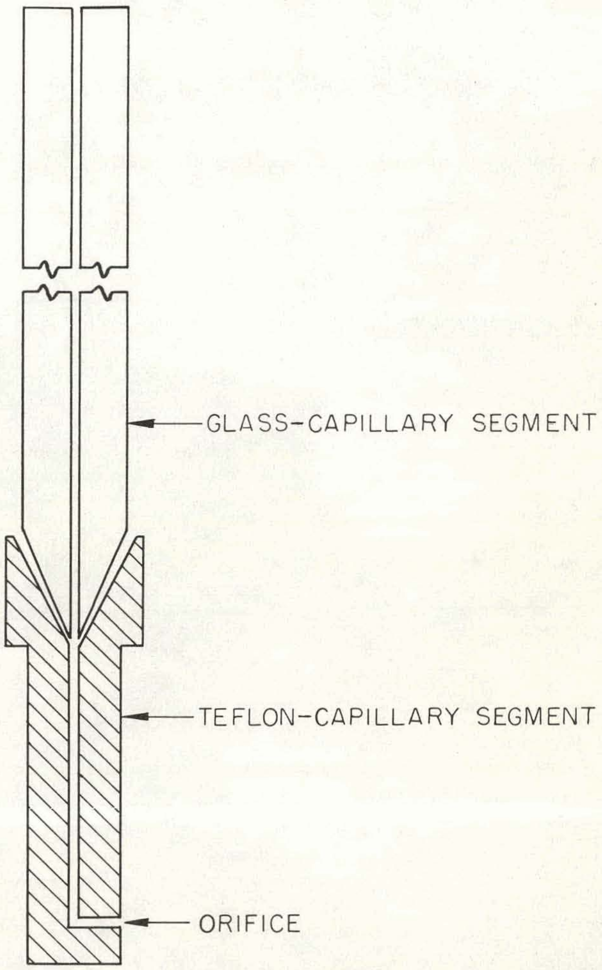

Fig. 4.1. Diagram of a Vertical-Orifice Teflon D.M.E. Capillary.

polarograph. The supplementary circuits and the recorder were checked out by H. C. Jones and W. L. Belew.[10]

Three additional vertical-orifice Teflon capillaries were subsequently made by the ORNL Fabrication Shops. The first received (116 × 134 μ orifice), together with a 100-μ-diam glass controlling capillary, was evaluated with 1×10^{-3} *M* $PbCl_2$ in 1 *M* HCl. The polarograms showed evidence of maxima of the second kind, possibly as a result of the very fast flow rate (*m* as great as 15 mg/sec), which might indicate that at sufficiently large *m*, maxima of the second kind can exist even with a vertical-orifice capillary. The polarograms obtained with the capillary were otherwise typical.

One of the three capillaries has a round, 115-μ-diam orifice (Fig. 4.2) of good geometry. It will be used in future work, together with a glass controlling capillary of smaller diameter to provide a slower flow rate.

As anticipated, it is possible to obtain polarographic data very rapidly with a vertical-orifice Teflon capillary. This work will be continued to perfect the capillary and to establish the optimum conditions for its use.

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[10] Analytical Instrumentation Group.

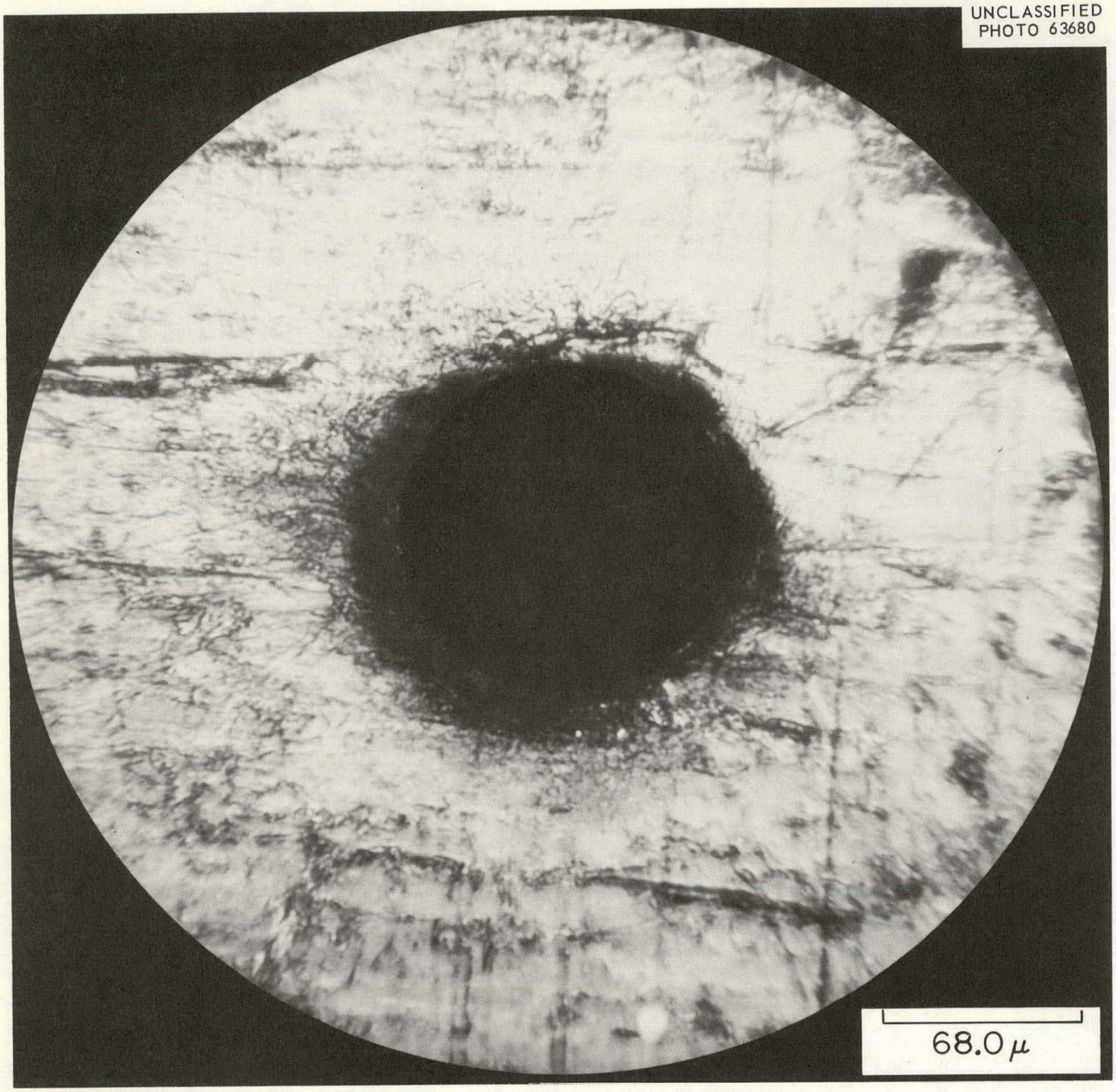

Fig. 4.2. Photomicrograph of Orifice of a Vertical-Orifice Teflon D.M.E. Capillary.

Comparison of a Pyrolytic Graphite Electrode and a Teflon D.M.E.

It is of interest to compare the performance of a pyrolytic graphite electrode and a Teflon D.M.E. for polarography in hydrofluoric acid and other glass-corroding media. For this purpose, the Y-12 Plastics Shop was requested to fabricate two pyrolytic graphite electrodes. These were received but have not yet been used.

ABSORPTION SPECTROPHOTOMETRIC STUDIES OF PLUTONIUM(IV) IN AQUEOUS NITRATE MEDIA[11]

D. A. Costanzo R. E. Biggers

The analysis of data from the absorption spectrophotometric studies discussed previously[12] was continued. Some objectives were to determine the kinetics of the polymerization of Pu(IV), the kinetics of the depolymerization of polymeric Pu(IV), and the properties of Pu(IV) polymer in solution under representative conditions of acidity, temperature, and ion concentrations encountered in fuel processing.

A CF memorandum on this work, issued earlier, was reissued[13] for external distribution. Preliminary data analyses by nonexact approximation methods were summarized in a report.[14] The complexity of the mathematical procedures and computations required for a meaningful and exact analysis of data from such reactive multicomponent systems necessitated the development of digital computation methods.

The data from the polymerization, disproportionation, and depolymerization experiments are being analyzed exactly by the computer methods developed for the analysis of spectrophotometric data from dynamic multicomponent systems (see "Computer Program for the Analysis of Spectrophotometric Absorption Data from Multicomponent Systems," this chapter). An article on this work is being submitted for publication in the *Journal of Inorganic and Nuclear Chemistry*.

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[11] In collaboration with the Chemical Technology Division.

[12] D. A. Costanzo and R. E. Biggers, "Absorption Spectrophotometric Studies of Plutonium(IV) in Aqueous Nitrate Media," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, pp 26–27.

[13] R. E. Biggers and D. A. Costanzo, *Hazards and Experimental Evaluation for: Studies on the Polymerization and Hydrolysis of Plutonium in Uranyl Nitrate Acid Solutions at Elevated Temperatures*, ORNL-TM-580 (May 22, 1963).

[14] D. A. Costanzo and R. E. Biggers, *A Study of the Polymerization, Depolymerization and Precipitation of Tetravalent Plutonium as Functions of Temperature and Acidity by Spectrophotometric Methods: Preliminary Report*, ORNL-TM-585 (July 1, 1963).

COMPUTER PROGRAM FOR THE ANALYSIS OF SPECTROPHOTOMETRIC ABSORPTION DATA FROM DYNAMIC MULTICOMPONENT SYSTEMS

R. E. Biggers D. A. Costanzo

Spectrophotometric study of the reaction kinetics of complex multicomponent systems has prompted the development of methods for the analysis of data from such systems. The complexity of the mathematical procedures for obtaining an exact and statistically meaningful analysis of the data necessitates the use of digital computation. Computer techniques are mandatory for dynamic systems of more than two components and are desirable even for two-component systems.

In the conventional method of analysis, linear and exactly determined simultaneous equations are used, that is, one wavelength is used per component. The accuracy of the results depends on the accuracies of the standard spectral data for each component and of the experimental absorption measurements. As the number of components increases, the method becomes increasingly sensitive to small errors in either the standard spectral data for each component or the experimental data at the set of selected wavelengths. However, more than one wavelength can be used for each component. The accuracy of the solution is thus increased by minimizing the statistical error for slight inaccuracies in either the standard spectral data or the experimental measurements. To do this, a least-squares solution must be made on the matrices involved. An example of this procedure, applied to a five-component system at equilibrium, is described by Sternberg, Stillo, and Schwendeman.[15]

When this method is used, the concentration of each component must remain unchanged over the time interval required to obtain absorbancy data for the multicomponent system at the set of wavelengths selected. Thus, the experimental data must represent an "instantaneous spectrum," that is to say, be time-independent.

If the system is undergoing reaction, use of the method will give erroneous concentration data for the individual components. The magnitude of the

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[15] J. C. Sternberg, H. S. Stillo, and R. H. Schwendeman, *Anal. Chem.* **32**, 84 (1960).

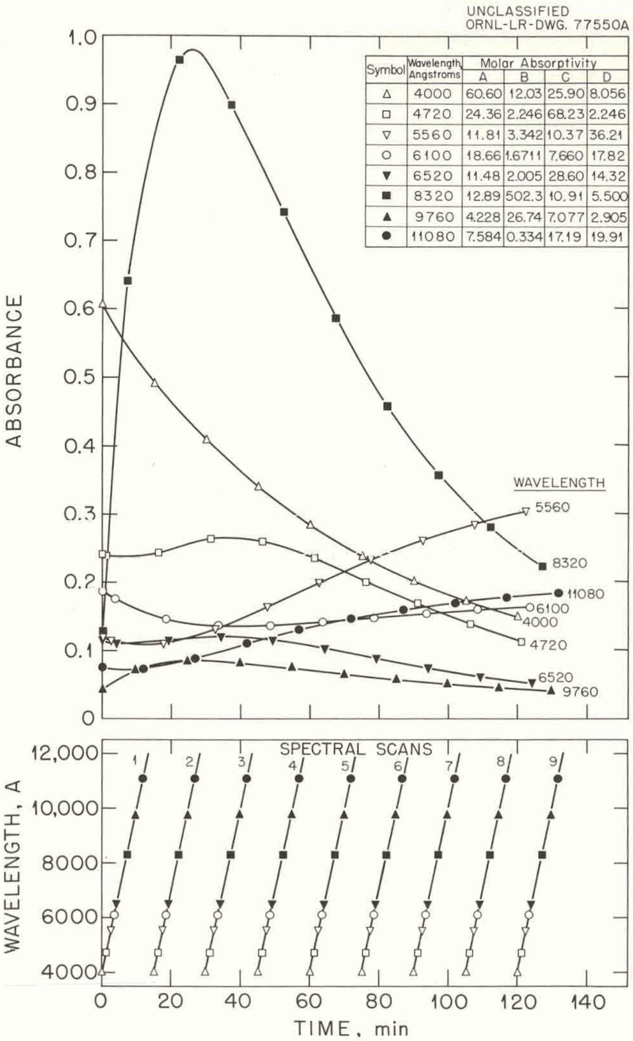
error will depend on the rate of change in the concentration of a particular component during the time interval necessary to obtain the absorbancy data and also on changes in the concentrations of any one or all the other components.

In order to analyze the spectrophotometric data from a dynamic system by digital computation, the absorbancy of the multicomponent system must be measured at each selected wavelength as a function of time, and sufficient data must be obtained to define exactly the absorbance-time behavior of the system. To make possible the analysis, a computer program for the IBM 7090 was written,[16] the latter part of which uses least-squares methods in matrix form. In the first part of the main program, analytical curve-fitting techniques are used to obtain polynomial functions which describe the change in absorbance of the mixture with time at each wavelength in the selected set. From the polynomials, an "instantaneous spectrum" is computed. For each experimental spectrum, an average time is selected with respect to the wavelength range and spectral scan rate used, and the "instantaneous spectrum" is computed at each of these average times. Analysis of the computed "instantaneous spectrum" by least-squares-matrix methods, which can also be applied to an equilibrium case, results in sets of equations from which the concentration of each component is calculated.

The program was first tested with the synthesized spectrophotometric absorption data for two parallel first-order reactions involving three absorbing components and for three series first-order reactions involving four absorbing components. For each case, the number of wavelengths selected was equal to twice the number of components. Figure 4.3 gives the absorption-time data at the selected set of wavelengths for the reacting system represented by the three series first-order reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D \, . \tag{4.8}$$

Each spectral scan corresponds to a spectrum that can be obtained with a recording spectrophotometer at a known, constant scan rate. The absorbance of the mixture was calculated at the indicated set of wavelengths at which the system absorbs.



Symbol	Wavelength Angstroms	Molar Absorptivity			
		A	B	C	D
△	4000	60.60	12.03	25.90	8.056
□	4720	24.36	2.246	68.23	2.246
▽	5560	11.81	3.342	10.37	36.21
○	6100	18.66	1.6711	7.660	17.82
▼	6520	11.48	2.005	28.60	14.32
■	8320	12.89	502.3	10.91	5.500
▲	9760	4.228	26.74	7.077	2.905
●	11080	7.584	0.334	17.19	19.91

Fig. 4.3. Absorbance-Time Curves for a System Containing Components *A*, *B*, *C*, and *D* in Series First-Order Reactions.

The results of the computer analysis of the absorption-time data (Fig. 4.3) for the four-component reacting system are given in Fig. 4.4. For each component, the concentration-time curves are shown. From this type of data, it is possible to determine the reaction kinetics for the system.

The results obtained for the analysis of the synthesized data for a three-component system (not given herein) and the four-component system mentioned above were excellent. With the exact synthesized absorption-time data, the concentrations of each component were determined to within ranges of relative standard deviation from 0.1 to 0.5% and of error from ±0.05 to ±0.1% over the entire course of the reaction.

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[16] By E. C. Long and A. L. Brooks of the Central Data Processing Center, ORGDP.

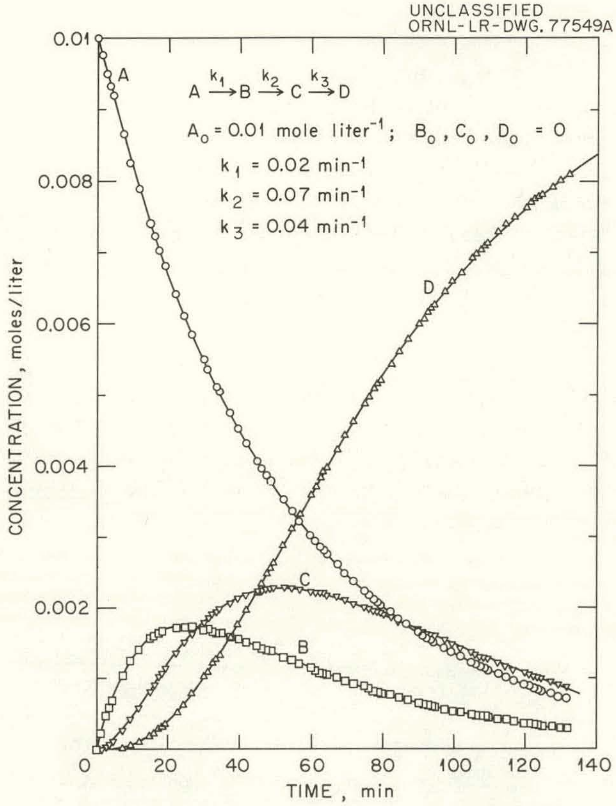

Fig. 4.4. Concentration-Time Curves for Components *A, B, C,* and *D* in Series First-Order Reactions.

Two different general types of curve-fitting, interpolation techniques have been investigated for use in the analysis of the absorption-time data. The first technique involves the fitting of the entire absorption-time curve at each wavelength to a single polynomial function whose order limit cannot exceed the number of absorption-time data points. The second technique investigated involves the fitting of the absorption-time curve in segments of moving point groups to quadratic functions or to rational fraction polynomials. An averaging method has also been used for both of these functions, involving all functions calculated from the point groups that pass through a given data point. The best of the latter methods involves the use of a quadratic function in conjunction with moving point group averaging.

For data which exhibits considerable statistical scatter, the single high-order polynomial is superior. However, enough data points are necessary to define the absorption-time behavior of the system. The exact number of points depends on the particular characteristics and reaction kinetics of the system under study. For those cases where the scatter is not significant, and where a large number of data points are not available, the moving point group technique must be used.

The program has been used for the analysis of the spectrophotometric data from a series of studies on the polymerization, disproportionation, and depolymerization of Pu(IV) in various nitrate media. The results obtained are very encouraging and indicate that the above type of mathematical and computational procedures should be adequate for analyzing the data from complicated nonequilibrium systems.

Reports are being prepared for open-literature publication on this method of analysis of data from dynamic systems, the results obtained by the use of this method for some multicomponent dynamic systems, and the computer programs.

PROGRAM FOR SPECTROPHOTOMETRIC STUDY OF SOLUTIONS AT HIGH TEMPERATURES AND HIGH PRESSURES[17]

R. E. Biggers

The program for the absorption spectrophotometric study of aqueous solutions at high temperatures and high pressures has been discussed;[18,19] a more extensive review of the program was given previously.[20,21] This work is being done jointly with R. G. Wymer.[22]

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[17] Program with the Chemical Technology Division.

[18] "High-Temperature Chemistry," *Chem. Technol. Div. Ann. Progr. Rept. May 31, 1963,* ORNL-3452, pp 211–15.

[19] R. E. Biggers, "Program for Absorption Spectrophotometric Study of Solutions at High Temperature and High Pressure," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962,* ORNL-3397, pp 27–32.

[20] "High-Temperature Chemistry," *Chem. Technol. Div. Ann. Progr. Rept. June 30, 1962,* ORNL-3314, pp 187–90.

[21] D. A. Costanzo and R. E. Biggers, "Absorption Spectrophotometric Studies of Plutonium in Solutions of $UO_2(NO_3)_2$, $Al(NO_3)_3$, and HNO_3 at Elevated Temperatures," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961,* ORNL-3243, pp 21–22.

[22] Chemical Technology Division.

A complete spectrophotometric system that can be operated at temperatures to at least 330°C and at pressures to at least 5000 psi with highly radioactive (alpha) solutions was designed under subcontract for ORNL by the Applied Physics Corporation (APC), Monrovia, California. The general features and details of this system are discussed more fully elsewhere.[23] A schematic layout of the absorption cells of the high-temperature, high-pressure spectrophotometer system and a photograph of the cell components are shown in Figs. 4.5 and 4.6. The layout of the principal components and the special features of the entire system have been presented previously.[21]

The design and development work on the subcontract between ORNL and APC, begun in March 1960, was finished, and the subcontract has been closed out. The prototype high-temperature, high-pressure absorption cell, fabricated by APC, and other equipment furnished to APC by ORNL were delivered to ORNL. The program for the construction of the high-temperature, high-pressure spectrophotometer system was approved.

A test facility to be used for elevated-temperature—elevated-pressure experiments with the cells was put into operation. It can be used for the hydrostatic and gas-pressure testing of the cells to 10,000 psi, with the cells at the maximum

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[23] R. E. Biggers and R. G. Wymer, *Status Report: Design and Development of a High-Temperature, High-Pressure Spectrophotometer System,* ORNL-CF-60-11-96 (Nov. 12, 1960).

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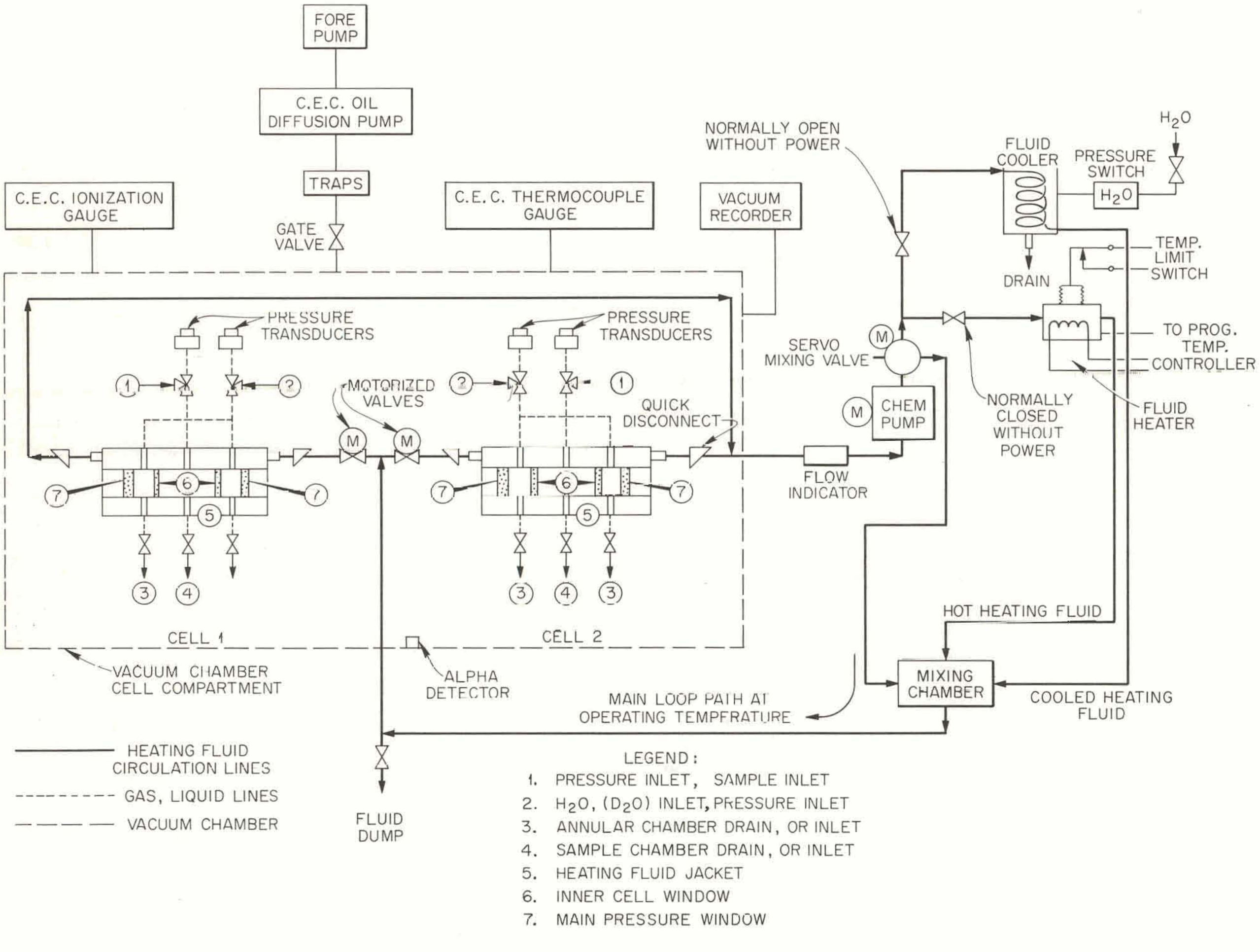

Fig. 4.5. Schematic Plan for High-Temperature High-Pressure Cells, Vacuum, and Heating System.

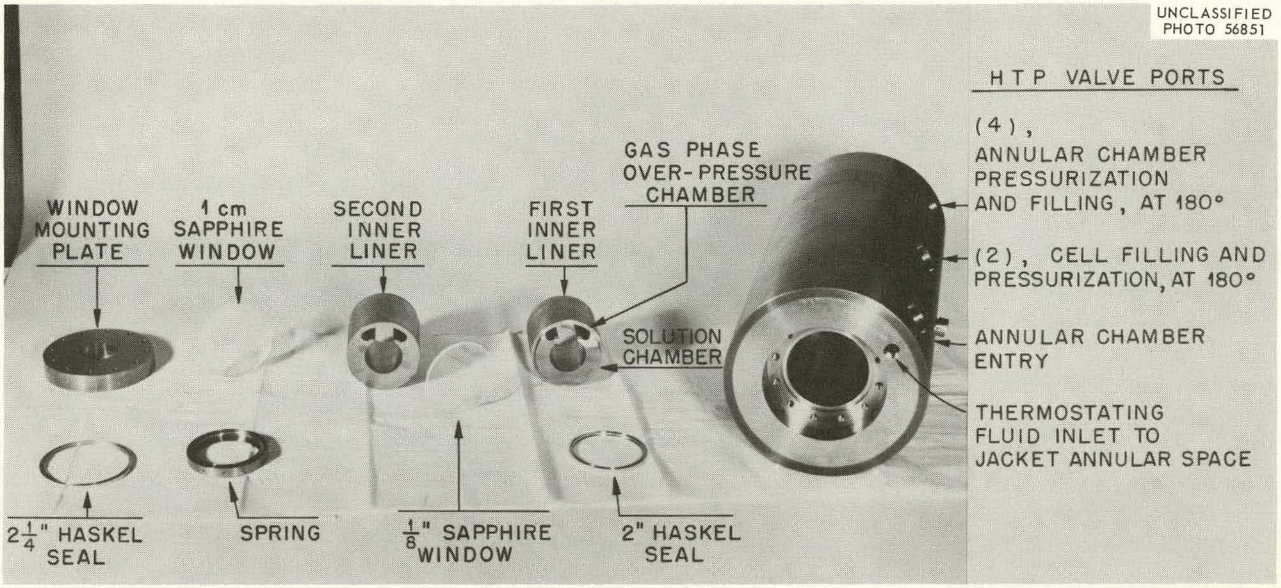

Fig. 4.6. ORNL High-Temperature High-Pressure Spectrophotometer Cell Assembly.

temperatures anticipated, and up to the critical point of water.

Some further refinements have been made in the cell design. It was found that the titanium spring, designed by APC and based on the Haskel seal design, was overstressed at the operating temperature and consequently lost its elasticity.

Its effective deflection range was considered to be too small. A new spring was designed for loading the inner Haskel seals of the cell. The spring must develop ~200-lb force at 400°C within a total linear space of 0.240 in. and with a very small deflection. This requirement has been met with a Bellville-type spring. Four such springs were constructed from 17-4-PH precipitation-hardened stainless steel. Calibrations at room temperature have confirmed the engineering design almost exactly. The springs are now being tested within the cell.

The prototype cell is being tested to determine leak-tightness and optimum operating and assembly procedures.

Several series of different kinds of tests were carried out with the prototype cell. The cell has been operated without leaks at 5000 psi and at 360°C simultaneously with a set of c-axis-oriented sapphire windows returned by APC with the cell. Prior to the test, it was noticed that the thick, external, main pressure windows exhibited radial striae. New and unstressed windows do not exhibit such striae. After several hours of leak-free operation at 360°C and 5000 psi, the windows fractured without rupturing and very slowly released the pressure. It was later found that these windows had been used by APC, who had severely stressed them thermally in an effort to find conditions that would fracture them. Sapphire cannot be heated or cooled at a rate exceeding ~3°C/min without the introduction of severe stresses. Additional tests with new sapphire windows are in progress, and other tests will be carried out while the spectrophotometer system is being constructed.

MEASUREMENT OF LIQUID DENSITIES AT HIGH TEMPERATURES AND HIGH PRESSURES

R. E. Biggers T. G. Rogers[24]

As an important adjunct to the high-temperature spectrophotometry program, an x-ray method was

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[24] Chemical Technology Division summer student.

devised for measuring the densities of aqueous solutions at accurately measured temperatures and pressures up to the critical points of the solutions. The method has been discussed previously.[20,21]

The liquid volume of a weighed solution of known composition is determined in an autoclave of suitable material, and an x-ray photograph is made to show the position of the vapor-liquid interface in a calibrated section of the autoclave. The density at any temperature is determined from the weight of solution and the location of the interface at that temperature. A prototype high-pressure autoclave was designed and made of titanium. The autoclave can be operated at pressures as high as 4000 psi at 400°C. It consists of a bulb section of about 4-ml volume that contains an internal thermocouple well, a uniform expansion section about 12 in. long, and a high-pressure closure head with a fitting that contains a titanium capillary which leads to a pressure transducer. Markers on the expansion section facilitate the location of the solution interface by x-ray measurements. Densities can be determined at 370 to 371°C within a range of maximum error of ±0.6%. As the temperature decreases, the error decreases. X-ray film can be driven past the slit in the system behind the autoclave at rates varying from ~0.05 to ~3 in./min. All the equipment has been installed and is being used with an existing 300-kv Norelco x-ray system.

The rate of leakage from the liquid-density autoclave does not exceed 2.9×10^{-4} ml of water per hour, that is, 0.002% of the autoclave volume per hour, at 4000 psi. Although this is an acceptable leakage rate for experimentation, attempt was made to reduce it further – to zero if possible. The conical high-pressure titanium seal at the top of the autoclave was changed from a 59°/60° to a 56°/60° cone-plug arrangement in order to obtain less surface contact area. The redesigned closure appears to be better; detailed studies of the leakage rate are in progress.

Difficulties with the present autoclave result from its being constructed entirely of titanium. This metal was used initially because it will contain chloride solutions at elevated temperatures and pressures without stress-corrosion cracking. However, it does not perform nearly as satisfactorily for the conical high-pressure seals as does stainless steel or other alloys. Also, the 0.035-in.-OD (0.015-in.-bore) titanium capillary leading to the pressure transducer has broken at the entry point to the high-pressure plug (but not at the weld). An autoclave will be constructed from stainless steel.

The various exposure, development, beam current, and voltage conditions necessary for the optimum x-ray photography of the autoclave within the furnace were established. Photographs were made with water and aqueous solutions of uranyl perchlorate and of uranyl sulfate. The films are very sharp and permit the accurate location of the liquid interface within the autoclave stem.

All the instrumentation for monitoring and controlling temperature and pressure has been installed and calibrated. The high-temperature furnace was tested, and power-input levels were established as a function of temperature. Temperature profiles of the furnace and autoclave were obtained. The autoclave is being calibrated with water from 25 to 370°C. Following the calibration, density measurements will be made on several solutions of interest.

A complete report on this work is being prepared for publication in the open literature.

COMPUTER PROGRAM FOR THE CONVOLUTE SMOOTHING OF DIGITIZED SPECTRAL DATA

R. E. Biggers T. G. Kabele[25]

The output of digitized spectral data from a spectrophotometer system[21,22] yields absorbance data as a function of wavelength. At high absorbances and low light levels, the "noise" associated with the output from the spectrophotometer may be significant, particularly when the multiplier phototube detector is used. With a strip-chart recording, the noise is usually manually averaged out. However, any given absorbance point punched out on a card may contain a noise contribution. Data points are obtained at moderately close wavelength intervals (1 A, or even smaller). A spectrum may contain 10,000 points or more; the number of points is determined by the wavelength-punching interval and the range of the spectrum. Therefore, manual averaging cannot be done, and a mathematical technique must be used.

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[25] Chemical Technology Division co-op student.

When a computer is used to make refined calculations from spectral data (e.g., concentrations, spectral-band resolutions, spectral-band profile models), the data should be as free as possible from the effects of random fluctuations. One of the simplest methods of smoothing is to take a moving average. This technique, however, is not useful for many types of data, particularly in the present case, because the peaks of the resulting spectrum tend to be distorted.

A set of computer programs and subroutines was written for the CDC 1604-A computer to smooth spectral data. A least-squares convolution smoothing technique, recently reported by Savitzky and Golay[26] and by Savitzky,[27] is used. The smoothed value for each point is obtained from the observations in the immediate neighborhood of each point by use of coefficients from orthogonal polynomials. This type of smoothing is an advantage because the nature of the spectrum changes radically from one end of the range to the other. The recording of many data points at close intervals is desirable; the number depends on the character of the spectrum. The present technique requires that the data points be equally spaced; this is usually true for digitally output data and is true in the present case. A convolution or fitting may be done for each point over a 3- to 15-point (odd) range by use of a cubic (or quadratic) function over the range of the convolute. The same technique can also be used to take the first, second, and third derivatives of curves, spectra, etc.

The programs are very flexible in that all probable combinations of experimental spectral data, optical-cell balance data, and conical-screen attenuator data can be handled and smoothed. Three versions of the smoothing programs were prepared to handle various combinations of spectral data, cell-balance data, and attenuator-suppression data. Subroutines were written to add attenuation data to the spectral data in those cases where conical screen attenuators are used to measure absorbances greater than 2.0. The choices of output for either the "rough" or "smoothed" data, or both, in any combination and for all versions of the program include: tabulating, CALCOMP curve-plotting, card-punching, and writing binary tapes. The various program versions use different compatible output subroutines.

RADIOLYSIS OF CHLORIDE SOLUTIONS

Hisashi Kubota

The acidity of 10 *M* LiCl solutions used to extract transuranic elements decreases as a result of the radiolysis induced by the high level of alpha activity. It is desirable to define the parameters associated with this behavior and to devise rapid and reliable ways to measure the change in acidity in such a system.

The loss of free acid is accompanied by the appearance of free chlorine in the solution. The study thus far has shown that the production of this free chlorine by radiolysis is not limited to concentrated lithium chloride solutions alone but is characteristic of all acid chloride systems. There is a critical chloride concentration (1.4 *M*) below which the chlorine is not formed. Acidity is a necessary condition for this reaction; however, there is little difference between the amount of chlorine formed in hydrochloric acid solutions and that formed in solutions having the same total chloride content but much lower acidity.

EFFECT OF RADIATION ON SODIUM CHLORIDE

Hisashi Kubota

Disposal in salt (sodium chloride) mines of highly radioactive wastes from nuclear-fuel reprocessing has been proposed. A demonstration experiment is planned in which canned, spent fuel elements will be stored in cavities in a salt mine. Therefore, the effect of radiation on the structural properties of salt and the possibility of radiolytic decomposition of salt are of considerable interest.

It is believed that structural damage will be minor since only that salt just at the periphery of the waste container could possibly receive doses large enough to cause a sizable reduction in structural strength. The possible release of

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[26] A. Savitzky and M. H. E. Golay, "Some Numerical Operations on Analytical Data," *15th Annual Summer Symposium*, Division of Analytical Chemistry, American Chemical Society, College Park, Md., June 13–15, 1962.

[27] A. Savitzky, Perkin-Elmer Corp., Norwalk, Conn., private communication to R. E. Biggers, October 1962.

gaseous chlorine to the mine atmosphere as a result of radiolytic decomposition of the salt is the more serious problem. The release of free halogens from alkali-metal halides is being studied intensively in the field of solid-state physics; such releases are theoretically possible.

A low dose of Co^{60} gamma irradiation colors reagent-grade sodium chloride yellow. The color changes to dark brown and finally to black as the dose is increased. When irradiated salt is dissolved in water, the solution has oxidizing power that can be determined iodometrically or by the *o*-tolidine test for free chlorine. With increase in irradiation dose, the G value for the production of this oxidant decreases from 9×10^{-3} at 10^6 rads to 7×10^{-4} at 10^9 rads. On the basis of these figures as the upper limit of possible chlorine release, salt in sealed containers was irradiated to determine the possibility and extent of this phenomenon. Since the salt near the storage cans would become heated, the irradiations were made at 60, 160, and 250°C.

After receiving a dose of 2×10^9 rads, the salt at 60°C turned black; that at 160°C, gray black; and that at 250°C remained white. Chlorine was not detected when the associated atmospheres were analyzed gas chromatographically. When the salt was dissolved in water, the oxidizing power was still present, irradiation at 250°C producing less than one-fifth that at 60°C.

When irradiated salt is heated, the color is annealed from the crystal body and the oxidizing power is reduced. The rate of annealing is a function of temperature; the color is gone completely within 4 hr at 250°C and within two weeks at 160°C. The net results of the combined effects of heating and irradiation are the creation of color centers and the annealing. The effects of irradiation should therefore be most severe at lower temperatures.

The release of enough chlorine to hinder disposal operations is believed to be unlikely. In the forthcoming demonstration experiment, the cavity atmosphere will be monitored for chlorine.

THERMAL STABILITY OF NATURAL SALT

Hisashi Kubota

When chunks of natural salt (sodium chloride) from the Carey Salt Mine, Hutchinson, Kansas, were heated, they shattered rather violently at 260 to 300°C. This disintegration is accompanied by release of steam. Laboratory tests indicate that the steam pressure or the thermal expansion of trapped water in the salt causes this phenomenon. Figure 4.7 is a photograph of a water inclusion, the so-called negative crystal, with an air bubble floating in the liquid.

The results of field tests in which heaters were placed in cavities in the salt wall or floor showed that salt in place in the mine also shatters at ~280°C. Therefore, the strength of materials used in waste-disposal operations in salt mines must be considered so that safety hazards resulting from salt fracture will not be created.

The thermal stability of salt from various mines throughout the country was determined. All dome-type salt tested was stable to heat up to 600°C. Most of the bedded salt shattered at temperatures in the range from 260 to 380°C; that from the Retsof Mine in New York was stable up to 600°C.

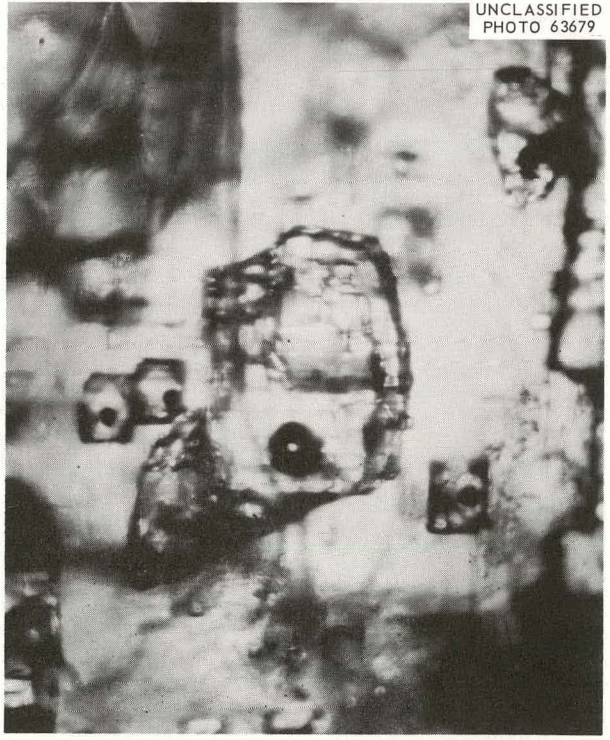
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Fig. 4.7. Liquid Inclusion in Rock Salt. Reduced 17%.

5. Reactor Projects

J. C. White
A. S. Meyer

GAS-COOLED REACTOR PROJECT ANALYSES

A. S. Meyer J. E. Attrill
C. M. Boyd

Helium Analysis

A. S. Meyer C. M. Boyd

The research and development work concerning the process analysis of helium blanket gas and the application of ionization detectors to the determination of permanent-gas impurities in helium has been reported in the progress reports of the Gas-Cooled Reactor Project.[1,2]

PROCESS CHROMATOGRAPHY FOR ENGINEERING TESTS

J. E. Attrill

A Beckman model 120-A process chromatograph and infrared analyzer was reconditioned and adapted for the analysis of samples from the atmosphere of hydrogen autoclave tests. This instrument was adapted to continuously determine methane, nitrogen, carbon monoxide, and carbon dioxide in hydrogen gas. It has been tested and put on standby in preparation for the start-up of this loop.

A Greenbrier model 112 process chromatograph has also been adapted to monitor gases in a high-temperature steam-graphite loop. This instrument has been set to analyze a sample that contains 60 to 100% hydrogen; 0 to 20% carbon dioxide; 0 to 10% carbon monoxide; and <1% oxygen, nitrogen, and methane together.

A calibration curve must be used in determining hydrogen in the designated range, because the plot of peak height vs concentration of hydrogen does not pass through the origin even though the relationship is linear. The linearity is brought about by using a mixed carrier gas that contains 8% hydrogen in helium.[3] Other components appear to give a linear response, and peak height is proportional to concentration in the ranges used.

DEVELOPMENT AND EVALUATION OF METHODS FOR THE ANALYSIS OF RADIOACTIVE MSRE FUEL

R. F. Apple

Evaluation of methods for analyzing radioactive MSRE fuel has continued. To simulate, as closely as possible, the operating conditions necessary, the mock-up hot-cell facility and the high-level radiation hot cells were used in most of this work.

A procedure for the dissolution of the salt was established which yields a sulfate solution of the fluoride salt fuel. The solution is essentially free of fluoride ions. The salt is dissolved by heating it in a mixture of boric, nitric, hydrochloric, and sulfuric acids until fumes of sulfur trioxide are evolved. Sufficient water is added to make the solution 1 M in H_2SO_4. About 3 hr is required to dissolve a 1-g portion of salt. This time is about that required to dissolve a similar quantity of simulated nonradioactive fuel.

The following methods were tested in the Analytical Chemistry mockup cell and found satisfactory (the first method, for zirconium, was taken from ref 4):

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[1] A. S. Meyer and C. M. Boyd, "Equipment for Helium Analyses," *Gas-Cooled Reactor Program Semiann. Progr. Rept. Mar. 31, 1963*, ORNL-3445, pp 334–36.

[2] C. M. Boyd and A. S. Meyer, Jr., "Determination of Permanent Gas Impurities in Helium," *Gas-Cooled Reactor Program Semiann. Progr. Rept. Sept. 30, 1963*, ORNL-3523 (to be published).

[3] T. Johns, *The Measurement of Hydrogen in Process Streams by Gas Chromatography*, Scientific and Process Instruments Division, Beckman Instruments Co., Fullerton, Calif., Aug. 3, 1961.

[4] J. G. Surak and Hisashi Kubota, "Amperometric Titration of Zirconium with Cupferron," presented at the 144th National Meeting, American Chemical Society, Los Angeles, Calif., Mar. 31–Apr. 5, 1963.

Determination	Method	Relative Standard Deviation (%)
Zirconium	Amperometric	1.5
Uranium	Polarographic	2.5
Uranium	Coulometric	0.5
Fluoride	Pyrolysis	1.0
Chromium	Amperometric	1.6

AMPEROMETRIC DETERMINATION OF CHROMIUM IN MSRE FUEL

R. F. Apple H. E. Zittel

An amperometric method for the titration of Cr^{6+} with ferrous sulfate was developed for the determination of chromium in solutions of MSRE fuels. A titration cell assembly, which incorporates a pyrolytic graphite electrode and an S.C.E., was designed especially for use in this method. Chromium is oxidized to Cr^{6+} with argentic oxide in 0.5 M H_2SO_4. The Cr^{6+} is subsequently reduced to Cr^{3+} by ferrous sulfate. This reduction causes a decrease in diffusion current, which is measured electrically. The progress of the titration is followed by means of an ORNL model Q-1160 polarograph with the pyrolytic graphite electrode at +1.0 v vs the S.C.E. The titration is continued until a sharp deflection in the titration curve is observed. If the MSRE fuel is dissolved in sulfuric acid, the titration of chromium can be performed without any prior separations. When the determination is made routinely, the relative standard deviation for titration of 10- to 50-μg quantities of chromium is 1%, which is the ultimate precision expected. A description of this work is being submitted to *Analytical Chemistry* for publication.

REDUCING POWER IN MSRE FUEL

R. F. Apple I. B. Rubin

Measurement of U^{3+} in MSRE fuel is important because of the possible deposition of UF_3 in the reactor. No reaction is known that is specific for U^{3+}. From the determination of "reducing normality" made by measuring the hydrogen evolved when the fuel is dissolved in acid, U^{3+} has been estimated. Other reduced species, such as CrF_2 and structural metals, also contribute evolved hydrogen. In tests of a modified "reducing normality" procedure in which MSRE fuel samples were dissolved in fused $KHSO_4$-H_3BO_3, evolution of hydrogen was incomplete. Surprisingly, the UF_3 appears to be insoluble or sparingly soluble in the fused solvent.

In a series of dissolution tests conducted under an inert atmosphere, 0.5-g unreduced samples of the MSRE salt dissolved completely in 10 min in $KHSO_4$(3 g)–H_3BO_3(0.5 g) at 300°C. When the molten solvent was filtered under inert gas through a fine-porosity fritted disk, no insoluble material remained on the frit. When this dissolution test was repeated with UF_3 added to the MSRE salt, ~90% of the UF_3 remained on the filter. The evolution of hydrogen from MSRE salts to which CrF_2 was added indicated that the Cr^{2+} was oxidized to Cr^{3+} with a stoichiometric evolution of hydrogen. This dissolution technique, therefore, appears to offer potential as a specific method for U^{3+} either via the preoxidation of other reducing species followed by the conventional evolution of hydrogen from the unreacted UF_3 or, more sensitively, by separation of the UF_3 by filtration followed by the determination of uranium in the residue (e.g., by measurement of fluorescence).

Since pure UF_3 is not available, the equilibrium solubility of UF_3 in $KHSO_4$(3 g)–H_3BO_3(0.5 g) and the possible kinetics of the dissolution are being studied by measuring the concentration of uranium in the washes obtained after successive washings of UF_3 samples with the molten $KHSO_4$-H_3BO_3 solvent.

RATE OF REMOVAL OF CARBON DIOXIDE FROM WATER IN AN MSRE PUMP DEMONSTRATION SYSTEM

R. F. Apple

Relative to the removal of xenon from the MSRE, studies of the rate of removal of carbon dioxide from water used in an MSRE pump demonstration were continued. The rate of carbon dioxide removal is being determined by pH measurements and by titrating the free carbon dioxide with a solution of sodium hydroxide.[5] Under the present

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[5] C. P. Hoover, *Water Supply and Treatment*, p 132, Bulletin 211, National Lime Association, Washington, D.C., 1941.

pump modifications, the removal rate is about 50% of the theoretical rate. Although carbon dioxide is $\sim 10^4$ times more soluble in water than xenon is in MSRE fuel, the data obtained from these experiments will be used to predict the rate of xenon removal during normal MSRE operation.

NEW ALKALI-METALS ANALYTICAL FACILITY

Gerald Goldberg

Because of the rapidly expanding technology associated with the determination of interstitials (oxygen, carbon, and hydrogen) as contaminants in the alkali metals, a fully equipped analytical laboratory was set up in Building 2011. The facilities of this new laboratory will be used for the routine analysis of alkali metals and for further development, when warranted, of existing methods for the determination of the contaminants.

The laboratory is equipped with a plastic-domed, high-vacuum dry box, which was set up by the Materials Compatibility Group of the Metals and Ceramics Division. Oxygen-sensitive metals can be Heliarc welded within this dry box under an inert atmosphere. The laboratory also contains two stainless steel hoods, ample workbench and table space, a storage area, several high-temperature furnaces, and a change room. The proposed addition of a flame spectrophotometer will make the laboratory virtually self-sufficient. Figure 5.1 shows a section of the laboratory.

DETERMINATION OF HYDROGEN IN THE ALKALI METALS

Gerald Goldberg

It has become necessary to determine hydrogen in NaK in connection with a long-range loop program undertaken by the Reactor Division. Several loops are being fabricated to assist in the examination of the effects of adding various amounts of hydrogen to the circulating NaK in the loops. Fortunately, a method exists for the determination of hydrogen (as the hydride) in sodium, potassium, and NaK.[6] The pressing problem was to sample the NaK while the loop was operating at both elevated temperature and pressure and then to transfer the sample to the analytical apparatus.

With the cooperation of several members of the Reactor Division, a sampler (Fig. 5.2) was designed whereby a metal bucket is lowered into the NaK under various conditions of temperature and pressure and ~ 2 g of sample is obtained. This bucket is transferred from the bucket sampling apparatus to a glass vial, which is then sealed under vacuum to protect the NaK from contamination. An unexpected advantage is that surface tension keeps the NaK from spilling, even if the bucket is inverted. The vial is placed in an inert-atmosphere dry box and is broken open; the bucket that contains the NaK is transferred to the reaction vessel. The alkali metal is then removed by the amalgamation procedure, which in turn leaves only the unreacted hydrides, oxides, and carbon compounds in the reaction vessel. The reaction vessel is next connected to the gas-transfer apparatus. Deaerated water is added under vacuum to the residue, and the liberated hydrogen is determined by gas chromatography. A blank correction is not needed.

Figure 5.3 shows the apparatus used for the liberation and transfer of the hydrogen. The evacuated sample bulb is connected to the uppermost part of the Toepler pump. The cold trap and the section of the pump located above the upper valve are both connected to a common manifold, which is connected, in turn, to both vacuum and helium lines. The pump controller, pictured in the foreground, was designed to pump the mercury past the upper contact of the pump and thus to force all the liberated gas into the sample bulb.[7]

Several samples have been taken from the first NaK loop to determine the oxide content of the NaK. The results are in close agreement with those recorded by the plugging meter that is connected to the loop.

DETERMINATION OF FREE ALKALI METAL IN ALKALI-METAL HALIDES

Gerald Goldberg

One phase of the molten-salt spectrophotometry work conducted by J. P. Young (see "Spectrophotometric Studies of Molten-Salt Systems" in

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[6] Gerald Goldberg, "Determination of Hydrogen in the Alkali Metals," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962,* ORNL-3397, p 52.

[7] Gerald Goldberg, A. S. Meyer, Jr., and J. C. White, "Determination of Oxides in Fluoride Salts by High-Temperature Fluorination with Potassium Bromotetrafluoride," *Anal. Chem.* **32**, 314 (1960).

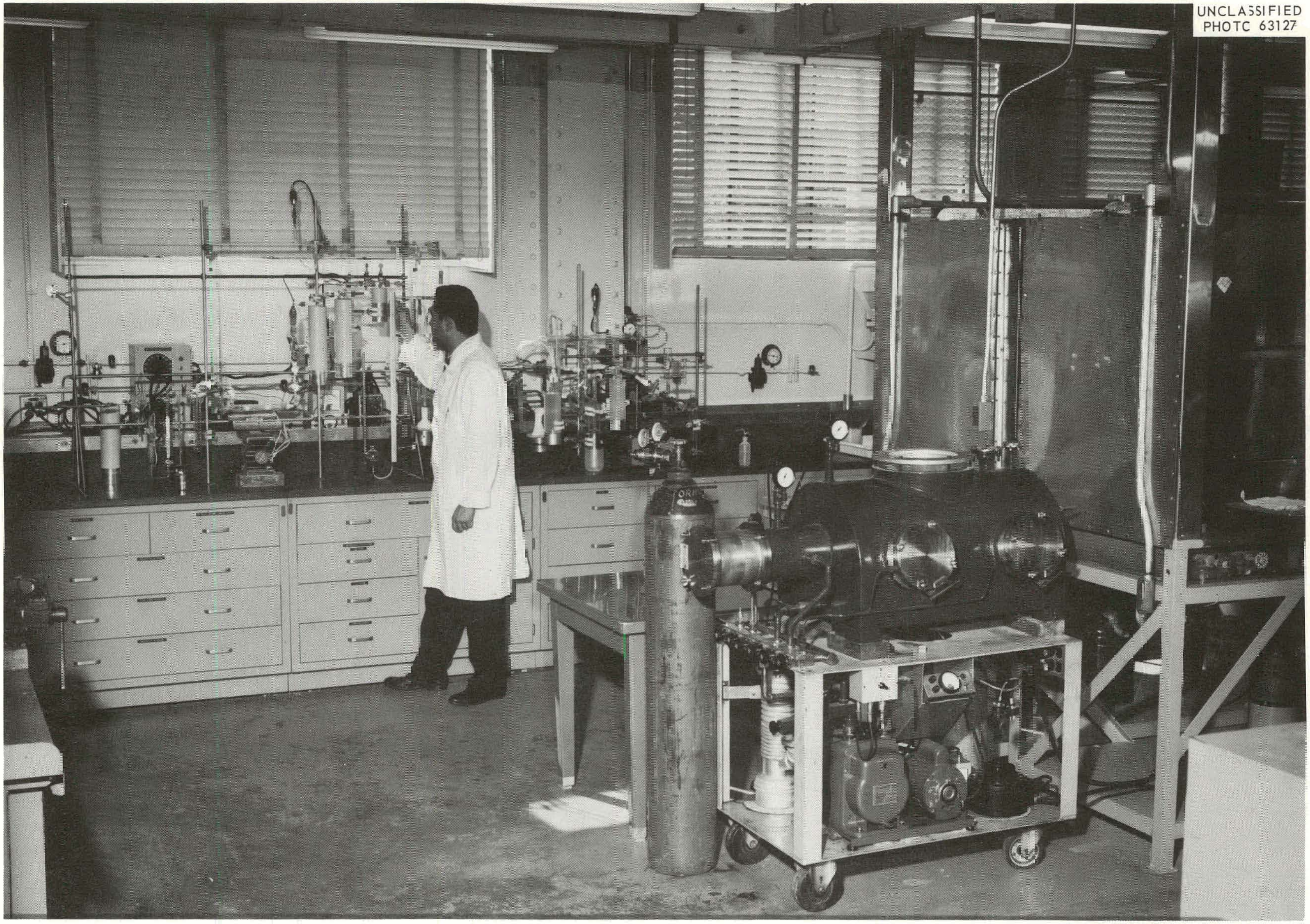

Fig. 5.1. Partial View of New Alkali Metals Analytical Facility. (Left to right: carbon-in-sodium apparatus; hydrogen-in-NaK apparatus; second, portable, vacuum dry box; and stainless steel hoods.)

Chap. 3 of this report) involved the addition of a few milligrams of alkali metal to various alkali-metal halides. Young was interested in the spectrum of the free alkali metal, if discernible, at temperatures above the melting point of the salts. Although the alkali metal was added to the salt with all due precaution, it was thought that all the metal would not remain in an uncombined state and that the initial weight of the metal added would not suffice for the calculations involved. It was therefore necessary to determine the amount of free alkali metal that remained after the experiment was conducted.

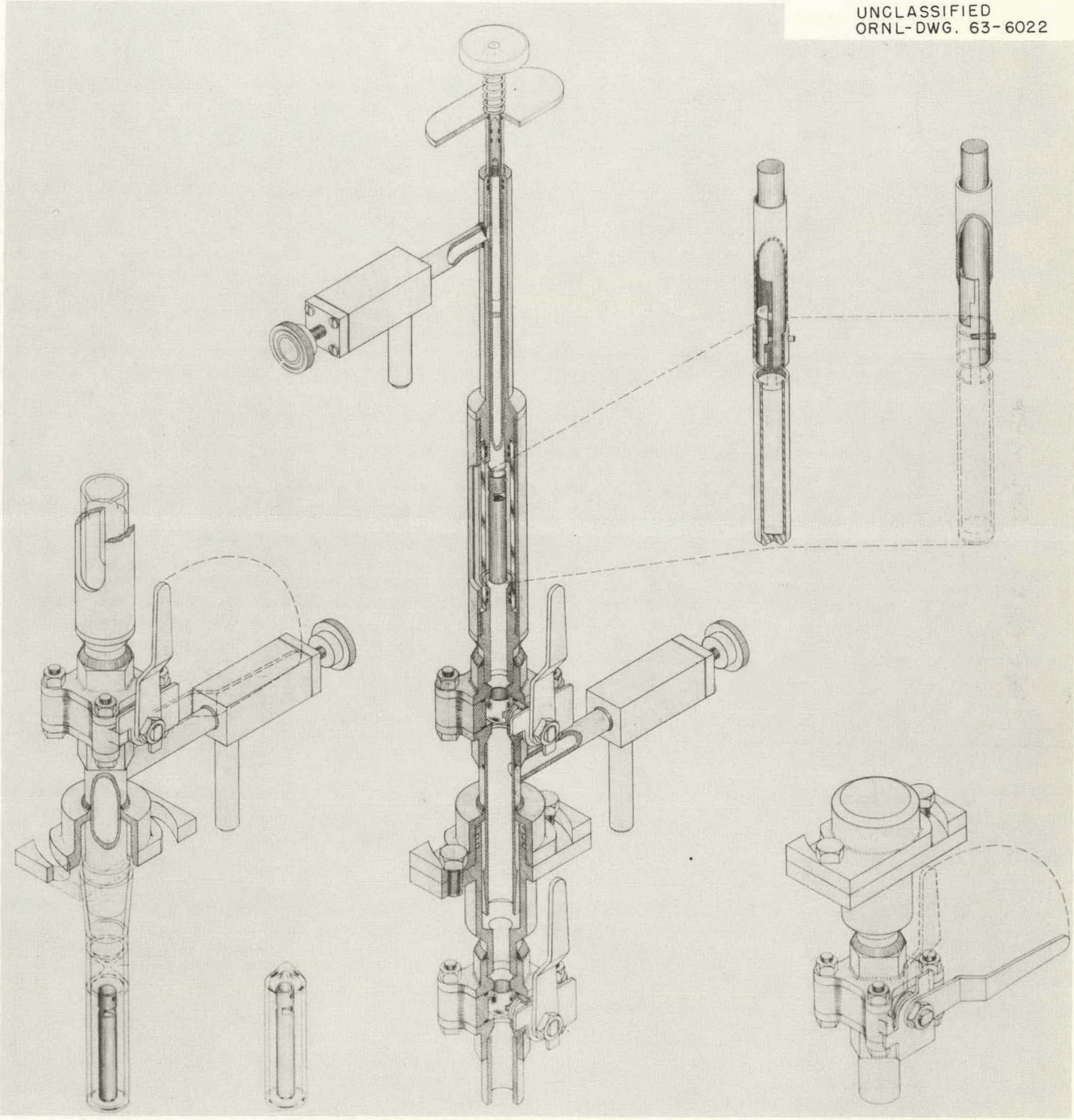

Fig. 5.2. NaK Sampler Assembly.

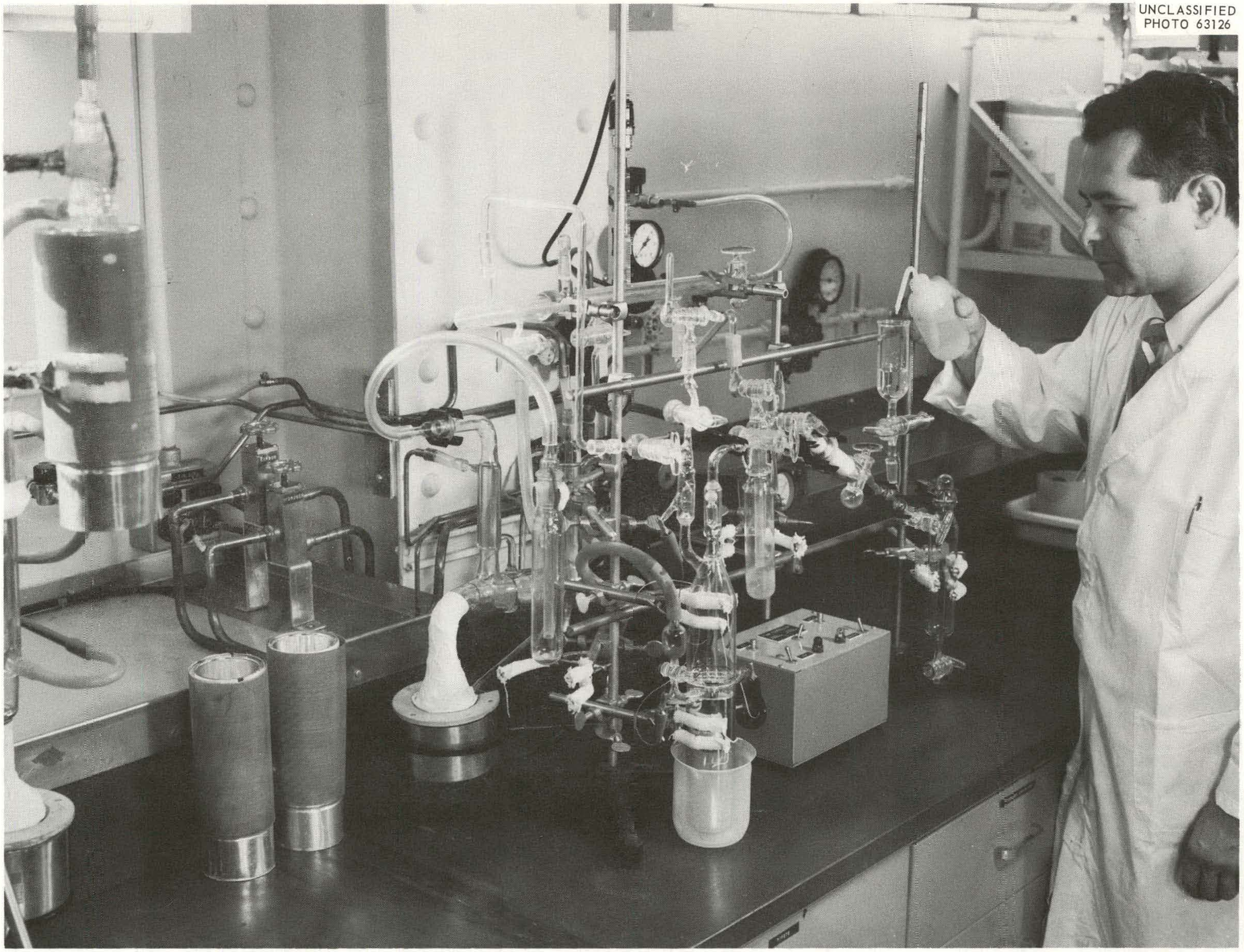

Fig. 5.3. Apparatus for the Determination of Hydrogen in Alkali Metals. (Right to left: reaction vessel, water-addition funnel, $MgClO_4$ drier, cold traps, and Toepler pump.)

The sample was transferred, under inert atmosphere, to a reaction vessel (Fig. 5.3). The vessel was evacuated, and deaerated water was then added to it under vacuum. The reaction proceeded smoothly, hydrogen being liberated as a result of the reaction of the alkali metal with the water. By means of the Toepler pump, the hydrogen was transferred to an evacuated, calibrated sample bulb through the magnesium perchlorate drying tube and the cold trap. The amount of hydrogen liberated, as a direct function of the free alkali metal present, was determined by gas chromatography.

DETERMINATION OF CARBON IN SODIUM

Gerald Goldberg

In conjunction with the AEC Sodium Component Development Program, an apparatus was designed and constructed for determining microgram amounts of carbon in sodium metal (Fig. 5.4). The apparatus consists of an oxygen-purification system, an ignition tube, a series of cold traps, and a capillary-manometer measuring system. The sodium metal is converted to the oxide in an atmosphere of pure oxygen at a reduced pressure and low temperature within the quartz ignition tube. The oxide, along with any carbon present, is then heated to 1100°C in the presence of pure oxygen at a reduced pressure. The resulting carbon dioxide is isolated in a capillary U-tube, and the pressure of the carbon dioxide is measured manometrically.

The oxygen is purified by passing it over hot cupric oxide and through Ascarite and Anhydrone. The gas is then liquefied in a cold trap cooled with liquid nitrogen. The overpressure of oxygen in the cold trap is used as the source of purified oxygen that is admitted to the ignition tube.

To protect the quartz ignition tube, the quartz boat that contains the sodium sample is first placed in a short length of quartz tubing, which is plugged at each end with quartz wool. This assembly is placed in the ignition tube. (The ignition tube is loaded within an inert-atmosphere dry box and is then connected to the apparatus.) During ignition, a pressure of ~800 μ of oxygen is maintained within the tube by partially throttling the flow of oxygen to which the apparatus is exposed. Any carbon monoxide formed is converted to carbon dioxide as the gas passes through a second tube of hot cupric oxide.

The first cold trap is simply a length of tubing packed with glass beads. It is cooled to the temperature of Dry Ice–acetone to trap moisture and to precool the carbon dioxide that is collected in the second trap, which is cooled with liquid nitrogen.

After ignition, the system is evacuated to less than 1 μ of pressure; the capillary U-tube is cooled with liquid nitrogen, and the collection trap, immediately preceding the U-tube, is warmed to the temperature of Dry Ice–acetone to facilitate the transfer of the carbon dioxide to the U-tube. The pressure of the carbon dioxide that is now isolated in the U-tube is measured on the calibrated mercury manometer.

The manometer was calibrated by first determining the cross section (S) of a measured length of the capillary. This was accomplished by weighing the volume of mercury contained in this measured length. Next, the manometer was zeroed at atmospheric pressure by means of a leveling bulb. The stopcocks at either end of the U-tube were then closed, and the leveling bulb was lowered to near the bottom of the manometer. The manometer reading was recorded (X_1). The U-tube was again exposed to atmospheric pressure, and a second reading was taken with the leveling bulb still in position near the bottom of the manometer (X_2). The atmospheric pressure (h) was also recorded. According to Boyle's law, the calibrated volume (V) is determined from the equation:

$$V = \frac{SX_1(h - X_2 + X_1)}{X_2 - X_1} . \qquad (5.1)$$

Three blank runs were made on the apparatus. The three values for a 1-hr ignition period ($\frac{1}{2}$ hr at 1100°C) were: 0.70, 0.75, and 0.72 cm. In micrograms of carbon (W), the average is 5.2 μg. This value is calculated from the equation:

$$W = 12.01X\left(\frac{V + SX}{RT_s}\right), \qquad (5.2)$$

where:

12.01 = gram atomic weight of carbon,

X = manometer reading, mm,

$V = 1120\ \text{mm}^3$,

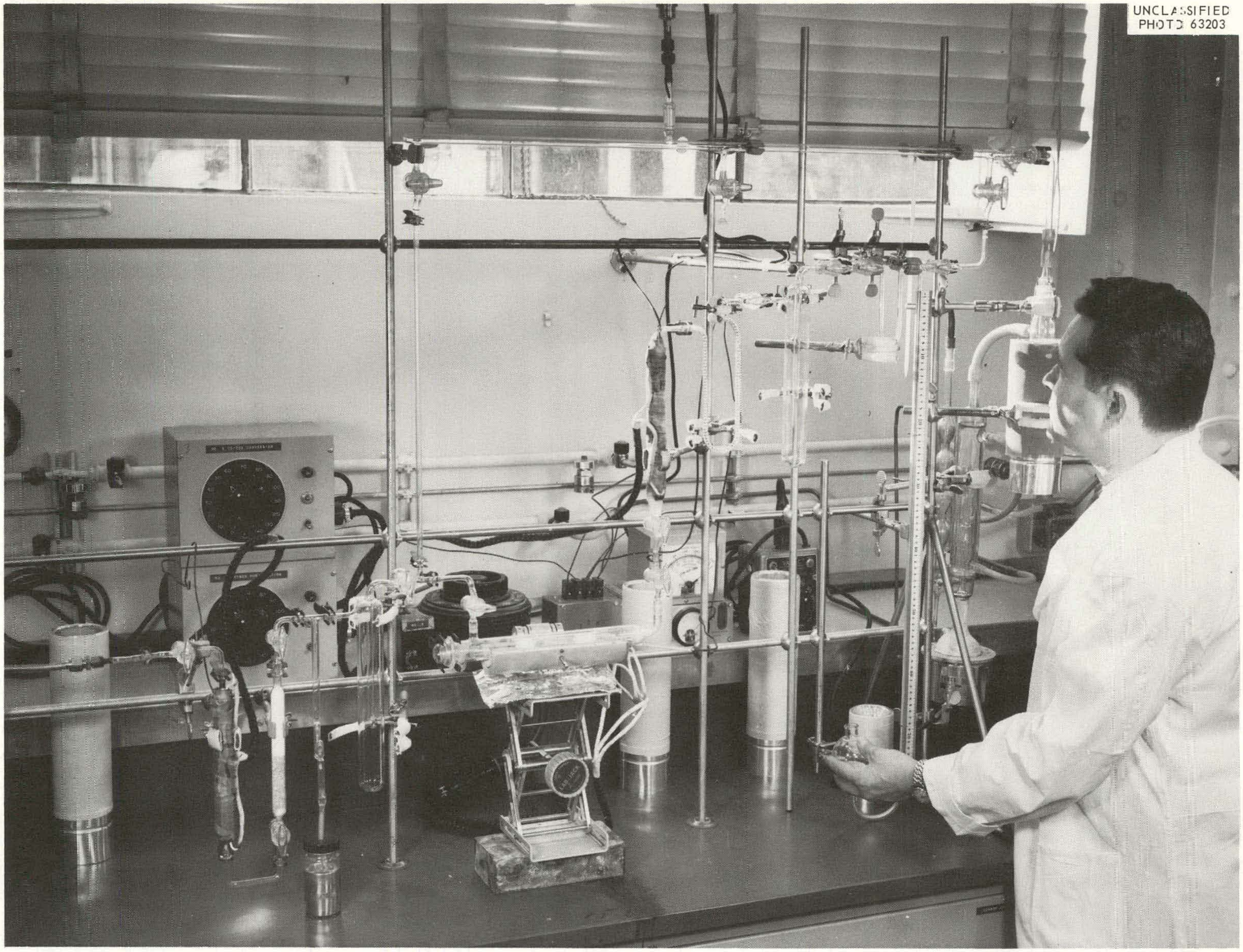

Fig. 5.4. Apparatus for Determination of Carbon in Sodium.

$S = 0.912\ \text{mm}^2$,

$R = 62.36$ liters (mm Hg) $\text{mole}^{-1}\ \text{deg}^{-1}$,

T = room temperature, °C,

$T_s = 273 + T$.

A sample of sodium that weighed ~0.5 g was placed in the quartz boat. (No attempt was made to maintain the purity of this sample.) The ignition tube was first exposed to a partial pressure of oxygen, and then the furnace was turned on. At 300°C the sodium began to burn rapidly with little attendant sputtering. The temperature was then raised to 1100°C. The carbon dioxide evolved was collected but not measured. A second heating of this sample gave rise to approximately the average blank. A further examination of the gas in the U-tube indicated that there was no moisture present. The round-robin samples of sodium for carbon content will be determined soon by this method.

REACTION OF POTASSIUM WITH DRY OXYGEN

Gerald Goldberg

Two experiments were conducted to determine whether dry oxygen reacts with potassium metal at elevated temperatures. In the first experiment, a 1-in.-diam Pyrex cylinder that contained 15 g of potassium was connected to a high-vacuum stopcock. The stopcock, in turn, was sealed to a 25-cc manifold to which a Hastings-gage tube was connected. The system was then evacuated. Dry oxygen, obtained as the overpressure from oxygen liquefied in a trap cooled with liquid nitrogen, was introduced into the manifold at a pressure of 2 mm. The potassium was heated to 100°C, and the stopcock was opened. The pressure dropped rapidly to 10 μ. The surface of the potassium first exhibited a purple discoloration; then a white deposit formed rapidly. The temperature of the potassium was raised to 175°C, and a second volume of oxygen was added at 2 mm of pressure. After the reaction, the pressure within the manifold remained greater than 1 mm.

In the second experiment, a Pyrex container in the form of a modified Erlenmeyer flask was connected to the high-vacuum stopcock and the manifold. The flask contained 50 g of potassium, a 3-in.-diam surface of which was exposed to the oxygen. The potassium was heated to 135°C, and ten successive additions of dry oxygen were made at a pressure of ~1 mm. The reading on the Hastings gage dropped rapidly to 0 μ after each addition. Apparently, the large surface area of the potassium retarded the formation of a protective film of oxide on its surface, and the larger amount of potassium caused more of the oxide to dissolve. Unless some combination of surface tension and surface area tends to produce a cohesive oxide film that retards further oxide formation, the reaction between dry oxygen and potassium should proceed until all the potassium is converted to potassium oxide.

DETERMINATION OF OXYGEN IN ALKALI METALS

Gerald Goldberg

In addition to the routine application of the amalgamation apparatus[8] to the determination of oxygen in sodium, potassium, and NaK samples, a number of capsule tests were run to further investigate the reliability of the method. One series of tests involved the recovery of oxygen from potassium contained in niobium capsules and to which mercuric oxide had been added as a spiking agent. These sealed capsules were heated at temperatures in the range from 200 to 800°C. Control samples that did not contain mercuric oxide were also run at these same temperatures.

In all cases the recovery of oxygen was low. At 200°C there appeared to be little or no reaction between the mercuric oxide and potassium. From 400 to 800°C there may have been complete reduction of the mercuric oxide by the potassium. The low recovery of oxygen as K_2O was possibly due to the reaction of the K_2O with the niobium metal as evidenced by the large quantity of niobium found in the residues after amalgamation. In a more recent test, niobium foil and wire were sealed in a niobium capsule together with KO_2. The capsule was heated to 800°C. When the capsule was opened, it was found that the KO_2 had been reduced to potassium metal and that the niobium metal had been partially converted to the oxide.

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[8] J. C. White, A. S. Meyer, and Gerald Goldberg, "Determination of Oxygen in Higher Alkali Metals," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, p 41.

In order to determine whether the mercuric oxide did, in fact, react to any extent with the potassium metal, additional tests were run at 400 and 600°C with potassium contained in nickel capsules. Niobium capsules that contained potassium were spiked with K_2O to check further on the effect of a high oxygen concentration on the niobium metal. In both series of tests the recovery of oxygen was low. Evidently HgO does not react readily with potassium metal. In the case of the niobium capsules, milligram amounts of niobium, possibly as the oxide, were found in the residues after amalgamation. The existence of niobium oxide would account for the low recovery of oxygen as K_2O. (The oxygen is calculated on the basis of a flame spectrophotometric determination of the potassium present in a dilute acid solution of the residue after amalgamation.) An alternative possibility is that some K_2O is lost to the drained amalgam during analysis.

In a previous test[9] both K_2O and KO_2 were added to 5-g samples of potassium of high purity that were contained in amalgamation reaction vessels. Essentially quantitative recoveries of the oxides were attained after amalgamation. It is therefore doubtful that the oxide is partially lost to the amalgam. This premise is also substantiated by the continued precision of results of replicate samples at various oxygen levels. To investigate this possibility further, however, the product from the first amalgamation of a sample of high oxygen content will be collected in a molybdenum capsule under vacuum. The capsule will contain a strip of zirconium of known oxygen content. This capsule will be sealed, and a gettering experiment will be conducted at an elevated temperature to determine whether oxygen is picked up by the zirconium; this oxygen would be attributed to entrained K_2O in the amalgam.

A test was run to determine the recovery, by amalgamation, of oxygen added as Na_2O to a sample of sodium. The capsule was heated at 400°C for 24 hr. Recovery was 80% complete based on the assumption of 100% purity of the Na_2O and no pickup of oxygen by the capsule material. A second such test gave almost 100% recovery. This test indicates that the modified amalgamation procedure is definitely applicable to samples of sodium metal.

Several samples of potassium were examined for possible off-gassing during amalgamation. After the first amalgamation in vacuum, the reaction vessel was connected to an apparatus used to dry and to transfer gases to an evacuated sample bulb by means of a Toepler pump. In no case was there any evidence that any of the noncondensable gases (oxygen, hydrogen, nitrogen) were liberated during amalgamation.

A simple distillation method for determining oxygen in potassium and sodium was studied further, and the results from it were compared with results from the amalgamation method. The sample and its containment material (tubing section or capsule) are placed in a nickel cup. The nickel cup is enclosed in a nickel pot, which has an externally cooled coil connected to the inside of the cover flange. This operation is done within a dry box. The pot is removed from the box, and the lower section is placed in a furnace. The pot is then evacuated and heated to distill the alkali metal to the surface of the cooled coil. When distillation is complete, the nickel cup and containment material are removed, and the residual alkali-metal oxide is dissolved and analyzed in the same manner as in the amalgamation procedure.

Preliminary distillation results from loops that contained sodium show reasonable agreement with amalgamation results in the range of 200 ppm or less of oxygen at distillation temperatures of 500 to 600°C. Results from samples of potassium are far less encouraging. It appears that the distillation temperature for potassium is more critical than for sodium and is in the narrow range from 350 to 375°C. Also, the quenching technique for the capsule tests appears to be inadequate for both metals – and possibly more so for potassium because of the increased oxygen solubility in potassium as opposed to sodium. Analysis of the metal in sections of the quenched capsule showed that both oxygen and the niobium corrosion product were distributed inhomogeneously in the metal.

Some capsules that contained spiked metal were divided into two sections for comparative analysis by both methods. In most cases the results by amalgamation were lower than by distillation. The solutions of the residues from the samples analyzed by the amalgamation method were cloudy with suspensions of niobium oxide. The solutions

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[9] Gerald Goldberg, "Determination of Oxygen in Higher Alkali Metals," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 51.

of the residues from the distillation procedure contained several milligrams or more of shiny niobium metal particles.

It may be that the niobium oxide formed by the oxidation of the capsule during the test is reduced by the alkali metal during the distillation period.

Other niobium capsules that contained spiked metal were divided into three sections. In some cases the upper and lower sections were analyzed by distillation, and the center section by amalgamation. In other cases the upper and lower sections were analyzed by amalgamation, and the center section by distillation. In all cases, results from the analysis of the center section were far lower than those from the upper and lower sections. Also, results of the analysis of the upper and lower sections did not agree. Further experiments will be conducted to develop a suitable technique for providing replicate samples that can be compared by both methods.

The first of a series of round-robin samples of potassium for oxygen analysis were received from NASA. The oxygen content was indicated to be <35 ppm. These samples were handled in a routine manner in that each of the two tubes of sample was cut into three sections within a dry box, and each of these sections was placed in a separate amalgamation reaction vessel. Table 5.1 gives the results of the analysis.

An article that describes the application of the modified amalgamation technique to the determination of oxygen in potassium and NaK was prepared for publication in the open literature. This same topic is the subject of a paper submitted for presentation at the Conference on Applied Spectroscopy and Analytical Chemistry to be held in Pittsburgh in March 1964.

Table 5.1. Results of Analysis of NASA Round-Robin Samples of Potassium

Sample Tube	Section	Sample Weight (g)	Oxygen (ppm)
B-16	Top	1.51	22
	Middle	1.49	26
	Bottom	1.45	24
B-20	Top	1.43	21
	Middle	1.54	19
	Bottom	1.47	22

6. Effects of Radiation on Analytical Methods

J. C. White
P. F. Thomason

EFFECTS OF GAMMA RADIATION ON THE SPECTROPHOTOMETRIC DIMETHYLGLYOXIME METHOD FOR NICKEL

H. E. Zittel

A study of the effect of gamma radiation on the spectrophotometric dimethylglyoxime method for nickel is near completion. Dimethylglyoxime (I) is much less resistant to radiation than is the nickel dimethylglyoxime complex. The effect of the radiation on I is very complicated; the value depends largely on the concentration of I. For 1×10^{-5} and 1×10^{-3} *M* solutions of I, the radiation damage is of the order of 1×10^{-10} and 1×10^{-9} mmole ml^{-1} rad^{-1}, respectively. The form of I is also a factor that affects the radiation damage. A postirradiation effect occurs when a solution of I in ethyl alcohol is used, but not with an aqueous solution of the sodium salt of I; the role of ethyl alcohol in this apparent anomaly is being studied. Identification of the radiolysis products is being attempted. The apparent shift in the absorption peak caused by radiation is also being studied. Possibly I exists in two forms – acid and basic – that absorb at ~225 and ~265 mμ, respectively. Any change in their relative proportions with change in pH brought about by radiation tends to shift the absorption peak. Thus, the relationship between the absorbance and concentration is nonlinear. Data from experiments in which buffered media were used support this postulation.

EFFECT OF GAMMA RADIATION ON ARSENAZO III SOLUTIONS

G. L. Kochanny

The compound 1,8-dihydroxynaphthalene-3,6-disulfonic acid-2,7-bis-(azo-2)-phenylarsonic acid, known as arsenazo III (I), in the form of the disodium salt (II) is used widely as a reagent for the photometric determination of many elements. It is an especially useful reagent for several lanthanides and actinides (see "Studies on Arsenazo III," in Chap. 14 of this report). In view of the current interest in the use of II either in the presence of or for the analytical estimation of radioactive isotopes, its radiation stability was studied.

Pure II (99+%) was obtained from H. L. Holsopple.[1] Solutions of this reagent were irradiated in a Co^{60} source at a dose rate of 3 kilorads/min. Change in the concentration of II was observed spectrophotometrically at the following absorption-spectra maxima: 537 mμ for acetic acid solutions, 542 mμ for hydrochloric acid and sulfuric acid solutions, and 560 mμ for distilled water solutions.

In the strong-acid media studied, the rate of radiolytic decomposition is greatest for the lowest reagent concentration (2.5×10^{-5} *M* II) and the highest acid concentration (9 *N*) studied. For 1×10^{-4} *M* and 2.5×10^{-5} *M* solutions of the reagent in 9 *N* HCl, the average rates of decomposition of II are 2×10^{-6} and 4×10^{-6} mole/liter per kilorad of absorbed gamma radiation, respectively. For a 1×10^{-4} *M* solution of II in 1 *N* HCl, the average rate of decomposition is 9×10^{-7} mole liter^{-1} kilorad^{-1}.

For absorbed gamma doses below 72 kilorads, II is exceptionally stable in 1 *N* acetic acid. A 1×10^{-4} *M* solution of II in 1 *N* acetic acid decomposes at a rate of 9×10^{-8} mole liter^{-1} kilorad^{-1} until a total dose of 72 kilorads has accumulated. At this point, the rate of decomposition becomes $\sim 2 \times 10^{-6}$ mole liter^{-1} kilorad^{-1}. Upon termination of the irradiation, decomposition continues as a postirradiation effect.

The effects of radiation on various metal-II complexes are now being studied. The results of this work will determine the practicability of using II as a chromogenic reagent in the presence of radiation.

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[1] H. L. Holsopple, "Synthesis of o-Nitrophenylarsonic Acid, o-Aminophenylarsonic Acid, and Arsenazo III," ORNL-TM-625 (July 12, 1963).

EFFECTS OF GAMMA RADIATION ON SPECTROPHOTOMETRIC THIOCYANATE METHODS FOR MOLYBDENUM, IRON, AND URANIUM

Lucy E. Scroggie

Investigations of the effects of Co^{60} gamma radiation on spectrophotometric methods for the determination of molybdenum, iron, and uranium as thiocyanate complexes were completed. Papers that describe this work are being prepared for publication.

Preliminary studies on the thiocyanate–stannous chloride spectrophotometric method for the determination of molybdenum[2] are reported.[3] To determine the effects of gamma radiation on the color of the molybdenum thiocyanate complex, a series of butyl acetate extracts of the complex prepared by the procedure[2] was subjected to gamma radiation at various levels. The difference between the spectral absorbances of the irradiated solutions and of unirradiated control solutions was taken as a measure of the damage to the complex caused by the radiation; the absorbances were measured at 470 mμ – the wavelength of analytical interest. The absorbance of the complex decreases with increasing radiation dose – markedly at low doses – until the radiation damage approaches a constant value. The complex is essentially destroyed by radiation doses greater than about 1.4×10^4 rads. Errors as great as 55% can be caused by doses of 3.4×10^3 rads, depending on the molybdenum concentration.

The effects of gamma radiation on the procedure of Woods and Mellon[4] for the determination of iron as the thiocyanate complex in acetone-water medium were studied. Sets of solutions of known iron concentrations prepared by the procedure were subjected to radiation of various intensities. The absorbance of iron thiocyanate, measured at 478 mμ, increases with increasing radiation dose, reaches a maximum between 1×10^5 and 2×10^5 rads, and decreases gradually as the dose is increased further. Errors of from 8 to 22% can be caused by a dose as small as 1.7×10^4 rads, depending on the iron concentration.

The effects of gamma radiation on the spectrophotometric ammonium thiocyanate method for the determination of uranium[5] were investigated. Series of solutions of known uranium concentrations, both with and without stannous chloride as a reducing agent, were subjected to gamma radiation. Aqueous solutions of uranium thiocyanate that contain stannous chloride show a decrease in absorbance, measured at 380 mμ, with increasing radiation dose until a visible dispersion of elemental sulfur appears and thus causes an apparent increase in absorbance. The damage per unit of radiation is less severe for high levels of radiation and for low uranium concentrations. Less than about 2% error is caused by radiation doses of less than 6.8×10^3 rads. The absorbance of the uranium complex in solutions that contain no stannous chloride increases with increasing radiation dose, again due to the turbidity of elemental sulfur produced by radiolysis. The damage per unit of radiation is less severe for high radiation levels and of approximately the same magnitude for different uranium concentrations. Appreciable error (2 to 13%) is caused by radiation doses of less than 3.5×10^3 rads.

The effects of gamma radiation on uranium thiocyanate in the acetone-water medium recommended by Crouthamel and Johnson[6] were studied. Solutions of known uranium concentrations, both with and without stannous chloride, were irradiated. The absorbance of the complex, measured at 375 mμ, decreases with increasing dose, markedly at doses less than 3×10^5 rads and then more gradually, when stannous chloride is present. The damage per unit of radiation is less severe at high radiation levels, but the color of the complex is destroyed and therefore is worthless from an analytical standpoint after a dose of 5×10^5 rads has been absorbed. Errors less than 10% would

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[2] T. C. Rains and L. J. Brady, "Molybdenum, Spectrophotometric Thiocyanate–Stannous Chloride Method," Method Nos. 1 215010 and 9 00715010 (5-10-57), *ORNL Master Analytical Manual*, TID-7015, sec 1 (April 1958).

[3] Lucy E. Scroggie, "Effects of Gamma Radiation on the Thiocyanate–Stannous Chloride Spectrophotometric Method for Molybdenum," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 55.

[4] J. T. Woods and M. G. Mellon, "Thiocyanate Method for Iron. A Spectrophotometric Study," *Ind. Eng. Chem., Anal. Ed.* **13**, 551 (1941).

[5] U. Koskela and C. E. Lamb, "Uranium, Spectrophotometric Ammonium Thiocyanate Method," Method Nos. 1 219210 and 9 00719210 (R. 10-9-61), *ORNL Master Analytical Manual*, TID-7015, suppl 4 (June 1962).

[6] C. E. Crouthamel and C. E. Johnson, "Spectrophotometric Determination of Uranium by Thiocyanate Method in Acetone Medium," *Anal. Chem.* **24**, 1780 (1952).

be caused by doses not exceeding 2×10^4 rads. Solutions that contain no stannous chloride exhibit an increase in absorbance with increasing radiation dose, marked at low doses and more gradual for doses greater than about 1×10^5 rads. The damage per unit of radiation is less severe at high radiation levels. However, errors exceeding 40% can be caused by a dose of 1.7×10^4 rads, depending on the uranium concentration.

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7. X-Ray and Spectrochemical Analyses

X-RAY AND SPECTROCHEMICAL ANALYSES (X-10)

M. T. Kelley
Cyrus Feldman

X-Ray Analysis

H. W. Dunn

Determination of Gd_2O_3 in Gd_2O_3-Al_2O_3 Ceramic by X-Ray Fluorescence. – Pure specimens of Gd_2O_3 and Al_2O_3 were ignited overnight in an electric muffle to eliminate H_2O and CO_2 from the Gd_2O_3 and to convert the Al_2O_3 to corundum, which is nonhygroscopic. Standard mixtures having Gd_2O_3 contents in the range from 60 to 80 wt % were prepared from these oxides.

Standards and specimens of the Gd_2O_3-Al_2O_3 ceramic were reduced to ~250-mesh particles with a ball-shaker mill; tungsten balls and hardened steel end plates were used in the specimen container. Six grams of borax ($Na_2B_4O_7 \cdot 10H_2O$) was fused in a platinum dish, 1 g of powdered sample and 0.2 g of Co_3O_4 were added, and the mixture was ignited overnight at 1000°C. It was necessary to perform the ignition in an electric muffle, since the use of a Meker burner caused reduction of Co_3O_4 to cobalt, which alloyed with the platinum dish. The melt was cooled, powdered, and mixed with an equal weight of corn starch. This mixture was compressed to a pellet at 40,000 psi. The intensities of the Gd $L\beta_1$ and Co $K\alpha$ lines were measured with a General Electric XRD-3 diffractometer. Weight percent Gd_2O_3 was read from a curve showing Gd $L\beta_1$/Co $K\alpha$ intensity ratios as a function of standard composition. The standard counting error for these ratios was consistently less than 1%.

Neighboring Edge Effect in X-Ray Absorption-Edge Analysis. – Although matrix composition normally has negligible effect on results obtained by x-ray absorption-edge analysis, distortions occur when minor amounts of one element are determined in the presence of major amounts of another element having an absorption edge near the edge being measured (e.g., Mo in Nb, W in Ta, Zr in U). To obtain accurate results, it is necessary to prepare synthetic standards that closely match the samples in matrix composition.

X-Ray Absorption-Edge Analysis of Radioactive Solutions. – To make possible x-ray absorption-edge analysis of radioactive solutions in a conventional laboratory without exceeding tolerances on contamination or radiation level, a disposable polystyrene solution cell was designed. This cell, which has a volume of ~0.4 ml, will be filled at the point of origin of the sample and sealed with a suitable adhesive tape. It can then be transported to the x-ray laboratory in a shielded container, analyzed, and discarded without exposing the laboratory or persons to hazardous amounts of contamination or radiation.

Atomic Absorption Analysis

S. R. Koirtyohann   Cyrus Feldman

Effect of Hollow-Cathode Current on Absorption of Light by Sample Vapor. – The resonance absorption line of a cool monatomic vapor is always narrower than the corresponding line emitted by the hollow cathode. The effect of cathode current can therefore be either positive or negative, depending on the ratio of signal intensity to background intensity in the light emitted by the hollow cathode. If this ratio is high, the predominant effect is a decrease in absorption with increasing current, because the increase in Doppler and pressure broadening at higher currents makes the emission line broader than the absorption line. If the ratio is low, the effect is the opposite; the signal now consists mostly of continuum, and the total signal detected is determined by the bandwidth of the monochromator. This bandwidth is always much greater than the width of the line. Thus, there is little absorption of the light emitted by such a source at low currents, and more absorption at higher currents. If a sufficiently high current can be reached, the absorption should begin to decrease again for the reasons given above.

An experiment was made to compare this phase of the performance of the demountable hollow cathode,[1] operating in a continuous stream of argon, with that of a commercially available sealed-off hollow cathode.[2] The results, obtained with a 1-μg/ml solution of lead by the absorption-tube technique (Fig. 7.1) described previously,[3] are shown in Table 7.1. They indicate that the spectral width of the line emitted by the demountable cathode varies only slightly with current. At low currents, the sealed-off cathode emits relatively little of the absorbable Pb 2833 A radiation; at higher currents, it gives about the same performance as the demountable source. Higher currents shorten the life of the commercial tube and are not recommended by the manufacturer. The demountable cathode is thus less current-sensitive than is the sealed cathode under the preferred working conditions, although it is also less convenient for routine use.

Table 7.1. Absorbance of Pb 2833 A Radiation by Vapor from a 1-μg/ml Solution of Lead

Current (ma)	Absorbance	
	Demountable Hollow Cathode	Sealed-off Hollow Cathode
10	0.138	
15		0.060
20	0.135	0.090
30	0.127	0.114
40	0.120	0.127

Use of Long Absorption Tubes. – The absorbance of a column of atomic vapor can be increased by increasing the number of absorbing particles in the light path. The obvious advantage to be gained by lengthening the absorption tube (Fig. 7.1) is limited by the tendency of free metallic atoms to combine with oxygen as they travel down the tube and/or to deposit on the walls of the tube. If the flame gases show continuous absorption at the wavelength of interest, lengthening the tube past the point where free atoms exist will increase background absorption without a corresponding increase in signal absorption.

Figure 7.2 shows that extending the tube increases the absorbance in the case of lead, which forms an easily dissociated oxide, and that the improvement ceases at a tube length of ~25 cm in the case of magnesium, which forms a difficultly dissociated oxide.

Molecular Absorption and Scattering. – Resonance radiation emitted by the hollow cathode is absorbed by the atomic species being determined, but it may also be absorbed by molecular fragments or scattered by particles in the flame. When the insertion of sample vapor into the optical path causes a decrease in the intensity of the resonance radiation transmitted, it is necessary to measure the extent to which this may have been due to molecular band absorption and/or scattering. This is most readily done with the aid of a sample known to be completely free of the element being determined. If such a sample is not available, a measurement of absorbance at a closely neighboring wavelength, by use of a line that is not absorbed by this element, will serve the same purpose.

Figure 7.3 shows spectral "absorption" curves obtained with moderately concentrated solutions of sulfuric acid, aluminum nitrate, and sodium

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[1] G. K. Werner *et al.*, "Further Investigations in the Spectro-Isotopic Assay Technique for Lithium," *J. Opt. Soc. Am.* **45**, 202–5 (1955).

[2] Jarrell-Ash Co., Newton, Mass.

[3] Cyrus Feldman, S. R. Koirtyohann, and T. S. Krishnan, "Use of Demountable Hollow Cathode," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, pp 60–61.

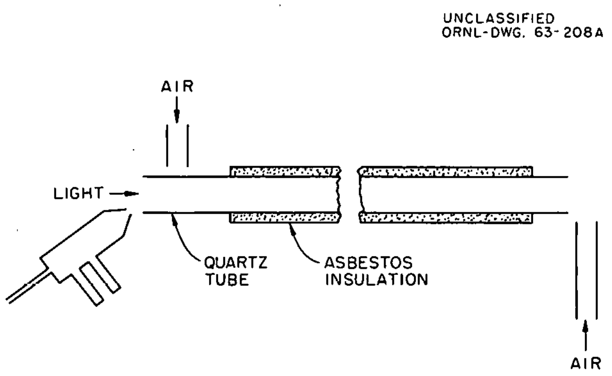

Fig. 7.1. Burner and Tube Arrangement for Long Absorption Path Lengths.

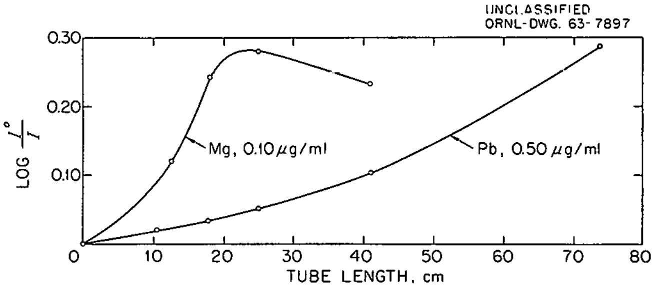

Fig. 7.2. Effect of Tube Length on Absorption.

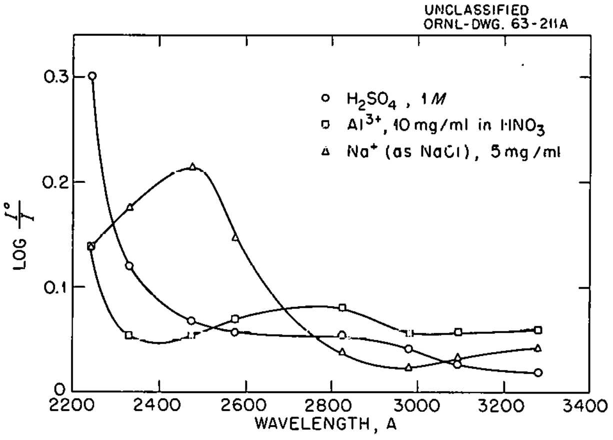

Fig. 7.3. Apparent Absorption from Materials in the Flame; 25-cm Tube.

chloride. At the total solute concentration ordinarily used (1 mg of metal per ml), however, interference due to this factor is not usually serious. Table 7.2 shows the maximum error that would be caused by failing to correct for continuous absorption and/or scattering in several typical situations. These corrections are of the order of thousandths of a percent in metal-to-metal terms. Their importance depends, of course, on the concentration level of the element determined.

Applications and Sensitivity Limits. – All the elements listed in Table 7.3 were determined in water and in the aqueous phase remaining after the extraction of uranium. Bismuth and antimony were determined in air dust; cadmium in urine and in U-Al alloys (without chemical separation); lead in air dust, blood, and urine; tellurium in urine; magnesium in solutions of sodium chloride; and zinc in copper alloys. The sensitivities listed in Table 7.3 refer to solutions that contained no other solutes. As in emission flame photometry, any anions or other solutes that reduce the volatility of the species being determined will reduce the sensitivity of the method.

Determination of Tin. – The detectability of tin by flame-emission methods is limited by the difficulties of dissociating SnO in the gas phase and of exciting those Sn atoms that are produced. By the atomic absorption method, with air substituted for oxygen in the Beckman oxyhydrogen burners used in the end-fed absorption-tube technique, a sensitivity limit of 0.5 μg/ml (1% absorption) was attained for tin in dilute nitric acid. The presence of substantial concentrations of hydrochloric acid or hydrobromic acid reduced the sensitivity.

Flame Photometry

T. C. Rains Cyrus Feldman

Determination of Cesium in Sea Water. – In the application of the ammonium phosphomolybdate (I) collection procedure to sea water, flocculation of aluminum hydroxide was difficult to achieve. Prolonged standing (e.g., overnight) led to partial dissolution of I and to loss of cesium. It was found that the floc (and the cesium) could be collected efficiently by centrifugation. The sea

Table 7.2. Maximum Error Introduced by Ignoring Corrections for Continuous Absorption and/or Scattering in Analyzing Salt Solutions by Atomic Absorption

Solute		Maximum Error (μg/ml)			
Identity	Concentration (mg/ml)	Pb 2833 A	Mg 2852 A	Zn 2138 A	Cd 2288 A
Na^+	1	0.1	0.005	0.005	0.02
Al^{3+}	1	0.07			0.004
Ca^{2+}	1	0.05		0.005	
H_2SO_4	(0.1 *M*)	0.02		0.010	

Table 7.3. Detection Sensitivities by Atomic Absorption by Use of the End-Fed Absorption Tube

Aqueous solutions; oxyhydrogen flame

Element	Line (A)	Concentration Giving 1% Absorption (μg/ml)
Bi	2230	0.1
Cd	2288	0.001
Cu	3247	0.005
Hg	2537	0.5
Mg	2852	0.001
Mn	2795	0.005
Ni	2320	0.01
Pb	2833	0.02
Sb	2176	0.1
Sr	4607	0.1
Te	2143	0.02
Tl	2768	0.05
Zn	2138	0.0005

water samples tested contained 3 to 4 μg of cesium per liter. An article that describes this work was accepted for publication in *Analytical Chemistry*.

The cesium content of I obtained from different sources varied considerably. The preparations tested gave the following results (μg of Cs per g of I): Bio-Rad Laboratories, Richmond, California, <0.05; Chemical Procurement Laboratory, College Point, New York, <0.05; Shattuck Chemical Company, Denver, Colorado, 0.5; Kanto Chemical Company, Tokyo, Japan, 0.6.

Tissue Analysis

S. R. Koirtyohann Cyrus Feldman

Volatilization of Metals During Ashing. – The experiments on the volatilization of metals during ashing described previously[4] were repeated with 2.7 g of liver ash. The only trap found to contain volatilized material was the first trap, which was cooled with Dry Ice. Results agree essentially with those reported earlier; the only losses observed were (in percent of the amount of the element originally present in the ash): Cu, 0.06; Ni, 10; and Al, 2.

In view of Schroeder's[5] finding that the concentration of vanadium in human fat is >1 ppm, the volatilization of vanadium during ashing was studied. Ashing-loss experiments similar to those reported previously showed no vanadium (i.e., <2 μg) present in the traps, whereas 3 μg was found in the ash, which amount corresponds to a vanadium concentration of 0.03 μg/g in the original sample.

To prevent loss of vanadium, a second sample of fat was saponified before it was ashed. The ash solution was extracted with a solution of 8-hydroxyquinoline in chloroform, and the extract was examined spectrographically. No vanadium was detected; thus, an original concentration of <0.1 μg/g was indicated. Vanadium added to an aliquot of the sample solution was recovered completely.

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[4] S. R. Koirtyohann and Cyrus Feldman, "Tissue Analysis," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, pp 62–64.

[5] H. A. Schroeder, Dartmouth Medical School, Hanover, N. H., private communication to S. R. Koirtyohann, July 23, 1963.

Tape Readout for Quantometer. — A readout device designed by R. K. Adams[6] was attached to the Quantometer. This device punches on paper tape results obtained from standards and samples. By means of a code written by C. D. Martin,[6] the results are converted to chemical concentration and are typed in tabular form. Elimination of the associated clerical work saves ~20% of the cost of analysis of tissues.

X-RAY AND SPECTROCHEMICAL ANALYSES (Y-12)

A. E. Cameron

J. A. Norris

Multiplier Phototube Testing Program

J. A. Norris

To select the best multiplier phototubes for direct-reading spectrochemical analyses, two test devices were rebuilt to conserve space and to accelerate testing. The first is a rack-mounted light-tight box that contains a tritium-activated phosphor source (4000-A peak intensity) with an externally controlled iris diaphragm for adjusting the light level. The multiplier phototube (side-window 1P28 or similar tube) is mounted ~6 in. from the light source. The output of the phototube is sensed by a vibrating-reed electrometer and is recorded on a Brown recorder. The absolute level and variability of the background current are measured; also, the absolute level and stability of response to the constant light source are monitored. Variations of more than one order of magnitude between different tubes of the same type are commonly found.

The second test apparatus is a light-tight attachment to a Beckman model DU spectrophotometer. This apparatus is so designed that the multiplier phototube can be moved horizontally across the light path, and the response of the photosensitive surface recorded. The change in response with changing angle of incident light can also be tested. By use of sources of different wavelengths, the relative responses of different tubes of one type or of tubes of different types can be measured. Typical recordings of a tube tested under these conditions are shown in Fig. 7.4. Recording A shows the response of dark current; B, constant light; and C, the response profile with incident light perpendicular to the photosensitive surface. With this equipment, representative tubes manufactured by RCA (1P28, 1P21), Toshiba (MS-9SY), and Hamamatsu (R-136) were tested.

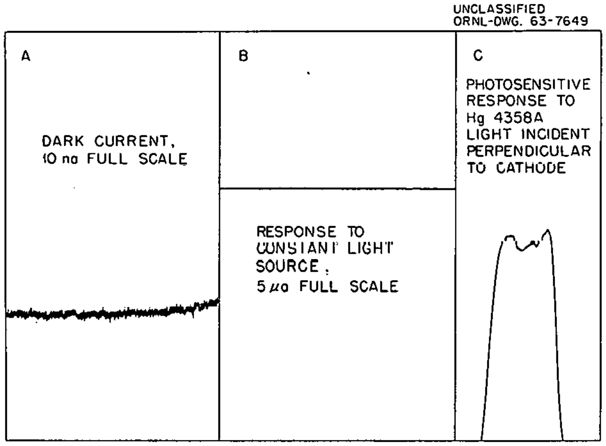

Fig. 7.4. Test Response of Hamamatsu R-136 Multiplier Phototube.

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[6] Instrumentation and Controls Division.

8. Mass Spectrometry

A. E. Cameron

ANALYTICAL MASS SPECTROMETRY

J. R. Sites

A series of quartz capsules that contained UO_2-Al fuel pellets and various contaminant gases were analyzed. A vacuum-tight, bakeable, demountable, capsule-breaker tube is used to sample the gases remaining after the baking. A second gas sample is taken after the tube is evacuated and the residue is baked at 600°C.

The space for the high-alpha, double-magnet, mass spectrometry laboratory was renovated. Most of the basic vacuum and electronic equipment is ready to be assembled. The detection and data-handling equipment will arrive soon.

It was demonstrated that the five-filament sample wheel in the 12-in., 90° mass spectrometer can be used to analyze 15 rare-earth samples in one day.

A routine based on a daily isotopic standard was devised and used to analyze about 200 potassium samples; this routine requires a double-filament sample and ionizing subassembly. The precision achieved in isotopic measurements by means of the routine is significantly better than the precisions reported by three other laboratories.

A manual, *Isotopic Mass Spectrometry of the Elements*, based on techniques now in use by the Analytical Mass Spectrometry Section, was compiled and is being published. It contains outlines of the procedures for determining each of 63 polynuclidic elements. A summary of these techniques was presented at the meeting of the ASTM Committee E-14 in May at San Francisco.

MASS SPECTROMETRY RESEARCH

J. F. Burns

The discovery of a rather complicated structure in the ionization-efficiency curves for the rare gases that could not be explained in terms of known auto-ionizing processes was reported in 1960.[1] Since that time, auto-ionization from the discrete atomic levels of krypton and xenon, which lie between the two members of the doublet ground state of those atoms, was reported.[2,3] In addition, the ionizations resulting from transitions to the individual vibrational levels of the N_2^+ ion were resolved, but the curves have not been published. Several of the more serious sources of error inherent in the method of measurement were identified, and procedures were developed to eliminate them. The unambiguous correspondence between the structure observed in the ionization efficiency curves for krypton, xenon, and nitrogen and that predicted from optical spectroscopic data indicates that at least part of the additional structure is real and arises from some ionization process not observed by previous investigators. The potentialities of the present experimental apparatus have been exhausted, and a new instrument is being designed that will overcome the limitations of the one now in use.

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[1] J. F. Burns, "Mass Spectrometry Research and Development," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 35–36.

[2] J. F. Burns, "Experimental Detection of Auto-Ionizing Transitions in Krypton by Electron Impact," *Nature* **192**, 651 (1961).

[3] J. F. Burns, "Auto-Ionization and the Ionization Efficiency Curves of Krypton and Xenon," presented at the 3rd International Conference on the Physics of Electronic and Ionic Collisions, London, July 22–26, 1963.

9. Infrared Spectroscopy

C. A. Horton Lucy E. Scroggie

A method was developed for encapsulating hazardous or radioactive solid samples for infrared examination. A 0.5- to 2.5-mg portion of the sample is diluted with 325 mg of dry, powdered, infrared-quality potassium bromide in a small, metal, capsule ball mill placed on a Wig-L-Bug agitator. The mixture is introduced into an evacuable die that contains a 0.5-in.-OD metal ring and is tamped flat. The plunger is inserted, the die is evacuated for 3 to 5 min, and a pellet is pressed at 8 tons pressure for 12 min. Both the plunger and bottom of the die are then removed, and 25 to 30 mg of dry potassium bromide is spread over each of the exposed surfaces of the pellet. The sandwich is then re-pressed at 10 tons pressure for 12 min. The encapsulated pellet is removed from the die. All these steps are carried out in facilities provided with shielding, safety, and radiation control adequate for the material of interest. For further protection, the pellet may be mounted in a suitable holder and encased in a 0.5-mil-thick polyethylene bag. If the composite is stable and of sufficiently low radiation level, the prepared sample may be examined in spectrophotometers located in noncontrolled areas.

Detection of anions in aqueous solution with an attenuated total reflectance unit was studied briefly. By means of a silver chloride prism, sulfate and uranyl ions in aqueous solutions can be detected in concentrations as low as 0.4 and 0.07 *M*, respectively.

Waxes obtained as by-products of the hydrolysis of uranium carbides with water or nitric acid were studied. These materials are methanol-soluble but are insoluble in carbon tetrachloride and benzene. Among the functional groups confirmed for some of these products were: nitrite and nitrate esters, ordinary ester, δ-lactone, olefin, aldehyde, carboxylic acid, and probably alcohol. Brief attempts were made to separate the mixtures by paper chromatography and by selective solubility in mixed organic solvents.

Thallium bromide and thallium chloride were studied as matrices for thorium oxides in pellets for infrared examination. For both compounds, pellets that contained 10 mg of ThO_2 per 400 mg of matrix had greater transmittance than did pellets having potassium bromide as a matrix.

The hydrogen-bonding of 4-sec-butyl-2(α-methylbenzyl)phenol (I), designated BAMBP, in various solvents and the character of its cesium adducts were investigated. Figure 9.1 shows the absorption bands in the region of the stretching vibration of the hydroxyl ion for various solvents

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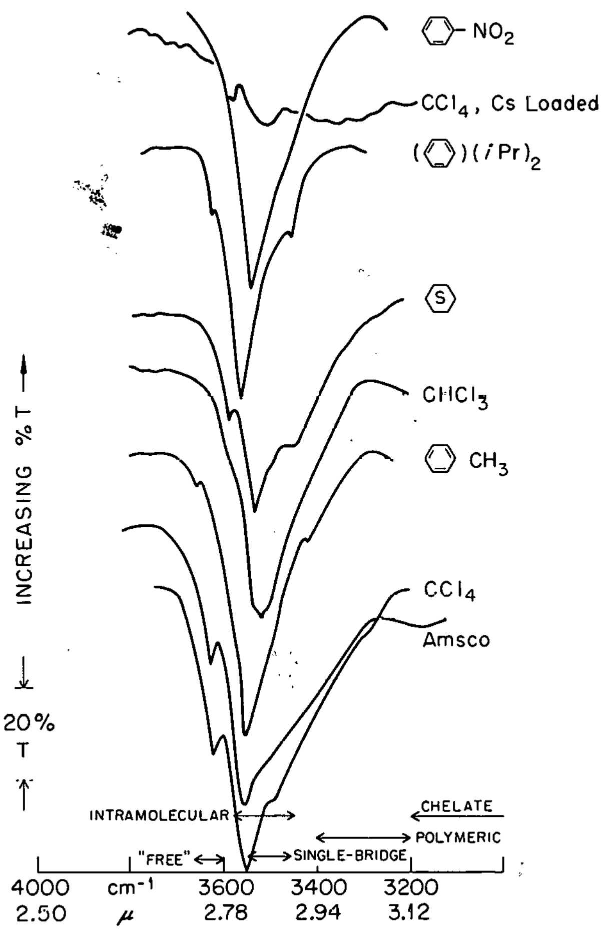

Fig. 9.1. Variation of OH Stretching Vibration of 4-sec-Butyl-2(α-methylbenzyl)phenol for Various Media.

and one cesium adduct. The change in amounts of "free," single-bridge, intramolecular, and polymeric character of the partially hydrogen-bonded hydroxyl vibration for 1 *M* I in various solvents is evident. None of these solutions showed "chelate" hydroxyl vibrations in the 2600 to 2300 cm^{-1} region except those that contained the cesium adduct. This adduct was made under loading conditions with a determined mole ratio of 4 of I to 1 of Cs^+. Another adduct made under loading conditions with a 2 : 1 mole ratio of I to Cs^+ absorbed almost entirely in the polymeric hydroxyl region and only slightly in the chelate region. The change in ratio of these various hydroxyl vibrations was also followed after dilution of the solutions with more of the same solvents.

Table 9.1 lists most of the various types of samples investigated qualitatively by infrared spectroscopy during the year. In addition, semiquantitative or quantitative studies were made of the isomeric content of diethylbenzenes and of solutions of di-sec-butylphenylphosphonate in diethylbenzene.

Table 9.1. Types of Samples Examined by Infrared Spectroscopy

Organometallic and Organic	
Benzyltributylphosphonium tetrachloronickelate(II)	Nicotinamide ribose phosphate
Tetra-*n*-butylammonium tetrabromonickelate(II)	Modified nicotine ribose phosphate
Acetylacetone	Perfluorotrialkylamine
Arsenazo III	Phenols, substituted
Arylphosphonium halides	Phenols, substituted, nitrated
Bathophenanthrolines	Metal adducts of substituted phenol
Chlorinated biphenyl	Ribose phosphate
Cyclopentanecarboxylic acid	Sorbitan monooleate
Di-*sec*-butylphenylphosphonates	Tetrabutylammonium halides
Dibutylthiophosphate salts	Tributyl phosphate
2,3-Dichloroacrylonitrile	Degraded oils
Diethylbenzenes	Fluorothene sheet
Nitrated diethylbenzenes	Neoprene O-ring extract in CCl_4
Di-2-ethylhexylphosphoric acid	Permatrex hydraulic fluids
3,9-Diethyltridecanone-6	Residue from HNO_3 dissolution of uranium carbides
3,9-Diethyltridecanol-6	Rubber
Diisopropylbenzene	Teflon-type grease
N-Methylnicotinamide iodide	Urine fractions
Inorganic	
$CrF_{2.445}$	FeF_2 (crystal)
NiO	KCl (single crystals)
$NiSO_4$	LiF (single crystals)
TlBr	Rare-earth-metal manganites
TlCl	$2NaF \cdot ZrF_4$ eutectic
UO_2	$2LiF \cdot UF_4$ eutectic
LiF powder	$5LiF \cdot BeF_2 \cdot ZrF_4$ eutectic
ThO_2 powders	$8LiF \cdot BeF_2 \cdot ZrF_4$ eutectic

10. Optical and Electron Microscopy

M. T. Kelley
T. E. Willmarth
H. W. Wright T. G. Harmon

ELECTRON MICROSCOPY OF RADIOACTIVE MATERIALS

Methods for the preparation of irradiated material for electron microscopy were developed or modified. Barnes, Burton, and Scott[1] describe a method for the replication of surfaces for electron microscopy by the pressure molding of polystyrene. The method was adapted to remotely controlled replication by use of the pressure device shown in Fig. 10.1. A weight is used to apply a load of about 1 kg to a guided central shaft connected to a slightly tapered head, which rests on the sample material. The sample is placed on a piece of $\frac{1}{16}$-in.-thick polystyrene sheet, which rests on a polished metal block. The block is heated to ~160°C by a remotely controlled heater. On cooling, the sample is easily removed from the polystyrene, and the polystyrene from the metal block. The radioactivity of successive replicas is monitored until one is found that is within safe limits. A positive replica is then made from the polystyrene mold by the evaporation of silica or carbon onto its surface. Standard techniques are used for dissolving the polystyrene and collecting the replica film. If preferred, polyethylene or isobutyl methacrylate can be used instead of polystyrene. Special jigs can be used for samples of various shapes. If one is interested in the identification of surface material, enough such material is usually stripped along with the negative replica and is transferred to the positive replica for use in electron-diffraction studies of a selected area.

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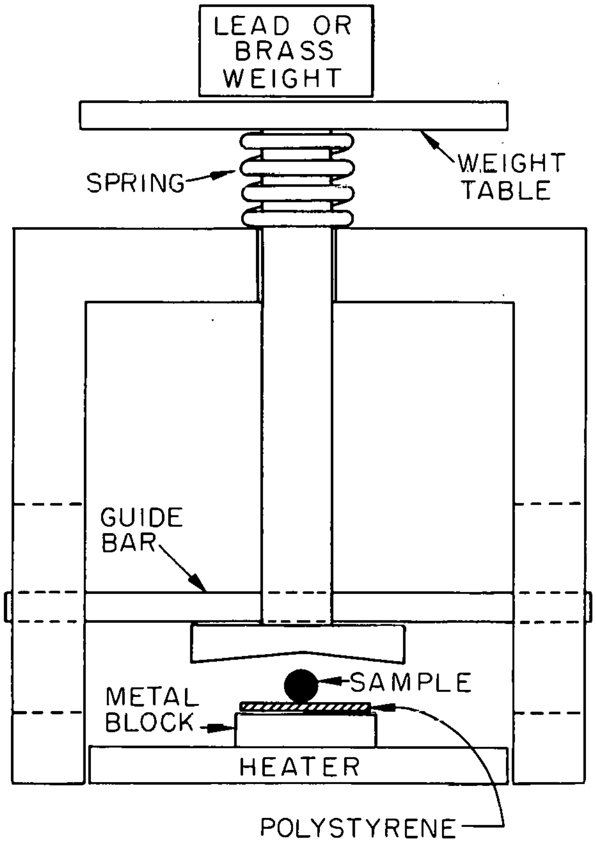

Fig. 10.1. Device for Pressure Replication by Use of Polystyrene or Polyethylene Sheet.

The electrostatic device for collecting radioactive particulates[2] (Fig. 10.2) was fabricated. After a promising test run, the electrostatic precipitator was included in the U-Al alloy fission product release experiment conducted by G. W. Parker and group.[3] Figure 10.3 shows a repre-

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[1] R. B. Barnes, C. J. Burton, and R. G. Scott, "Electron Microscopical Replica Techniques for the Study of Organic Surfaces," *J. Appl. Phys.* 16, 730–39 (1945).

[2] M. T. Kelley *et al.*, "Optical and Electron Microscopy," *Anal. Chem. Ann. Progr. Rept. Dec. 31, 1962,* ORNL-3397, pp 67–70.

[3] Reactor Chemistry Division.

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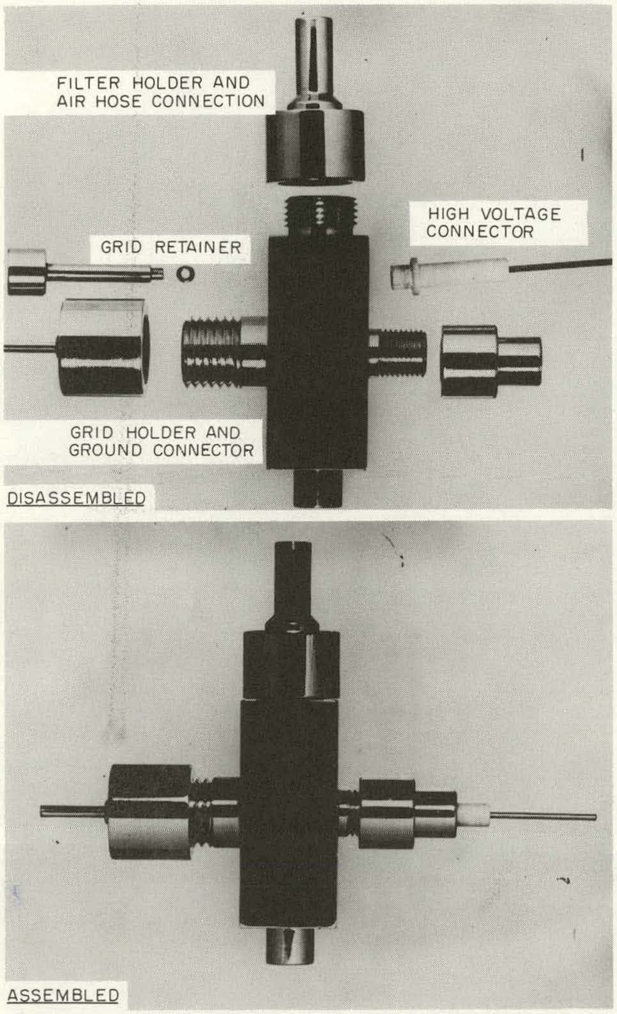

Fig. 10.2. Electrostatic Particle Collector for Electron Microscopy.

sentative field of particulate material collected electrostatically on the carbon substrate of the electron microscope grid during the experiment. The solid opaque particles appear to be U-Al alloy; the less dense, halo-surrounded particles appear to be a cesium compound – possibly the iodide. In current runs, selected-area electron diffraction will be used to establish more definitely the identity of the collected particles.

One of the research groups has requested a system by means of which a number of these devices can be used for collecting dust samples and can be individually and automatically closed or opened at set times or temperatures.

INSTRUMENTATION

A Philips 200B electron microscope, which has a resolution of the order 5 to 10 A, was purchased and should be in operation by December 1963.

RESEARCH ASSISTANCE

A wide variety of materials of interest in nuclear technology and other fields were studied by electron and optical microscopy and by electron diffraction for research groups in other divisions. Examples of the materials and the studies are: films of evaporated silver, for structural changes produced by varying the nature of the receiving strata and the rate of deposition; fractured surfaces of beryllium oxide exposed to various neutron doses at elevated temperatures; lithium-beryllium fluoride crystals, for effect of electron bombardment; glass and asbestos fibers exposed in a fluorine atmosphere; membranes used in saline water experiments; carbon-coated uranium oxide–thorium oxide spheres; spheres of thorium sol gel; thorium oxide particles in thorium and in molybdenum matrices; neodymium hydroxide precipitated at 100°C; Zircaloy exposed to 0.05 M H_2SO_4 at 296°C for two months; nickel and thorium exploded in nitrogen; the surface structure of sapphire crystals; the surfaces of gold-electroplated steel seals; uranium oxides and niobium oxides; the surface of a copper-coated single crystal of silicon; tantalum, tungsten, aluminum, and magnesium powders; silver-impregnated polypore filters; synthetic magnetite; films from molten salt experiments; and latex hydrosols.

Additional thin films, produced by vaporization, were provided to the Physics and Chemistry Divisions for use as targets and solid-state detectors.

Fig. 10.3. Particles Collected by the Electrostatic Precipitator in Line During the Fission Product Release Experiment.

11. Nuclear and Radiochemical Analyses

J. C. White
W. S. Lyon

MEASUREMENT OF RADIOACTIVITY

Nuclear Decay Scheme of Lu^{177m}

J. S. Eldridge Peter Crowther[1]

Work to characterize the decay of Lu^{177m} was begun. B. S. Weaver,[2] with whom this work was jointly done, provided sources of irradiated Lu_2O_3 from which he first observed this long-lived isomer that decays with a half-life of 170 days.[3] Jorgensen, Nielsen, and Sidenius,[4] from preliminary studies of this nuclide, report gamma rays of 100 to 400 kev and indicate that Lu^{177m} lies about 1200 kev above the level in Lu^{177}.

The gamma-ray spectrum of Lu^{177m} was measured with various source-to-detector geometries. Gamma photons as energetic as 1.4 Mev, with some coincident sum events as high as 1.6 Mev, were observed. A typical gamma-ray spectrum of Lu^{177m} is shown in Fig. 11.1. Gamma-gamma coincidence measurements are being made to resolve this complex decay.

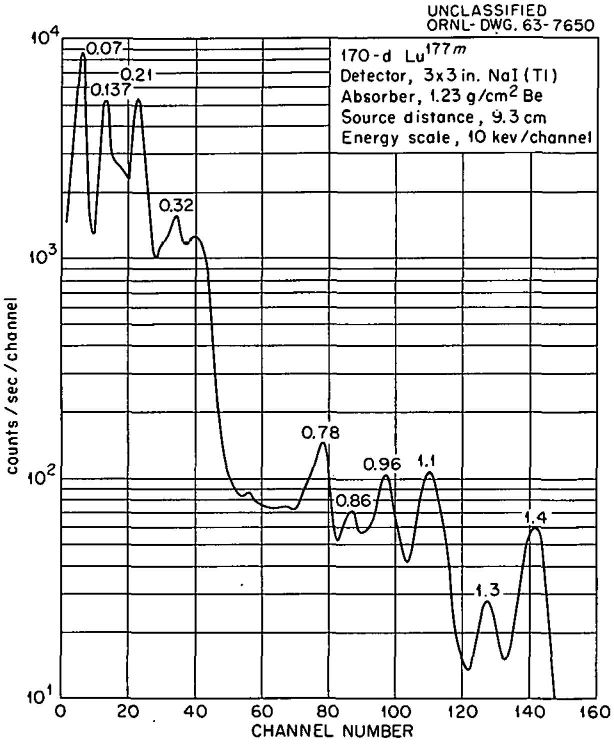

Fig. 11.1. Gamma-Ray Spectrum of 170-day Lu^{177m}.

Gamma-Ray Branching in Mo^{99}

Peter Crowther[1] J. S. Eldridge

To measure absolute disintegration rates and gamma-ray branchings in Mo^{99}, a new liquid-liquid extraction technique for the separation of molybdenum and technetium was developed. Sixty-eight-hour Mo^{99} was separated from its 6-hr Tc^{99m} daughter by extraction of the Tc^{99m} into a chloroform-pyridine solution of tetraphenylarsonium chloride. Three such extractions were made to ensure quantitative separation. Figure 11.2 shows the gamma-ray spectrum of Mo^{99} taken immediately after separation. For comparison, the gamma-ray spectrum of an equilibrium mixture of Mo^{99}-Tc^{99m} is shown in Fig. 11.3. To determine the absolute disintegration rate of source mounts, 4π beta-gamma coincidence measurements were made on the separated Mo^{99}. Gamma-ray emission rates were determined by gamma-ray spectrometry. From these measurements, the branching of the 0.74- plus 0.78-Mev gamma rays in Mo^{99} was found to be (16.5 ± 0.1)% of the decays. Others[5] had assigned a

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[1] Temporary alien employee, South African Atomic Energy Board, Pelindaba, Pretoria, South Africa.

[2] Chemical Technology Division.

[3] B. S. Weaver and J. R. Collins, *A Second Isomer of* Lu^{177} (unpublished report), Dec. 29, 1960.

[4] M. Jorgensen, O. B. Nielsen, and G. Sidenius, "Three-Particle Excitation in Lu^{177}," *Phys. Letters* 1, 321 (1962).

[5] *Nuclear Data Sheets*, vol 5, Natl. Acad. Sci.—Natl. Res. Council, Washington, D.C., 1962.

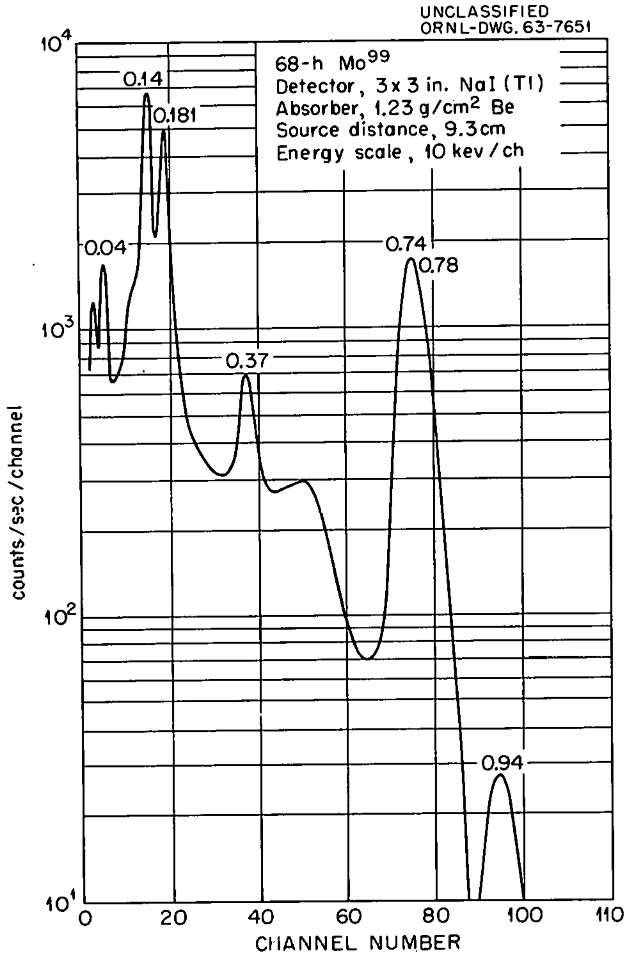

Fig. 11.2. Gamma-Ray Spectrum of 68-hr Mo^{99} Immediately After Separation of Tc^{99m} Daughter.

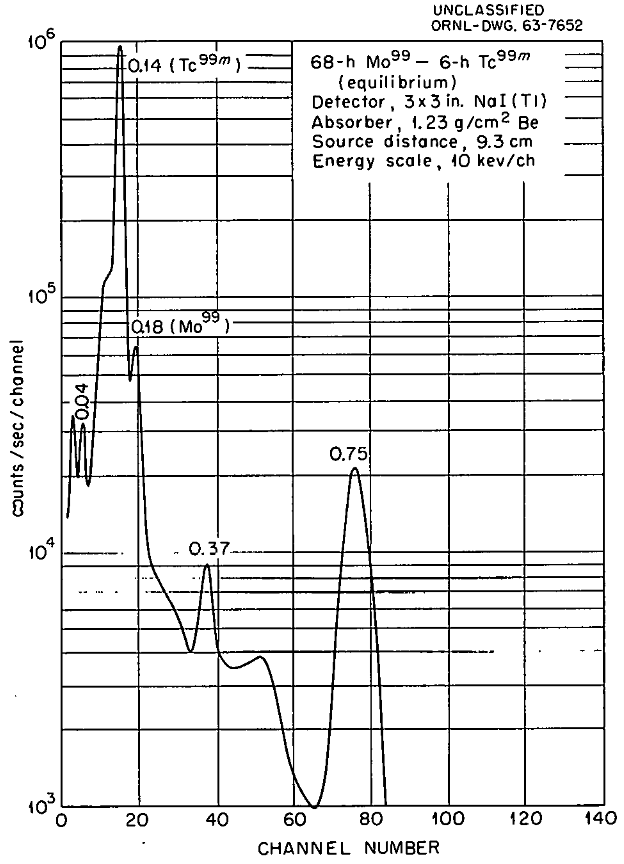

Fig. 11.3. Gamma-Ray Spectrum of 68-hr Mo^{99}–6-hr Tc^{99m} Equilibrium Mixture.

value of 14% to this branching. Work to further characterize this nuclide will be done. The results will be valuable to workers who wish to determine burnup and total fissions by means of gamma-ray spectrometry.

Gamma-Ray Branchings in the Decay of 54-min In^{116}

Peter Crowther[1] J. S. Eldridge

Gamma-ray branchings in some of the major transitions in 54-min In^{116} were determined by absolute gamma-ray spectrometry on sources that were calibrated by 4π beta-gamma coincidence measurements. Table 11.1 lists gamma-ray energies and observed intensities for the measured transitions.

Spectral determinations were made at several distances in order to check for sum-coincidence effects in the above branching ratios. The gamma ray at 1.77 Mev was found to be the only transition exhibiting sum-coincidence effects. The value listed in Table 11.1 for this gamma ray is the observed branching ratio at 9.3 cm from a 3 × 3 in. NaI detector.

The decay of this nuclide was followed over a period of 12 half-lives by use of the scaler-time mode of operation in the 512-channel analyzer. The decay data were analyzed by the CLSQ Decay Curve Analysis Program[6] in the IBM 7090 computer,

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[6] J. B. Cumming, *Radiochemical Techniques. Application of Computers to Nuclear and Radiochemistry* (ed. by G. D. O'Kelley), NAS-NS-310 (March 1963).

Table 11.1. Gamma-Ray Branchings in 54-min In^{116}

Energy (Mev)	Branching Ratio ($\gamma/d \times 100$)
1.09	54.6
1.28	85.8
1.49	7.0
1.77	4.1[a]
2.09	16.9

[a] This observed value would be the upper limit of this transition. Sum-coincidence corrections have not been made.

The least-squares fit of the data gave a half-life value of 53.73 ± 0.06 min.

Figure 11.4 gives a typical gamma-ray spectrum of In^{116} showing the levels at which the photopeaks were fitted by a graphical technique.

Gamma-Ray Branchings in the Decay of Cl^{38}

J. S. Eldridge Peter Crowther[1]

Previous workers have characterized the decay of 37-min Cl^{38} by use of beta-ray spectrographs and Compton spectrometers. The gamma-ray branchings in the decay scheme were redetermined; considerable discrepancies from literature values were observed. The 1.64- and 2.19-Mev gamma rays are present to the extent of 31 and 42%, respectively, of the decays. The ratio of these intensities is thus seen to be 1.36 compared with the literature value of 1.13. By use of a "pair" spectrometer, workers in the ORNL Chemistry Division have recently determined this ratio to be 1.37. Measurements of beta-particle energies in coincidence with these gamma rays will be made, and the results will be submitted for publication.

During the experiments leading to the gamma-ray branching results, some interesting effects were observed due to scattering of the 5.0-Mev beta particles present in the decay of Cl^{38}. The beta particles were being scattered into the side of the detector. (Lucite shields will be made to reduce these scattering effects.) Figure 11.5 shows the gamma-ray spectrum of Cl^{38} under conditions

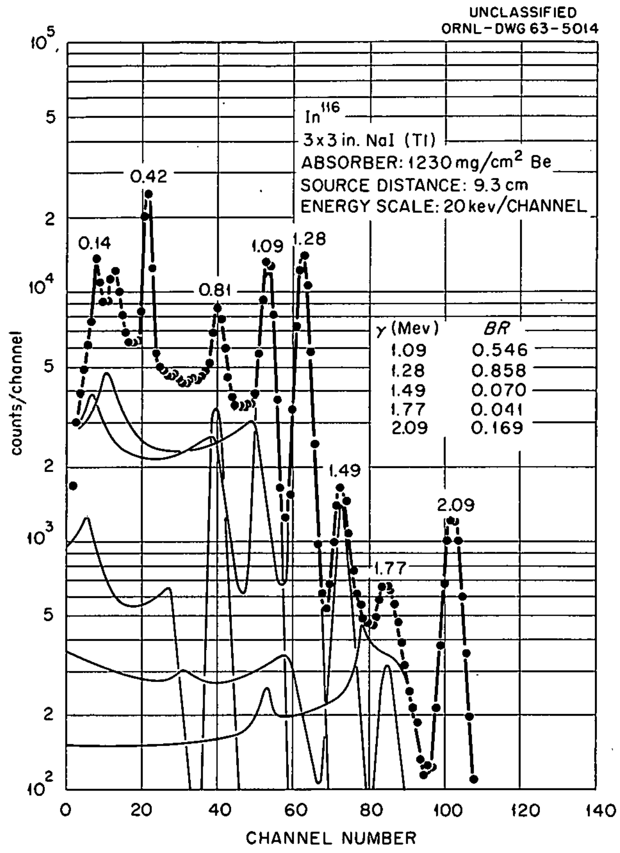

Fig. 11.4. Gamma-Ray Spectrum of 54-min In^{116} Illustrating Graphical Procedures Used in Determining Gamma-Ray Branchings.

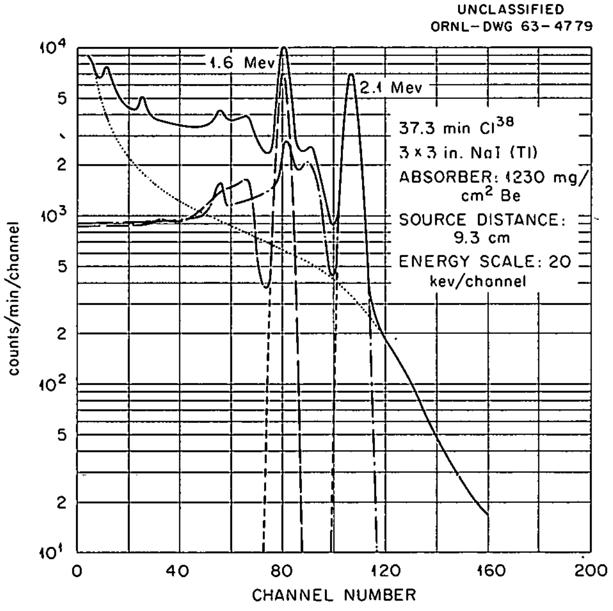

Fig. 11.5. Gamma-Ray Spectrum of 37-min Cl^{38} Illustrating Beta-Particle Scattering into the Detector Side.

where beta-particle scattering into the detector side was important. The dashed line indicates the contribution due to bremsstrahlung and scattered electrons. This contribution under the 2.19-Mev photopeak was reduced by a factor of 10 with suitable shields on the detector side.

Decay of Ba^{131}-Cs^{131}

W. S. Lyon

The absolute intensities of eight gamma rays emitted following electron capture in Ba^{131} were determined to be

Gamma Ray (Mev)	Absolute Intensity
0.130	0.28
0.220	0.28
0.380	0.16
0.496	0.60
0.600	0.032
0.820	0.0034
0.910	0.0009
1.04	0.017

The method used was to prepare Ba^{131} free from its Cs^{131} daughter, allow the Cs^{131} activity to grow in, separate the Cs^{131} activity from the parent and measure its activity, measure the gamma activity of the Ba^{131} by gamma-ray spectrometry, and calculate the absolute amount of Ba^{131} from parent-daughter growth relationships. The half-life of Cs^{131} was determined to be 9.83 ± 0.28 days. The ratio of the pile neutron-activation cross sections for the production of Ba^{131} and Ba^{133} was found to be $\sigma_{130}/\sigma_{132} = 1.36 \pm 0.08$.

A paper on this subject was published.[7]

Negatron Emission from Te^{129m}

J. S. Eldridge Peter Crowther[1]

Previous work[8] has shown that separation of Te^{129} isomers is possible by chemical means. During the course of examination of gases released from MSRE experimental capsules, TeF_6 gas samples were examined.[9] Gamma-ray spectrometry showed an unreported 0.7-Mev gamma ray accompanying the decay of the 33-day Te^{129} isomer. A possible negatron emission of 1.53 Mev from the 33-day isomer was reported;[10] however, no gamma-ray emission was reported. The presence of the 0.7-Mev gamma ray indicates that Te^{129m} must undergo negatron emission of ~0.8 Mev in its decay. Experiments are being continued to characterize both the Te^{129} and Te^{129m}.

Nuclear Decay Scheme Studies: S^{37}

J. F. Emery

A low-yield gamma ray found in 5.07-min S^{37} (abundance 0.30%)[11] has been confirmed from pair spectrometer data.[12] Table 11.2 summarizes the data.

Table 11.2. Intensities of Gamma Rays Observed in the Decay of S^{37}

S^{37} Gamma Ray (Mev)	Pair Spectrometer	Gamma-Ray Spectrometer
3.1	1	1
3.70 ±0.02	0.0028 ±0.0003	0.0032
3.95 ±0.05	0.0003 ±0.0001	Not observed

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[7] W. S. Lyon, "Decay of ^{131}Ba-^{131}Cs," *J. Inorg. Nucl. Chem.* 25, 1079 (1963).

[8] R. R. Williams, Jr., "Chemical Consequences of Isomeric Transition in Tellurium," pp 220–31 in *Radiochemical Studies: The Fission Products* (ed. by C. D. Coryell and N. Sugarman), book I, part II, McGraw-Hill, New York, 1951.

[9] J. S. Eldridge, "Applications of Gamma-Ray Spectrometry in Reactor Problems," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 92.

[10] W. E. Graves and A. C. G. Mitchell, "Disintegration of Te^{129}," *Phys. Rev.* 101, 701 (1956).

[11] J. F. Emery, "New Nuclear Data," *Anal. Chem. Research and Development Quart. Progr. Rept. July 15, 1963* (unpublished report).

[12] B. L. Robinson, Physics Department, Case Institute of Technology, Cleveland, Ohio, private communication to J. F. Emery.

180° Compton-Scattered–Annihilation Gamma-Ray Sum Peak Observed in Gamma-Ray Spectrometry

W. S. Lyon

The presence of an anomalous gamma-ray photopeak at ~700 kev in the gamma-ray spectra of certain positron-emitting nuclides (notably Cu^{64}) has been explained. The gamma-ray spectrum of Cu^{64} is measured at a high geometry without surrounding absorber (Fig. 11.6) and then with absorber (Fig. 11.7). The presence of the ~700-kev gamma-ray photopeak in Fig. 11.7 is apparent. This photopeak has been shown to arise from summing in the crystal of one 510-kev annihilation gamma ray with the 180° Compton-backscatter gamma ray from either the coincident 510-kev annihilation gamma ray or another coincident gamma ray. A note on this subject was accepted for publication as "Correspondence" in *Analytical Chemistry.*

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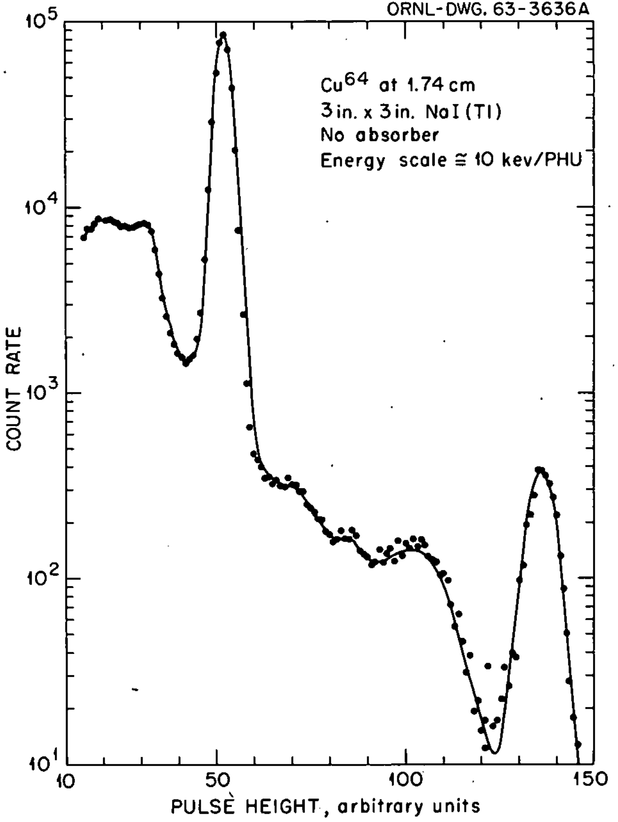

Fig. 11.6. Gamma-Ray Spectrum of Cu^{64} (High Geometry; No Absorber).

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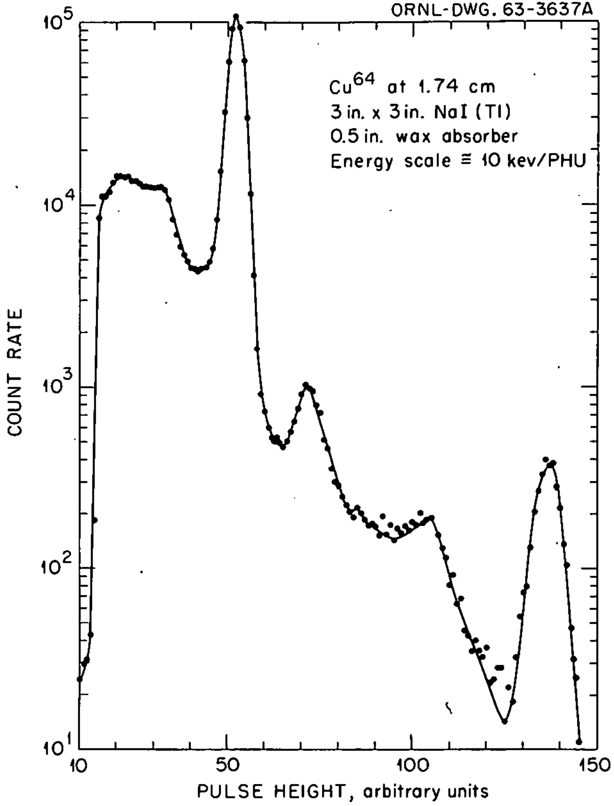

Fig. 11.7. Gamma-Ray Spectrum of Cu^{64} (High Geometry; Absorber Surrounding Source).

Nuclear Spectroscopy of Even Isotopes in the Osmium Region

T. H. Handley

To obtain more data on the systematics of nuclear levels in even-even nuclei, a number of osmium nuclei ($186 \leqq A \leqq 192$) are being investigated with iridium sources produced in the 86-in. cyclotron. The complex disintegration spectra are analyzed with permanent-magnet conversion-electron spectrographs. Some measurements are made with scintillation counters. The available data are being arranged in decay schemes and interpreted by use of the unified model of the nucleus. This work was done jointly with B. Harmatz.[13] A paper on this subject will be submitted for publication in *The Physical Review.*

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[13] Electronuclear Division.

Direct Nondestructive Method for the Determination of Cf^{252}

F. L. Moore J. S. Eldridge

A new, direct, nondestructive method for the determination of Cf^{252} was developed. Prompt gamma rays coincident with the spontaneous fission of Cf^{252} are measured on a gamma scintillation spectrometer. The technique is rapid for either the qualitative or quantitative determination of Cf^{252} in the presence of associated fission products and actinide elements. As little as 10^{-2} ng of Cf^{252} can be measured quantitatively. Several useful analytical and process applications of the method are discussed in a paper submitted for publication in *Analytical Chemistry.*

Determination of the Yields of Krypton and Xenon Nuclides in Uranium Fission

R. L. Hahn

A vacuum system was designed and built for measurement of yields of krypton and xenon nuclides from uranium fission.[14] The uranium metal foil, after irradiation in the Oak Ridge Research Reactor, is placed in the vacuum system and is dissolved in concentrated HCl–30% H_2O_2; krypton and xenon carrier gases are also introduced into the system during this step. The gaseous products are then passed through traps that contain: Ascarite, to remove excess HCl; CuO, at 425°C, to convert excess hydrogen to H_2O; $Mg(ClO_4)_2$, to remove H_2O; and activated charcoal, at −195°C, to collect the krypton and xenon. These noble gases are then eluted with helium from the charcoal – krypton at room temperature and xenon at 240°C. The gaseous samples are collected in small glass bulbs so that the decay of the various nuclides can be followed by gamma-ray spectrometry. Determinations of the elution peaks by assay of the radioactive products, as well as decay-curve analyses of the data obtained from the separated gases, indicate that the separation of krypton and xenon is a highly efficient process.

Determination of the Half-Life of a Short-Lived Isomer of Sn^{127}

R. L. Hahn

In conjunction with some radiochemical fission studies, the half-life of a short-lived isomer of Sn^{127} was determined. Previously reported values for the half-life of this nuclide are 4.6 ± 0.4 min[15] and 2.5 ± 1.0 min.[16] In this work, uranium that had been irradiated in the ORR for 20 sec was dissolved in 6 *M* HCl that contained H_2O_2 and both tin and antimony carriers. After NH_4SCN was added to the solution, the tin was separated from the uranium and antimony by extraction into ethyl ether.[17] Periodic milkings of the daughter activity, Sb^{127}, were then used to determine the

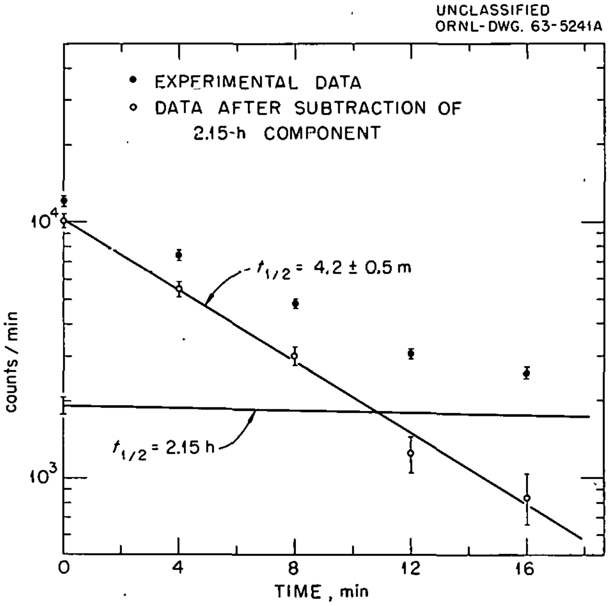

Fig. 11.8. Data for the Determination of the Half-Life of an Isomer of Sn^{127}.

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[14] F. F. Momyer, Jr., *The Radiochemistry of the Rare Gases,* NAS-NS-3025 (October 1960).

[15] E. Hagebo, A. Kjelberg, and A. C. Pappas, "Radiochemical Studies of Isotopes of Antimony and Tin in the Mass Region 127–130," *J. Inorg. Nucl. Chem.* **24**, 117 (1962).

[16] B. J. Dropesky and C. J. Orth, "A Summary of the Decay of Some Fission Product Tin and Antimony Isotopes," *J. Inorg. Nucl. Chem.* **24**, 1301 (1962).

[17] G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry,* pp 135–37, Wiley, New York, 1957.

half-life of the short-lived parent, Sn^{127}. Figure 11.8 shows the results of a least-squares fit[18] to the data; the half-life value was found to be 4.2 ± 0.5 min.

Half-Life Measurements

S. A. Reynolds

Determinations of half-lives by direct gamma-decay measurements[19] are in progress. The results of previous work of this type have been published.[20,21] Recent values[22] for the half-life of Cs^{137} range from 27 to 33 yr, although the observations do seem to be "converging" toward a value of ~30 yr. In the present program, the decay of four Cs^{137} sources has been followed for 4 yr, and the current result is 30.7 ± 0.6 yr at a 95% confidence level. In collaboration with E. I. Wyatt,[23] the decay of a source of Ba^{133} has been studied for 1.7 yr; the result thus far is 10.2 ± 0.8 yr, in approximate agreement with earlier values of 10.7 yr[21] and 9.5 yr.[24]

RADIOCHEMICAL STUDIES

Extraction of Cesium and Rubidium with 4-sec-Butyl-2-(α-methylbenzyl)phenol

W. J. Ross

Possible analytical applications of 4-*sec*-butyl-2-(α-methylbenzyl)phenol (I) as an extractant were investigated. This reagent is an excellent extractant of cesium from strongly basic solution.[25]

A survey of the extraction characteristics of microgram quantities of 49 elements from solutions that were 1 *M* in NaOH and 0.2 *M* in tartaric acid showed that only the group IA and IIA elements are extracted by 1 *M* I in cyclohexane. The degree of extractability of elements decreases markedly with decreasing atomic weight. The extracted species are readily back-extracted into dilute acid solutions.

A method was developed for the isolation and determination of radiotracer and milligram amounts of cesium and rubidium by extraction with I and is being prepared for publication.

Liquid-Liquid Extraction of Cesium with 2-Thenoyltrifluoroacetone

Peter Crowther[1] F. L. Moore

A new, rapid, highly selective liquid-liquid extraction method for cesium was developed. Recent means of inhibiting the hydrolysis of 2-thenoyltrifluoroacetone provide the basis for the quantitative extraction of cesium under a variety of conditions. Small amounts of lithium markedly enhance the extraction of cesium with 2-thenoyltrifluoroacetone. Highest extraction is obtained in the presence of lithium with 2-thenoyltrifluoroacetone dissolved in solvents that contain the nitro group (e.g., 98% for nitromethane and nitrobenzene). Efficient extraction of other alkali elements is possible under certain conditions. The method is applicable for either trace or macro quantities of cesium. Several practical applications are proposed, both for the analytical chemist and the separations technologist, in the purification of cesium and gross removal of fission products.

This work has been completed and is described in detail in a paper to be published in *Analytical Chemistry*.

Selective Liquid-Liquid Extraction of Radiotin with 2-Thenoyltrifluoroacetone

J. R. Stokely[26] F. L. Moore

A new and highly selective method for the radiochemical purification of tin was developed. The

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[18] J. B. Cumming, "CLSQ, The Brookhaven Decay Curve Analysis Program," pp 25–33 in *Radiochemical Techniques. Applications of Computers to Nuclear and Radiochemistry* (ed. by G. D. O'Kelley), NAS-NS-3107 (March 1963).

[19] E. I. Wyatt, "Gross Gamma," Method No. 9 0733002 (8-14-53), *ORNL Master Analytical Manual;* TID-7015, sec 9.

[20] H. W. Wright *et al.*, "Half-Lives of Radionuclides. I," *Nucl. Sci. Eng.* 2, 427 (1957).

[21] E. I. Wyatt *et al.*, "Half-Lives of Radionuclides. II," *Nucl. Sci. Eng.* 11, 74 (1961).

[22] L. A. Dietz, C. F. Pachucki, and G. A. Land, "Half-Lives of Cesium-137 and Cesium-134 as Measured by Mass Spectrometry," *Anal. Chem.* 35, 797 (1963).

[23] Radioisotopes-Radiochemistry Group.

[24] S. Katcoff, "Half-Life of Ba^{133}," *Quart. Progr. Rept. Oct. 1–Dec. 31, 1951*, BNL-149, pp 23–24.

[25] K. B. Brown, *Chemical Technology Division, Chemical Development Progress Report for January–March 1962*, ORNL-TM-181 (July 10, 1962).

[26] Temporary summer employee, Clemson College, Clemson, S.C.

method is based on the extraction of radiotin from a dilute sulfuric acid–chloride medium into 0.5 *M* 2-thenoyltrifluoroacetone in hexone. Excellent separation of radiotin is achieved from fission products, heavy elements, and corrosion products. The method and several useful applications of it are discussed in a paper to be submitted for publication in *Analytical Chemistry*.

Extraction with Sulfur-Containing Organophosphorus Compounds

T. H. Handley

The solvent-extraction properties of the sulfur analogs, both neutral and acid, of those organophosphorus compounds that have been used so extensively in solvent extraction were investigated. These sulfur analogs have one or more oxygen atoms replaced by sulfur atoms. The neutral esters, trialkyl phosphorothioates, selectively extract Ag^+ and Hg^{2+} from a nitric acid medium. In general, the acid esters, dialkylphosphorothioic and -dithioic acids, extract from mineral acid solutions those metal ions that form insoluble sulfides. Dialkylphosphorothioic acids appear to be more selective extractants than are the corresponding dithioic acids. The effects of various organic solvents, concentration of mineral acid, and concentration of dialkylphosphorothioic and -dithioic acids were studied. The relative order of extraction and the limits of extraction were determined. The nature of the zinc di-*n*-butylphosphorothioate and -dithioate complexes as they exist in the aqueous and organic phases were investigated. A paper on this subject was published.[27]

Chemical Effects of Isomeric Transitions: Separation of Isomers of Te^{127}, Te^{129}, and Te^{121}

R. L. Hahn

The problem of the chemical separation of radioactive isomers of tellurium was investigated.[28] The separation efficiencies obtained with end-window beta-particle detectors for Te^{127} and Te^{129} are significantly less than unity and are in agreement with the values determined by Williams.[29] It is demonstrated, however, that these values are not proper in that they have not been corrected for differences in detection efficiencies for the different beta particles observed. Use of gamma-ray spectrometry has overcome this difficulty. The percent of isomer separation can be determined independently of detection efficiency by measuring the relative rate of growth of an individual gamma ray from a sample in which the equilibrium between metastable- and ground-state isomers has been disturbed by the chemical separation (see Fig. 11.9). The separation

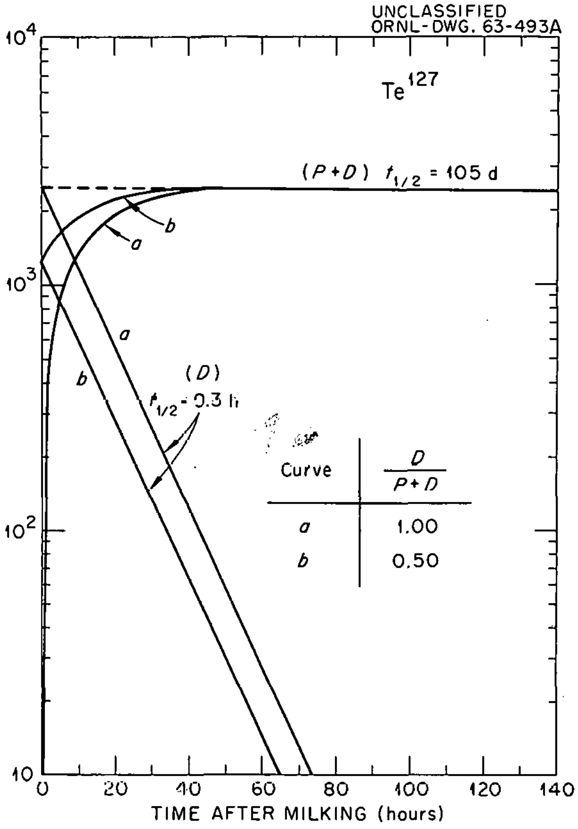

Fig. 11.9. Radioactive Growth and Decay for Te^{127} with Curves for Parent (P) and Daughter (D). [The ratio, $D/(P + D)$, is a measure of the efficiency of separation of the isomers. Curve *a* represents complete separation of parent and daughter.]

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[27] T. H. Handley, "Extraction with Sulfur-Containing Organophosphorus Compounds," *Nucl. Sci. Eng.* **16**, 440 (1963).

[28] R. L. Hahn, "Study of Separations of Isomers of Tellurium Isotopes," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 83.

[29] R. R. Williams, Jr., "Nuclear Chemistry of Tellurium: Chemical Effects of Isomeric Transition," *J. Chem. Phys.* **16**, 513 (1948).

efficiencies for Te^{127} and Te^{121} were found to be 0.984 ± 0.022 and 1.0 ± ~0.05, respectively. These results also were used in support of the concept that the chemical properties of the unstable tellurium species formed in internal conversion are essentially independent of the details of the nuclear decay and are the same for all tellurium nuclides that decay via highly converted isomeric transitions. These results were applied to the study of the decay of Te^{129}. The separation factors determined for the 0.475-, 1.12-, and 0.027-Mev gamma rays in Te^{129} were 0.952 ± 0.007, 0.863 ± 0.020, and 0.254 ± 0.005, respectively. These values were used to obtain relative gamma-ray transition probabilities in Te^{129} through an analysis of the dependence of the isomer separation process on nuclear-decay parameters.

An article that describes this work in detail was accepted for publication in the *Journal of Chemical Physics.*

Investigation of the separation of the isomers of Te^{127} and Te^{129} will continue. The effects of various chemical media, such as 6 *M* NaOH and 6 *M* $HClO_4$, on the separation process are being studied. Preliminary results indicate that the separation efficiencies are very dependent on the nature of the chemical environment and that, for a given environment, the separation efficiencies for Te^{127} and Te^{129} are similar.

LIQUID SCINTILLATORS

Unique Liquid Scintillator for Detection of Neutrons

H. H. Ross R. E. Yerick[30]

Boron-loaded liquid-scintillator systems have been used extensively for the detection of neutrons.[31–34] However, these systems have a number of drawbacks, the most serious of which probably is the small pulse-height output from interactions with thermal neutrons. A new liquid-scintillator system was developed; it exhibits a pulse height from 5 to 25 times higher for thermal neutrons than that of conventional boron-loaded

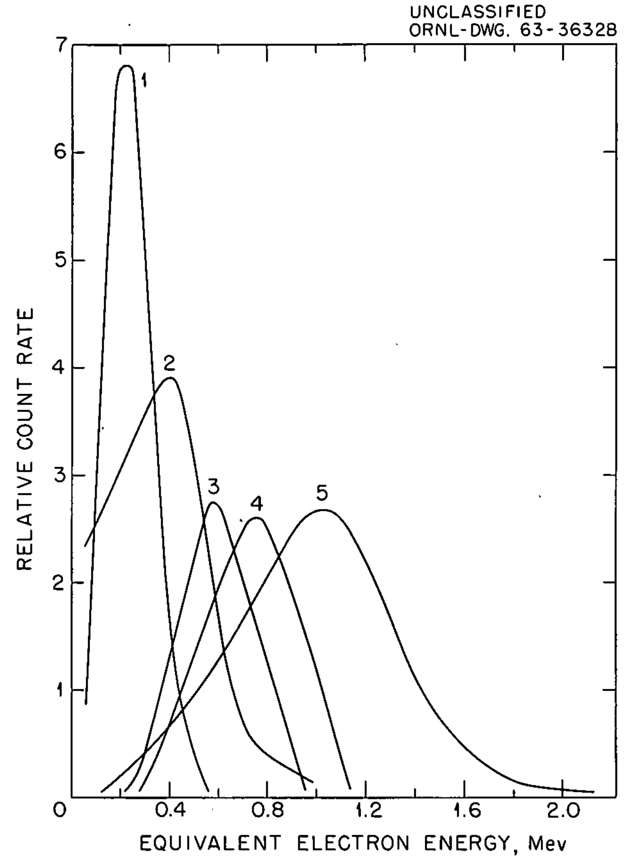

Fig. 11.10. Neutron Spectra with Various Nonaqueous Liquid Scintillation Mixtures That Contain Li^6 Salicylate.

Mixture	Composition				
	Dioxane (ml)	Li^6 Salicylate (g)	Naphthalene (g)	PPO^a (g)	$DMPOPOP^b$ (g)
1	20	0.35			
2	20	0.35	2		
3	20	0.35	2	0.14	
4	20	0.35	2		0.006
5	20	0.35	2	0.14	0.006

[a] PPO = 2,5-diphenyloxazole.

[b] DMPOPOP = 1,4-*bis*-2-(4-methyl-5-phenyloxazolyl)-benzene.

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[30] Research participant, Lamar State College of Technology, Beaumont, Tex.

[31] C. O. Muehlhause and G. E. Thomas, Jr., "Two Liquid Scintillation Neutron Detectors," *Nucleonics* 11, 44 (1953).

[32] F. Reines *et al.*, "Detection of Neutrons with a Large Liquid Scintillation Counter," *Rev. Sci. Instr.* 25, 1061 (1954).

[33] L. M. Bollinger and G. E. Thomas, "Boron-Loaded Liquid Scintillation Neutron Detectors," *Rev. Sci. Instr.* 28, 489 (1957).

[34] G. E. Thomas, "A Boron-Loaded Liquid Scintillation Neutron Detector Using a Single Photomultiplier," *Nucl. Instr. Methods* 17, 137 (1962).

systems. This new system is unique in that the functions of neutron target and scintillation fluor are combined in a single chemical compound and that the scintillator will perform efficiently in aqueous systems — even in pure water.

The unique target-fluor material is Li^6 salicylate. The lithium undergoes the $Li^6(n,\alpha)T$ reaction; the Q of the reaction is 4.8 Mev. This released energy is deposited in the system and causes other lithium salicylate molecules to scintillate with an emission maximum at 410 mμ.

The scintillator material is characterized by being very soluble in water, dioxane, and other polar solvents, easy to prepare and purify, relatively inexpensive, and essentially 100% efficient in some systems. Figure 11.10 shows the response of the scintillator, in various nonaqueous solvent systems, to thermal neutrons. Figure 11.11 shows similar responses in semiaqueous systems.

In cooperation with the Physics Division and the Instrumentation and Controls Division, work is being continued to determine other characteristics of the scintillator.

Glass-Loaded Liquid Scintillator

Gerald Goldstein

Work is continuing on the development of a glass-loaded liquid scintillator.[35] A small-scale scintillator (3 × 3 in.) was prepared with 50/80 mesh particles of Bausch and Lomb No. 617366 glass in a 1-g/liter solution of *p*-bis-2-(5-naphthyloxazolyl)-benzene, designated α-NOPON, in toluene (8%)–1-methylnaphthalene. Figure 11.12 shows pulse-height spectra for various gamma energies. The lower-energy pulses seem to represent scintillations produced in the glass itself, and the higher-energy pulses are due to scintillations produced in the liquid by Compton electrons. A model on a larger scale is planned; a glass being developed for this purpose by the Kimble Glass Company will be used.

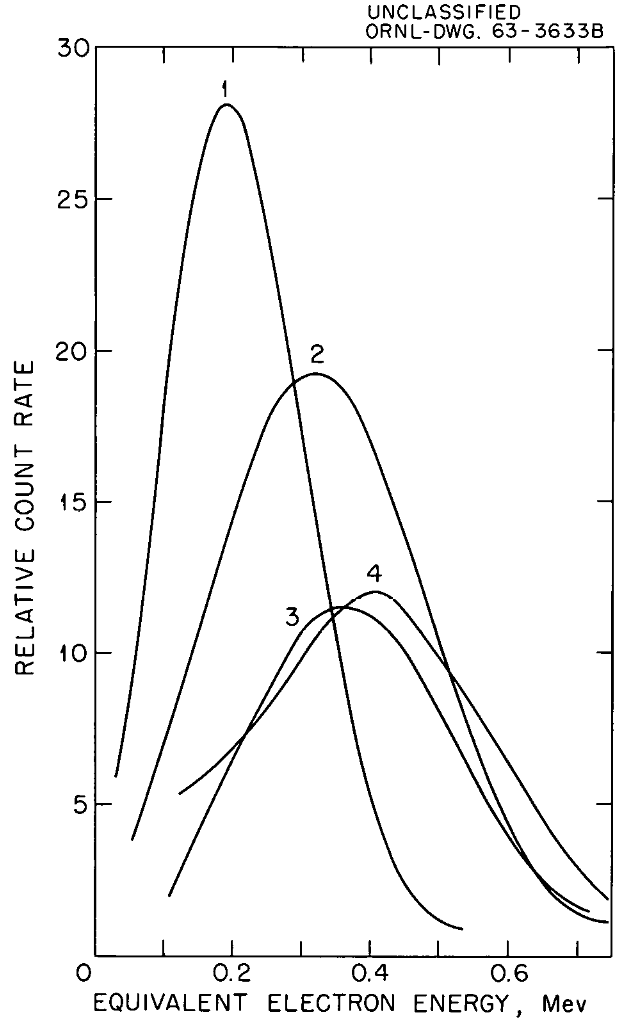

Fig. 11.11. Neutron Spectra with Various Liquid Scintillation Mixtures That Contained Water and Li^6 Salicylate.

	Composition					
Mixture	Dioxane (ml)	Li^6 Salicylate (g)	Naphthalene (g)	Water (ml)	PPO[a] (g)	DMPOPOP[b] (g)
1	20	2	2	1	0.14	0.006
2	20	2	2	0.5		
3	20	1	2	0.5		
4	20	1	2	0.5	0.14	0.006

[a] PPO = 2,5-diphenyloxazole.

[b] DMPOPOP = 1,4-*bis*-2-(4-methyl-5-phenyloxazolyl)-benzene.

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[35] Gerald Goldstein, "Liquid Scintillation Development," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 110.

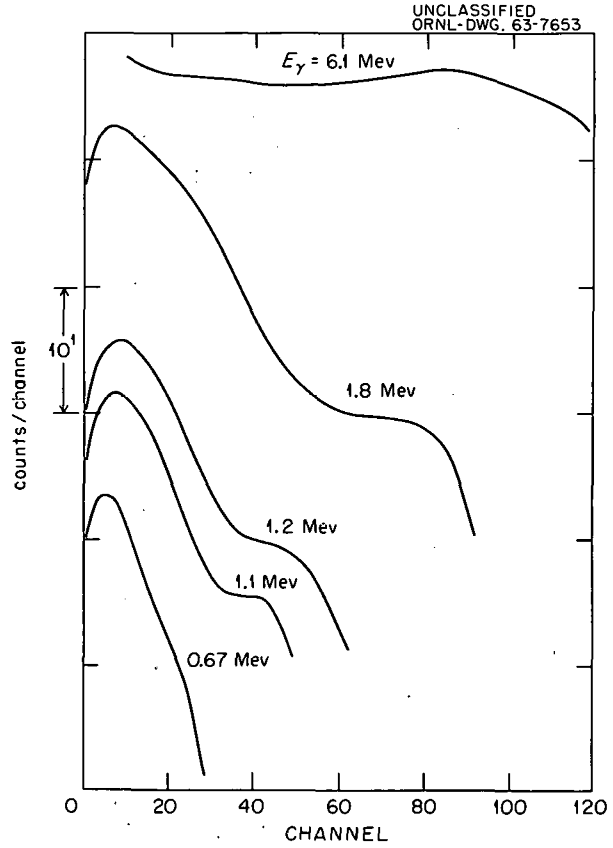

Fig. 11.12 Pulse-Height Spectra Obtained with a 3 × 3 in. Glass-Loaded Liquid Scintillator.

Liquid Scintillation Counting of C^{14} by Use of a "Balanced Quenching" Technique

H. H. Ross

Liquid scintillation counting is one of the most valuable techniques for the radioassay of alpha-,[36] beta-,[37] weak-gamma-,[38] and x-ray-emitting[39] nuclides. However, the method has the practical disadvantage that certain materials, when present in the sample, can quench the light output of the scintillator solution. Therefore, the observed activity of each quenching sample must be corrected for counting efficiency.[40–43]

A new method was developed for liquid scintillation counting of C^{14} at a constant, known efficiency in quenched samples. This technique reduces the manipulation and calculation problems inherent in other methods of yield correction and avoids the radiochemical contamination inherent in the internal-standard method. Once initial counting conditions have been established for a given type of sample, count rate can be read directly from the instrument at the predetermined counting efficiency. This technique is insensitive to errors caused by differences in activity levels from sample to sample and also to small shifts in instrument operating parameters. The method does *not* require the use of instruments having dual scalers and is ideally suited for routine counting of similar types of samples in any activity range.

A paper that describes this work was accepted for publication in the *International Journal of Applied Radiation and Isotopes*.

LOW-LEVEL RADIOCHEMICAL STUDIES

Low-Level Radiochemical Analyses

S. A. Reynolds C. L. Burros

A program of study of low-level analyses was initiated. It includes literature surveys, study of current practices in the ORNL Analytical Chemistry Division and elsewhere, recommendations of improved techniques, and consultation on special problems. The first task, a review of techniques

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[36] D. L. Horrocks, "Alpha Particle Energy Resolution in Liquid Scintillator," pp 17–20 in *Oak Ridge Radioisotope Conference*, Apr. 1–3, 1963.

[37] M. S. Raben and N. Bloembergen, "Determination of Radioactivity by Solution in a Liquid Scintillator," *Science* 114, 363 (1951).

[38] R. E. Yerick and H. H. Ross, "Liquid Scintillation Counting of Iodine-129 and Iodine-125," pp 20–21 in *Oak Ridge Radioisotope Conference*, Apr. 1–3, 1963.

[39] R. J. Dern and W. L. Hart, "Doubly Labelled Iron. I. Simultaneous Liquid Scintillation Counting of Isotopes Iron-55 and Iron-59 as Ferrous Perchlorate," *J. Lab. Clin. Med.* 57, 322 (1961).

[40] E. N. Hayes, "Liquid Scintillators: Attributes and Applications," *Intern. J. Appl. Radiation Isotopes* 1, 46 (1956).

[41] C. T. Peng, "Liquid Scintillation Counting of Some Sulfur-35 Labelled Organic Compounds," p 198 in *Liquid Scintillation Counting* (ed. by C. G. Bell and F. N. Hayes), Pergamon, New York, 1958.

[42] L. A. Baillie, "Determination of Liquid Scintillation Counting Efficiency by Pulse Height Shift," *Intern. J. Appl. Radiation Isotopes* 8, 1 (1960).

[43] H. H. Ross and R. E. Yerick, "Quantitative Interpretation of Color Quenching in Liquid Scintillator Systems," *Anal. Chem.* 35, 794 (1963).

for determining very low levels of Sr^{90}, was completed (see below), and information has been forwarded to those concerned. Plans were made for adding a second NaI(Tl) crystal to the existing 200-channel system, thus making possible the simultaneous collection of data on two samples. In confirmation of the results of others,[44,45] Mn^{54} has been identified in fallout samples. Figure of merit (see "Optimum Counting Methods and Tracers," in this chapter) is of special importance in low-level work.

Sr^{90} Determinations and Low-Level Beta Counting

S. A. Reynolds C. L. Burros

The problem of determining low-level Sr^{90} in environmental samples was investigated. Factors limiting the sensitivity of the method are background, blank, and efficiency. The current local background is 0.7 count/min; other typical values vary from 0.5 to 2 counts/min.[46–51] Representative blank values (dis/min) are: <0.9,[52] 0.4 to 1,[49] and <0.6.[53] Recent local blanks were 0.7 ± 0.2 dis/min. Efficiencies are now ~17% for Sr^{90} and ~28% for its Y^{90} daughter and are to be increased by use of a higher support for the samples. Some United States Public Health Service workers[47] achieve ~40% efficiency for Y^{90} at the cost of "several" contaminated windows, and another establishment has ~33% efficiency.[53]

The limit of measurement for Y^{90}, equivalent to three times the standard deviation of the background[54] and based on the assumption of zero blank, would be: for a 1-hr count, 1.2 dis/min; 1000-min count (16.7 hr), 0.3 dis/min. Of the present background, ~0.1 to 0.2 count/min appears to be due to C^{14} in the mounting card, since it is "stopped" by thin aluminum foil; it is not worthwhile or feasible to reduce this. The use of overnight counting periods, with background determinations being made during the weekend, yields increased sensitivity. Under ideal conditions about 16 overnight counts can be made per week. It is necessary to monitor power-line voltage, noise, and temperature of the counting room; fluctuations in these will occasionally cause invalid data. Purification of reagents, especially strontium and yttrium carriers, should result in smaller blanks. Those requesting analyses can secure best values by submitting large samples when possible. This procedure will also aid in solving the problem of obtaining a representative sample of the material of interest. Even in sampling precipitation, inhomogeneities of 10 to 15% arise.[55] If only Sr^{90} values are desired, counting its Y^{90} daughter[56] is desirable because of specificity and higher efficiency. This counting is already done on some samples.

Strontium-90 in water is reported routinely at the 0.01-dis min^{-1} ml^{-1} level, with $\leqq$10% uncertainty, both calculated and as observed by use of different methods on duplicate samples. This uncertainty is in accord with the findings of a relative standard deviation of ~10% during the 1961 program of the AEC Health and Safety Laboratory.[52] In a recent series of duplicate analyses at levels of 0.2 to 3 dis min^{-1} ml^{-1}, the predicted average relative standard deviation of counting was 10%, and the observed average relative standard deviation, from differences in duplicates, was 11.6%. A set of 11 soil samples was analyzed, at ORNL and at

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[44] H. Krieger and J. Kearney, U.S. Public Health Service, Taft Center, unpublished data.

[45] T. R. Folson *et al.*, "Manganese-54 and Zinc-65 in Coastal Organisms of California," submitted for publication.

[46] E. I. Wyatt, ORNL, unpublished data.

[47] U.S. Public Health Service, Taft Center, unpublished data.

[48] L. Henley, ORNL, unpublished data.

[49] E. P. Hardy, Jr., J. Rivera, and R. Frankel, *Health and Safety Laboratory Fallout Program Quart. Sum. Rept. June Through Sept. 1961*, HASL-115 (Oct. 1, 1961).

[50] H. D. LeVine, L. Charlton, and R. T. Graveson, *Low Background Nuclear Counting Equipment*, HASL-60 (Mar. 23, 1959).

[51] U.S. Public Health Service, N.E. Rad. Health Lab., unpublished data.

[52] E. P. Hardy, Jr., J. Rivera, and R. Frankel, *Health and Safety Laboratory Fallout Program Quart. Sum. Rept. Dec. 1961 Through March 1, 1962*, HASL-122 (April 1962).

[53] E. P. Hardy, Jr., *Quart. Sum. Rept. March 1, 1961 Through June 1, 1961, Fallout Program*, HASL-113 (July 1, 1961).

[54] B. Kahn and S. A. Reynolds, "Determination of Radionuclides in Low Concentrations in Water," *J. Am. Water Works Assoc.* 50, 613 (1958).

[55] E. P. Hardy, Jr., *Quart. Sum. Rept. June 1, 1962, Through Sept. 1, 1962. Health and Safety Laboratory Fallout Program*, HASL-131 (Oct. 1, 1962).

[56] B. Kahn *et al.*, *Analysis for Radionuclides in Aqueous Wastes from an "Atomic" Plant*, p 38, STP-235, ASTM, Philadelphia, 1958.

the Public Health Service Taft Center, at levels of 100 to 4800 pc/kg; the average difference (after one obvious "outlier" was discovered) was 15%. In a set of analyses reported recently, the total disintegration rates for the various samples ranged from <2 to ~15 dis/min, with a standard deviation of 1.9 to 2.7 dis/min. The weights represented were 0.02 to 1.5 g – rather small for measuring natural levels of Sr^{90}.

Optimum Counting Methods and Tracers

S. A. Reynolds

It is sometimes necessary to select the optimum technique for measuring a given radionuclide in radiochemical or tracer work or to choose the best radiotracer for a given task. The choice depends on the efficiencies and backgrounds of the available instruments, which are suitably indicated by a numerical quantity called the *figure of merit*. This is defined as the reciprocal of the relative standard deviation of a count taken for unit time, with background also for unit time: thus,

$$M = S/\sigma = S/(S + 2B)^{1/2}\,, \qquad (11.1)$$

where

M = figure of merit (dimensionless),

S = net count rate of sample, counts/min,

σ = standard deviation of net rate, counts/min,

B = background, counts/min.

Note that the value of M is not an intrinsic quality of the counter but depends on the count rate (S) and, therefore, the disintegration rate of the sample. In comparing counters, or choosing one of two or more tracers, it is necessary to specify the disintegration rate. Qualitatively, one chooses the instrument of highest efficiency for large disintegration rates and low background for low disintegration rates. A quantitative treatment, similar to that of Miller,[57] has been made for the nuclides Sr^{85}, Sr^{89}, Cs^{137}, and Ce^{144}, as measured by several commonly used counters. For example, the beta-active Sr^{89} is shown to be superior to Sr^{85} as a strontium tracer at low activity. The detailed method will be given in the *ORNL Master Analytical Manual*, and, since the material has been favorably received by several specialists, it will be submitted for possible publication in the "Correspondence" section of *Analytical Chemistry*.

Natural Radionuclides

S. A. Reynolds

The program[58,59] of development of methods for natural radioelements has been completed, and all such work has been transferred to appropriate routine-analysis groups. Table 11.3 shows typical recent values for the routine, simultaneous, gamma-spectrometric determination of thorium[60] by the 2.62-Mev peak of Tl^{208}, uranium (or radium)[58,59] by the 1.76-Mev peak of Bi^{214}, and

Table 11.3. Results of Typical Gamma Analyses

Sample	Components		
	Th (ppm)[a]	U (ppm)	K (%)
1	74, 75	17	4.1
2	81, 83	19	4.2
3	86	22	4.1
4	92	27	4.3
5	123	36	4.0
6	240, 244, 248	59	4.3
G1[c]	51 (51 to 52)[b]		4.4 (4.5)
W1[c]	2.7 ±0.5	0.4 ±0.2	0.56 ±0.04
	(2.1 to 3.4)	(0.28 to 0.52)	(0.53)

[a] Two or more results; two independent spectrometers.

[b] Values in parentheses are published or accepted.

[c] U.S. Geological Survey standards.

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[57] C. E. Miller, *Neutron Activation Analysis Methods for the Group VIII Elements*, ORNL-2715 (May 5, 1959).

[58] S. A. Reynolds and T. H. Handley, "Natural Radionuclides," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 63–65.

[59] C. L. Burros and S. A. Reynolds, "Natural Radionuclides," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, pp 59–61.

[60] S. A. Reynolds, "Determination of Thorium in Granite by Gamma Spectrometer and by Radiotracer," *Talanta* 10, 611 (1963).

potassium by the 1.46-Mev peak of K^{40}. Samples 1 through 6 are fractions of the same granite of increasing sieve number (decreasing particle size); the results show the typical increase in thorium and uranium content.

APPLICATION OF COMPUTERS

Equilibrium Distribution of Metal-Ion Complexes

Gerald Goldstein

Although excellent compilations of successive stability constants of metal-ion complexes are available,[61,62] obtaining specific information from these data can require tedious and troublesome calculations. For practical purposes, diagrammatic representation is usually more useful; consequently, equilibrium data for the formation of metal complexes with inorganic ligands are being compiled in the form of distribution diagrams (fraction of each species present vs ligand concentration), with the necessary calculations and plotting performed by means of a high-speed computer. Three examples are shown in Figs. 11.13, 11.14, and 11.15. For the analytical chemist, these plots have the advantages that one can tell at a glance the ligand concentration tolerable before complexation of a metal ion begins and the species actually present in a solution at a given ligand concentration. These diagrams can also serve as guides for the preparation of solutions which contain a desired species that might be useful, for example, in ion-exchange

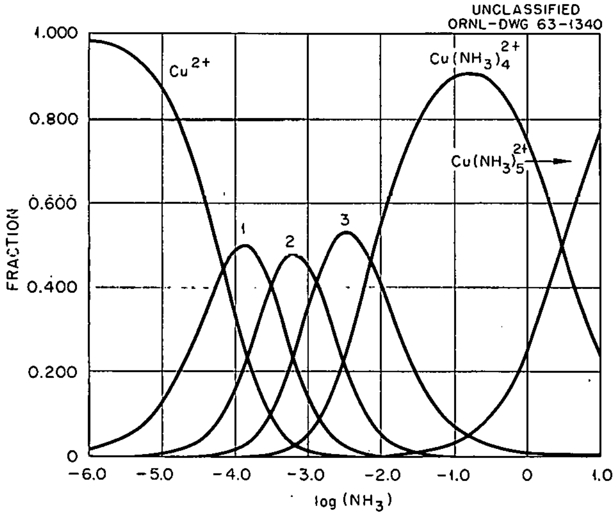

Fig. 11.14. Copper(II) Ammines.

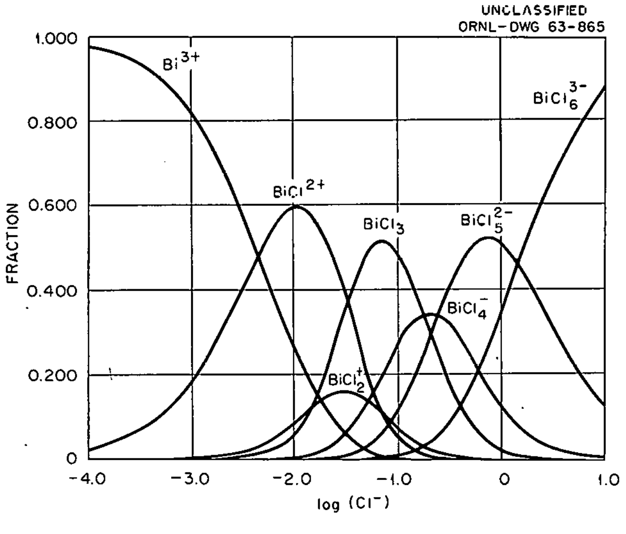

Fig. 11.13. Bismuth Chloro Complexes.

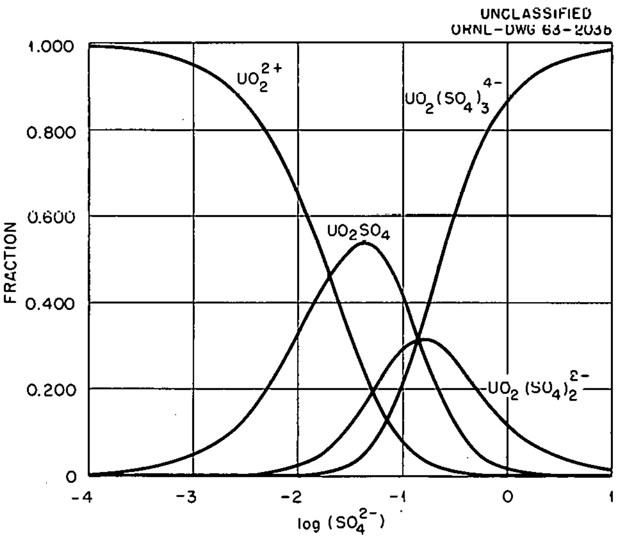

Fig. 11.15. Uranyl Sulfate Complexes.

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[61] J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, *Stability Constants Inorganic Ligands*, part II, Spec. Publ. No. 7, Chemical Society, London, 1958.

[62] K. B. Yatsimirskii and V. P. Vasilev, *Instability Constants of Complex Compounds*, Pergamon, New York, 1960.

separations or the extraction of ion-association compounds.

Diagrams have been compiled for fluoride, chloride, bromide, iodide, ammonia, sulfate, and nitrate complexes. Compilations are being made for cyanide, thiocyanate, and thiosulfate complexes and for complexes of the transuranium elements.

Computer Applications in Nuclear Analyses

J. S. Eldridge

Use of computers is an important tool in radiochemical and nuclear analyses. Applications in which computers are used are: analysis of multicomponent decay curves, resolution of complex gamma-ray spectra into their components, "pooling" of multiple spectra into standard response functions, and routine data handling – including curve plotting and background correction. Some of the computer applications make use of programs developed at other laboratories with minor modifications.

The decay-curve-analysis procedure uses a program developed by Cumming.[63] A least-squares procedure is used in an iterative routine starting from a set of trial values for the analysis of single- or multicomponent decay curves. The computer program gives a considerable saving in time over graphical procedures, and the results are not subjective. Error estimates are more meaningful than those inferred from graphical analyses. This program has been applied extensively for decay-curve analysis of data obtained from scaler-time mode of the multichannel analyzers.

A program for the resolution of complex gamma-ray spectra was written at the Central Data Processing Facility for use with the standard-response function library. This program is now being tested. It consists of least-squares fitting of an experimental spectrum with spectra from the standard-response library. When tested and perfected, this program should result in improvements in many analytical spectrometry problems.

To check for nonstatistical counting behavior and for gain-shift effects, spectra from multiple determinations are combined by means of a computer program developed at the Central Data Processing Facility for the IBM 7090. This program is being used in the collection of spectra for the standard-response function library.

A program that has found wide application in nuclear analyses was written by R. L. Ferguson[64] for use on the CDC 1604 computer and Calcomp plotter. The program converts gamma-ray spectral data from typewriter or paper-tape readout to magnetic tape for making three-decade semilogarithmic plots on the Calcomp plotter. The program contains background-correction and channel-summation provisions. This program has been adopted by the Radioisotopes-Radiochemistry Laboratory and has resulted in considerable saving of technician and multichannel-analyzer time.

Electronic Resolution of Gamma-Ray Spectra

J. S. Eldridge

Collection of standard-response curves from calibrated sources is under way.[65] Nuclides comprising the standard-response-curve "library" are standardized by absolute counting techniques, and three source mounts from each standard solution are prepared. Each of the three standard mounts is then counted twice in the multichannel spectrometer (Fig. 11.16). This spectrometer consists of a 3 × 3-in. NaI(Tl) detector housed in the lead shield, a 512-channel analyzer, and appropriate data-reduction equipment. A computer-type paper-tape-handling system is used to speed the acquisition and reduction of data. Data from six spectra and two background determinations for each nuclide are transmitted to the IBM 7090 facility, where a computer program is used to "pool" the data into a master spectrum characteristic of that nuclide and spectrometer gain setting.

To date, the standard-response-curve library consists of data for 25 nuclides.

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[63] J. B. Cumming, *Radiochemical Techniques. Application of Computers to Nuclear and Radiochemistry* (ed. by G. D. O'Kelley), NAS-NS-3107 (March 1963).

[64] Chemistry Division.

[65] J. S. Eldridge, "Electronic Resolution of Gamma-Ray Spectra," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, pp 88–89.

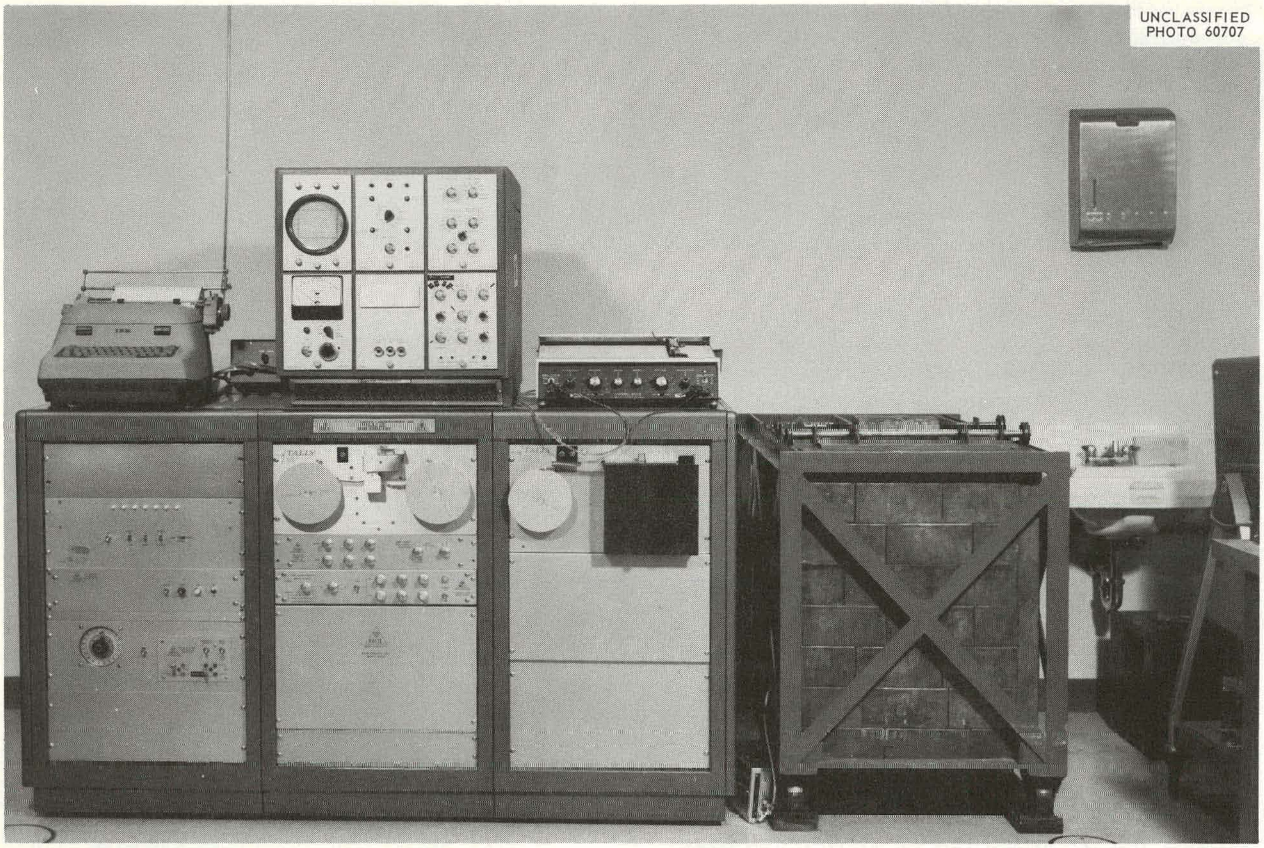

Fig. 11.16. Photograph of 512-Channel Spectrometer Used for Standard-Response-Function Collection.

Computer Program for the Calculation of Absolute Activities, Fluxes, and Cross Sections

F. F. Dyer E. Ricci

A FORTRAN program is being prepared for the calculation of absolute activities of radionuclides. The program will handle several spectra, each having a number of photopeaks. Heath's gamma-spectrometry method is used in the calculations. Since a procedure of this kind must follow directions that depend on the characteristics of each photopeak, the program will be a compromise between man-made and computer-made decisions. The code is being written for the IBM 7090 computer. Use will be made of existing subroutines for linear and nonlinear least-squares fittings of Gaussian curves to the photopeaks. Dead-time and escape-peak corrections are included.

The flux at which a nuclide was produced or the cross section of a nuclear reaction can be calculated for any number of peaks, if desired. The program will also calculate errors of the absolute activities, fluxes, and cross sections by means of propagation-of-error formulas. The flexibility of decisions in this program should allow the user to combine it at will with existing programs, such as spectrum plotting, least-squares fitting of decay curves, etc.

Second-Order Interference in Activation Analysis

E. Ricci F. F. Dyer

Activation analysis for submicrogram amounts of elements requires high-sensitivity techniques. Sensitivity is enhanced by using high fluxes and/or long times of irradiation. However, second-order nuclear reactions may become significant under these conditions. Second-order interference may be defined as the systematic error introduced in activation analysis by successive nuclear reactions of the type

$$ {}_{Z-1}E^{A-1}(n,\gamma)_{Z-1}E^{A} \xrightarrow{\beta^-} {}_{Z}E^{A}(n,\gamma)_{Z}E^{A+1} \,. \quad (11.2)$$

Interference may be appreciable for the element ${}_{Z}E$ if it is determined in a matrix that contains large amounts of element ${}_{Z-1}E$. An example is the reaction

$$\mathrm{Cu}^{63}(n,\gamma)\mathrm{Cu}^{64} \xrightarrow[\beta^+,\ \mathrm{EC}]{\beta^-} \mathrm{Zn}^{64}(n,\gamma)\mathrm{Zn}^{65} \quad (11.3)$$

in the determination by activation analysis of zinc in a copper matrix by measurement of Zn^{65}. If this second-order reaction takes place extensively, part of the final Zn^{65} activity is independent of the original amount of zinc in the sample. Thus, the most important assumption of activation analysis, that is, the proportionality of activity to mass, is not borne out.

Twenty-two cases, important in activation analysis, were found to show second-order interference, and they are listed in Table 11.4.

Table 11.4. Element Systems That Exhibit Second-Order Interference in Activation Analysis

Activation Analysis for	Measured Nuclide	Activation Analysis for	Measured Nuclide
Al in Mg	Al^{28}	As in Ge	As^{76}
P in Si	P^{32}	Br in Se	Br^{82}
Cl in S	Cl^{38}	Y in Sr	Y^{90}
Sc in Ca	Sc^{46}	Sb in Sn	Sb^{122}
V in Ti	V^{52}	Sb in Sn	Sb^{124}
Mn in Cr	Mn^{56}	I in Te	I^{128}
Co in Fe	Co^{60}	La in Ba	La^{140}
Cu in Ni	Cu^{66}	Ta in Hf	Ta^{182}
Zn in Cu	Zn^{65}	Au in Pt	Au^{198}
Ga in Zn	Ga^{70}	Tl in Hg	Tl^{204}
Ga in Zn	Ga^{72}	Tl in Hg	Tl^{206}

Calculations were made by the computer code CRUNCH,[66] which permits estimation of the interference for each case in an activation analysis. A variety of irradiation times and neutron fluxes was included. Figure 11.17 shows results of calculations for the example of Eq. (11.3), as well as for the case of P in Si, Sc in Ca, and Co in Fe. The ordinates of Fig. 11.17 are expressed as micrograms of element ${}_{Z}E$ which would produce an activity of radionuclide ${}_{Z}E^{A+1}$ equal to the interfering activity ${}_{Z}E^{A+1}$ produced from 1 g of element ${}_{Z-1}E$. This quantity is termed the interference. The interferences for each case are plotted as double curves for a thermal neutron flux of 5×10^{15} neutrons $\mathrm{cm}^{-2}\ \mathrm{sec}^{-1}$. The upper and lower curves correspond to resonance-to-thermal flux ratios of $\frac{1}{10}$ and $\frac{1}{30}$, respectively; the Stoughton and Halperin[67] conventions for effective activation cross sections were used in the calculations. At a constant irradiation time, the interference is directly proportional to the thermal neutron flux; therefore, the interference can be easily calculated for other flux values.

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[66] M. P. Lietzke and H. C. Claiborne, *CRUNCH — An IBM-704 Code for Calculating* N *Successive First-Order Reactions*, ORNL-2958 (Oct. 24, 1960).

[67] R. W. Stoughton and J. Halperin, "Heavy Nuclide Cross Sections of Particular Interest to Thermal Reactor Operation: Conventions, Measurements, and Preferred Values," *Nucl. Sci. Eng.* **6**, 100 (1959).

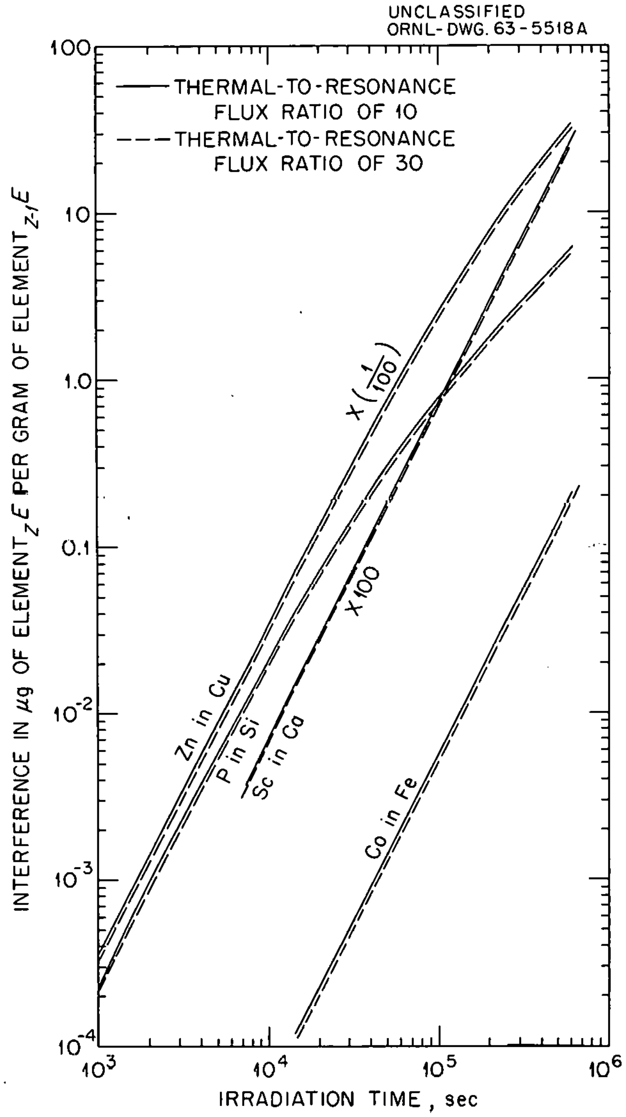

Fig. 11.17. Second-Order Interference in Activation Analysis (Thermal Neutron Flux = 5×10^{15} Neutrons cm^{-2} sec^{-1}).

APPLICATION OF RADIOISOTOPES IN ANALYTICAL CHEMISTRY

This program has continued, as reported previously.[68,69] A review article was published,[70] as were an article on the determination of thorium[71] and one on the determination of alkaline-earth elements and thorium.[72]

Radioisotopes in Electroanalysis

S. A. Reynolds

A preliminary survey is being made of possible applications of radioisotopes in such electroanalytical methods as polarography[73] and electrodeposition.[74] An area of potential interest is a study of anomalous co-deposition of tin with antimony.[74,75] The radioisotopes Sb^{124} and Sn^{113} will be used in the study of this phenomenon.

Measurement of Wear Rates in Automotive Engines by Liquid Scintillation Counting of Fe^{55}

H. H. Ross

The radiotracer method of determining wear rates in automotive engines has been used extensively.[76] The method consists in irradiating an engine part in a thermal-neutron flux, installing the irradiated part in a test engine, and determining the amount of radioactivity that becomes suspended in the

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[68] S. A. Reynolds, "Application of Radioisotopes in Analytical Chemistry," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, pp 35–37.

[69] S. A. Reynolds, "Determination of Alkaline-Earth Elements," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, pp 75–78.

[70] S. A. Reynolds and G. W. Leddicotte, "Radioactive Tracers in Analytical Chemistry," *Nucleonics* **21**(8), 128 (1963).

[71] S. A. Reynolds, "Determination of Thorium in Granite by Gamma Spectrometry and by Radiotracer," *Talanta* **10**, 611 (1963).

[72] S. A. Reynolds, "Determination of Thorium and Alkaline-Earth Elements by Isotope Dilution," *Proceedings of the Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962*, TID-7655, pp 288–90.

[73] W. B. Schaap and E. Wildman, "Applications of Radioisotopes in Polarography," *Proceedings of the Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., Oct. 9–11, 1962*, TID-7655, pp 302–11.

[74] S. A. Reynolds, *Studies on the Electrolytic Separation and Determination of Tin, Antimony, and Bismuth with Controlled Cathode Potential*, ORNL-1557 (July 6, 1953).

[75] A. Brenner, *Electrodeposition of Alloys*, Academic Press, New York, 1963.

[76] P. L. Pinotti, D. E. Hull, and E. J. McLaughlin, "Radioactive Tracers Used in Research on Engine Wear," *S.A.E. Quart. Trans.* **3**, 634 (1949).

engine oil while the engine is run under a given set of test conditions. The amount of radioactivity in the oil is usually assayed by counting the gamma radiation from Fe^{59}.

A new technique for determining wear rates of selected engine parts was developed and demonstrated for piston rings. In this technique, Fe^{55} instead of Fe^{59} is used as the radiotracer. The method consists in extracting the wear debris from the circulating oil, separating the iron from other radionuclides in the wear debris (Co^{60}, Mn^{54}), dissolving the iron in a liquid scintillator medium, and counting the 5.9-kev x ray of Fe^{55}. The wear rate is determined by comparison with unused piston rings irradiated at the same time as the test rings.

The advantages of using Fe^{55} are: its longer half-life (2.6 years compared with 45 days for Fe^{59}), its greater abundance (typically, several times as much Fe^{55} is produced as Fe^{59}), reduced radiation hazard if the Fe^{59} is allowed to decay for several months, and ease of calibration for the determination of absolute wear rates.

For piston rings irradiated for 28 days in the ORR, a minimum detectable wear of 106 μg was obtained with 10-ml samples of oil taken from a total of 4000 ml of circulating oil.

This work was done jointly with R. P. Gardner[77] and J. W. Dunn.[78]

Selective Determination of Mercury by Isotopic Exchange with Mercuric Di-*n*-butylphosphorothioate in an Extraction System: Alternate Displacement Method with Silver Di-*n*-butylphosphorothioate

T. H. Handley

A rapid and precise isotopic exchange method was developed for the determination of 10^{-7} to 10^{-2} g of mercury. The organic phase of the system is a CCl_4 solution of mercuric di-*n*-butylphosphorothioate; the aqueous phase is a mineral-acid solution ($\geqq 0.2$ N) of the sample. The Hg^{2+} of the mercuric di-*n*-butylphosphorothioate exchanges with the Hg^{2+} of the sample. The D_{Hg} is measured by means of Hg^{203}, which is either added as a tracer to the aqueous phase or incorporated as a label in the mercuric di-*n*-butylphosphorothioate. A simple proportional relationship exists between D_{Hg} and the concentration of mercury. Chloride interferes; sulfate, nitrate, phosphate, and acetate do not. Of the metal ions tested, only Pd^{2+}, Au^{+}, and Cu^{+} interfere seriously; Cu^{2+}, Bi^{3+}, Pb^{2+}, Cd^{2+}, In^{3+}, and Zn^{2+} do not interfere when present in a mole ratio to Hg^{2+} as high as 10^4. When Ag^{+} is present in a mole ratio to Hg^{2+} of 10^3, the error is about -3%. The analysis of standard solutions of Hg^{2+} gave recoveries of 99 to 101%; the standard deviation of the recoveries was about 1%.

In an alternative method, the extractant is silver di-*n*-butylphosphorothioate. The Ag^{+} in the complex is displaced by an equivalent amount of Hg^{2+} from the sample, and Ag^{110} is exchanged with inactive silver. A paper on this subject was accepted for publication in *Analytical Chemistry*.

Determination of Beryllium by the Photoneutron Method

Gerald Goldstein

The photoneutron method previously described[79] was used to determine beryllium in solutions. The sensitivity was good (<1 mg of Be per ml), and there were virtually no interferences. Radiation hazard from the Sb^{124} gamma source was small. A complete report of this work has been published.[80]

APPLIED RADIOCHEMICAL STUDIES

Applications of Gamma-Ray Spectrometry in Reactor Problems

J. S. Eldridge

Gamma-ray spectrometry has continued to be useful in nondestructive assay problems.[81] Specimens irradiated in the Materials Test Reactor for

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[77] Measurement and Controls Laboratory, Research Triangle Institute, Durham, N.C.

[78] Department of Mathematics, North Carolina State College, Raleigh.

[79] G. Goldstein, "Determination of Beryllium by the Photoneutron Method," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 78.

[80] G. Goldstein, "Determination of Beryllium by the Photoneutron Method," *Anal. Chem.* 35, 1620 (1963).

[81] J. S. Eldridge, "Application of Gamma-Ray Spectrometry in Reactor Problems," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 92.

in-pile testing of MSRE systems were examined for residual activity approximately one year after they were discharged from the reactor. These specimens were too radioactive (300 to 400 mr/hr) for routine measurements in the control laboratory. Radioactive species found in the specimens at the time of measurement were Zr^{95}-Nb^{95}, Ru-$Rh^{103,106}$, and Ce-$Pr^{141,144}$. Gas samples collected from MSRE capsules were also assayed with this technique. The nuclides Kr^{85}, $Te^{129,129m}$, and Xe^{133} have been found in the gas samples.

Uranium and Fission Product Gamma Measurements

S. A. Reynolds

Measurements of gamma activity were made on enriched (93%) UNH, natural uranium, and fission product mixtures that consisted of Zr^{95}-Nb^{95}, Ru^{103}, and Ru^{106}. H. A. Parker[82] furnished the measured quantities of radioisotopes. The radiochemical purity of the uranium materials was checked by gamma spectrometry.

A conventional 4π gamma ionization chamber was employed; in terms used herein, its sensitivity was 1000 mv per 1 μc of Co^{60} or per 1.5 μg of Ra. Samples of 100-ml volume were measured. Also, two Analytical Chemistry Division standard well-type scintillation counters were used in three ways: without absorber, with 1.2-g/cm^2 Al absorbers, and with 5-g/cm^2 Pb absorbers. Samples of 1-ml volume were counted. Typical data are given in Tables 11.5 and 11.6. The natural-U values and self-absorption effect (differences between 2-*M* and 100-g/liter solutions) are consistent with those reported previously.[83] External-radiation measurements are also being made on a large volume of UNH solution. Preparation of a paper for publication in *Nuclear Science and Engineering* is contemplated.

Table 11.5. Results of Gamma Scintillation Counting with Aluminum Absorber

Uranium Material	Concentration of FP[a] (μc per g of U)	Gamma Activity (counts min^{-1} ml^{-1}) Gross	Gamma Activity (counts min^{-1} ml^{-1}) Net FP	Gamma Activity (counts/min per mg of U)
		× 10^4	× 10^4	
Natural U (100 g/liter)	0	0.96		56
	3.4×10^{-2}	1.20	0.24	
	3.4×10^{-1}	2.99	2.03	
	1.0	6.79	5.83	
Natural UNH (2 *M*)	0	3.96		83
	3.4×10^{-2}	4.84	0.88	
	3.4×10^{-1}	12.51	8.53	
Enriched U (100 g/liter)	0	41.3		4.13×10^3
	3.4×10^{-2}	41.5	~0.2	
	3.4×10^{-1}	43.3	2.0	
	1.0	47.1	5.8	

[a] FP = fission products.

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[82] Radioisotopes-Radiochemistry Group.

[83] S. A. Reynolds, "Measurement of Uranium Beta and Gamma Radiations," *Anal. Chem. Div. Quart. Progr. Rept. Jan. 10, 1951*, ORNL-955, pp 58–63.

Table 11.6. Results of Gamma Scintillation Counting with Lead Absorber

Uranium Material	Concentration of FP[a] (μc per g of U)	Gamma Activity (counts $\min^{-1}$ ml^{-1}) Gross	Gamma Activity (counts $\min^{-1}$ ml^{-1}) Net FP	Gamma Activity (counts/min per mg of U)
		$\times 10^4$	$\times 10^4$	
Natural U (100 g/liter)	0	0.048		4.8
	3.4×10^{-2}	0.161	0.113	
	3.4×10^{-1}	1.121	1.07	
	1.0	3.25	3.20	
Natural UNH (2 *M*)	0	0.245		5.2
	3.4×10^{-2}	0.733	0.49	
	3.4×10^{-1}	4.96	4.71	
Enriched U (100 g/liter)	0	0.19		19
	3.4×10^{-2}	0.30	0.11	
	3.4×10^{-1}	1.26	1.07	
	1.0	3.4	3.2	

[a] FP = fission products.

This work was done jointly with E. D. Arnold.[84]

Quantitative Analysis of Decay Products of Fission-Produced Krypton and Xenon Isotopes

F. F. Dyer

Many experiments were made by the Irradiation Engineering Section of the Reactor Division to measure the release rates of krypton and xenon radionuclides from reactor fuel elements during neutron irradiations. Fuel elements were irradiated in the ORR. Radiochemical measurements needed in this work were made.

The method of Townley *et al.*[85] was used. It consists in blowing helium over a fuel element in a reactor and allowing the gas to pass through a Cottrell precipitator. As the helium passes by the fuel element, it picks up the fission gases and carries them to the precipitator. Positively charged daughter products are deposited on a negatively charged aluminum collector rod. After a predetermined deposition time, the rod is cut into 1-in. segments, and daughter radionuclides are measured as a function of distance along the rod.

The release rates of Kr^{91}, Xe^{137}, Xe^{140}, and Xe^{141} were of major interest. These rates were determined by measuring the disintegration rates of Sr^{91}-Y^{91}, Cs^{137}, Ba^{140}-La^{140}, and La^{141}, respectively. The La^{141} was separated radiochemically and was beta counted under the direction of E. I. Wyatt.[82] Other radionuclides were determined nondestructively by gamma spectrometry, by summing areas under appropriate photopeaks, or by applying Heath's method of calculation.[86] Data obtained from the radioactivity measurements have helped to optimize the experimental conditions for the collection of samples.

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[84] Chemical Technology Division.

[85] C. W. Townley *et al.*, "An Improved Technique for the Determination of Short-Lived Fission-Product Gases," *Nucl. Sci. Eng.* 13, 297 (1962).

[86] R. L. Heath, *Scintillation Spectrometry Gamma-Ray Spectrum Catalogue*, IDO-16408 (July 1, 1957).

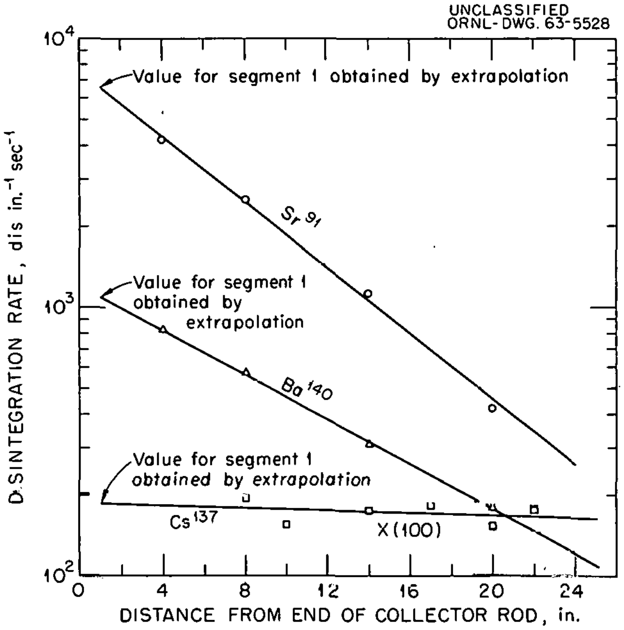

Fig. 11.18. Disintegration Rates of Daughter Activities from Fission Gases Found on Collector Rod – A Typical Experiment.

Results for the disintegration rates of Sr^{91}, Cs^{137}, and Ba^{140} in a typical experiment are shown in Fig. 11.18.

Computer analyses of the gamma-ray spectra will now be obtained. A least-squares fitting code will be used.

Investigation of Strontium Titanate

S. A. Reynolds E. I. Wyatt[82]
H. A. Parker[82]

Methods were required for measurement of Sr^{90} in $SrTiO_3$ powder contained on filter papers and in similar samples and of Sr^{90} in solution, the latter related to solubility studies.[87] The filter samples were measured both by beta-radiation reading and by bremsstrahlung counting with a scintillation spectrometer. Levels were microcuries to millicuries. The spectrometer was also used to measure a trace of Cs^{137} in $SrTiO_3$ for purposes of identification. The Sr^{90} content of solutions was determined by "gross beta" counting, recounts being made after two weeks to assure equilibrium of Y^{90}. It was found that the solutions were usually deficient in Y^{90}, indicating nondissolution or deposition after dissolving. A recent Sr^{90}-Y^{90} standard obtained from the International Atomic Energy Agency was used for calibrations involved in the solution work.

Chemistry of Pressurized-Water In-Pile Loop of the Oak Ridge Research Reactor

T. H. Handley

In an effort to obtain more precise information on the decontamination of Pressurized Water Reactor coolant by inorganic materials at elevated temperatures, a series of bench tests was conducted. The detailed results are found in the Army Reactor Program status reports.

A sampling system for in-pile experiments was constructed for use in further study of the efficiency of various inorganic high-temperature absorbents for removing ionic impurities from the loop water. The new system is expected to give more exact information both on the absorption process and on the characterization of particulate and ionic impurities circulating in the loop water.

ACTIVATION ANALYSIS

Preparation of a Guide on Activation Analysis

F. F. Dyer W. S. Lyon
J. S. Eldridge E. Ricci
R. L. Hahn H. H. Ross
J. E. Strain

Material has been written, assembled, edited, and forwarded to the AEC Division of Isotopes Development for publication in the form of a guide to activation analysis. The compilation contains a comprehensive survey of background information necessary for an understanding of activation analysis, together with detailed descriptions of techniques used in the application of nuclear analysis methods.

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[87] A. F. Rupp, *Newsletter on DID Programs for August 1963*, Sept. 5, 1963.

Table 11.7. Examples of Applications of Neutron Activation Analysis

Sample	Elements Determined
Aluminum	Au
Beryllium	Br, Mn, Sc
Bismuth	Cu, Mn, Na, Sb
Copper	Cr, Fe, Ru, Sb, Sc, Zn
Iron	Ag, As, Au, Br, Co, Cr, Cu, Cs, K, Mo, Na, Ni, Sb, Se, Ta, W
Silicon	Au
Titanium	Co, Fe, Ni
Zirconium	Au, Fe, Ta, W
Fe_3O_4	Co, Cr, Sc
Zr-Hf alloy	Hf
Body fluids	Co, Ir
Construction material	Co, Cr, La, Mn, Na, Ni, Sb, Sc, Th
Geyser water	Cs
Rubber	Cl
Spring water	Cs
Water	In

Research Applications of Neutron Activation Analysis

W. T. Mullins

Neutron activation analysis has continued to be applied to the determination of a number of elements in a variety of matrices. Table 11.7 lists a number of such analyses that were made. Nondestructive determinations include gold in silicon, aluminum, and zirconium; bromine in beryllium; chlorine in rubber; sodium in water; and hafnium in Zr-Hf alloy. The remainder of the analyses involved chemical separation.

Neutron Flux Perturbation in Activation Analysis

S. A. Reynolds W. T. Mullins

Some effects of the physical characteristics of samples and of comparators in activation analysis were evaluated in an experimental program. Induced specific activities in dilute aqueous solutions were compared with those in solid elements or compounds irradiated under the same conditions. Three factors that affect the neutron flux were investigated: thermal neutron self-shielding by solid materials, resonance neutron self-shielding, and enhancement of thermal flux by moderation within the aqueous samples.

The first effect can be computed with reasonable accuracy by using well-known equations. Self-shielding of resonance neutrons cannot be calculated rigorously; therefore, an empirical approach was used. It was assumed that an "effective thickness" exists, which is a function of the ratio of the resonance integrals of the absorbing element and of cobalt. This function was then substituted in an empirical equation for self-shielding in cobalt. Enhancement of thermal activation by moderation of neutrons was studied by irradiations with and without water in commonly used types of containers. Effects of the three factors were computed separately and combined to obtain the actual attenuation of the neutron flux. Agreement between computed and observed values was satisfactory. Details of this work were reported in a conference[88] and in a paper.[89] Findings are similar to, but more extensive than, those of others.[90–92]

Reactor Fast-Neutron Cross Sections of the Reactions $Ti^{46}(n,p)Sc^{46m}$ and $Al^{27}(n,p)Mg^{27}$

E. Ricci

Experiments were made at the "rabbit" facility of the ORR to examine the possibilities for the use of short-lived Sc^{46m} (19.5 sec) in fast-neutron activation for titanium. A preliminary value was

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[88] S. A. Reynolds, "Neutron Flux Perturbation in Activation Analysis," pp 24–26 in *Oak Ridge Radioisotope Conference*, Apr. 1–3, 1963.

[89] S. A. Reynolds and W. T. Mullins, "Neutron Flux Perturbation in Activation Analysis," *Int. J. Appl. Radiation Isotopes* **14**, 421 (1963).

[90] E. C. Lightowlers, "Determination of Submicrogram Quantities of Manganese, Sodium, and Copper in Natural Diamonds by Neutron Activation Analysis," *Anal. Chem.* **35**, 1285 (1963).

[91] G. R. Choppin, *Experimental Nuclear Chemistry*, Prentice-Hall, New York, 1961.

[92] O. T. Høgdahl, *Neutron Absorption in Pile Neutron Activation Analysis*, MMPP-226-1 (December 1962).

obtained for the average cross section[93] ($\bar{\sigma}$) of the reaction $Ti^{46}(n,p)Sc^{46m}$ for reactor fast neutrons: $\bar{\sigma} = 0.094 \pm 0.013$ mb. This low value results in poor activation-analysis sensitivity.

In these experiments, the reaction $Al^{27}(n,\alpha)Na^{24}$ was used as a fast-flux monitor ($\bar{\sigma} = 0.6$ mb). By measurement of Mg^{27} in the irradiated aluminum monitor, the average cross section of the reaction $Al^{27}(n,p)Mg^{27}$ was also confirmed[93] to be 2.8 mb.

Nuclear Methods of Determining Oxygen

L. C. Bate

A literature survey was conducted to learn what nuclear methods have been used to determine oxygen. The nuclear reactions primarily used are: $O^{16}(t,n)F^{18}$ ($t_{1/2}$, 112 min); $O^{16}(n,p)N^{16}$ ($t_{1/2}$, 7.35 sec); and $O^{16}(\gamma,n)O^{15}$ ($t_{1/2}$, 124 hr). Charged-particle reactions are also included. The results of this survey were reported.[94]

Comprehensive Nomograph for Calculating Absolute Activities Obtained After Irradiation and Decay

E. Ricci

A set of two nomographs was prepared for use in nuclear analysis calculations. The first nomograph calculates the saturation activity of any radioisotope per gram of irradiated element for any values of flux and cross section. The second nomograph gives the actual absolute activity obtained after certain irradiation and decay times; these times may cover a wide range.

The nomographs are versatile. Charged-particle currents, resonance, fast, and thermal fluxes, as well as average or thermal cross sections or resonance integrals, can be entered. These features should make the nomographs useful in various fields, such as activation analysis, monitoring of fluxes or charged-particle currents, production and use of radioisotopes, etc.

Comprehensive Scheme for Neutron Activation Analysis

W. J. Ross

Development work on the separation procedure previously reported[95] was completed, and the method was prepared for publication. The separations have been made >95% quantitative for all elements except antimony, rhenium, and iridium. Supplementary chemical separations were developed to remove overshadowing gamma activities from individual groups of nuclides or to isolate nuclides of interest from each of these groups. The method has been used successfully on a service basis for the analysis of aluminum, beryllium, and beryllium hydroxide.

FORENSIC AND BIOLOGICAL APPLICATIONS OF ACTIVATION ANALYSIS

Application of Neutron Activation Analysis to Physical Evidence

L. C. Bate G. W. Leddicotte[96]
J. F. Emery W. S. Lyon
M. J. Pro[97]

The identification of the automobile lacquers, soots, and soils discussed previously[98,99] has been completed, and an article on this work was accepted for publication in the *International Journal of Applied Radiation and Isotopes.*

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[93] D. J. Hughes, *Pile Neutron Research*, Addison-Wesley, Cambridge, Mass., 1953.

[94] L. C. Bate, "Nuclear Methods of Oxygen Analysis," *Nucleonics* 21(7), 72 (1963).

[95] W. J. Ross, "Comprehensive Scheme for Neutron-Activation Analysis," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, pp 95–99.

[96] Present address: Union Carbide Nuclear Company, Tuxedo, N.Y.

[97] Alcohol and Tobacco Tax Laboratory, Internal Revenue Service, Treasury Department, Washington, D.C.

[98] L. C. Bate *et al.*, "Use of Neutron-Activation Analysis in the Identification and Comparison of Physical Evidence for Enforcement Purposes," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 105.

[99] L. C. Bate, M. J. Pro, and G. W. Leddicotte, *Identification and Comparison of Physical Evidence for Law Enforcement Purposes by Neutron Activation Analysis*, ORNL-TM-363 (Sept. 11, 1962).

Use of Neutron Activation Analysis to Identify Sources of Drugs

L. C. Bate M. J. Pro[97]

Neutron activation analysis was used to compare and identify drugs. Phenobarbital and meperidine samples from different sources[98] were irradiated, and the resulting induced radionuclides were identified by nondestructive gamma-ray spectrometry. The results obtained indicate that the method can be used to differentiate sources of drugs. An article about this work was accepted for publication in the *International Journal of Applied Radiation and Isotopes.*

Forsensic Science Applications: Physical Evidence

J. F. Emery

The New York Police Department requested assistance in the comparison of small quantities of steel obtained from different sources. The samples were irradiated in the pneumatic tube of the ORR for 10 min. The radioisotopes Cr^{51} and Fe^{59} were found in all the samples. The specific activity of Fe^{59} was the same in all three samples; the specific activity of Cr^{51} was the same in the first and third samples but was 10 times higher in the second sample. However, the third sample contained a large amount of W^{187}. On the basis of these results, it was concluded that the three steel samples are all different.

Forensic Science Applications: Heroin

J. F. Emery

The New York City Police Department and the Bureau of Narcotics sought assistance in determining the similarity of a number of heroin samples.

In one such study for the Bureau of Narcotics, a particular sample of heroin was compared with five other heroin samples. Each sample was irradiated for 5 min at a neutron flux of 6.0×10^{13} neutrons cm^{-2} sec^{-1} and was allowed to decay for 5 days. The gamma-ray spectra of the heroin samples were compared. The sample in question was found to contain a considerable quantity of Au^{198} activity, whereas the other five samples had only Br^{82} activity. The dissimilarity of this one sample clearly indicated that it did not have the same origin as the other five.

The New York Police were interested in identifying a small amount of heroin found in some personal property with one of three larger quantities of the drug. After neutron irradiation of the drugs and a suitable decay period, the gamma-ray spectra from trace impurities were compared; the small heroin sample did not match exactly any of the larger quantities. However, the small quantity of heroin appeared qualitatively similar to two of the larger quantities.

This work was done for the court during a recess called for the purpose. During the recess, one of the two defendants pleaded guilty, and the evidence was not needed for disposition of the case. A third defendant pleaded guilty to conspiring to violate New York's narcotics laws by bringing $3,500,000 worth of heroin into the United States.

Forensic Science Applications: Identification of the Origin of Opium

J. F. Emery

The application of activation analysis to the identification of the origin of opium, grown throughout the world, was begun about two years ago.[100] Raw opium samples from ten different sources were analyzed. The results indicated that opium is reasonably homogeneous with enough variety of trace elements in each opium sample to warrant a full-scale investigation.

Of some 270 opium samples received, 107 were selected for analysis.[101] They included samples from 15 nations, as well as samples grown in different years in one locality and different varieties of opium.

Each sample was ground into a fine powder. Two 100.0 ± 0.5 mg portions were encapsulated and

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[100] G. W. Leddicotte, J. F. Emery, and L. C. Bate, *The Assay, Characteristics, Composition, and Origin of Opium. I. The Preliminary Study on the Use of Activation Analysis in the Determination of the Origin of Opium*, unpublished report, Feb. 26, 1962.

[101] J. F. Emery, "Determination of Trace Elements in Raw Opium by Neutron-Activation Analysis," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 107.

then irradiated in the ORR for 20 min at a neutron flux of 5×10^{13} neutrons cm^{-2} sec^{-1}. Gamma-ray spectra were obtained from each sample. To facilitate the analysis of each spectrum, comparison programs were designed for the IBM 7090 and CDC 1604 computers. The program for the 7090 computer consists in searching for photopeaks, locating the photopeaks by channel number rather than by gamma-ray energy, and integrating between minima on each side of the photopeak. Only the ten photopeaks having the largest areas are used for comparison purposes. If an "unknown" sample matches one of the samples in the library of gamma-ray spectra, the computer output will give the sample number and "fit factor " (e.g., sample 809 matches 168 with a fit factor of 71.31). The best fit factor is 100.00. The fit factor is calculated by the computer from the difference in areas and peak-channel numbers of the ten selected areas of the compared and library spectra. When each opium gamma-ray spectrum was compared with the library, the best fit factor obtained was 74.09. This matched a sample from Turkey with one from India.

The comparison program for the CDC 1604 computer was designed to use the entire gamma-ray spectrum. Each spectrum was divided into the same 13 groups. These were selected on the basis that a gamma ray most likely to appear in the spectrum would be centered in one of the groups. The program provides for correcting each spectrum for background, summing the channels that are included in each group, and obtaining the standard deviation of the net count in each group. Preselected limits of agreement are determined by $k\sigma$, where k may have any reasonable value. For matching each sample of the library to the remainder of the library, six values of k were selected: 1, 2, 3, 4, 5, and 10. The smaller the value of k, the better is the agreement between any two spectra that match. The best agreement was 3σ; only three spectra matched out of 107.

Both programs are being evaluated for dependence upon variations in decay time and reproducibility of a given spectrum.

It is anticipated that in the near future the Bureau of Narcotics will send "unknown" samples of opium for identification by neutron activation and computer comparison techniques.

Activation Analysis of Hair

L. C. Bate

Neutron activation analysis was used to study the trace elements associated with hair. In previous studies,[102–105] organic solvents have been used for cleaning hair prior to analysis. At this laboratory, the cleaning of irradiated hair with detergents [Kyro EO (ref 106)] and shampoos showed that the elements Na, Br, Cl, Mn, Zn, Sb, Cr, Ag, Sc, Hg, and Se are removed in greater amounts than with organic solvents. It appears that the elements are removed from the surface rather than leached from the hair and that postirradiation washing with detergent is necessary for measurement of the trace elements in hair. (The nonionic detergent, Kyro EO, is advantageous where preirradiation washing is required, since it leaves less residual sodium than shampoos.) Table 11.8 compares the relative amounts of

Table 11.8. Removal of Na and Br from Irradiated Hair by Washing

Wash	Br[a]		Na[a]	
	Before	After	Before	After
Detergent	53	3	25	2
Aerosol-DT (1%)	25	15	20	13
Alcohol-acetone	50	49	38	38
Carbon tetrachloride	37	34	24	22
Lacquer solvent	30	26	38	30
Amyl acetate	30	28	23	20
Benzene	18	18	29	29

[a] Intensity based on peak heights of 0.77 and 1.37 for Br and Na, respectively.

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[102] T. F. Dutcher and S. Rothman, "Iron, Copper, and Ash Content of Human Hair of Different Colors," *J. Invest. Dermatol.* 17, 65 (1951).

[103] P. Flesch, "The Role of Copper in Mammalian Pigmentation," *Proc. Soc. Exptl. Biol. Med.* 70, 79 (1949).

[104] R. E. Jervis, "Neutron Radioactivation Helps Solve Crimes," *Can. Nucl. Technol.*, p 21 (Winter 1962).

[105] A. K. Perkons and R. E. Jervis, "Applications of Radio-Activation Analysis in Forensic Investigations," *J. Forensic Sci.*7, 449 (1962).

[106] Alkylphenol ethylene oxide condensate type, Procter and Gamble Co., P.O. Box 599, Cincinnati.

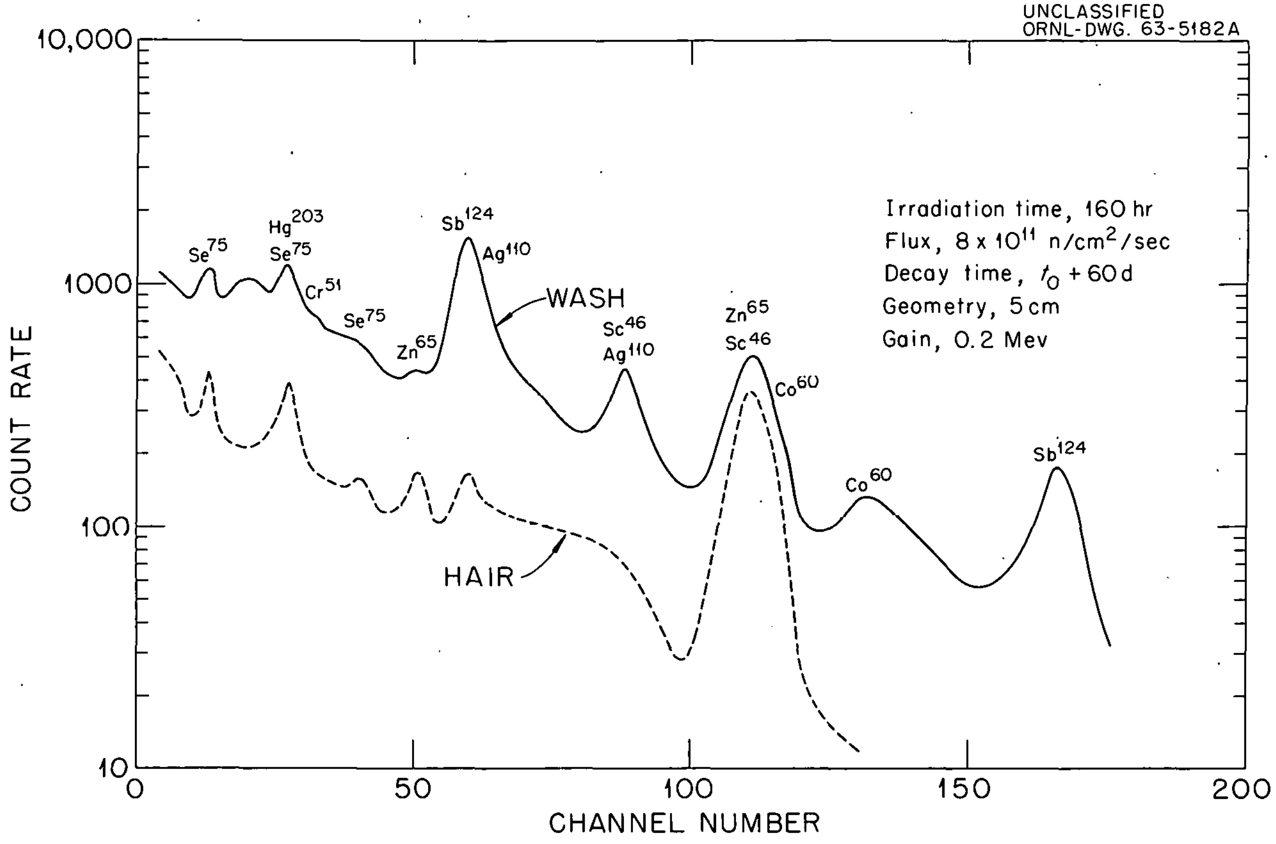

Fig. 11.19. Long-Lived Radionuclides in Hair and Wash Solution.

sodium and bromine removed from irradiated hair by one wash with various wash solutions. Figure 11.19 indicates results from a typical washing experiment.

Other studies of the washing of hair *in situ* with shampoo show that the Na and Br decrease after washing, and then the content of Na and Br begins to increase with time. The use of hair conditioners after washing leaves large amounts of sodium on the hair.

Hair Analysis (L. C. Bate, W. B. Healy[107]). – After hair is adequately cleaned, it can be analyzed nondestructively; therefore, samples can be retained for forensic use as physical evidence.

The sample is neutron irradiated for 150 hr, washed with detergent to remove surface material, dried, weighed, and mounted for counting. The wash solution is saved for the determination of surface material. The hair is counted with a multichannel analyzer, and the data obtained are compared with standards irradiated with the samples. With long irradiation times, an element whose half-life is 10 hr or greater can be determined. When the amount of sample is limited, the irradiated sample can be reirradiated after a 3-week decay for measurement of the short-half-lived radionuclides. Typical concentrations of trace elements found in hair are listed in Table 11.9. The trace elements vanadium, chlorine, and iodine are detected occasionally. The wash solution is also analyzed after Na and Br have decayed out. The long-lived radioelement contents of the wash and hair are compared in Table 11.10. As shown, the amount of trace element in the wash can be a considerable portion of the total present in the original hair. Thus, the elements present in the wash, as well as in the hair, should be considered in forensic identification.

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[107] Department of Scientific and Industrial Research, Soil Bureau, Lower Hutt, New Zealand.

Table 11.9. Trace-Element Content of Hair

Hair	Color	Concentration (μg/g)									
		Zn	Ag	Hg	Au	Mn	Cu	Al	Sb	Co	Se
1	Gray and black	149	1.0	1.6	0.008	0.12	26.0	2.4	ND	ND	ND
2	Black	88	0.42	8.9	0.016	0.49	20.0	4.0	ND	ND	ND
3	Black	51	1.6	2.1	0.012	1.5	21.0	8.5	0.51	ND	ND
4	Dark red	206	ND[a]	1.6	0.025	0.20	7.9	5.0	ND	ND	0.80
5	Blonde	151	ND	49.0	0.032	0.66	21.0	4.5	ND	0.43	ND

[a] ND = not detected.

Three samples of hair from the same individual were taken at 3-month intervals. The samples were irradiated, washed, and analyzed for trace elements. The bromine present, which was not removed by washing, is also included. These data presented in Table 11.11 show the reproducibility of trace-element determination at these levels.

Wool Analysis (L. C. Bate, W. B. Healy[107]). – Difference in trace-element composition of vegetables produced locally in two new Zealand areas, Napier and Hastings, result from local soil differences.[108] Dental surveys[109] have shown that there is a much lower prevalence of dental caries in children raised in Napier than in children raised in Hastings. Nutritional experiments with rats[110]

Table 11.10. Trace Elements in Hair and Wash Solutions

Sample		Concentration (μg/g)			
		Zn	Hg	Sb	Se
1	Hair	105	2.0	0.1	0.4
	Wash	65	0.7	0.8	0.03
2	Hair	120	3.0	0.5	0.4
	Wash	79	0.4	0.9	0.01
3	Hair	106	1.8	0.3	0.4
	Wash	66	ND[a]	0.7	0.06
4	Hair	133	0.8	0.2	0.4
	Wash	105	0.5	1.1	0.08
5	Hair	127	1.5	1.3	0.6
	Wash	124	1.1	2.7	0.09

[a] ND = not detected.

Table 11.11. Variation of Trace-Element Content in Hair

Sample	Concentration (μg/g)					
	Cu	Au	Zn	Br	Hg	Se
1	13 ± 4	0.020 ± 0.004	232 ± 25	1.2 ± 0.2	8.1 ± 2.5	0.9 ± 0.4
2	15 ± 3	0.010 ± 0.002	296 ± 11	2.5 ± 0.6	4.8 ± 1.8	1.1 ± 0.5
3	15 ± 2	0.014 ± 0.003	320 ± 30	2.7 ± 0.8	16 ± 2	0.8 ± 0.3

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[108] W. B. Healy, T. G. Ludwig, and F. L. Losee, "Soils and Dental Caries in Hawke's Bay, New Zealand," *Soil Sci.* 92, 359 (1961).

[109] T. G. Ludwig, W. B. Healy, and F. L. Losee, "An Association Between Dental Caries and Certain Soil Conditions in New Zealand," *Nature* 186, 695 (1960).

[110] T. G. Ludwig, R. S. Malthus, and W. B. Healy, "An Association Between Soil Conditions and Dental Caries in Rats," *Nature* 194, 456 (1962).

have shown that the differences in the trace-element content of the vegetables (fed as an ash supplement to caries-inducing diet) produce differences in caries prevalence.

As part of the soils-caries study, an animal experiment was conducted in New Zealand in which twin male lambs were separated at weaning and grazed on the pasture carried by these two different soils. When fully grown, the sheep were killed, and a number of tissue samples were taken for analysis. Activation analysis shows that the wool from sheep raised on the higher-manganese pastures is higher in manganese than wool from the twin sheep raised on lower manganese pastures (Table 11.12). The differences in wool manganese appear to be greater than the differences noted for manganese in soft tissues, such as liver, kidney, spleen, and pancreas. Although the two pastures appeared to be similar in zinc content, the wool from sheep raised in the Napier area was generally higher in zinc.

Separation of Sodium from Biological Materials

Nicolaas Spronk[111]

Because the abundance of sodium in biological material ranges from 300 to 10,000 times the abundance of some metallic elements, the determination of these elements, particularly copper, by activation analysis is difficult.

The induced Na^{24} has a 15-hr half-life; the induced Cu^{64} has a half-life closely similar, 12.9 hr. If one measures Cu^{64} in this material by gamma spectrometry using the 0.51-Mev annihilation gamma photopeak, this photopeak is usually obscured by the Compton spectrum from the Na^{24}; hence, the need to separate the Cu^{64} and the Na^{24}. Most previous work has involved separating the element sought from the matrix material.[112,113] The separation method studied here is to use anion exchange[114] to remove the bulk of the Na^{24}. The Cu^{64} fraction is measured by gamma-ray spectrometry, and any contribution to the Cu^{64} 0.51-Mev gamma-ray peak area from Na^{24} is corrected by instrumental techniques. The method is being evaluated using synthetic solutions of sodium and copper. These are evaporated and the residue irradiated in the ORR for 20 min at a thermal neutron flux of 3.8 × 10^{13} neutrons cm^{-2} sec^{-1}. This irradiated residue is leached with 12 *M* HCl, diluted 1:1 with water, and eluted through Dowex 1-X10. The elution removes Na^{24} and leaves Cu^{64} on the resin column vial, which is counted on a 3 × 3 in. NaI crystal. Table 11.13

Table 11.12. Manganese and Zinc Content of Wool

Wool Sample Pair	Concentration (μg/g)			
	Manganese		Zinc	
	Lamb A[a]	Lamb B[b]	Lamb A[a]	Lamb B[b]
1	1.5	0.4	96	106
2	1.3	0.6	108	580
3	0.5	0.6	89	109
4	2.8	0.3	103	168
5	1.9	0.5	93	169
6	0.7	0.9	113	127
7	1.2	0.2	101	124
8	0.9	0.2	92	103
9	1.2	0.2	94	89

[a] Lamb A raised in the Hastings area. Mean pasture content: Mn, 115 ppm; Zn, 26 ppm.

[b] Lamb B raised in the Napier area. Mean pasture content: Mn, 35 ppm; Zn, 25 ppm.

Table 11.13. Reduction in Sodium Content in Sodium-Containing Copper Solutions

	Original	After Elution	After Electronic Subtraction
Apparent copper content, counts per 2 min	10,000	7000	6000
Sodium content, counts per 2 min	54,000	1000	≦100
Ratio Cu/Na	0.2	7.0	60

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[111] Alien guest, Free University, Amsterdam, Netherlands.

[112] F. F. Dyer and G. W. Leddicotte, *The Radiochemistry of Copper*, NAS-NS-3027 (April 1961).

[113] W. T. Mullins and G. W. Leddicotte, *The Radiochemistry of Sodium*, NAS-NS-3055 (March 1962).

[114] K. A. Kraus and G. E. Moore, "Anion Exchange Studies VI," *J. Am. Chem. Soc.* 75, 1460 (1953).

gives preliminary data on the effectiveness of the combined technique; total counts in 0.47- to 0.54-Mev and 1.31- to 1.41-Mev peaks are compared.

In future work, attempt will be made to reduce the ~2000 counts per 2 min loss of Cu after elution (1000 counts per 2 min is due to Na^{24} contribution), as well as to reduce the Na remaining with the Cu^{64} after elution.

NEUTRON GENERATOR

Irradiation of Titanium with 14-Mev Neutrons

E. Ricci

To examine the possibilities of the fast-neutron activation analysis for titanium, the cross sections of the reactions $Ti^{46}(n,p)Sc^{46m}$ and $Ti^{46}(n,p)Sc^{46}$ were determined. Samples of "spec pure" titanium were irradiated with the 14-Mev neutrons of a neutron generator. The neutron flux was measured by the reaction $Si^{28}(n,p)Al^{28}$. The neutron output of the generator, during the irradiations, was monitored externally (in a relative manner) with a BF_3 tube. The results are listed in Table 11.14.

Two serious problems became apparent during these measurements. The first was the wide spread in published values[115] for the monitor reaction $Si^{28}(n,p)Al^{28}$. (The recent value 345 ± 40 mb[116] was used in these determinations.) This problem is directly related to the neutron energy distribution from the generator, which was unknown. The reaction $Al^{27}(n,\alpha)Na^{24}$ was tried as a flux monitor, since relevant data for its excitation function have been reported recently.[117,118] However, to use this or any other monitor reaction, the energy distribution of the neutrons emitted by the generator must be known. Since no reliable data for the titanium cross sections can be obtained without accurate flux measurements, the titanium research had to be postponed until that problem was solved. As the determination of the generator-neutron spectrum is an important problem in itself, it is reported separately.

Table 11.14. Cross Sections of 14-Mev Neutron Reactions That Produce Sc^{46m} and Sc^{46} from Natural Titanium

Nuclide Formed	σ^a (mb)	Standard Deviation (%)	Number of Determinations
Sc^{46m} (independent)	95 ± 28 (σ_1)	29.5	4
Sc^{46}	325 ± 84 (σ_2)	25.8	Calculated[b]
Sc^{46} (total)	420 ± 79 (σ)	18.8[c]	1

[a] σ = cross section if only (n,p) reactions are assumed.

[b] When Sc^{46m} is the result of the nuclear reaction, this nuclide immediately decays to its isomer Sc^{46}. Therefore, $\sigma = \sigma_1 + \sigma_2$, where σ and σ_1 are measured experimentally.

[c] This value was obtained by applying the statistical law of propagation of errors to the calculation of σ.

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[115] D. G. Gardner, "Trends in Nuclear Reaction Cross Sections (I). The (n,p) Reaction Induced by 14-Mev Neutrons," *Nucl. Phys.* 29, 373 (1962).

[116] J. M. Ferguson, W. E. Thompson, and B. D. Kern, *Cross Sections for the* $Mg^{24}(n,p)Na^{24}$, $Al^{27}(n,\alpha)Na^{24}$, $Si^{28}(n,p)Al^{28}$, $Cr^{52}(n,p)V^{52}$, *and* $Fe^{56}(n,p)Mn^{56}$ *Reactions*, USNRDL-TR-269 (Oct. 10, 1958).

[117] H. W. Schmitt and J. Halperin, "$Al^{27}(n,\alpha)Na^{24}$ Cross Section as a Function of Neutron Energy," *Phys. Rev.* 121, 827 (1961).

[118] J. P. Butler and D. C. Santry, "Excitation Curves for the Reactions $Al^{27}(n,\alpha)Na^{24}$ and $Mg^{24}(n,p)Na^{24}$," *Can. J. Phys.* 41, 372 (1963).

The second problem was the possible interference of the reactions (*n,np*) and (*n,d*) in the determination of the (*n,p*) cross sections. Since reactions (*n,np*) and (*n,d*) have been reported for several nuclides,[119,120] it appears possible that radionuclides of scandium might be formed by two or three reactions in the same irradiation, for example, $Ti^{46}(n,p)Sc^{46}$, $Ti^{47}(n,np)Sc^{46}$, and $Ti^{47}(n,d)Sc^{46}$. The data in Table 11.14 report (*n,p*) reactions only and, naturally, should be changed if significant values are found for the cross sections of the reactions (*n,np*) and (*n,d*). Values for these cross sections could be obtained by irradiating enriched isotopes of titanium and by comparing the results with those from irradiation of natural titanium.

Determination of Oxygen with the 14-Mev Neutron Reaction, $O^{16}(n,p)N^{16}$

J. E. Strain W. J. Ross

The present limit of sensitivity for determination of oxygen by the $O^{16}(n,p)N^{16}$ reaction is about 500 μg of oxygen due to the high background of oxygen that is in the polyethylene rabbits. Sensitivity can be improved by a factor greater than 10, it is believed, by an increase in counting efficiency, increase in flux by target redesign, and redesign of the rabbit system to accommodate a larger sample and at the same time to more effectively exclude oxygen and moisture. The system should make possible the determination of oxygen at the $\sim$10 ppm level in the maximum-size (18 g) sample.

Miscellaneous Use of the 14-Mev Neutron Generator

J. E. Strain W. J. Ross

The 14-Mev neutron generator has been used in the production of the nuclides of technetium by irradiation of separated isotopes of ruthenium, in irradiation of germanium and silicon semiconductors, in irradiation studies on liquid-liquid interfaces, in measurements of the cross sections of the isotopes of titanium, and in determination of P, O, N, and F in a variety of materials.

Measurement of Neutron Spectra Using Solid-State Detectors

J. E. Strain F. F. Dyer

Since the cross section of any neutron reaction is a function of the neutron energy, it is desirable in many experiments to know the energy distribution of the neutrons used. To this end, a commercially available neutron spectrometer was acquired to measure the neutron energy distribution from isotopic, accelerator, and reactor neutron sources. The detector consisted of a layer of Li^6F between two silicon diodes. The incident neutron interacts with the Li^6 to produce a triton and an alpha particle; the cumulative energy of these is 4.78 Mev plus the energy of the incident neutron.

A coincidence circuit is used to reduce background, and a summing unit is used to integrate the alpha and triton energies into a single pulse. This pulse is analyzed in a conventional pulse-height analyzer. The commercial sum-coincidence circuitry proved too slow (6 μsec) to reject the noise or background pulses produced by the fast neutron reaction on silicon, and the data obtained were therefore meaningless. By use of the same detectors, but a 60-nsec coincidence circuit built at ORNL, it was possible to obtain valid neutron spectra for the 14.7-Mev neutrons from the $T^3(d,n)He^4$ reaction, as well as for those from Am^{241}-Be neutron sources. Figure 11.20 shows a corrected Am^{241}-Be neutron spectrum obtained by means of the 60-nsec coincidence circuitry.

This work was performed jointly with E. H. Acree.[121]

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[119] D. L. Allan, "An Experimental Test of the Statistical Theory of Nuclear Reactions," *Nucl. Phys.* 24, 274 (1961).

[120] L. Colli *et al.*, "(*n,d*) Reactions with 14-Mev Neutrons on Al^{27}, Ca^{40}, Mn^{55}, Cu^{63}, Rb^{103}," *Nuovo Cimento* 14, 1120 (1959).

[121] Isotopes Division.

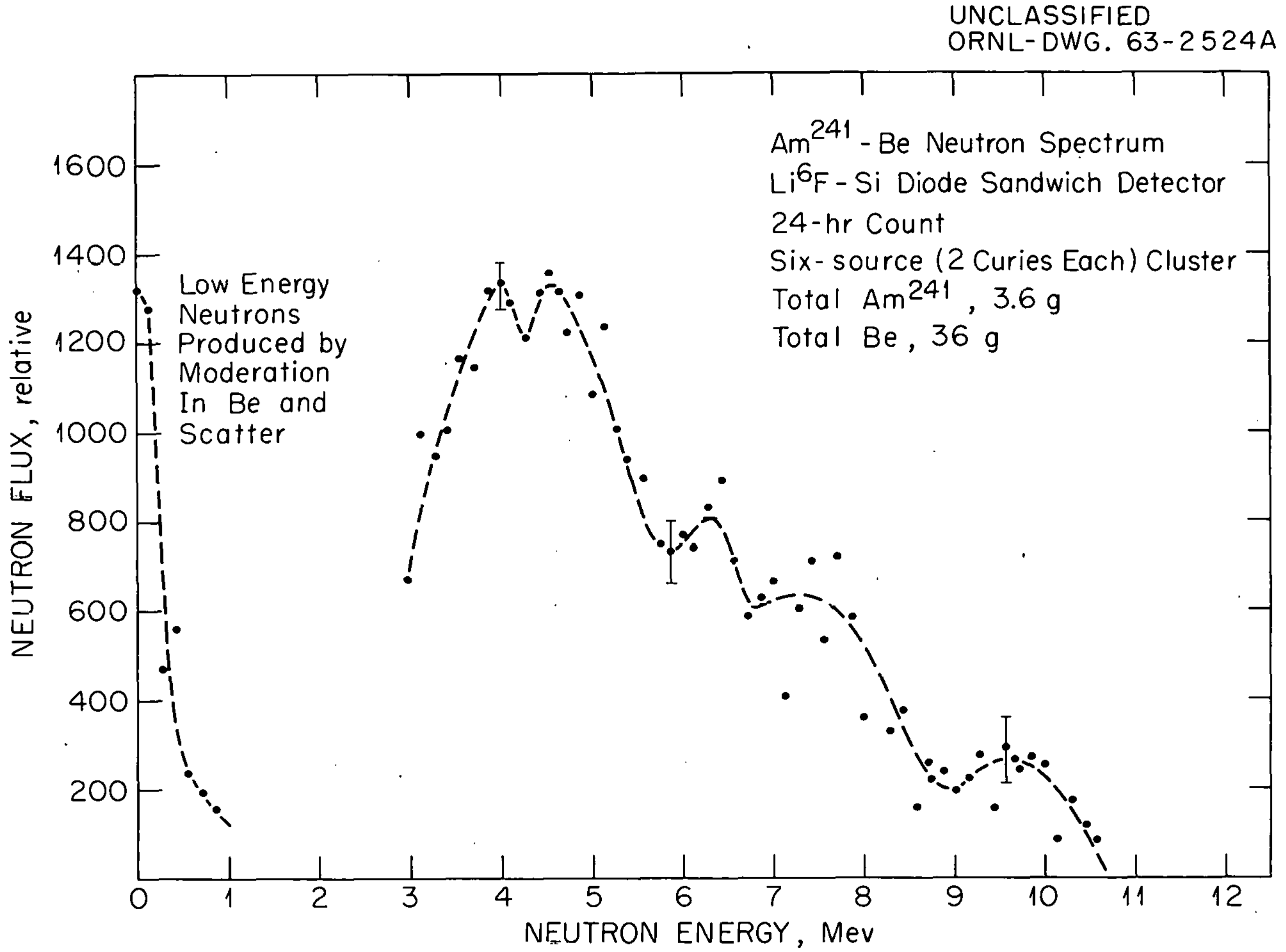

Fig. 11.20. Neutron Spectrum Produced by Am^{241}-Be Isotopic Neutron Sources.

Approximate Method for Calculating the Neutron Spectrum Produced by a 14-Mev Neutron Generator

E. Ricci

Experiments performed inside and outside the plastic rabbit assembly at the 14-Mev neutron generator indicate that the neutron spectrum is changed and the flux lowered by the assembly. An effort was made to calculate the neutron energy distribution by a simplified calculation which ignores the relatively unimportant effects of the energy spread of the impinging 150-kev deuterons and multiple scattering.

Energy Spread and Percentage of Nonscattered Neutrons. – The geometrical conditions of the neutron generator are shown in Fig. 11.21. For the extreme angles geometrically possible, the tables of Fowler and Brolley[122] and probability calculations show that the percentage of neutrons which hit the sample without being previously scattered is 69.9%, their energies being between 14.7 and 14.9 Mev. This result is obtained by first calculating the groups of neutrons which are scattered by aluminum, oxygen, and hydrogen.

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[122] J. L. Fowler and J. E. Brolley, Jr., "Monoenergetic Neutron Techniques in the 10- and 30-Mev Range," *Rev. Mod. Phys.* **28**, 103 (1956).

Subgrouping of the Scattered Neutrons According to Their Energies. – The aluminum- and oxygen-scattered neutron groups mentioned above may each be subdivided into two or more energy subgroups. The number of subgroups and their energy limits are set arbitrarily according to the shape of the corresponding scattering angular distribution curves.[123] The relative percentages of neutrons in each subgroup are calculated by integration of these curves.

The final results of this subgrouping procedure are listed in Table 11.15. The histogram of Fig. 11.22 was drawn from these results. It shows a sharp peak at 14.8 ± 0.1 Mev and clearly points

Table 11.15. Calculated Energy Grouping for Neutrons Emitted by a 14-Mev Neutron Generator[a]

Scattering Element	Energy Interval (Mev)	Neutrons (%)	
		In Interval	Total per Scattering Element
(No scattering)	14.7–14.9	69.6	
Hydrogen	0–14.9	8.2	8.2
Oxygen	11.3–13.8	3.4	9.3
	13.8–14.9	5.9	
Aluminum	12.2–13.5	1.3	12.9
	13.5–14.2	2.6	
	14.2–14.9	9.0	
Total		100.0	

[a] As seen by a pellet attached to the aluminum end cap (see Fig. 11.21).

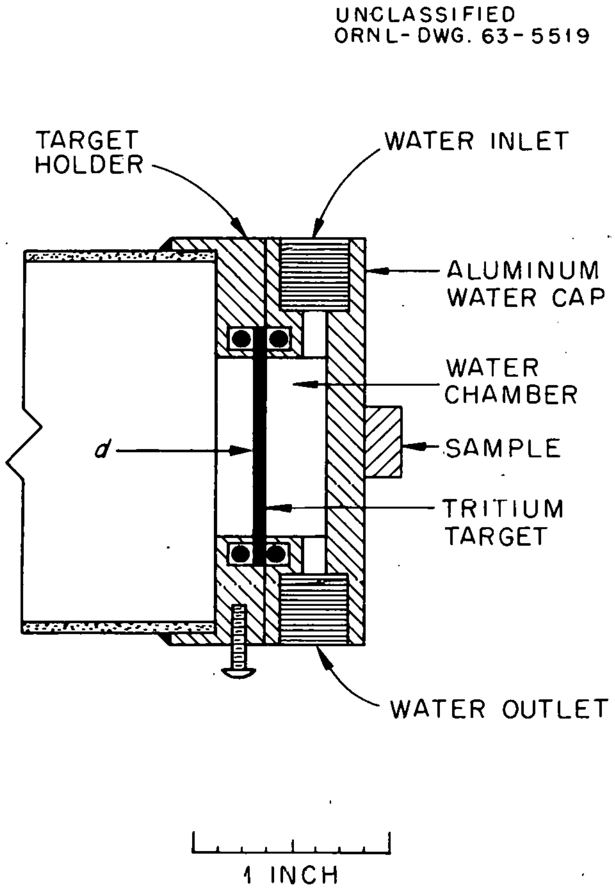

Fig. 11.21. Sample-Irradiation Geometry Assumed in the Neutron-Spectrum Calculation.

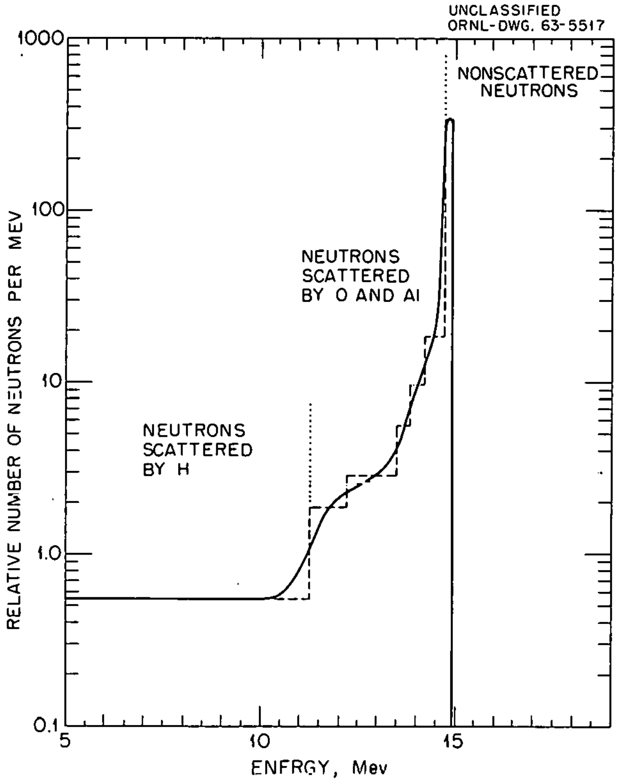

Fig. 11.22. Calculated Neutron Spectrum Seen by a Sample Attached to the End Cap of a 14-Mev Neutron Generator.

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[123] M. D. Goldberg, V. M. May, and J. R. Stehn, *Angular Distributions in Neutron-Induced Reactions*, BNL-400, 2d ed. (February 1963).

out the influence of the scattered neutrons on the shape of the neutron spectrum (left slope of the peak).

Catalog of 14-Mev Neutron Reactions

J. E. Strain W. J. Ross

The 150-kv neutron generator has been used primarily to investigate the feasibility of performing activation analyses with unmoderated 14-Mev neutrons. The cross section and sensitivity of each neutron reaction that yields gamma-emitting nuclides have been established for the lighter elements ($4 < Z < 31$) and are given in Table 11.16.

Table 11.16. Nuclear Reactions Obtained with Unmoderated 14-Mev Neutrons

Element Irradiated	Reaction Observed	$t_{1/2}$ of Product	ΔTime			Cross Section (mb)		Major Photopeak Height (counts/g)[b]
			Irradiation	Decay	Count	Calculated	Literature[a]	
B	$\mathrm{B}^{11}(n,p)\mathrm{Be}^{11}$[c]	13.7 s	10 s	1.6 s	18 s	5.5		250
	$\mathrm{B}^{11}(p,n)\mathrm{C}^{11}$	20.4 m	5 m	1.6 s	1 m	0.9		2,000
N	$\mathrm{N}^{14}(n,2n)\mathrm{N}^{13}$	10.1 m	5 m	1.6 s	1 m	6.7	5.7	40,000
O	$\mathrm{O}^{16}(n,p)\mathrm{N}^{16}$	7.4 s	10 s	1.6 s	24 s		49 ± 50%	2,500[d]
F	$\mathrm{F}^{19}(n,\alpha)\mathrm{N}^{16}$	7.4 s	10 s	1.6 s	18 s			1,500
	$\mathrm{F}^{19}(n,p)\mathrm{O}^{19}$	29 s	10 s	1.6 s	18 s	109	135	3,800
	$\mathrm{F}^{19}(n,2n)\mathrm{F}^{18}$	112 m	2 m	60 m	1 m	60	61	4,700
Na	$\mathrm{Na}^{23}(n,p)\mathrm{Ne}^{23}$	40 s	40 s	80 s	18 s	53	34	4,300
	$\mathrm{Na}^{23}(n,\alpha)\mathrm{F}^{20}$	11.6 s	10 s	1.6 s	12 s	104		11,000
Mg	$\mathrm{Mg}^{24}(n,p)\mathrm{Na}^{24}$	15 h	1 m	18 m	1 m	189	191	210
	$\mathrm{Mg}^{25}(n,p)\mathrm{Na}^{25}$	60 s	1 m	35 s	30 s	144	45	800
	$\mathrm{Mg}^{26}(n,\alpha)\mathrm{Ne}^{23}$	40 s	1 m	35 s	30 s			e
Al	$\mathrm{Al}^{27}(n,p)\mathrm{Mg}^{27}$	9.5 m	5 m	1 m	1 m	78	52.4	60,000
	$\mathrm{Al}^{27}(n,\alpha)\mathrm{Na}^{24}$	15 h	5 m	2 h	5 m	115	79 ± 20%	2,300
Si	$\mathrm{Si}^{28}(n,p)\mathrm{Al}^{28}$	2.3 m	2 m	1 m	1 m	221	220	66,000
	$\mathrm{Si}^{29}(n,p)\mathrm{Al}^{29}$	6.56 m	2 m	1 m	1 m	83	101 ± 30	500
P	$\mathrm{P}^{31}(n,\alpha)\mathrm{Al}^{28}$	2.3 m	1 m	2.4 s	1 m	124	146 ± 20%	45,000
	$\mathrm{P}^{31}(n,2n)\mathrm{P}^{30}$	2.5 m	1 m	2.4 s	1 m	10.5		27,000
Cl	$\mathrm{Cl}^{35}(n,2n)\mathrm{Cl}^{34}$	32.4 m	5 m	60 m	5 m	5.2	3.5 ± 45%	5,000
	$\mathrm{Cl}^{37}(n,p)\mathrm{S}^{37}$	5.0 m	5 m	1 m	1 m	28	33 ± 20%	1,100
K	$\mathrm{K}^{39}(n,2n)\mathrm{K}^{38}$	8.0 m	10 m	1 m	1 m	4	10 ± 55%	14,000
	$\mathrm{K}^{41}(n,\alpha)\mathrm{Cl}^{38}$	37.5 m	20 m	20 m	10 m	26	31 ± 35%	2,900
	$\mathrm{K}^{41}(n,p)\mathrm{A}^{41}$	1.8 h	20 m	20 m	10 m	42	81 ± 40%	5,000
Ti	$\mathrm{Ti}^{46}(n,p)\mathrm{Sc}^{46m}$	20 s	1 m	1 s	18 s	72		f
	$\mathrm{Ti}^{48}(n,p)\mathrm{Sc}^{48}$	44 h	1 m	1 h	10 m	132	93 ± 35%	360
	$\mathrm{Ti}^{50}(n,p)\mathrm{Sc}^{50}$	1.7 m	1 m	1 m	1 m	27		210
	$\mathrm{Ti}^{46}(n,2n)\mathrm{Ti}^{45}$	3.1 h	1 m	1 h	10 m	54		800
V	$\mathrm{V}^{51}(n,p)\mathrm{Ti}^{51}$	5.8 m	5 m	20 m	1 m	48	27	10,000
	$\mathrm{V}^{51}(n,\alpha)\mathrm{Sc}^{48}$	44 h	5 m	5 h	10 m	34	29	720
	$\mathrm{V}^{51}(n,\gamma)\mathrm{V}^{52}$	3.8 m	5 m	1 m	1 m	18	24[g]	5,200

Table 11.16 (continued)

Element Irradiated	Reaction Observed	$t_{1/2}$ of Product	ΔTime			Cross Section (mb)		Major Photopeak Height (counts/g)[b]
			Irradiation	Decay	Count	Calculated	Literature[a]	
Cr	$Cr^{52}(n,p)V^{52}$	3.76 m	0.5 m	7 m	0.5 m	82	77	880
	$Cr^{50}(n,2n)Cr^{49}$	42 m	5 m	1 h	5.0 m	27		660
Mn	$Mn^{55}(n,\gamma)Mn^{56}$	2.58 h	30 s	2 m	1 m	26	25[h]	1,200
	$Mn^{55}(n,\alpha)V^{52}$	3.76 m	30 s	72 m	10 m	27	30 ± 12 mb[h]	650
Fe	$Fe^{56}(n,p)Mn^{56}$	2.58 h	1 m	70 m	10 m	104	110	6,200
	$Fe^{54}(n,2n)Fe^{53}$	9 m	1 m	3 s	1 m	21	10	750
Co	$Co^{59}(n,\alpha)Mn^{56}$	2.58 h	5 m	100 m	1 m	42	27–39	750
	$Co^{59}(n,2n)Co^{58}$	72 d	5 m	119 h	20 m	1040		900
Ni	$Ni^{58}(n,p)Co^{58}$	72 d	5 m	140 h	20 m	281	310	120
	$Ni^{58}(n,2n)Ni^{57}$	37 h	5 m	25 m	5 m	35	22	400
	$Ni^{62}(n,p)Co^{62}$	13.9 m	5 m	1 m	1 m	106		400
Cu	$Cu^{63}(n,2n)Cu^{62}$	9.9 m	20 s	30 s	1 m	560	450–550	40,000
	$Cu^{65}(n,2n)Cu^{64}$	12.8 h	20 m	17 h	20 m	950	970	35,000
Zn	$Zn^{64}(n,p)Cu^{64}$	12.8 h	5 m	23 h	20 m	163	216–590	1,700
	$Zn^{64}(n,2n)Zn^{63}$	38 m	5 m	1 m	1 m	157	150	30,000
	$Zn^{66}(n,p)Cu^{66}$	5.1 m	5 m	1 m	1 m	101	80	~1,000
	$Zn^{67}(n,p)Cu^{67}$	59 h	5 m					

[a] R. J. Howerton, *Tabulated Neutron Cross Sections 0.001–14.5 Mev*, UCRL-5226 (1959).

[b] Neutron flux of 5×10^8 neutrons cm^{-2} sec^{-1}, 3 × 3 in. NaI crystal, 4.0-cm Lucite β^- absorber, 4.2-cm source-crystal distance.

[c] H_3BO_3 irradiated.

[d] 5.6-Mev pair peak.

[e] Ne^{23} ± Na^{25} ~2500 counts/g at 0.41 Mev.

[f] Sc^{46m} ± Sc^{47} ~9600 counts/g at ~9.16 Mev.

[g] D. J. Hughes and R. B. Schwartz, Supplement to BNL-325 (1957).

[h] D. J. Hughes and J. A. Harvey, *Neutron Cross Sections*, BNL-325 (1955).

12. Inorganic Preparations

M. T. Kelley
D. E. LaValle
R. B. Quincy

The preparation of pure, anhydrous, fused, and sublimed salts continued to occupy the major portion of the time.

The Ion Spectroscopy Laboratory of the Metals and Ceramics Division was provided with substantial quantities (~100 g) of fused, anhydrous, solvent media such as the eutectics LiCl-KCl, NaI-KI, and LiI-KI and the salts $AlCl_3$, $BiCl_3$, CsBr, and CsI. Smaller amounts of other anhydrous compounds used in connection with the solvent media, such as $NiBr_2$, NiI_2, CaH_2, $TiCl_3$, VCl_3, Na_2S, $Ni(NO_3)_2$, Cs_2ZnCl_4, and $CuCl_2$, were also provided. Most of the solvent salts were prepared by methods described in previous reports, but the $AlCl_3$ has not yet been successfully fused. Of the other compounds, anhydrous $Ni(NO_3)_2$ was prepared by an adaptation of methods of Ferraro, Katzin, and Gibson[1] and of Guntz and Martin.[2] The compounds $TiCl_3$, VCl_3, CaH_2, and NbO_2 were prepared according to known methods,[3] and Cs_2ZnCl_4, $CuCl_2$, and Na_2S by ordinary methods of dehydration. Procedures had to be modified for the preparation of some iodides because of the wide variation in the behavior of these substances toward container materials.

The High Temperature and Structural Chemistry Group of the Chemistry Division continued to request anhydrous halides of the alkaline-earth and rare-earth metals. These also were prepared mostly by the methods noted above, again with special treatment for some of the iodides.

The work for the Nuclear Physics and Neutron Diffraction Group of the Physics Division was limited to the preparation of some alloys of the rare-earth metals with each other and of a series of ternary oxides of rare-earth metals with manganese (manganites). An analogous new compound was $ScMnO_3$. Some further studies were made on the H_2 and D_2 absorption in and evolution from Pd-Ni alloys.

Preparation of the Fe^{57} compounds $Fe^{57}F_2$, $KFe^{57}F_3$, $LaFe^{57}O_3$, and $Fe_3^{57}O_4$ was the sole work performed for the Nuclear Physics and Low Temperature Group of the Physics Division.

The Radiation Chemistry Group of the Chemistry Division was provided with ~50 g of Li^6NO_3 and ~300 g of Li^7NO_3; the respective isotopes in the metallic form were used as starting materials.

The continuing investigation into the chemistry of rhenium, in connection with the work of the Inorganic and Physical Chemistry Group of the Chemistry Division, has led to the solution of some problems. A comparatively simple method for the preparation of significant quantities of ReF_4 from ReF_6 by reduction with rhenium metal was developed, and the x-ray structure of the compound was fairly well established. The compound K_2ReF_6,[4] which had previously seemed to exist in forms of several colors, has now been determined to be pink in its pure state. This compound has also been prepared directly from $KReO_4$ by a modification of the method of Ruff and Kwasnik[5] for the first time since their original description of the method. The decomposition product of $(NH_4)_2ReF_6$[6] was tentatively identified as ReNF. The existence of the compound $ReBr_4$ described by Colton and Wilkinson[7] could not be confirmed. The acid H_2ReBr_6 does not deposit an

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[1] J. R. Ferraro, L. I. Katzin, and G. Gibson, "The Reaction of Thorium Nitrate Tetrahydrate with Nitrogen Oxides. Anhydrous Thorium Nitrate," *J. Am. Chem. Soc.* **77**, 327 (1955).

[2] A. Guntz and F. Martin, "Sur la préparation des nitrates anhydres de manganese, cuivre, nickel, cobalt," *Bull. Soc. Chim. France* [4] 5, 1004 (1909).

[3] G. Brauer (ed.), *Handbuch der präparativen anorganischen Chemie*, 2d ed., vol II, F. Enke, Stuttgart, 1960.

[4] D. E. LaValle, "Inorganic Preparations," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1960*, ORNL-3060, pp 15–16.

[5] O. Ruff and W. Kwasnik, "Rheniumfluoride," *Z. Anorg. Allgem. Chem.* 219, 65 (1934).

[6] M. T. Kelley, D. E. LaValle, and R. B. Quincy, Jr., "Inorganic Preparations," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, pp 112–13.

[7] R. Colton and G. Wilkinson, "Halide Compounds of Rhenium," *Chem. Ind.* (London) **1959**, 1314.

insoluble $ReBr_4$ that is analogous to the ReI_4 described by Peacock, Welch, and Wilson;[8] however, a thermal decomposition product, $ReOBr_4$, has been isolated and characterized. About 170 g of K_2ReI_6 was prepared for calorimetric studies by modifying the general method of using $KReO_4$ to one taking advantage of the higher solubility of $HReO_4$, and thereby minimizing the hydrolytic problem involved in the concentration of solutions of this compound.

Some work was initiated for the Salt Separation Chemistry of Protactinium from Irradiated Thorium Group of the Reactor Chemistry Division; it requires experiments toward the production of $AlCl_3$. About 20 g of this material in fairly high purity was provided. The purification of 100-g quantities, and more, of commercial or otherwise available $ThCl_4$ and $ZrCl_4$ is in process.

In the preparation of high-purity compounds, the Pure Materials Group of the Solid State Division was provided with a KCl product that is sufficiently pure to challenge the limitations of analytical methods and subsequent crystal-growing operations. A particular brand of reagent-grade KCl was treated by extraction with 2-thenoyltrifluoroacetone—hexone, crystallization, fusion, passage of a 1:1 Cl_2-HCl gas mixture through the melt, purging with argon, and filtration into a cold receiver. Of the chief contaminants, bromine and calcium were reduced to <3 ppm, and OH^- to <1 ppm. Only sodium remains analytically significant at a concentration of 4 ppm.

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[8] R. D. Peacock, A. J. E. Welch, and L. F. Wilson, "Three Iodides of Rhenium," *J. Chem. Soc.* 1958, 2901.

13. Organic Preparations

J. C. White
P. F. Thomason
H. L. Holsopple

Organic compounds were prepared and purified on request from the Chemical Technology, Analytical Chemistry, and Metallurgy Divisions. These compounds either were not readily available from commercial sources or were available in impure form only and required purification. A summary of this program follows.

COMPOUNDS PREPARED

Ammonium Pyrrolidinedithiocarbamate

Ammonium pyrrolidinedithiocarbamate (57 g) was synthesized by the reaction of pyrrolidine, carbon disulfide, and ammonium hydroxide in ethyl alcohol.[1] The white crystalline product was purified by recrystallization twice from ethyl alcohol. Elemental analysis gave the following results (in mole percent):

Component	Theoretical	Found
Carbon	36.6	37.1
Sulfur	39.0	38.3
Nitrogen	17.0	16.7

Monoacid Esters

Eighteen new monoacid esters were prepared for testing as extractants in the fission product recovery program being carried out by the Chemical Technology Division. Stoichiometric quantities (0.3 mole) of six cyclic anhydrides of dibasic

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[1] H. Malissa and E. Schöffmann, "Über die Verwendung von substituierten Dithiocarbamaten in der Mikroanalyse. III," *Mikrochim. Acta* 1955, 187.

acids (maleic, succinic, phthalic, tetrahydrophthalic, 1,2-cyclohexanedicarboxylic, and 5-norbornene-2,3-dicarboxylic) were cleaved by 0.5 mole of each of three long-chained alcohols (dodecyl, tridecyl, and heptyldecyl) to yield the monoacid esters. Carbon and hydrogen determinations were made on each of the compounds, and refractive index measurements on the liquid samples; the results are presented in Table 13.1. The details of this work are reported elsewhere.[2]

Tetrahedral Nickel Compounds

Two tetrahedral nickel compounds, tetra-*n*-butylammonium tetrabromonickelate(II) and benzyltributylphosphonium tetrachloronickelate(II), were synthesized for the Metallurgy Division by reacting the appropriate nickel halide with tetra-*n*-butylammonium bromide and benzyltributylphosphonium chloride, respectively. Results of elemental analysis were in good agreement with theoretical values (Table 13.2). The details of this work are reported elsewhere.[3]

Table 13.1. Results of the Analyses of Eighteen Monoacid Esters

Monoacid Ester	Carbon (mole %)		Hydrogen (mole %)		n_D^{20}
	Calcd.	Found	Calcd.	Found	
Monododecyl maleate	67.6	68.5	9.9	10.4	(Solid)
Monododecyl succinate	67.1	67.6	10.6	10.7	(Solid)
Monododecyl phthalate	71.8	72.2	9.0	9.3	(Solid)
Monododecyl tetrahydrophthalate	71.0	70.3	10.1	10.0	(Solid)
Monododecyl 1,2-cyclohexanedicarboxylate	70.6	68.8	10.7	10.1	1.4683
Monododecyl 5-norbornene-2,3-dicarboxylate	72.0	72.3	9.8	9.7	(Solid)
Monotridecyl maleate	68.4	68.7	10.1	10.1	1.4662
Monotridecyl succinate	68.0	68.1	10.7	10.6	1.4547
Monotridecyl phthalate	72.4	72.1	9.3	9.3	1.5000
Monotridecyl tetrahydrophthalate	71.6	71.7	10.3	10.3	1.4770
Monotridecyl 1,2-cyclohexanedicarboxylate	71.1	71.0	10.8	10.8	1.4718
Monotridecyl 5-norbornene-2,3-dicarboxylate	72.5	71.7	10.0	9.7	1.4840
Monoheptyldecyl maleate	71.1	70.8	10.8	10.7	1.4653
Monoheptyldecyl succinate	70.7	70.8	11.3	11.2	1.4559
Monoheptyldecyl phthalate	74.2	74.2	10.0	9.9	(Solid)
Monoheptyldecyl tetrahydrophthalate	73.5	72.9	10.9	10.7	1.4752
Monoheptyldecyl 1,2-cyclohexanedicarboxylate	73.1	72.8	11.3	11.1	1.4712
Monoheptyldecyl 5-norbornene-2,3-dicarboxylate	74.2	73.3	10.5	10.9	1.4761

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[2] H. L. Holsopple, *Syntheses of Some New Mono-Acid Esters*, ORNL-TM-631 (July 19, 1963).

[3] H. L. Holsopple, *Syntheses of Two Tetrahedral Nickel Compounds*, ORNL-TM-635 (July 26, 1963).

Table 13.2. Composition of Two Tetrahedral Nickel Compounds

Component	Mole Percent			
	In Tetra-*n*-butylammonium Tetrabromonickelate(II)		In Benzyltributylphosphonium Tetrachloronickelate(II)	
	Theoretical	Found	Theoretical	Found
Carbon	44.5	43.9	58.3	58.5
Bromide	37.0	37.0		
Nitrogen	3.25	3.19		
Chloride			18.1	17.6
Phosphorus			7.9	7.8

Organophosphorus Compounds

A number of organophosphorus compounds were requested by the Chemical Technology Division in order that the influence of alkyl chain length and branching on fission product decontamination, extractability of uranium and thorium, and solubility of the uranium and thorium adducts in the water-Amsco solvent-extraction system can be evaluated.

Di-2-ethylhexylcarboxylic Acid

Attempts to prepare and purify di-2-ethylhexylcarboxylic acid have met with only limited success. An intermediate compound, 2-ethylhexylbromide, was synthesized in good yields by reacting 2-ethylhexyl alcohol and phosphorus tribromide. Theoretically, the alkyl halide can be reacted with diethyl malonate in an alcoholic sodium ethoxide solution to give a dialkyl malonate. This, on alkaline hydrolysis, should yield the corresponding alkyl malonic acid, which can be decarboxylated to the monocarboxylic acid. The product recovered actually consisted of a mixture of acids, none of which has been completely characterized. Efforts to effect a reasonable separation of pure product will continue.

Di-octylphenyl Acid Phosphate

The preparation of alkyl esters of phosphoric acid by the reaction of an alcohol with phosphorus pentoxide is well known. As yet, attempts to prepare mono- and di-octylphenyl acid phosphate by an analogous reaction using P_2O_5 and pure octylphenol, recrystallized from *n*-heptane, have been unsuccessful. However, a quantity of di-octylphenyl acid phosphate was prepared for the Chemical Technology Division. This compound was purified from a commercial mixture of mono- and dihydrogen phosphate esters by hydrolyzing polyphosphates with 6 *M* HCl; extracting with petroleum ether; and partitioning away phenols, inert materials, and trialkyl phosphates with petroleum ether. Following acidification with HCl, the di-compound was extracted into petroleum ether, which was evaporated to yield 120 g of 96.3% dioctylphenyl acid phosphate.

COMPOUNDS PURIFIED

Tetrapentylammonium Bromide

Tetrapentylammonium bromide (25 g) was purified for the Metallurgy Division by dissolving the compound in ethyl alcohol, decoloring the solution with bone black, and filtering it. The solid product was recovered by use of the freeze-dry technique for removal of liquid.

Ethyl Cyanide

Ethyl cyanide (200 g), also called propionitrile, was purified by vacuum distillation for use in gas chromatographic studies being carried out by the Reactor Projects Group of the Analytical Chemistry Division.

Phenol

Phenol (300 g) was purified by vacuum distillation for use by the General Analyses Laboratory in the preparation of reagents.

CURRENT PROGRAMS

The Chemistry Division has requested an evaluation of an electrochemical method for the reduction of pyridine to a mixture of dipiperidyl isomers. The Chemical Separation of Isotopes Group of that division has, in addition, requested the synthesis of a quantity of methyl isocyanide.

The Chemical Technology Division has requested 1 kg of 6-amino-3,9-diethyltridecane. A secondary alcohol having the desired alkyl chain has been oxidized to a ketone. This ketone will be converted to an oxime that can be catalytically hydrogenated to the amine desired.

The Radiochemical Research Group has requested a quantity of *N*-trisubstituted borazine compounds. Work has been started on this program.

Part II. Analytical Development

J. C. White
P. F. Thomason

14. Methods Development

DETERMINATION OF FREE ACID IN TRAMEX PROCESS SOLUTIONS

D. A. Costanzo

A study was undertaken to determine the applicability of polarography for the measurement of free acid in Tramex process solutions, which contain Al^{3+}. The potentiometric titration method generally used to determine free acid requires a complexing agent to prevent the hydrolysis of Al^{3+} during the titration of the acid with base. In the polarographic method the complexing agent is not required.

In this study the D.M.E. was used. The effect of lithium chloride concentration (0.56 to 13.2 *M*) on the half-wave potential ($E_{1/2}$) of the $2H^+ \rightarrow H_2 \uparrow$ reduction and on the ratio of diffusion current to hydrogen ion concentration (i_d/C) was determined. The half-wave potential was observed to shift linearly to a less negative potential and the ratio i_d/C to decrease nonlinearly with increase in lithium chloride concentration. For a solution that contains 2 millimoles of HCl per liter, the shift in $E_{1/2}$ vs the S.C.E. is from −1.67 v in 0.56 *M* LiCl to −0.96 v in 13.2 *M* LiCl, and the decrease in i_d/C is from 8.7 to 1.5 μa/m*M*, respectively. At a given concentration of lithium chloride, i_d/C is constant over the range of hydrogen ion concentration studied (i.e., 1 to 10 m*M*); Al^{3+} does not interfere. For a given hydrogen ion concentration, the diffusion current remains constant with increase in aluminum chloride concentration.

Aluminum ion was also observed to exhibit an analytically useful reduction wave in concentrated solutions of lithium chloride. The half-wave potential for Al^{3+} in 11.2 *M* LiCl is −1.55 v vs the S.C.E. compared with −1.85 v in 0.56 *M* LiCl. The i_d/C for Al^{3+} in 11.2 *M* LiCl is ~5 μa/m*M*. The shape of the irreversible wave was observed to depend on the acidity. In acid solution of 11.2 *M* LiCl, i_d/C was constant over the concentration range studied (i.e., 1 to 10 m*M* $AlCl_3$).

The polarographic studies will be continued to determine the possible interferences by other hydrolyzable cations for the determination of free acid in simulated Tramex process solutions. Also, the polarographic behavior of the rare-earth-element and other electroactive ions will be studied in concentrated solutions of lithium chloride.

DETERMINATION OF LEAD IN BONES

Lucy E. Scroggie

Eleven fragments of prehistoric bones were submitted for lead determination. Following dissolution of the material in an HNO_3-$HClO_4$ mixture, the lead was extracted from ammoniacal citrate solution into a 0.1% solution of dithizone in hexone and was determined by atomic absorption spectrometry. The lead content of the samples ranged from 0.5 to 17 ppm.

TITRIMETRIC DETERMINATION OF MERCURY(II)

Lucy E. Scroggie

The titration of Hg^{2+} in nitric acid solution with standard thiocyanate solution using Fe^{3+} as indicator[1] was investigated as a rapid method for the determination of milligram amounts of Hg^{2+} in calciner waste. The method was also adapted for the determination of submilligram amounts of mercury by spectrophotometric detection of the end point. The two methods were applied successfully with the desired speed and accuracy; two technicians were able to analyze 150 samples in three days.

CONDUCTOMETRIC TITRATION OF FREE ACID IN DAREX SOLUTIONS

Lucy E. Scroggie

Conductometric titration was investigated as the most promising method for the detection of the free-acid end point in Darex solutions. The high-sensitivity, direct-reading, linear, recording conductivity titrator developed by T. R. Mueller and R. W. Stelzner[2,3] was used in the investigation; this work was done with T. R. Mueller.

Darex solutions are nitric acid–hydrochloric acid solutions that contain the following approximate concentrations of hydrolyzable metal ions: Fe^{3+}, 1.15 *M*; Cr^{3+}, 0.38 *M*; Ni^{2+}, 0.18 *M*; Mn^{2+}, 0.04 *M*; and Ru^{3+}, 0.9 m*M*. The acid content varies from about 0.5 to 5 *N*. Darex feed contains 1.0 *M* Al^{3+} and large amounts of H_3PO_3, H_3BO_3, and NaH_2PO_2, in addition to the above ions.

Most methods for determining free acid in solutions of hydrolyzable metal ions are based on preliminary removal of cations by such techniques as ion exchange, on complete complexation of cations by groups other than the hydroxy group, or on precipitation of the cations in some sparingly soluble form. Synthetic Darex solutions and solutions of the individual metal ions with various acid concentrations were used to test the efficiency of many of the complexing agents reported as effective for similar purposes. The complexing agents that were studied either singly or in combination are oxalate, tartrate, fluoride, EDTA, α, α-dipyridyl, and thiocyanate. All these, with the exception of thiocyanate, exhibit some acid-base characteristics that interfere in the titration of known amounts of acid. Thiocyanate ion greatly improves the sharpness of the breaks in the conductometric titration curves for Fe^{3+}, Cr^{3+}, Ni^{2+}, and Mn^{2+}. The ratio of thiocyanate to metal ion is not critical; thiocyanate present in mole ratios to metal ion from 6 : 1 to 10 : 1 for Fe^{3+}, 3 : 1 to 8 : 1 for Cr^{3+}, 2 : 1 to 6 : 1 for Ni^{2+}, and 2 : 1 to 8 : 1 for Mn^{2+} has very little effect on the recovery of the acid.

Further work required to establish conditions for the conductometric titration of free acid in Darex solutions was postponed while the titrator is being modified and improved.

ANALYSIS OF ERBIUM MANGANATE

A. L. Travaglini

It was of interest to determine the oxidation state of manganese in erbium manganate and to confirm the formula, $ErMnO_3$. To do this, the compound was dissolved in boiling concentrated H_3PO_4. Erbium was determined by precipitation with cupferron,[4] ignition of the precipitate at 1000°C for several hours, and weighing the residue as Er_2O_3. Manganese was determined gravimetrically as $MnNH_4PO_4 \cdot H_2O$.

Preliminary attempts to determine the oxidation state of manganese in the compound were unsuccessful; the work was postponed.

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[1] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, revised ed., p 575, Macmillan, New York, 1943.

[2] T. R. Mueller and R. W. Stelzner, "Automatic, Recording Conductometric Titrator," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1961*, ORNL-3243, p 5.

[3] T. R. Mueller and R. W. Stelzner, "High Sensitivity, Direct-Reading, Linear, Recording Conductivity Titrator," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 6.

[4] A. I. Popov and W. Wendlandt, "Cupferron and Neocupferron Complexes of the Rare Earth Elements," *Anal. Chem.* **26**, 883–86 (1954).

CHARACTERISTICS OF VAPOR PHASE INHIBITOR-260

A. L. Travaglini

The mechanism of the rust-inhibiting action of vapor phase Inhibitor-260, which is dicyclohexylammonium nitrite–diisopropylammonium nitrite, is not understood. Analyses were made in an effort to determine the mechanism. The compound is water-soluble and has a low vapor pressure (~0.1 that of mercury) at room temperature. On being heated, it decomposes without melting and leaves a brown residue. The results of the infrared analysis of the residue showed no ammonia or amine groups, no cyclohexyl groups, and only a small amount of propyl group. From this information, it is postulated that the rust inhibition[5] may be due to a tightly adsorbed monolayer of amine on the metal surface, the passivating effect of nitrite ion, or a combination of the two. The compound probably arrives at the metal surface through a process of sublimation and condensation.

POLAROGRAPHIC DETERMINATION OF NITRATED 4-*sec*-BUTYL-2(α-METHYLBENZYL)-PHENOL (BAMBP) DISSOLVED IN AMSCO

A. L. Travaglini

To study the nitration of 4-*sec*-butyl-2(α-methylbenzyl)phenol (I), sometimes called BAMBP, aliquots of 1 *M* solution of I in Amsco were added to aliquots of HNO_3 solutions that varied in concentration from 0.1 to 3 *M*. The mixtures were agitated mechanically for periods ranging from 1 to 76 hr. The extent of nitration of I was measured by determining polarographically the nitro content of the organic phase. The supporting electrolyte was anhydrous methanol that was 0.1 *M* in $LiClO_4$ and 0.05 *M* in $HClO_4$. This supporting electrolyte can retain in solution as much as 10 v/v % of the Amsco-I solution.

To determine the effect of the concentration of Amsco and I on diffusion current and $E_{1/2}$ values, standard solutions of 10^{-5} *M* *o*-nitrophenol in supporting electrolyte that contained from 0 to 10 vol % unnitrated I in Amsco were made. Polarograms of these solutions showed that the diffusion current remained constant at 0.16 to 0.17 μa, whereas the $E_{1/2}$ varied from approximately −0.24 to −0.35 v vs the S.C.E. as the percent of I in Amsco increased.

Results of the polarographic analyses showed that the amount of nitration of I depends on the length of contact, temperature, and the concentration of the HNO_3. As much as 20% nitration occurred.

DETERMINATION OF PHENOLS BY NONAQUEOUS TITRIMETRY

J. R. Lund

The properties of 4-*sec*-butyl-2(α-methylbenzyl)phenol, called BAMBP, and *p*-chloro-*o*-benzylphenol are being investigated by members of the Chemical Technology Division. These phenols, dissolved in a variety of diluents such as carbon tetrachloride, diisopropyl benzene, Amsco 125-82, kerosene, *n*-octane, and a 50-50 mixture of kerosene and Solvesso-100, are being tested as extractants for removing cesium from waste-processing solutions.

The concentration of the phenol was determined by titration with tetrabutylammonium hydroxide in a medium of pyridine. The details of the method have been described.[6]

DETERMINATION OF LITHIUM IN BERYLLIUM OXIDE

J. R. Lund

To learn the fate of the lithium produced by the $Be^{10}(n,\alpha)Li^7$ reaction, lithium was determined in beryllium oxide that had been exposed to various levels of neutron irradiation. Samples of BeO, obtained from the Reactor Chemistry Division, were ground to ~200 mesh, then dissolved in an HNO_3-$HClO_4$ mixture that contained a few drops of hydrofluoric acid. The lithium content of these solutions was determined flame photometrically by T. C. Rains.[7]

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[5] H. R. Baker, "Volatile Rust Inhibitors," *Ind. Eng. Chem.* **46**, 2592 (1954).

[6] Corinne C. White, "Determination of Phenols by Nonaqueous Titrimetry," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 120.

[7] X-Ray and Spectrochemical Analysis Group.

POTENTIOMETRIC TITRATION OF TECHNETIUM(VII) WITH CHROMIUM(II) SULFATE BY USE OF A PYROLYTIC GRAPHITE INDICATING ELECTRODE

Anne A. Terry[8]   P. F. Thomason

The reductometric titration of NH_4TcO_4 in 3 *M* H_2SO_4, with Cr^{2+} as the titrant, was studied by use of the ORNL model Q-1728 automatic titrator. A pyrolytic graphite electrode was found to be a more suitable indicating electrode than is platinum. Pertechnetate ion (TcO_4^-) is reduced to Tc^{3+} in one step; the relative standard deviation of the reduction is ~1% in the range from 1 to 6 mg of Tc. Figure 14.1 shows the titration curve for the reduction of Tc^{7+} to Tc^{3+} with Cr^{2+}.

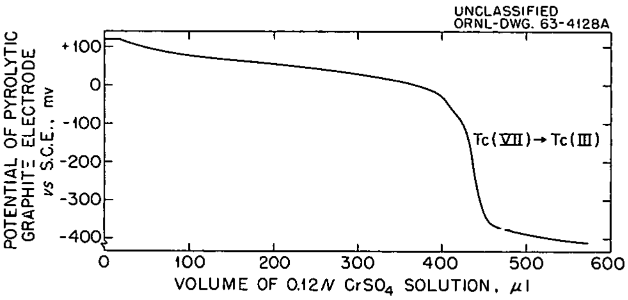

Fig. 14.1. Curve for $Tc^{7+} \rightarrow Tc^{3+}$ Potentiometric Reduction with Cr^{2+}.

DETERMINATION OF RHENIUM(III) IN A RHENIUM COMPOUND

J. R. Lund

According to Ryabchikov, Zarinskii, and Nazarenko,[9] Re^{3+} in 8 *M* HCl is quantitatively oxidized to Re^{4+} with ceric sulfate. As a result of titrations of test portions of a sample of solid $ReBr_4$ received from the Inorganic Preparations Group, the Re^{3+} content of the $ReBr_4$ was found to be less than 0.2%.

DISSOLUTION OR DECOMPOSITION OF VARIOUS MATERIALS

J. R. Lund   Hisashi Kubota
P. F. Thomason

Wichers, Schlecht, and Gordon[10] described a procedure for dissolving materials in hydrochloric acid by heating the reaction mixture in a sealed tube at a temperature between 100 and 350°C. The scope of this procedure was extended by the use of acids other than hydrochloric and to decompose certain types of organic compounds being prepared for elemental analysis. The use of the sealed-tube technique to decompose organic compounds with fuming (90%) nitric acid was of particular value when quantitative retention of volatile combustion products (i.e., halogens, sulfur, phosphorus, and mercury) was desired. When it was desired to retain halogen during decomposition of the sample, an excess of silver nitrate was added to the reaction mixture; the resulting product was a coarse, easily filterable silver halide. Any premature reaction between an organic compound and the acid was prevented by separating them with a layer of ice. First, the acid and silver nitrate (if used) were introduced into the glass tube, which was immersed in a Dry Ice alcohol bath. When the mixture was well chilled, distilled water was added until a $\frac{1}{8}$- to $\frac{1}{4}$-in.-thick layer of ice covered the acid. After the organic sample was added, the contents of the glass tube were kept cold until the tube had been sealed. The successful attempts at dissolution or decomposition are indicated in Table 14.1.

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[8] Research participant, Texas Woman's University, Denton.

[9] D. I. Ryabchikov, V. A. Zarinskii, and I. I. Nazarenko, "Electrolytic Preparation of Rhenium(III) Compounds," *Russ. J. Inorg. Chem.* (English Transl.) 6, 580 (1961).

[10] E. Wichers, W. G. Schlecht, and C. L. Gordon, "Preparing Refractory Oxides, Silicates, and Ceramic Materials for Analysis, by Heating with Acids in Sealed Tubes at Elevated Temperatures," *J. Res. Natl. Bur. Std.* 33, 451 (1944).

Table 14.1. Dissolutions Effected by Heating with Concentrated Acids in Sealed Tubes

Material	Solvent	Oxidant
Single Pieces or Chips		
Rh (massive metal)	HCl	HNO_3
Ir (massive metal)	HCl	HNO_3
ThO_2 (0.97)–UO_2 (0.03)	HCl	None
$TbIr_2$ (filings)	HCl	HNO_3
$HoIr_2$ (filings)	HCl	HNO_3
Powdered Samples		
IrO_2	HCl	$HClO_4$
Rh_2O_3	HCl	$HClO_4$
Organic Compounds (Liquids or Solids)		
Halogen compounds[a]	HNO_3 (90%)	
Sulfur and phosphorus compounds[b]	HNO_3 (90%)	

[a] Includes 2-ethyl-1-hexyl chloride, bromide, and iodide; benzyltributylphosphonium chloride; tetrapentylammonium bromide; tetra-*n*-butylphosphonium tetrachloronickelate(II); tetra-*n*-butylammonium tetrabromonickelate(II).

[b] Includes $[(C_4H_9O)_2P(O)S]_2Hg$, $(C_4H_9O)_2P(O)SCu$, $[(C_4H_9O)_2P(S)S]_2Hg$, and the corresponding parent acids.

POLAROGRAPHIC DETERMINATION OF CADMIUM IN HFIR FUEL PLATES

A. L. Travaglini Lucy E. Scroggie
J. R. Lund

Cadmium (0.05 to 0.2%) in the form of cadmium glass (a mixture of the oxides of cadmium, zirconium, zinc, barium, strontium, titanium, and silicon) is added to HFIR fuel plates, which contain aluminum, uranium oxide, and boron carbide. The fuel plates are dissolved for analysis with nitric and hydrochloric acids. Preliminary work indicated that a polarographic determination, using the standard-addition technique, was rapid and reliable. Actual analyses of the solutions gave results that were usually low, perhaps only a few percent but sometimes as much as 25%. Analysis of the insoluble residue (B_4C and SiO_2) from the acid reflux showed that essentially all the cadmium was dissolved by the procedure; other techniques also failed to indicate any manner by which cadmium losses could occur. Therefore, studies were initiated to develop conditions that would give the desired accuracy.

Polarograms of 1 *M* HCl solutions of cadmium isolated from the cadmium glass by several dissolution, fusion, and extraction procedures were ill-defined. Polarograms of ammoniacal (pH 9) tartrate solutions of the residue from the dissolution of the glass in $HClO_4$-HF mixtures had good cadmium waves that yielded good results, but solutions of actual and synthetic fuel plates under the same conditions gave polarograms in which the cadmium waves were overlapped by two others such that no useful measurements could be made.

In the procedure adopted, precipitation with ammonium hydroxide removed interfering ions from HFIR fuel-plate solutions. Well-shaped, reproducible curves were obtained. Cadmium added as aliquots of standard cadmium solution to both synthetic and actual fuel-plate solutions was completely recovered. Following removal by centrifugation of the precipitate resulting from the addition of ammonium hydroxide to the sample solution in 1 *M* NH_4Cl, cadmium is reduced at about -0.92 v vs the S.C.E.

STUDIES ON ARSENAZO III

Hisashi Kubota R. F. Apple

Arsenazo III (1,8-dihydroxynaphthalene-3,6-disulfonic acid-2,7-bis[(azo-2)phenylarsonic acid]) (I), in the form of the disodium salt (II), is a very useful and sensitive reagent for the quantitative determination of microgram quantities of thorium.[11,12] Therefore, it has been used extensively to determine thorium in small samples of

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[11] V. M. Vladimirova and N. K. Davidovich, "Determination of Thorium in Materials Containing Niobium by Means of Arsenazo III," *Zavodsk. Lab.* 26(11), 1210 (1960) [transl.: *Ind. Lab.* (USSR) 26, 1395 (1960)].

[12] S. B. Savvin, "Analytical Use of Arsenazo III," *Talanta* 8, 673 (1961).

granites. Savvin,[12] who first reported the reagent, describes its use in the determination of most of the lanthanides and actinides. The sensitivity and proved performance of II for determining thorium prompted a closer look into its use for other actinides and the lanthanides. The study has confirmed Savvin's claims of this reagent's versatility.

The molar absorptivities of the II complexes of several actinides and lanthanides are listed in Table 14.2. The sensitivity of II for rare-earth elements is about twice that of arsenazo, which has been reported to be ~28,000 liters mole^{-1} cm^{-1}.[13] The highest sensitivity for the tetravalent actinides is attributed to a 2 : 1 mole ratio of reagent to metal as compared with a 1 : 1 ratio for the lanthanides. The compositions of the complexes were verified by Job's plots.

Compound II has the advantage of forming colored compounds in acid medium. The lanthanides form complexes in acetic acid (~1 *M*), whereas the actinides generally require higher acid content (1 to 9 *M* HCl). The high acid content minimizes hydrolysis.

Beer's law plots for various metal-II complexes show a positive deviation from the ideal absorbancy-concentration relation. Repeated trials have shown that this deviation is a real effect. As yet, no good reason for it has been postulated.

Table 14.2. Sensitivity of Disodium Arsenazo III for Various Lanthanides and Actinides

Element	Molar Absorptivity of Disodium Arsenazo III Complex (liters mole^{-1} cm^{-1})	
	ORNL Value	Savvin Value
Ce	69,000	47,000
Dy	65,000	
Eu	40,000	
La	53,000	45,000
Sc	13,000	19,000
Sm	56,000	
Y	53,000	55,000
Th	108,000	133,000
U^{4+}	100,000	100,000
Zr	100,000	120,000

GAS CHROMATOGRAPHIC ANALYSIS OF AROCLOR 1248

A. D. Horton

Aroclor 1248, a high-boiling organic chloride, is used as a lubricant in the machining of certain metals. This compound has caused various allergic reactions in persons exposed to it. The tolerance level has been set at 0.5 ppm (0.5 mg of liquid per liter of air). The use of the argon beta-ionization detector is required to detect it in this concentration.

A chromatogram of Aroclor 1248 obtained with a 6-ft × ¼-in.-OD Apiezon "L" column, operated at an argon flow of 60 cc/min and a temperature of 250°C. shows a complex mixture of 15 or more compounds. Figure 14.2 is a composite chromatogram of the Aroclor 1248 liquid and vapor samples. The dotted lines represent peaks that appear in the liquid samples but not in the vapor samples.

Four samples of air contaminated with Aroclor were analyzed by injecting 5-cc portions into the Apiezon "L" column. The resulting chromatograms were identical with those obtained when vapor withdrawn from the neck of a bottle that contained liquid Aroclor 1248 was injected into the column. The results (μl of liquid per cc of air), based on the first major peak in the liquid Aroclor chromatogram, were: 0.006, 0.006, 0.008, and 0.011. The data are given on a volume of liquid per volume of air basis because physical data on the mixture are not available. Lack of information on the composition of Aroclor 1248 precludes a statement that the peaks found in the chromatogram of the liquid, but not in that of the vapor, are those of the active components of this mixture.

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[13] J. S. Fritz, Marlene J. Richard, and W. J. Lane, "Spectrophotometric Determination of Rare Earths," *Anal. Chem.* **30**, 1776 (1958).

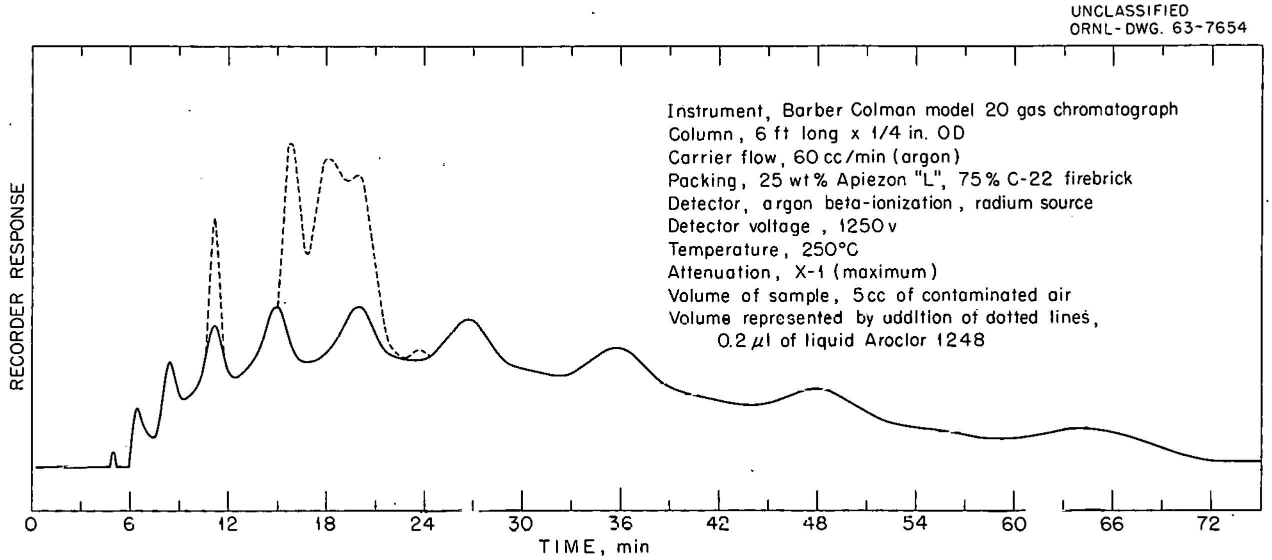

Fig. 14.2. Gas Chromatogram of Aroclor 1248.

GAS CHROMATOGRAPHIC DETERMINATION OF THE CRESOLS

A. D. Horton

A gas chromatographic method was developed for the determination of *o*-, *m*-, and *p*-cresols; benzaldehyde; phenol; and benzyl alcohol. It was used to analyze the oxidation products of gamma-irradiated toluene. This method is adapted from that of Paterson,[14] who resolved a similar mixture on a 4-m column of Chromosorb, coated with 5 wt % tricresyl phosphate and 3 wt % phosphoric acid, at 140°C. A 10-ft × $\frac{1}{4}$-in. copper column packed with 40/50-mesh glass beads, coated with 0.15 wt % tricresyl phosphate and 0.09 wt % phosphoric acid, was operated at an argon flow of 30 cc/min and a temperature of 110°C. The hydrogen flame ionization detector was used to monitor the eluate from the column. As little as 0.01 μl/ml of each of the components in the mixture was determined by this method.

The advantages of this column over that of Paterson[14] are: a 25- instead of a 40-min analysis time, 110 instead of 140°C column temperature, and a 10- instead of 13.1-ft column.

ANALYSIS OF PYROLYSIS PRODUCTS OF BIPHENYL

J. E. Attrill

As part of the organic moderator coolant program, products from the thermal decomposition of biphenyl were studied with the Reactor Chemistry Division. Gas chromatography was chosen for the analytical portion of this study because it is fast, simple, and can be used to analyze gases, liquids, and solids with little change in procedure or instrumental parameters. Samples of purified biphenyl were sealed in Pyrex containers in the absence of air and were heated for periods of 8 to 48 hr at temperatures from 320 to 346°C. The solids, liquids, and gases formed were analyzed[15] in an attempt to study the mechanisms and rates of reaction. The products formed were similar to those found on radiolysis of the same compounds;[16] therefore the identification of components was simplified somewhat.

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[14] A. R. Paterson, "Gas Chromatographic Separation of Close Boiling Isomers," pp 323–26 in *Gas Chromatography* (ed. by H. J. Noebels, R. F. Wall, and N. Brenner), Academic Press, New York and London, 1961.

[15] L. B. Yeatts, Jr., J. E. Attrill, and W. T. Rainey, Jr., *Gas Chromatographic Analysis of Biphenyl Pyrolytic Products*, ORNL-TM-523 (Mar. 13, 1963).

[16] R. T. Keen *et al.*, *Methods for Analysis of Polyphenyl Reactor Coolants*, NAA-SR-4356 (Jan. 30, 1961).

The possibility of surface area and catalytic effects on the rate was studied by placing quantities of materials with large surface area, such as glass wool, steel wool, and iron wool, in with the biphenyl during pyrolysis. An excess of pure oxygen was also added to one series of samples to study its effect. About 100 samples have been analyzed to provide data for calculating the course and rate of the reaction. Early quantitative data indicate the possibility that a biphenyl molecule splits to form phenyl radicals, which either hydrogenate to produce benzene or react with biphenyl to form terphenyls, quaterphenyls, and hydrogen. Traces of other gases may be formed by cracking of aromatic bonds. A good material balance is often obtained from the amounts of benzene, hydrogen, and polyphenyls found.

Part III. Service Analyses

A summary of the service analyses made by the laboratories of the Analytical Chemistry Division is given in the table below.

Summary of Analytical Service Work

	Average Number in Group		Number of Results Reported																											
			For ORNL																				For Others							
Group Making Analyses	Scientists	Technicians	Analytical Chemistry	Biology	Chemical Technology	Chemistry	Electronuclear	Finance and Materials	Health	Health Physics	Inspection Engineering	Instrumentation and Controls	Isotopes	Metals and Ceramics	Neutron Physics	Operations	Physics	Plant and Equipment	Reactor	Reactor Chemistry	Solid State	Thermonuclear	General Electric	K-25	Miscellaneous	Paducah	Special Projects	TVA	Y-12	Total
Low-Radiation-Level Radiochemical Laboratory	2	2			146					3,866					69	11												65	22	4,183
Mass Spectrometry Analyses[a]	8	7	130	395	2,166	40	25	2650					5,426	2,078	42	32	236		5,360	5,320	50	80			305				580	24,930
Methods Development	5		50	5	920	203			36				10	240			12		34	249		2								1,766
Optical and Electron Microscopy[a]	3	2	44		356	181				202		5	65	136		20	122			321	1			1					94	1,553
Process Analyses																														
General Analyses Laboratory	10	17	71		38.166	495	7		1650	336	27		217	5,967	80	524	15	10	897	3,319	486	184								52,478
General Hot Analyses Laboratory	10	15			19,345		1			23			1,715		93	4,298	3		206	1,521										27,230
High-Level Alpha Radiation Laboratory	3	5			14,373					3			1,518																35	15,937
Materials Testing Laboratory	5	10	39		14,124	384			119	120	20	7	132	11,131	37	46	31	16	704	3,843	46								34	20,848
Radioisotopes-Radiochemistry Laboratory	6	15	33	28	7,538	114			91	1,474			12,503	1,615	63	7,197	184		2,169	8,670	495	4	694		18	88			131	43,130
Reactor Engineering Services Analytical Chemistry Laboratory	1	3			408	3				633		3	7	256	8				3,803	2,730		19					8		89	7,971
Spectrochemistry Laboratory[a]	2	2	184	8	142	246				146			10,641	306	96	27	185		2,018	2,654	122	291							940	18,010
X-Ray and Spectrochemical Analyses[a]	9	5	47		3,123	747	36		5560	17,724		46		1,216		406	96		172	3,216	401									32,804
Total	64	83	598	436	100,807	2413	69	2650	7456	24,527	47	61	32,234	12,945	488	12,561	884	26	15,363	31,843	1601	580	694	1	323	88	8	65	1925	250,840

[a] These groups also do research and development work; therefore, in these groups the average number of persons may be greater than the number of persons who have done service work.

15. Quality Control

C. D. Susano
C. K. Talbott Bobby J. Ginocchio

A marked improvement occurred in the overall quality level of the analytical work for the 12-month period July 1962 through June 1963. This improvement has come about primarily as a consequence of increases in the control limits of colorimetric determinations of thorium and uranium from 2% to 4% and from 4% to 5%, respectively. Although some improvement in quality level has occurred in the General Hot Analyses Laboratory, the level is still too low, because of the wide fluctuations in the fluorometric determination of small quantities of uranium. The 2S, or 95% confidence, limit for this determination is now at 15% and should be raised to 20% at the earliest possible date. The number of control determinations was increased during this period by ~20% over the number made last year, primarily to bring about a better degree of control over the work being performed in the laboratories. The additional control tests were spread out uniformly over those determinations that are made in appreciable volumes.

The distribution of these control tests by laboratories is shown in Table 15.1. The amount of quality control work done in the High-Level Alpha Radiation Laboratory was inconsequential during this period. The number of control tests and their specific characteristics are shown more appropriately in Table 15.2.

Table 15.1. Distribution by Laboratories of Control Tests for July 1962 Through June 1963

Laboratory	Number of Control Results		Quality Level (%)[a]	
	Total	Outside Fixed Limits	1962	1963
General Hot Analyses	1460	145	85	88
High-Level Alpha Radiation			68	
Materials Testing	1215	50	88	97
General Analyses	1646	101	91	94
Reactor Engineering Service	168	7	95	96
Total	4489	Total 303	Av 85	Av 94

[a] Control results within prescribed 2S limits.

Table 15.2. Distribution by Methods of Control Results for July 1962 Through June 1963

Type of Method	Constituent	Number of Control Programs		Number of Control Results	
Colorimetric (spectrophotometric)	Aluminum	1		1111	
	Chloride	1		3	
	Chromium	2		177	
	Copper	1		2	
	Iron	2		292	
	Manganese	1		17	
	Mercury	1		10	
	Molybdenum	1		21	
	Nickel	3		197	
	Thorium	4		735	
	Titanium	1		7	
	Uranium	3	21	1074	2646
Coulometric	Uranium	2	2	540	540
Fluorometric	Uranium	3	3	571	571
Gravimetric	Carbon	3		280	
	Molybdenum	1		1	
	Nickel	1		12	
	Silicon	1	6	10	303
Potentiometric	Uranium	1	1	23	23
Volumetric	Aluminum	1		109	
	Chromium	1		17	
	Nitrate	2		170	
	Phosphorus	1		10	
	Sulfate	1		78	
	Sulfur	1	7	22	406
Total			40		4489

16. Low-Level Radiochemical Laboratory

M. T. Kelley
C. L. Burros

The Low-Level Radiochemical Laboratory reported 4179 results. Most of the results (~90%) were for the Health Physics Division in connection with their ecological, waste-disposal, and area-monitoring programs. Samples were of the same types as those analyzed in past years.

17. Mass Spectrometric Analysis

A. E. Cameron
J. R. Sites

The Mass Spectrometry Laboratory reported over 25,000 results on some 3200 samples. This work included the isotopic analyses of the following 45 elements: Li, B, C, O, Ne, Si, S, Ar, K, Ca, Ti, Cr, Fe, Ni, Cu, Zn, Ga, Ge, Br, Kr, Rb, Sr, Zr, Mo, Cd, In, Sn, Te, Xe, Cs, Ba, La, Sm, Eu, Gd, Dy, Er, Yb, Lu, Ta, W, Re, Os, Pb, and U.

Mass spectrometric analysis was continued on samples from thermal-diffusion experiments and production, from fission product gases, and from uranium burnup experiments. Dozens of cylinders of helium and argon were certified as to their contaminants at the low-ppm level. Helium contained in several trailers was certified for the liquid helium plant, the Reactor Chemistry Division, and the Metals and Ceramics Division. Special high-pressure gas mixtures made in the Analytical Chemistry Division were analyzed.

The Kilorod Program was supported by analyzing the off-gases from baked fuel sections and by checking the uranium isotopic analysis of the U^{233} material at several stages of the production plant.

A set of calcium samples were analyzed isotopically to help check the feasibility of using a stable-isotope spike (Ca^{48}) to determine the rate of metabolism of calcium in an individual. The tests were done in Sweden. A set of gallium samples were analyzed to determine the isotopic separation of a certain chemical-exchange system. Some very radioactive samples were analyzed for the Isotopes Division, including some europium samples for a control rod study and some irradiated samarium samples.

18. Spectrochemical Analysis Laboratory

A. E. Cameron

Zell Combs J. A. Norris

Over 1000 samples were analyzed in the Spectrochemical Analysis Laboratory and ~18,000 results were reported. Forty-five percent of the samples originated in the Isotopes Division and included the stable isotopes of: B, Br, Cd, Ca, Cr, Cu, Dy, Er, Eu, Gd, Hf, In, Fe, La, Pb, Li, Lu, Mg, Mo, Ni, Os, Re, Ru, Sm, Si, Sr, S, Ta, Te, Sn, Ti, W, Yb, Zn, and Zr. Beryllium metal and oxide accounted for 85 samples, 72 samples were aluminum metal for specification testing, and over 30 samples were from the LiF crystal growth program.

The Paschen Direct Reader was shut down on March 5, 1963, for renovation of the laboratory and was returned to service on October 1, 1963.

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19. Process Analyses

L. T. Corbin

The number of analyses performed increased by 6%, and the number of personnel increased by 1.5%. These increases have resulted from work relative to the Transuranium Program. The work of each of the process analyses laboratories is discussed below.

HIGH-LEVEL ALPHA RADIATION LABORATORY

J. H. Cooper

The High-Level Alpha Radiation Laboratory reported 15,929 results. Of these, 95% were for the Chemical Technology Division and 5% were for the Isotopes Division. Most of the analyses were made on materials from the Transuranium Element Processing Program. Samples of curium from various Tramex type solutions were analyzed for fission products. The concentrations of cesium, strontium, and ruthenium were determined by existing methods. Zirconium was determined by extraction into thenoyltrifluoroacetone. Both cerium and promethium were extracted into 2-ethylhexylphenylphosphoric acid in heptane from a 1 *M* α-hydroxyisobutyric acid–0.01 *M* pentasodium diethylenetriaminepentaacetate solution.

Samples of uranium from the Sol-Gel process were analyzed by gamma spectrometry to determine the rate of growth of the U^{232} daughters. Samples were scanned periodically on the gamma spectrometer, and the growth of 2.6-Mev Tl^{208} was followed. This particular isotope was chosen because its position in the gamma spectrum leaves it free from the interfering peaks of other gamma emitters.

Three new instruments were obtained. A windowless gas proportional counter was put into use for counting the number of spontaneous fissions in Cf^{252} samples. Because of the insignificant difference between the alpha energies of Cf^{252} and Cm^{242}, alpha spectrometry can not be used to determine Cf^{252}. The vacuum-tube multichannel analyzer was replaced by a transistorized model having an integrator-resolver attachment, a typewriter data print-out, and an X-Y plotter. An alpha counter (gas proportional type) with data print-out and an automatic sample changer was obtained. The sample changer can accommodate 50 sample plates at one time. The counter will operate for a preset time or preset number of counts and will automatically print out sample number, total number of counts, duration of the counting in minutes, and counts per minute.

GENERAL ANALYSES LABORATORY

W. R. Laing

A total of 52,451 results were reported during the year. Several new methods were placed in service. The permeability of small graphite cylinders to He, Ar, N_2, and CO_2 was measured for the Reactor Chemistry Division. The diffusion of thorium in graphite specimens was also measured. A new method for the dissolution of UO_2 samples for nitrogen determination[1] was tested and was found to be satisfactory. The American Public Health Association standard methods for cyanide and phenol were put into use for the analysis of plant waste water. The need for hardness titrations at levels < 1 ppm required the conversion of a Beckman model B spectrophotometer into a spectrophotometric titrator. This titrator, attached to a Moseley X-Y recorder, was used to titrate free HF in solutions that contain $H_4NbO_2F_5$ and HF. Thorium is the titrant and Thoron is the indicator (see "Modification of the Beckman Model B Spectrophotometer for Continuous Recording of Spectrophotometric Titration Curves" in Chap. 1 of this report). An apparatus for the measurement of the helium density of small samples[2] was added to the BET surface-area apparatus. The relative standard deviation for the measurement of a 1-cc sample was 0.3%.

A method was developed for measuring the density of the pyrolytic graphite coating of the fuel particles for the AVR pebble-bed reactor. The method consists in screening, crushing, and rescreening operations; a double acid leach; and a float-sink separation. The density of the separated coatings was measured by means of the helium densitometer mentioned above.

A precise method was developed to determine boron in ½-in.-diam punchings from HIFR fuel plates. These punchings contained aluminum, uranium, and boron (50 to 250 μg) as B_4C. The punchings were dissolved in HCl-HNO_3. The B_4C was collected on filter pulp and fused with Na_2CO_3. An acid solution of the melt was passed through Dowex 50W resin, and the boric acid was titrated. The relative standard deviation was 1.5%.

GENERAL HOT ANALYSES LABORATORY

C. E. Lamb

New devices were developed and a number of methods were established for the remotely controlled analysis of MSRE fuel-salt samples. The new devices included a decoupler for removing a salt-filled copper ladle from an MSRE transport container, a capsule aligner for assembling a pulverizer-mixer capsule, and a powder-transfer device for removing crushed and blended salt from the pulverizer-mixer capsule (see "Remotely Operated Equipment for Analysis of Radioactive Samples," in Chap. 1 of this report). A specially designed apparatus for the remotely controlled pyrolytic determination of fluoride[3] was constructed and tested. An electrochemical cell was developed to perform amperometric, polarographic, or coulometric titrations by electrode substitution. Methods tested in the mock-up hot cell with synthetic MSRE salt samples were the spectrophotometric determinations of iron with o-phenanthroline and nickel with dimethylglyoxime, and the amperometric titrations of Cr^{6+} with ferrous sulfate (see "Amperometric Determination of Chromium in MSRE Fuel," in Chap. 5 of this report) and zirconium with cupferron.

A gas chromatograph[4] with columns designed for remotely controlled use with radioactive gases was placed in service. It was used to analyze gas samples received from the Chemical Technology Division's study of the dissolution of irradiated uranium carbide.

A large number of samples that contained concentrated U^{233} were expected to be received at the start-up of the Kilorod Pilot Plant. Laboratory space was not available for the addition of the glove boxes needed to meet the radiation-contamination safety requirements. Therefore, a standard

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[1] Z. M. Turovt͡seva and L. L. Kunin, *Analysis of Gases in Metals*, Consultants Bureau, New York, 1961. (Tr. from Russian by J. Thompson.)

[2] R. G. Gutmacher, J. E. Harrar, and R. K. Pearson, *Some Recently Developed Chemical and Physical Analytical Methods*, UCRL-6639 (Apr. 30, 1961).

[3] R. H. Powell and O. Menis, "Separation of Fluoride from Inorganic Compounds by Pyrolysis," *Anal. Chem.* 30, 1546 (1958).

[4] A. D. Horton and A. S. Meyer, "Gas Chromatographic Analysis of Radioactive Samples," *Anal. Chem. Div. Ann. Progr. Rept. Dec. 31, 1962*, ORNL-3397, p 48.

laboratory hood was sealed with a Lucite front that contained glove ports, and a sealed transfer port was added to connect the modified hood with an adjoining hood. In another hood, an equilibrium pressure apparatus was installed for use in determining total gases in solid samples of ThO_2-$U^{233}O_2$.

Assistance was given to the Chemical Technology Division in their evaluation of a process for the separation of curium from irradiated americium-curium. The work was done entirely in an HRLAF cell.

MATERIALS TESTING LABORATORY

L. J. Brady

The Materials Testing Laboratory reported some 20,800 analytical results. Of this total, ~68% were for the Chemical Technology Division, 18% for the Reactor Chemistry Division, 5% for the Metals and Ceramics Division, and 3% for the Reactor Division.

The staff of the Materials Testing Laboratory was decreased from 16 to 15 employees.

The determination of the thorium content of granite from the Conway deposits, and from other sources, was continued.

Fused fluoride salts were analyzed for major components and for such trace impurities as oxygen and sulfur. The hydrogen evolution method[5] was used to determine the trivalent uranium fluoride content of MSRE-type fuel salt samples.

Arsenazo III,[6] as a chromogenic reagent, has been applied in the spectrophotometric determination of thorium in low concentration and of various rare-earth elements when they occur singly.

The method of Katz *et al.*[7] was used to determine organic carbon in aqueous solutions. In this procedure, the carbon is oxidized by persulfate in the presence of Ag^+ as catalyst, and the carbon dioxide is collected in a sodium hydroxide solution in the inner cell in the combustion-diffusion vessel. The alkaline carbonate solution is then siphoned from the vessel and is titrated.

A new model 154-D Vapor Fractometer with a column-switching reverse-flow accessory was put into operation and is being used to determine O_2, N_2, H_2, CH_4, CO, and CO_2 on the same sample. The other Fractometer is now being used to determine helium in the presence of nitrogen carrier gas. Since the fittings for the sampling loops of both instruments are interchangeable, only one manifold is required to measure the volume and pressure of samples prior to the analyses.

Solutions of lithium derived from studies of the chemical separation of isotopes were evaporated, and the lithium was then converted to the iodide salt preparatory to the determination of the ratio of the isotopes by mass spectrographic analysis.

RADIOISOTOPES-RADIOCHEMISTRY LABORATORY

E. I. Wyatt

Although the overall work load did not increase, the amount of neutron activation work did. This included 1600 determinations of trace elements and about 2500 determinations of neutron flux with the aid of monitors. Elemental sulfur was found to be unreliable as a threshold monitor when exposed to temperatures above 300°C during neutron irradiation. Induced P^{32} is not dispersed homogeneously throughout the sulfur mass because phase changes occur in the sulfur as the temperature increases. Much of the P^{32} is plated onto the quartz vial. After having been irradiated at temperatures high enough to melt the sulfur, the vials explode violently when they are opened. An attempt is being made to overcome this problem by the use of sulfide compounds.

Trace elements were determined in several unusual matrices, including greases, cutting oils, tapes, inks, gasket materials, foods, bones, kidney and lung tissues, and explosive grade NH_4NO_3. Keysort data cards were punched to furnish a ready source of information needed in nuclear analysis. Nuclear constants and other pertinent nuclear data recorded on the punched cards provide a rapid means of obtaining information such as sample size, irradiation time, and identification of radionuclides.

The use of computers was extended to include many of the calculations necessary to routine radiochemical analysis and for the reduction of

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[5] J. C. White *et al.*, *Determination of Trivalent Uranium in Fluoride Salt Mixtures by the Modified Hydrogen Evolution Method,* ORNL-2043 (Feb. 28, 1956).

[6] S. B. Savvin, "Analytical Use of Arsenazo III," *Talanta* **8**, 673 (1961).

[7] J. Katz *et al.*, "Analytical Procedures Using a Combined Combustion-Diffusion Vessel," *Anal. Chem.* **26**, 1503 (1954).

data obtained on punched tape from multichannel pulse-height analyzers.

The determination of fission yields from $Am^{241,242}$ was continued; a paper on the subject was presented at the New York meeting of the American Nuclear Society.

A comparison of analytical results on "standard" solutions received by the Radioisotopes-Radiochemistry Laboratory during the year is given in Tables 19.1 and 19.2.

Table 19.1. Results Obtained on Standard Solutions of Radioisotopes from Nuclear-Chicago Corporation

Isotope	Radioactivity ($dis\ sec^{-1}\ ml^{-1}$)	
	Reputed	Found
	$\times 10^5$	$\times 10^5$
P^{32}	3.38	3.37
Na^{24}	9.41	9.46
Au^{198}	7.81	7.65

Table 19.2. Results Obtained on Standard Solutions of Radioisotopes from International Atomic Energy Agency

Isotope	Radioactivity ($\mu c/g$)	
	Reputed	Found
Co^{60}	10.1	10.1
Au^{198}	24.75	24.6

HIGH-RADIATION-LEVEL ANALYTICAL FACILITY

L. G. Farrar

New operations performed in the High-Radiation-Level Analytical Facility (HRLAF) include the separation of americium and curium from fission products. Both ion-exchange and solvent-extraction techniques were used. The separation processes were contained in removable cubicles installed in the work cells to effect containment and the removal of waste materials and contaminated equipment.

Contamination difficulties were experienced in handling samples removed from the containment cubicles. The samples contained alpha activity as high as 2×10^{12} dis/min and proved hazardous to handle in an ordinary work cell.

To facilitate future work involving high-level alpha-emitting materials, two of the HRLAF work cells were sealed in glove-box fashion. These two cells will give double containment at all times and will permit bag-out removal of sample dilutions and waste materials from the cells.

Alpha contamination of manipulators has increased the cell downtime required for all manipulator repairs. There is some evidence that highly radioactive alpha emitters, such as curium, will migrate through the manipulator booting materials now in use. A better manipulator booting material and more efficient means of manipulator decontamination are being sought.

Cell No. 4 in the HRLAF was used to check out MSRE analytical procedures under hot-cell conditions and to check modified equipment being used in the hot cell for the first time.

The spread of radioactive contamination due to the sparking of hot materials in the arc stand of the optical spectrograph in cell No. 6 was diminished. A new filtering and washdown exhaust duct was installed over the arc stand, and a new arc stand that will permit remote maintenance is now in use.

The scrub exhaust for the acid fume hood in cell No. 7 was redesigned to permit remote removal of apparatus and materials, cleanup, and more efficient scrubbing.

During the routine maintenance of manipulators, all light-duty slave hands were replaced by heavy-duty tongs; also, the open-face wrist assemblies were replaced by closed-face assemblies to prevent rupture of manipulator boots. The routine maintenance in the HRLAF has included the decontamination of 17 work cells and 87 manipulator repairs.

20. Reactor Engineering Service Laboratory

A. E. Cameron
C. K. Talbott

The Reactor Engineering Service Analytical Chemistry Laboratory made ~8000 analyses on some 2900 samples. Of these, about 60% were submitted by the Reactor Division, 30% by the Reactor Chemistry Division, and the remainder were derived from ten other sources. The samples consisted principally of dye solutions; water; ThO_2 and slurries thereof; high-alloy steel; solutions of HCl, HNO_3, KOH, NaOH, HF, LiCl, and UO_2SO_4; TiO_2 and slurries thereof; and corrosion scale samples. Analyses were made less frequently on a variety of materials such as graphite, aluminum, insulation, and plastic products. About 150 cylinders of mixed gases were prepared during this period. Methods of analyses included volumetric analysis, gravimetry, spectrophotometric and potentiometric titrations, spectrophotometry, polarography, thermogravimetry, and gasometric analysis. Physical measurements were made on many of the samples; the measurements included pH, conductance, particle-size distribution, specific gravity, and zeta potential.

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Part IV. ORNL Master Analytical Manual

21. ORNL Master Analytical Manual

M. T. Kelley
Helen P. Raaen

CUMULATIVE INDEXES TO THE *ORNL MASTER ANALYTICAL MANUAL*

Helen P. Raaen

The Division of Technical Information uses an IBM 7090 computer program to prepare key-word indexes to the Laboratory reports. The program is a modification of one developed by Bell Telephone Laboratories, Inc., and was obtained through SHARE. Ann S. Klein[1] suggested that the program, with minor modifications, could be used to produce a key-word index to the *ORNL Master Analytical Manual*, the permuted words being taken from the titles of the methods. A sample index, produced in a pilot run made on 12 selected method titles, proved that the program was applicable. The sample index was distributed within the Division for evaluation and comment; it was received favorably.

Complete information on all unclassified methods contained in the *Manual* was then computer processed. The following cumulative indexes to the *Manual* for the period 1953 (the time of its inception) through 1962 were thus provided: key-word index, bibliographic index, author index, and method-number cross indexes. The indexes are bound together in a document entitled *Indexes to the Oak Ridge National Laboratory Master Analytical Manual (1953–1962)*. The document contains an introduction in which the following are discussed: organization of the *Manual*, availability of the *Manual* and individual methods, numbering of methods, format of the indexes, procedures for using the indexes, suggested format for references to methods, and suggested uses for the indexes. The document is available from the Office of Technical Services, United States Department of Commerce, Washington, D.C. 20230, at a price of $2.50. The indexes will be updated annually; they will possibly be issued as a companion document to each annual supplement of TID-7015.

The indexes provide a composite of complete information about the *Manual* and were prepared to facilitate its use. As a result of their existence, the files on the *Manual* are easier to maintain and the updating of the *Manual* is simplified.

The computer input information for the indexes was extracted from the files and put in proper format by Bobby J. Ginocchio,[2] Beverly S. Varnadore, and Doris L. Willson. The computer work was supervised by Ann. S. Klein.[1]

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[1] Technical Information Division.

[2] General Analyses Laboratory.

MAINTENANCE OF THE *ORNL MASTER ANALYTICAL MANUAL*

Helen P. Raaen
Authors of Methods

The fifth supplement to the reprinted form of the *ORNL Master Analytical Manual* was prepared. It contains the new methods and the revisions issued in 1962. This supplement is available from the Office of Technical Services, United States Department of Commerce, Washington, D.C. 20230, at a price of $8.00; it is designated TID-7015 (Suppl. 5).

Eighteen new methods were added to the *Manual*; of these, three were for the purpose of record only. Revisions to 13 methods were issued. Two obsolete methods were discontinued. In addition to these methods, 55 methods have been edited and are being prepared for issue. The Table of Contents for the *Manual* was revised to bring it up to date. (See "Presentations of Research Results.")

A survey was made to determine what methods, now contained in the *Manual*, are no longer used; what revisions to existing methods are needed; and what new methods are required for current or anticipated analytical work, particularly work related to the MSRE and TRU programs. The results of the survey appear as method-writing assignments made to persons in the Analytical Chemistry Division. Subsections 9 02 and 9 06 of the *Manual* have been designated to contain the MSRE and TRU methods, respectively.

Presentation of Research Results

Several of the presentations listed below were made jointly with members of other divisions. In these cases the member of the Analytical Chemistry Division is indicated by a single asterisk.

PUBLICATIONS

Books, Theses, Monographs

AUTHOR(S)	TITLE	PUBLISHER
Dunn, H. W.	"Absorption Edge Analysis," pp 16–18 in *The Encyclopedia of X-Rays and Gamma Rays*, ed. by G. L. Clark	Reinhold, New York, 1963
Kelley, M. T.	"Microanalytical Techniques in the Analysis of Highly Radioactive Materials," pp 937–57 in *Microchemical Journal Symposium Series*, vol 2, ed. by N. D. Cheronis	Interscience, New York, 1962
Moore, F. L.	"High-Molecular-Weight Amines – Versatile Modern Extractants," pp 345–55 in *Analytical Chemistry 1962*, ed. by P. W. West, A. M. G. Macdonald, and T. S. West	Elsevier, New York, 1963
Mullins, W. T.	"Neutron Radioactivation Analysis of Minor Elements in Ultrapure Beryllium and Its Compounds," pp 648–53 in *The Encyclopedia of X-Rays and Gamma Rays*, ed. by G. L. Clark	Reinhold, New York, 1963
Reynolds, S. A.	"Radiochemical Methods," pp 7.14–7.39 in *Handbook of Analytical Chemistry*, ed. by L. Meites	McGraw-Hill, New York, 1963
White, J. C.	"Solvent Extraction," pp 181–200 in "Industrial and Natural Products and Noninstrumental Methods" of *Standard Methods of Chemical Analysis*, vol IIA, ed. by F. J. Welcher	Van Nostrand, Princeton, N.J., 1963

Articles

AUTHOR(S)	TITLE	PUBLICATION
Armento, W. J.,[1] C. E. Larson	"Determination of Sulfate with Chromium-51"	*Anal. Chem.* 35, 918 (1963)
Bate, L. C.	"Nuclear Methods of Oxygen Analysis"	*Nucleonics* 21(7), 72 (1963)
Cameron, A. E.	"The Determination of Atomic Weights by Mass Spectrometry"	*Anal. Chem.* 35, 23A (1963)
Crowther, P.,[2] D. M. Kemp[3]	"A Kinetic Study of the Reduction of Vanadium(V) Cupferrate by Chloroform"	*Anal. Chim. Acta* 29, 97 (1963).
Goeking, C. F., Jr., C. L. Ghann, E. I. Wyatt	"Chlorostannate Method for Separation of Cesium"	*Anal. Chem.* 35, 1434 (1963)
Goldstein, G.	"Determination of Beryllium by the Photoneutron Method"	*Anal. Chem.* 35, 1620 (1963)
	"Effect of Concentration on the Partition of Osmium Tetroxide Between Aqueous Solutions and Carbon Tetrachloride"	*Inorg. Chem.* 2, 425 (1963)
Goldstein, G., D. L. Manning, H. E. Zittel	"Vanadyl Ion as a Back-Titrant for Indirect Amperometric Titrations with (Ethylenedinitrilo)tetraacetic Acid. Application to the Determination of Al^{+3}, Zr^{+4}, and Th^{+4} in Fluoride-Bearing Materials"	*Anal. Chem.* 35, 17 (1963)
Hahn, R. L., W. S. Lyon	"Internal Conversion Coefficients in the Decay of Au^{199}"	*Phys. Rev.* 130, 306 (1963)
Handley, T. H.	"Di-*n*-butyl Phosphorothioic Acid as an Extractant for Metal Ions"	*Anal. Chem.* 35, 991 (1963)
	"Extraction with Sulfur-Containing Organophosphorus Compounds"	*Nucl. Sci. Eng.* 16, 440 (1963)
Handley, T. H., Raquel H. Zucal,[4] J. A. Dean[5]	"Zinc Complexing Properties with Dialkylphosphorodithioic Acids"	*Anal. Chem.* 35, 1163 (1963)
Hitchcock, R. B.,[6] J. A. Dean,[5] T. H. Handley	"Tri-*n*-butylphosphine Sulfide as an Organic Extractant"	*Anal. Chem.* 35, 254 (1963)

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Horton, A. D., A. S. Meyer, Jr., J. L. Botts	"Adaptation of a Gas Chromatograph for the Analysis of Radioactive Gas Samples"	*Anal. Chem.* 35, 1988 (1963)
Kochanny, G. L., Jr.,* A. Timnick,[7] C. J. Hochanadel, C. D. Goodman	"Radiation Chemistry Studies of Water as Related to the Initial Linear Energy Transfer of 11-Mev to 23-Mev Protons"	*Radiation Res.* 19, 462 (1963)
Kubota, H., J. G. Surak[8]	"Automatic, Amperometric, Cupferron Titration of Zirconium in Highly Radioactive Solutions"	*Anal. Chem.* 35, 1715 (1963)
Lyon, W. S.	"Decay of Ba^{131}-Cs^{131}"	*J. Inorg. Nucl. Chem.* 25, 1079 (1963)
Manning, D. L.	"Voltammetry of Iron in Molten Lithium Fluoride—Potassium Fluoride—Sodium Fluoride"	*J. Electroanal. Chem.* 6, 227 (1963)
	"Voltammetry of Silver in Molten Sodium Nitrate—Potassium Nitrate. Use of a Controlled-Potential Polarograph and a Platinum Quasi-Reference Electrode"	*Talanta* 10, 225 (1963)
Manning, D. L., M. Blander,[9] J. Braunstein[10]	"Association Constants of Lead and Bromide Ions in Molten Sodium Nitrate—Potassium Nitrate Mixtures and Their Comparison with the Quasi-Lattice Theory"	*Inorg. Chem.* 2, 345 (1963)
Miller, F. J.	"The Pyrolytic Graphite Electrode as an Indicating Electrode for Potentiometric Titrations"	*Anal. Chem.* 35, 929 (1963)
Miller, F. J., H. E. Zittel	"Fabrication and Use of a Pyrolytic Graphite Electrode for Voltammetry in Aqueous Solutions"	*Anal. Chem.* 35, 1866 (1963)
	"Spectrophotometric Determination of Technetium with 1,5-Diphenylcarbohydrazide"	*Anal. Chem.* 35, 299 (1963)
Moore, F. L.	"Novel Radiotracer Method for Fluoride Determination"	*Anal. Chem.* 35, 1032 (1963)
	"Separation of Americium from Other Elements: Application to the Purification and Radiochemical Determination of Americium"	*Anal. Chem.* 35, 715 (1963)
Mountcastle, W. R., Jr.,[11] W. D. Shults,[12] P. F. Thomason	"Controlled-Potential Coulometric Determination of Indium"	*Anal. Chem.* 35, 871 (1963)

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[7] Michigan State University, East Lansing.

[8] Marquette University, Milwaukee, Wis.

[9] Research Department, Atomics International, Canoga Park, Calif.

[10] Chemistry Department, University of Maine, Orono.

[11] Temporary summer employee, Birmingham Southern College, Birmingham, Ala.

[12] Present address, Chemistry Department, Indiana University, Bloomington.

Rains, T. C., H. E. Zittel, Marion Ferguson	"Elimination of Anionic Interferences in the Flame Spectrophotometric Determination of Calcium. Use of Glycerol as a Releasing Agent"	*Talanta* 10, 367 (1963)
Reynolds, S. A.	"Determination of Thorium in Granite by Gamma Spectrometry and by Radiotracer"	*Talanta* 10, 611 (1963)
Reynolds, S. A., G. W. Leddicotte[13]	"Radioactive Tracers in Analytical Chemistry"	*Nucleonics* 21(8), 128 (1963)
Reynolds, S. A., W. T. Mullins	"Neutron Flux Perturbation in Activation Analysis"	*Intern. J. Appl. Radiation Isotopes* 14, 1421 (1963)
Ross, H. H., R. E. Yerick[14]	"Quantitative Interpretation of Color Quenching in Liquid Scintillator Systems"	*Anal. Chem.* 35, 794 (1963)
Shults, W. D.[12]	"Applications of Controlled-Potential Coulometry to the Determination of Plutonium. A Review"	*Talanta* 10, 833 (1963)
Shults, W. D.,[12] Louise B. Dunlap	"Controlled-Potential Coulometric Determination of Uranium(VI) in Uranium-Niobium Alloys"	*Anal. Chem.* 35, 921 (1963)
	"Determination of Uranium(VI) by Tri-*n*-octylphosphine Oxide Extraction and Coulometric Titration"	*Anal. Chim. Acta* 29, 254 (1963)
Terry, Anne A.,[15] H. E. Zittel	"Determination of Technetium by Controlled-Potential Coulometric Titration in Buffered Sodium Tripolyphosphate Medium"	*Anal. Chem.* 35, 614 (1963)
Zittel, H. E.	"Chromium(VI) 1,5-Diphenylcarbohydrazide Reaction and the Effect of Gamma Radiation on It"	*Anal. Chem.* 35, 329 (1963)
	"Effect of Gamma Radiation on Aqueous Solutions of Ethylenediaminetetraacetic Acid"	*Anal. Chem.* 35, 1528 (1963)
	"Effect of Gamma Radiation on Aqueous Solutions of (Ethylenedinitrilo)tetraacetic Acid"	*Anal. Chem.* 35, 1528 (1963)
Zucal, Raquel H.,[4] J. A. Dean,[5] T. H. Handley	"Behavior of Dialkyl Phosphorodithioic Acids in Liquid Extraction Systems"	*Anal. Chem.* 35, 988 (1963)

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[13] Present address, Union Carbide Corp., Nuclear Division, Tuxedo, N.Y.

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Reports

AUTHOR(S)	TITLE	REPORT NO.
Apple, R. F.	*The Amperometric Titration of Zirconium with Cupferron*	Jan. 1, 1963 (unpublished report)
Apple, R. F., J. C. White	*Preparation of Essentially Pure Lithium Fluoride — Removal of Magnesium*	ORNL-TM-637 (Aug. 2, 1963)
Baes, C. F., T. H. Handley*	*PWR Chemistry: Studies of the ORR In-Pile Loop*	TID-7641, entry 35, p 367 (October 1962)
Bate, L. C., Y. Wellwart,[16] J. R. Stokely[17]	*A Rapid Chemical Separation for Radio Manganese*	ORNL-TM-438 (Dec. 6, 1962)
Biggers, R. E., D. A. Costanzo	*Hazards and Experimental Procedure Evaluation for: Studies on the Polymerization and Hydrolysis of Plutonium in Uranyl Nitrate and Nitric Acid Solutions at Elevated Temperatures*	ORNL-TM-580 (May 22, 1963)
Cameron, A. E.	*Report of Foreign Travel, Analytical Chemistry Division, Harwell, England: Chemistry Division, Aldermaston, England: Max-Planck Institut für Chemie, Mainz, Germany: and I.A.E.A. Laboratory, Seibersdorf, Austria*	Aug. 19, 1963 (unpublished report)
Costanzo, D. A., R. E. Biggers	*A Study of the Polymerization, Depolymerization, and Precipitation of Tetravalent Plutonium as Functions of Temperature and Acidity by Spectrophotometric Methods: Preliminary Report*	ORNL-TM-585 (July 1, 1963)
Feldman, C., R. K. Dhumwad[18]	*An Atomic Absorption Tube for Use with an Atomizer-Burner. Application to the Determination of Mercury*	TID-7655 (Oct. 22, 1963)
Feldman, C., T. C. Rains	*The Collection and Flame Photometric Determination of Cesium*	TID-7655 (Oct. 22, 1963)
Guthrie, C. E., E. E. Beauchamp, L. T. Corbin,* T. J. Burnett, T. A. Arehart	*Operating Guide for Radiochemical Laboratories at Various Activity Levels*	Apr. 3, 1963 (unpublished report)

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[16] Israel Atomic Energy Commission, Soreq Research Establishment, Rehovoth, Israel.

[17] Temporary summer employee, Clemson College, Clemson, S.C.

[18] Atomic Energy Establishment, Trombay, India.

Holsopple, H. L.	*Determination of Optimum Conditions for Anodizing Aluminum Alloy 6061*	ORNL-TM-641 (Aug. 1, 1963)
	Syntheses of o-Nitrophenylarsonic Acid, o-Aminophenylarsonic Acid and Arsenazo III	ORNL-TM-625 (July 12, 1963)
	Syntheses of Some New Mono-Acid Esters	ORNL-TM-631 (July 19, 1963)
	Syntheses of Two Tetrahedral Nickel Compounds	ORNL-TM-635 (July 26, 1963)
Kelley, M. T.	*Analytical Chemistry Division Research and Development Quarterly Progress Report for Period Ending December 15, 1962*	Dec. 20, 1962 (unpublished report)
	Statistical Quality Control Report, Analytical Chemistry Division, January Through December 1962	Feb. 6, 1963 (unpublished report)
	Statistical Quality Control Report, Analytical Chemistry Division, January Through March 1963	May 28, 1963 (unpublished report)
	Statistical Quality Control Report, Analytical Chemistry Division, January Through June 1963	July 29, 1963 (unpublished report)
Kelley, M. T., C. D. Susano	*Annual Progress Report, Analytical Chemistry Division, for Period Ending December 31, 1962*	ORNL-3397 (Feb. 1, 1963)
Raaen, Helen P.	*Polarography in Glass-Corroding Media: A Research Proposal*	Dec. 20, 1962 (unpublished report)
Raaen, Helen P., ed., and authors of methods	*ORNL Master Analytical Manual* (Suppl 5)	TID-7015, suppl 5 (December 1963)
Raaen, Helen P.,* and Ann S. Klein, eds.	*Indexes to the ORNL Master Analytical Manual (1953–1962)*	TID-7015, Indexes (December 1963)
Scroggie, Lucy E.	*A Literature Survey of Sensitive Methods for the Determination of Dissolved Gases and Impurities in Reactor Coolant Water*	ORNL-TM-724 (Nov. 11, 1963)
Susano, C. D., H. P. House	*Proceedings of the Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology*	TID-7655 (Mar. 4, 1963)
White, J. C.	*Analytical Chemistry Research and Development Quarterly Progress Report for Period Ending December 15, 1962*	Jan. 11, 1963 (unpublished report)
	Analytical Chemistry Research and Development Quarterly Progress Report for Period Ending March 15, 1963	Apr. 15, 1963 (unpublished report)
	Analytical Chemistry Research and Development Quarterly Progress Report for Period Ending June 15, 1963	July 15, 1963 (unpublished report)
	Report on Foreign Travel of J. C. White	Aug. 16, 1963 (unpublished report)
Yeatts, L. B., Jr., J. E. Attrill,* W. T. Rainey, Jr.	*Gas Chromatographic Analysis of Biphenyl Pyrolytic Products*	ORNL-TM-523 (Mar. 13, 1963)

New Methods Issued to *ORNL Master Analytical Manual*

AUTHOR(S)	TITLE	NUMBER(S)	DATE
Horton, A. D.	"Paraffins, Permanent Gases, and Rare Gases, Gas Chromatographic Method"	1 221005 9 00721005	9-17-62
Kubota, H.	"Magnesium and(or) Yttrium, Disodium Dihydrogen Ethylenediaminetetraacetate Automatic Potentiometric Titration Method"	1 214721 1 219621 9 00714721 9 00719621	9-25-62
Layton, F. L.	"Ammonia, Spectrophotometric Sodium Phenate Method"	1 220020 9 00720020	9-25-62
Pruitt, M. E., R. R. Rickard	"Neptunium-237 or Neptunium-239 in Aqueous Solutions, Thenoyltrifluoroacetone Extraction—Tracer Method"	2 31532 9 008532	11-16-62
Rubin, I. B.	"Helium in Beryllium Oxide, Gas Chromatographic Method"	1 213590	7-31-62
Wyatt, E. I.	"Heavy Metals in Iodine-131, Product Solutions, Reflectance-Photometric Hydrogen Sulfide Method"	9 0732440	11-5-62
	"Manganese in Iodine-131 Product Solutions, Photometric Ammonium Persulfate Method"	9 0732481	10-15-62
	"Nitrate in Iodine-131 Product Solutions, Photometric Brucine Method"	9 0732560	1-30-63
	"Total Reducing Agents in Iodine-131 Product Solutions, Photometric Ceric Sulfate Method"	9 0732007	10-11-62

Revised Methods Issued to the *ORNL Master Analytical Manual*

AUTHOR(S)	TITLE	NUMBER(S)	DATE
Jones, H. C.	"Automatic Coulometric Titrator, ORNL Model Q-2005, Electronic, Controlled-Potential"	1 003029 9 003029	R. 7-15-63
Wyatt, E. I.	"Antimony-122, Product Analysis Guide"	9 0733040	R. 7-1-63
	"Arsenic-76, Product Analysis Guide"	9 0733063	R. 7-1- 63
	"Barium-133, Product Analysis Guide"	9 0733084	R. 7-1-63
	"Cadmium-115, Product Analysis Guide"	9 0733142	R. 7-1-63
	"Calcium-45, Product Analysis Guide"	9 0733151	R. 7-1-63
	"Cesium-137, Product Analysis Guide"	9 0733191	R. 7-1-63
	"Chlorine-36, Product Analysis Guide"	9 0733201	R. 8-15-63
	"Cobalt-60, Product Analysis Guide"	9 0733221	R. 8-15-63
	"Gallium-72, Product Analysis Guide"	9 0733311	R. 8-19-63
	"Hafnium-181, Product Analysis Guide"	9 0733341	R. 8-20-63
	"Lanthanum-140, Product Analysis Guide"		

Record Copies Issued to *ORNL Master Analytical Manual*

AUTHOR(S)	TITLE	NUMBER(S)	DATE
Koskela, U.	"Dissolved Oxygen in Steam and Water from the Homogeneous Reactor Test, Modified Winkler Method"	9 082229	7-5-63
Kubota, H.	"Hydrazine in Steam and Water from the Homogeneous Reactor Test, Spectrophotometric Method"	9 082230	7-10-63
Ross, W. J.	"Sulfur, Neutron Activation Analysis (Isotopic Carrier) Method"	5 11810	7-1-63

ORAL PRESENTATIONS

Seventh Conference on Analytical Chemistry in Nuclear Technology

Nearly 300 scientists, including 30 representatives from 11 foreign countries, attended the Seventh Conference on Analytical Chemistry in Nuclear Technology, which was held on October 8–10, 1963, in Gatlinburg, Tennessee. The ORNL Analytical Chemistry Division continued its sponsorship of this annual event.

The Conference Committee for this meeting was comprised of eight ORNL staff members: M. T. Kelley, Director of the Division, C. D. Susano, Associate Director, J. S. Eldridge, Cyrus Feldman, D. J. Fisher, D. L. Manning, R. W. Stelzner, and P. F. Thomason.

Two panel discussions were featured. W. S. Lyon moderated the panel on "The Availability and Use of Radioactivity Standards," M. T. Kelley led the discussion on "Recent Developments in Analytical Instrumentation." Members of the committee presided at the different sessions of the conference.

A total of 50 papers were presented at the meeting, five of which were presented by members of the ORNL staff.

In addition to the usual program, meetings were also held simultaneously by a subcommittee of the National Research Council on Radioactivity Standards and by a group of AEC spectroscopists.

Contrary to the precedent established through the first six conferences, the proceedings of the Seventh Conference will not be published.

The Eighth Conference in this series is tentatively scheduled to be held at the Mountain View Hotel, Gatlinburg, Tennessee, on October 6–8, 1964.

At Meetings of Professional Societies

AUTHOR(S)	TITLE	PRESENTED AT
Attrill, J. E.,[19] C. M. Boyd, A. S. Meyer, Jr.	"Gas Chromatographic Analysis of Helium at Reduced Pressures"	144th Meeting, American Chemical Society, Los Angeles, Calif., Mar. 31–Apr. 5, 1963
Barton, C. J.,[19] D. R. Cuneo, M. J. Kelley, J. E. Strain*	"Protactinium Stability in Thorium Nitrate–Nitric Acid Solutions"	Protactinium Chemistry Symposium, Gatlinburg, Tenn., Apr. 25, 1963

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[19] Speaker

Belew, W. L.,[19] D. J. Fisher, M. T. Kelley, J. A. Dean[5]	"Polarographic Determination of the Concentration of Metal Complexes in the Organic Phase Following Solvent Extraction"	145th Meeting, American Chemical Society, New York, N.Y., Sept. 8–13, 1963
Boegly, W. J., R. L. Bradshaw, F. M. Empson, H. Kubota,*[19] F. L. Parker	"Laboratory and Field Studies in Salt at Oak Ridge Since December 1961"	NAS–NRC Earth Sciences Committee Meeting, Washington, D.C., June 7, 1963
Burns, J. F.	"Auto-Ionization and the Ionization Efficiency Curves for Krypton and Xenon"	Third International Conference on Physics of Electronic and Atomic Collisions, University College, London, England, July 22–26, 1963
	"Auto-Ionizing Processes in the Rare Gases"	Fall Meeting, Southeastern Section, American Physical Society, Lexington, Ky., Nov. 7–9, 1963
Cameron, A. E.	"Evaporation Techniques in the Mass Spectrometry of Solids"	Eastern Analytical Symposium, American Chemical Society, New York, N.Y., Nov. 13–15, 1963
Chilton, J. M.,[19] R. A. Gilbert, R. E. Leuze, W. S. Lyon*	"A Redetermination of the Half-Life of Uranium-232"	144th Meeting, American Chemical Society, Los Angeles, Calif., March 31–April 5, 1963
Corbin, L. T.	"Analytical Methods and Remote Handling Facilities for the MSRE and TRU Programs at the Oak Ridge National Laboratory"	7th Annual Conference, Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 8–10, 1963
Corbin, L. T.,*[19] W. R. Winsbro, C. E. Lamb,* M. T. Kelley*	"Design and Construction of ORNL High-Radiation-Level Analytical Laboratory"	11th Hot Laboratory and Equipment Conference, New York, N.Y., Nov. 18–22, 1963
Crowther, P.,[2,19] F. L. Moore	"Liquid-Liquid Extraction of Cesium with 2-Thenolytrifluoroacetone"	9th Annual Meeting, American Nuclear Society, Salt Lake City, Utah, June 17–19, 1963
Crowther, P.,[2,19] J. S. Eldridge	"Instrumentation for Absolute Radioactivity Measurements"	7th Annual Conference, Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 8–10, 1963
Dunn, H. W.	"Present Status of the X-Ray Absorption Edge Method of Analysis"	Eastern Analytical Symposium, American Chemical Society, New York, N.Y., Nov. 13–15, 1963
Empson, F. S.,[19] H. Kubota*	"Problems in Disposal of Radioactive Liquid Wastes in Salt"	50th Meeting, American Institute of Chemical Engineers, Buffalo, N.Y., May 8, 1963
Feldman, C.	"The Porous Cup Revisited – Improvements in the Materials and Techniques"	14th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Mar. 4–8, 1963

Fisher, D. J.	"Applications of Operational Amplifiers in Analytical Instruments"	Chemistry Colloquium, Indiana University, Bloomington, Jan. 4, 1963
	"Recent Advances in Polarography"	Seminar, Department of Chemistry, Indiana University, Bloomington, Jan 3, 1963
Goldstein, G.	"Determination of Beryllium by the Photoneutron Method"	Oak Ridge Radioisotope Conference, Gatlinburg, Tenn., Apr. 1–3, 1963
	"The Use of Antimony-124 for the Analysis of Beryllium by the Photoneutron Method"	Oak Ridge Radioisotope Conference, Gatlinburg, Tenn., Apr. 1–3, 1963
Hahn, R. L.	"Chemical Effects of Isomeric Transitions: The Separation of the Isomers of Te-127, Te-129, and Te-121"	American Physical Society Meeting, Chicago, Ill., Oct. 18–19, 1963
Handley, T. H.	"Extraction with Sulfur-Containing Organophosphorus Compounds"	Solvent Extraction Chemical Symposium, Gatlinburg, Tenn., Oct. 23–26, 1962
Healy, W. B.,[19,20] L. C. Bate	"Activation Analysis of Wool with Special Reference to Manganese"	American Nuclear Society Meeting, New York, N.Y., Nov. 18–21, 1963
Horton, C. A.	"Use of Infrared Spectroscopy in Solvent Extraction Studies"	Infrared Institute, Canisius College, Buffalo, N.Y., Aug. 12–13, 1963
Kelley, M. T.	"Applications of Operational Amplifiers in Electroanalytical Chemistry at the Oak Ridge National Laboratory"	7th Annual Conference, Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 8–10, 1963
Kelley, M. T., D. J. Fisher,[19] W. L. Belew	"Recent Developments in Direct-Current Polarography"	Indiana University, Bloomington, Jan. 3–4, 1963
Kelley, M. T., D. J. Fisher,[19] H. C. Jones, W. L. Maddox, R. W. Stelzner	"Applications of Commercial Operational Amplifiers in Instrumentation for Chemcal Analysis"	144th Meeting, American Chemical Society, Los Angeles, Calif., Mar. 31–Apr. 5, 1963
Koirtyohann, S. R.,[19] C. Feldman	"Atomic Absorption Spectroscopy Using Long Absorption Path Lengths and a Demountable Hollow Cathode Lamp"	14th Annual Mid-America Spectroscopy Symposium, Chicago, Ill., May 20–23, 1963
Kopp, M. C.,[21] R. P. Gardner,[19,22] H. H. Ross	"A Wide Band-Pass Transistorized Ratemeter for Alpha Gauge Measurements"	Oak Ridge Radioisotope Conference, Gatlinburg, Tenn., April 1–3, 1963
Kubota, H., R. F. Apple,[19] H. L. Holsopple	"Arsenazo III, A Sensitive Spectrophotometric Reagent for Lanthanides and Actinides"	145th Meeting, American Chemical Society, New York, Sept. 8–13, 1963
Kubota, H.[19] J. G. Surak[8]	"Amperometric Titration of Zirconium with Cupferron"	144th Meeting, American Chemical Society, Los Angeles, Calif., Mar. 31–Apr. 5, 1963
	"Automatic, Amperometric Cupferron Titration of Zirconium in Highly Radioactive Solution"	144th Meeting, American Chemical Society, Los Angeles, Calif., Mar. 31–Apr. 5, 1963

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[20] Soil Bureau, Department of Scientific and Industrial Research, Wellington, New Zealand.

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[22] Research Triangle Institute, Durham, N.C.

Lyon, W. S.	"Application of Radioisotopes to Analytical Chemistry"	Program Review Meeting, Isotopes Development Center, Oak Ridge, Tenn., Oct. 22–23, 1962
	"Electronic Resolution of Gamma Ray Spectra"	Program Review Meeting, Isotopes Development Center, Oak Ridge, Tenn., Oct. 22–23, 1962
Mamantov, G.,[19,23] D. L. Manning*	"Voltammetry and Chronopotentiometry of Iron in Molten Fluorides"	Southeastern Regional Meeting, American Chemical Society, Charlotte, N.C., Nov. 14–16, 1963
Menis, O.[24]	"Chemical Principles in the Extraction of Elements with 1,1,1-Trifluoro-3,2-thenoylacetone (TTA)"	16th Annual Summer Symposium on Analytical Chemistry, University of Arizona, Tucson, June 19–21, 1963
Meyer, A. S., Jr., C. M. Boyd, J. E. Attrill[19]	"Gas Chromatographic Analysis of Helium"	144th Meeting, American Chemical Society, Los Angeles, Calif., Mar. 31–Apr. 5, 1963
Miller, F. J.,[19] H. E. Zittel	"Fabrication and Use of a Pyrolytic Graphite Electrode in Aqueous Solutions"	144th Meeting, American Chemical Society, Los Angeles, Calif., Mar. 31–Apr. 5, 1963
	"Use of the Pyrolytic Graphite Indicating Electrode in Voltammetry"	144th Meeting, American Chemical Society, Los Angeles, Calif., Mar. 31–Apr. 5, 1963
Moore, F. L.,[19] J. S. Eldridge	"Quantitative Determination of Californium-252 Using Prompt Gamma-Ray Measurements"	American Nuclear Society Meeting, New York, N.Y., Nov. 18–21, 1963
Norris, J. A.	"Direct Reading Analyses and Problems of Direct Concentration Print-Out"	New England Section, Society for Applied Spectroscopy, Boston, Mass., May 6, 1963
		Niagara Frontier Section, Society for Applied Spectroscopy, Niagara Falls, N.Y., May 7, 1963
	"Spectroscopy in the Atomic Energy Field"	14th Annual Mid-America Spectroscopy Symposium, Chicago, Ill., May 20–23, 1963
Reynolds, S. A.	"Iodine-131 in Water"	Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, Feb. 8, 1963
	"Radium-226 in Water"	Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, Feb. 7, 1963
	"Recent Radiochemical Work at ORNL"	Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio, Apr. 22, 1963
Reynolds, S. A.,[19] W. T. Mullins	"Neutron Flux Perturbation in Activation Analysis"	Oak Ridge Radioisotope Conference, Gatlinburg, Tenn., Apr. 1–3, 1963

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[23] Chemistry Department, University of Tennessee, Knoxville.

[24] Nuclear Materials and Equipment Corp., Apollo, Pa.

Ricci, E., F. F. Dyer[19]	"Second-Order Interference in Activation Analysis"	2nd Meeting, Society for Applied Spectroscopy, San Diego, Calif., Oct. 14–18, 1963
Rickard, R. R.,[19] C. F. Goeking, Jr., E. I. Wyatt	"A Study of the Fission Yields of Americium-241"	American Nuclear Society Meeting, New York, N.Y., Nov. 18–21, 1963
Ross, H. H.	"Modern Theory and Techniques of Liquid Scintillation Counting"	ORNL–ORINS Health Physics Training Program, Oak Ridge, Tenn., Sept. 27, 1963
	"The Role of Radiotracers in Analytical Separations"	Eastern Analytical Symposium, American Chemical Society, New York, N.Y., Nov. 13–15, 1963
	"Tritium Labeling Techniques"	89th ORINS Radioisotope Training Program, Oak Ridge, Tenn., May 15, 1963
	"Vapor Phase Chromatography"	88th ORINS Radioisotope Training Program, Oak Ridge, Tenn., Mar. 8, 1963
		89th ORINS Radioisotope Training Program, Oak Ridge, Tenn., May 9, 1963
		90th ORINS Radioisotope Training Program, Oak Ridge, Tenn., July 10, 1963
		91st ORINS Radioisotope Training Program, Oak Ridge, Tenn., Aug. 14, 1963
Ross, H. H.,[19] R. P. Gardner[22]	"An Alpha Gauge System for the Continuous Measurement of Gas Density, Gas Pressure, and Film Thickness"	Oak Ridge Radioisotope Conference, Gatlinburg, Tenn., Apr. 1–3, 1963
Ross, H. H., R. P. Gardner,[19,22] J. W. Dunn III[25]	"Wear Rates in Automotive Engines by Liquid Scintillation Counting of Iron-55"	American Nuclear Society Meeting, New York, N.Y., Nov. 18–21, 1963
Shaffer, J. H.,[19] G. M. Watson, D. R. Cuneo, M. J. Kelly, J. E. Strain*	"Recovery of Uranium and Protactinium from Molten Fluoride Systems by Precipitation as Oxides"	Protactinium Chemistry Symposium, ORNL Reactor Chemistry Division, Gatlinburg, Tenn., Apr. 25, 1963
Sites, J. R.	"Applications of Mass Spectrometry to Chemical Analysis"	Analytical Group, East Tennessee Section, American Chemical Society, Apr. 16, 1963
	"Isotope Dilution and Examples in the Fields of Stable Isotopes and Biology"	Analytical Group, East Tennessee Section, American Chemical Society, Apr. 16, 1963
Spitzer, E. J., J. R. Sites[19]	"Isotopic Mass Spectrometry of the Elements"	11th Annual Conference of Mass Spectrometry and Allied Topics, ASTM Committee E-14, San Francisco, Calif., May 19–24, 1963
Spronk, N.[26]	"Sodium Separation from Biological Material"	American Nuclear Society Meeting, New York, N.Y., Nov. 18–21, 1963

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[25] Department of Mathematics, North Carolina State University, Raleigh.

[26] Alien guest, Free University, Amsterdam, Netherlands.

Strain, J. E.	"Explanation and Demonstration of Neutron Activation Analysis"	AEC Exhibit, 145th Meeting, American Chemical Society, New York, N.Y., Sept. 8–13, 1963
	"Neutron Activation Analysis – Research Development"	Program Review Meeting, Isotopes Development Center, Oak Ridge, Tenn., Oct. 22–23, 1963
Susano, C. D.	"Over-All Analytical Services at Oak Ridge Installations"	Analytical Group, East Tennessee Section, American Chemical Society, Oak Ridge, Tenn., Feb. 13, 1963
Terry, Anne A.,[19,27] H. E. Zittel	"Determination of Technetium by Controlled-Potential Coulometric Titration in Buffered Sodium Tripolyphosphate Medium"	144th Meeting, American Chemical Society, Los Angeles, Calif., Apr. 4, 1963
White, J. C.	"Separations in Analytical Chemistry with Organophosphorus Compounds"	19th International Congress of Pure and Applied Chemistry, London, England, July 10–17, 1963
Yerick, R. E.,[19,28] H. H. Ross	"Liquid Scintillation Counting of Iodine-129 and Iodine-125"	Oak Ridge Radioisotope Conference, Gatlinburg, Tenn., Apr. 1–3, 1963
Young, J. P.	"Spectrophotometric Studies of Molten Fluoride Salts"	7th Annual Conference, Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 8–10, 1963
	"Windowless Spectrophotometric Cell for Use with Corrosive Liquids"	145th Meeting, American Chemical Society, New York, N.Y., Sept. 8–13, 1963

Under the ORNL Traveling Lecture Program

LECTURER	LECTURE TITLE	PRESENTED AT
Biggers, R. E.	"Absorption Spectrophotometric Studies of Solutions at High Temperatures and High Pressures"	Agricultural and Mechanical College of Texas, College Station, Feb. 19, 1963
		University of Mississippi, University, Feb. 21, 1963

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[27] Temporary summer employee, Texas Woman's University, Denton.

[28] Present adress: Department of Chemistry, Lamar State College of Technology, Beaumont, Texas.

Cameron, A. E.	"Geological Age Determinations by Isotopic Measurements"	Roanoke College, Salem, Va., Apr. 17, 1963
		Medical College of South Carolina, Columbia, Apr. 27, 1963
		Glenville State College, Glenville, W.Va., May 2, 1963
		Converse College, Spartanburg, S.C., Aug. 8, 1963
		Institute of Marine Science, University of Miami, Miami, Fla., Feb. 28, 1963
Thomason, P. F.	"Controlled-Potential Coulometry: New Analytical Tool in the Nuclear Energy Program"	Tuskegee Institute, Tuskegee Institute, Ala., Jan. 17, 1963
White, J. C.	"New Reagents for Separations in Analytical Chemistry by Solvent Extraction"	Tennessee Polytechnic Institute, Cookeville, Jan. 10, 1963
		Institute of Marine Science, University of Miami, Miami, Fla., Apr. 1, 1963
		University of Alabama, University, Apr. 3, 1963
		Carver Foundation, Tuskegee Institute, Tuskegee Institute, Ala., Apr. 4, 1963
		North Carolina State College, Raleigh, Oct. 24, 1963
Willmarth, T. E.	"Application of Electron Microscope Replica Techniques for the Study of Hard-Surface Biological Materials"	Medical and Dental School, University of Kentucky, Lexington, Feb. 22, 1963

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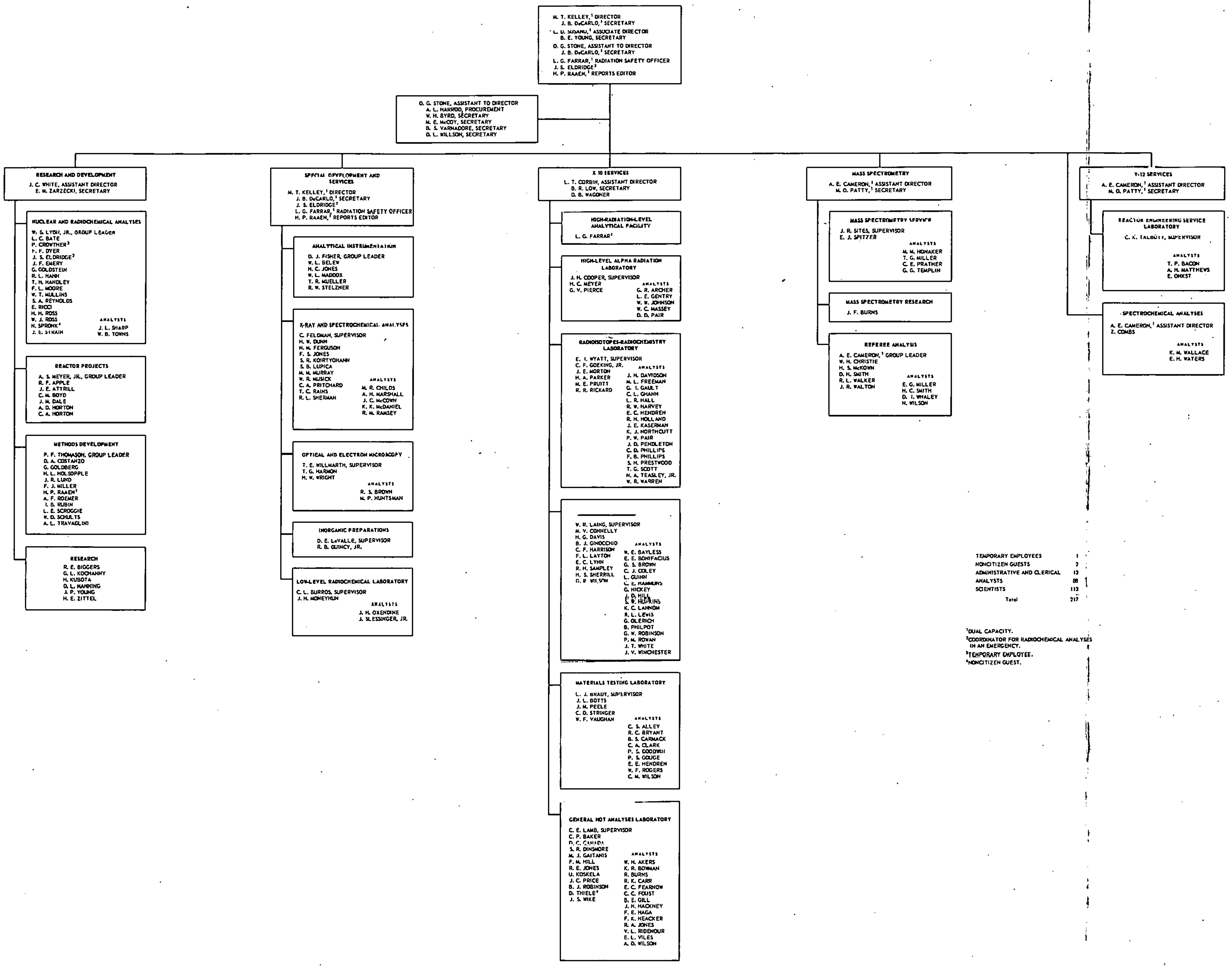

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[1] DUAL CAPACITY.

[2] COORDINATOR FOR RADIOCHEMICAL ANALYSES IN AN EMERGENCY.

[3] TEMPORARY EMPLOYEE.

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